Methane Hydrates, Truths and Perspectives

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Abstract

Global natural gas consumption is continuously increasing. This is the direct effect of the rapid growth in energy demand and the surge in the movement of coal-gas substitution undertaken by many industrialized countries to meet their electricity needs. In this energy consumption race, increasing efforts are used in anticipation of the coming gas revolution: methane hydrates. Methane hydrates constitute gas reservoirs trapped in crystalline structures within the ocean floor and in permafrost glacial regions. Recent assessments of available resources have reported huge economic potential. This article deciphers the stakes linked to the reserves estimates, scientific challenges and financial barriers standing in the way of their complex exploitation. It then offers a careful insight on the technical production requirements and the economic implications of the introduction of these resources on the gas market.

Keywords: *methane hydrate, energy economics, resources, natural gas, geopolitics*

1. Introduction

Natural gas is expected to play a crucial role in the context of future energy resources due to increasing levels of global consumption, stronger environmental pressure and the need for modern economies to rely on flexible and efficient electricity production sources. Primary energy consumption is expected to increase by a third between 2010 and 2035, driven by emerging countries, with China and India in the lead : according to the New Policies Scenario of the World Energy Outlook 2012, world demand will increase to almost 5 trillion cubic meters in 2035 compared to 3.4 trillion cubic meters today [2]. In order to meet this growing demand, coupled with the depletion of easily exploitable fossil fuels, consumer countries are seeking to diversify their energy portfolio. The exponential growth of shale gas and tight oil in the United States is a perfect illustration of the relentless pursuit between depletion of conventional reserves and exploitation of new resources made possible by the development of modern technologies. Unconventional gases might represent 50% of the 800 trillion cubic meters of ultimate recoverable resources and would be better distributed around the globe than conventional reserves [3].

Other potential sources concentrate large quantities of gas: methane hydrates. These crystalline formations, which remain stable under very strict pressure and temperature conditions, are present in the permafrost glacial regions and ocean floors. If deposits are not readily available, the estimated resources remain attractive: between 2.10^{14} and 3.10^{18} m^3 [1, 3], well beyond the current and future demand for natural gas. Therefore the exploitation of gas hydrate deposits can have a major impact on gas markets if the technical and economic feasibility of extraction is validated. Research programs on hydrates have increased over the past two decades, particularly in China, Japan, India and the United States [3].

2. Methane Hydrates: Origins and Characteristics

A clathrate is a chemical compound composed of a set of host molecules forming a solid lattice, and several thousands of "guest" molecules trapped within it. Hydrates are clathrates in which water is the host molecule trapping gas molecules: methane, but also ethane, propane and carbon dioxide [4]. Hydrates can trap large amounts of gas: ideally, reported at normal temperature and pressure, one cubic meter of methane hydrate is composed of 0.8 m^3 of water enclosing up to 164 m^3 of gas [4, 5]. The first scientific results on methane hydrates date from the early 19th century following their discovery in the laboratory by Sir Humphry Davy in 1810 [6]. In 1934, while the oil and gas industry were booming in the United States, Hammerschmidt discovered that the plugging of pipelines in the polar regions was due to the crystallization of hydrate and not to the presence of ice [7, 8]: identified as the nightmare of gas engineers, several research programs were launched and aimed at developing techniques inhibiting their formation. It was not until the mid-1960s that the first methane hydrates were found in the natural environment [9], in the sub ground sediments of gas fields in Messoyahka in western Siberia, in the Black Sea and in Alaska [10]. These findings were the starting point of the first research programs launched across the world [11, 12].

Formation and stability of methane hydrates require very accurate temperature and pressure conditions (high pressure and relatively low temperature), provided that the amounts of water and methane are available in sufficient quantities. These conditions are met in the glacial permafrost regions, within ocean sediments, and in some lakes. The formation of compounds occurs in a narrow sediment band called the *Hydrate Stability Zone*, parallel to the earth's surface. Several physicochemical factors have a strong impact on the size of the band: a high salinity level limits for example the formation of compounds, while the presence of other gases in deposits like carbon dioxide, sulfide hydrogen and heavier hydrocarbons such as ethane increase the stability area. Let's take, for example, the Gulf of Mexico: for pressure equivalent to 2500 meters, when the deposit is made up exclusively of pure methane, the base of the stability zone is characterized by a temperature of 21°C. For the same value of pressure, if the gas deposit is composed of 62% methane, 9% ethane and 23% propane, this characteristic temperature is then 28°C [11].

Methane from hydrate deposits is mainly of biogenic origin, namely coming from the degradation of organic matter by methanogenic bacteria in the sediment layers [8]. However, there are also pockets of methane hydrates of thermogenic origin, stemming from conventional hydrocarbon deposits after having migrated through geological faults. Hydrate deposits in the Gulf of Mexico, in the Messoyakha fields and the Prudhoe Kuparuk Bay in Alaska have been identified as a mixture of biogenic and thermogenic hydrates [9, 10, 13]. In the oceans, the pressure and the low temperatures encountered at depths greater than 300 meters can, theoretically, allow the formation of hydrates in the sedimentary layers. However, the gas concentration is generally too weak to allow the formation and stability of the compounds: no deposit has ever been found in the sediments of abyssal plains, the pockets being located only on the continental margins [9, 13-14]. It is therefore the availability of gas that mainly limits the formation of hydrates in natural environments. Finally, the stability zones along the margins depend heavily on the geothermal gradient - the increasing average temperature is 3-4°C for every 100 meters [15] - the probability of encountering deposits more than 2000 m depth is almost zero.

At the continental level, the areas where physicochemical conditions are met are mostly the polar continental regions where the average surface temperature is negative. The stability zone is located several hundred meters below the surface according to the geothermal gradient of the area. Due to their accessibility, current projects mostly focus on this type of deposit [13].

3. Resource Estimates

Following the discovery of the first natural hydrates in permafrost in 1965 by Makogon, two philosophies have long been opposed regarding the estimates of the gas hydrate reserves [17]. Some experts consider them inaccessible because of their dispersion and the complexity linked to their exploitation. It would make methane hydrates too risky in terms of investment. Conversely, others point to their omnipresence in the earth's surface, whether in permafrost or oceans, and the resulting economic and geostrategic potential. The principal estimates made since the 1970s are included in a segment extending from 2.10^{14} m^3 to 3.10^{18} m^3 [5].

Soviet geologists Trofimuk, Cherski and Tsarev provided the first estimate of the distribution and volume of submarine gas hydrate deposits, considering a surface of host sediments equivalent to 93% of the ocean surface. The obtained value of 3.10^{18} m^3 will then be reduced by refining the model to the continental shelf and abyssal plains. More recent estimates allowed the restriction of sediment areas that could harbor pockets of hydrate: the amount of trapped methane is then estimated between 0.2 and $6.8.10^{14}$ m^3 [18]. A recent publication by Klauda and Sandler [19], based on a thermodynamic model taking into account the effects of porosity and salinity reestimates these reserves much higher with $1.20.10^{17}$ m^3. The different figures show that the amount of methane trapped in gas hydrates, though certainly considerable, remains very difficult to assess. An average value commonly cited in the literature is $2.1.10^{16}$ m^3 [18], compared to conventional gas reserves estimated at $1.9.10^{14}$ m^3 [1].

Gas hydrates thus form naturally in permafrost regions and beneath the oceanic floor. Proven or estimated deposits are located in regions which are generally sensitive (low temperatures, difficult access, deep drilling), which complicates the exploration, development and delivery of the product to markets for which it is intended. Given these difficulties, most estimates are based on geological data obtained by seismic reflection which detects geochemical and geophysical anomalies [1, 11]. In some cases, direct sampling operations can be made, the samples being recovered by drilling or coring from the deck of a boat. Today the presence of submarine and land hydrates has been found in 23 sites by sampling and is suspected in 68 other sites [5, 27]. Scientists were able to recover hydrates in sediment cores extracted from shallow depths, between 10 and 30 meters of the seafloor in many parts of the world [11, 23], including the Gulf of Mexico, the Black Sea and the Caspian Sea, the Sea of Okhotsk and the Sea of Japan. Gas hydrates have also been found at greater depths beneath the seabed along the southeast coast of the United States on Blake Ridge, in the Gulf of Mexico, along the Central American gap, and off Peru and India [1].

In the 1990s, the growing appeal for methane hydrates as an energy source fostered the exploitation of the Canadian Mallik deposit. Mallik was and still is an ideal experimental site for developing an international cooperation and research program. Japanese scientists were very interested in the potential of hydrates that are present off their coast: they embarked on the adventure, the Mallik conditions presenting large similarities with the Japanese continental margins. The collaboration began between Japan, Canada and the United States, and the partnership first led to an initial drilling in 1998. The success of this first project led to the development of new drilling methods, coring and the evaluation of the strata constituting the pockets [18]. In 2011, the partners of the Mallik project expanded the field of cooperation and welcomed India, Germany and oil companies such as Chevron, BP and Burlington. Three extraction experiments were conducted and they confirmed that a reduction of pressure in the pockets allows gas production and extraction. A thermal stimulation test on the deposits was also conducted at the same time with an extracted gas flow equivalent to 1500 m^3 per day. If the production volume was very low compared to a conventional gas well, then the exploitation from hydrates was demonstrated for the first time to be possible [21].

Following the success of Mallik, the Japanese focused on the resources located in their territorial waters, especially in the area of Nankai. A Japanese national program was initiated in 2001 for a period of 16 years and is committed to studying the national deposits, testing production methods, and studying the resulting environmental impacts. Many other research programs were launched within the last decade.

4. Extraction Techniques

Methane production techniques are based on the dissociation of hydrates under specific conditions and use techniques similar to those used for conventional hydrocarbons. Many technical challenges are still being studied, such as maintaining optimal production rates during the extraction process, the long-term management of water production and understanding the behavior of hydrates at low temperatures and low pressure [10]. Ruppel [5] describes three methods of producing natural gas from gas hydrate deposits: thermal stimulation, depressurization and injection of inhibitors.

The thermal stimulation method consists of injecting steam or hot pressurized water in order to locally destabilize the hydrates, provoking an area of instability and thus allowing the freed gas to be extracted. This technique is not considered technically and economically viable when used alone because it is energy-intensive and has a low dissociation rate [20]. In terrestrial environments, it must be carefully controlled to minimize thawing permafrost which could lead to the release of methane into the atmosphere [5]. The second method, called depressurization, consists of lowering the pressure in the hydrate layer to cause dissociation. This technique is suitable for most deposits and is currently considered as the most economical [3]: the energy expenditure is limited and a significant volume of hydrate can be dissociated rapidly [4]. Because of its technical simplicity, it seems suitable for all types of exploitation of deposits over the long term. The thermal stimulation and depressurization methods were used together in the Mallik project [21]. Finally the last extraction technique uses the injection of inhibitors - such as some organic compounds (glycol, methanol) or ionic (salt water) - that modify the conditions of equilibrium (pressure-temperature) in the compounds. While this method does not pose major technical difficulties, it remains unattractive [11]: the volume of inhibitors required are substantial and the inherent costs very high, production yields collapse rapidly due to the dilution of inhibitors and the environmental risks are significant. The combination of the techniques might be a solution in a long-term perspective [3].

Many technological challenges remain with regards to the exploitation of hydrate deposits, and the principal results the scientific community have still rely on laboratory experiments and modeling. Field data is still missing and will be gathered over the long term. Research programs undertaken will therefore validate the feasibility of exploiting various types of deposits and consolidate existing theories.

5. Environmental Impact and Future Development Possibilities

5.1. A climate hazard?

The presence of significant gas hydrate deposits in sediments could have a significant influence on the climate if large quantities of gas were to be released. Methane has a warming impact that is 56 times greater than carbon dioxide over a period of twenty years [13, 29]. Thus, the reduction of hydrostatic pressure or a general increase in ambient temperature could trigger the dissociation of the compounds of some deposits [11], eventually increasing global warming and causing a chain reaction of degradation of other reservoirs [24, 25]. Note, however, that the conditions of temperature and pressure on the ocean floor - and therefore the geothermal gradient - change on temporal segments of hundreds or even thousands of years: hydrate pockets therefore are generally not affected in the short term. On the other hand, for surface deposits, the phenomenon of dissociation can be much faster: in the Gulf of Mexico and the American margin located in North of California, warm currents sometimes temporarily activate the dissociation of compounds, a phenomenon observable at the sediment-water interface level by the emission of gas bubbles [30].

The effects of the natural release of methane into the ocean is still widely debated because many parameters must be taken into account as (i) the amount and the transfer rate of methane in the sediments which depend on the bacterial activity at a local level, (ii) the volume of methane which is dissolved in the water column and (iii) the volume of methane finally escaping into the atmosphere [12, 31]. The real impact of dissociation - natural and accidental - of methane hydrates on climate change must be carefully studied to determine its real contribution to the environment. The effect is transposed to the polar regions, where an increase in the air temperature or the level of the sea may cause the dissociation of the compounds. Note that hydrate reservoirs play an important role on the stability of sedimentary layers that contain them. In case of disturbance of the deposits, these layers can be found weakened and cause landslides on the submarine continental slopes [1]. These instabilities can also occur on a smaller scale during drilling, therefore putting at risk offshore exploitation installations [5, 11] and there also releasing large amounts of gas into the atmosphere.

5.2. Or a game-changer?

The technological and economic potentials of methane hydrates are numerous. For instance, less conventional and still experimental techniques could replace the extracted methane from hydrates by carbon dioxide. The marine sequestration obviously requires a thorough knowledge of the solubility of CO_2 levels, the kinetics of the formation and the stability of the formed compounds [5, 11]. CO_2 hydrates are thermodynamically more stable than methane hydrates [32]. Recent experiments have shown that exposure of methane hydrates in CO_2 leads to a relatively rapid exchange process; the CO_2 hydrate formation is exothermic, the heat generated could even accelerate the dissociation reaction in the field and increase the rate of extraction of the original methane [33-35].

Finally, the physico-chemical properties of hydrates and their ability to store large quantities of methane make the transportation technology of gas particularly interesting in comparison to conventional methods of liquefaction. Refrigeration processes and cold storage may also make use of hydrates. The economic potential of methane hydrates is therefore immense, although the efforts of research and development remain substantial before reaching a viable economic development for the uses presented.

6. The Techno-economic Potential of Methane Hydrates

Natural gas is a typical example of market in which the structure and development do not entirely result from purely economic aspects. Given the massive levels of investment required, substantial freight costs, the heterogeneity of resources and the geographical dispersion of the main points of consumption, the growth of gas markets is closely linked to geostrategic issues. The natural gas market differs from other energy markets by the high costs inherent in transport, which are more or less equal to eight times those of oil [36, 37]. The last decade has been marked by an unprecedented production of literature on gas markets. If the intimately strategic aspect of energy resources and geopolitical hazards - including the disputes over the transportation of Russian gas through Ukraine between 2005 and 2010 [38] - are responsible for their presence in the headlines, a second explanation could be the understanding that the gas industry is a highly complex sector whose description and analysis requires a multidisciplinary perspective [36, 39-40].

The gas industry is subject at regular intervals to supply shocks. A substantial rise in US shale gas production in the last years provides a good example. Deposits of unconventional gas are important (deep gas, tight gas, gas-containing shales, coalbed methane excluding hydrates), so the current and expected impacts on gas markets are major. If the BP Statistical Review 2012 [42] estimated proven reserves of conventional gas at $1.9.10^{14}$ m^3 in 2010 - enough for 59 years of global production at current levels - unconventional gas, which are difficult to express in terms of resources, are likely to double the Reserves/Production (R/P) ratio [42-43]. The existence of these resources has long been known, but new technology and access to cheap drilling capacity mean that they have been slowly moving from unconventional to conventional reserves. The considerable progress made with deepwater production, for example, has had a similar effect.

The main factor determining the prospects for commercial exploitation of gas hydrates is the comparison between the costs of production and transportation and the likely range of market prices. Economically viable methods for safe methane extraction and minimization of the environmental impacts are necessary. Therefore the first deposits to be worked should be those containing the most optimal conditions according to the current accumulated scientific knowledge: important estimated volumes of hydrates, a sediment profile ensuring the sealing of the area, exploitation infrastructure and potential existing nearby transportation. Typically, the first exploitation fields could be those present in Alaska or the Mackenzie Delta in Canada, home of the first explorations and research programs [18, 1]. Other factors are likely to affect gas production from proven deposit reserves, such as the temperature of the area or the heterogeneity of the sedimentary layers: the rate of production on sites with significant volumes but non-optimal conditions can be greatly altered.

7. Conclusion

This article examines the state of technical knowledge and the economic potential of the exploitation of methane hydrate deposits. If the uncertainties related to production are still too important to come to a conclusion on the viability of the sector, future research and exploration will provide a more precise answer. Despite persistent questions, the application of technologies used in conventional production of oil and gas should lead to techniques adapted to hydrates. Ultimately, the multiplication of field data in the long term will be key in validating the models developed and will help draw a conclusion on gas deliverability from these untapped resources, and the impact their extraction would have on global warming.

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