



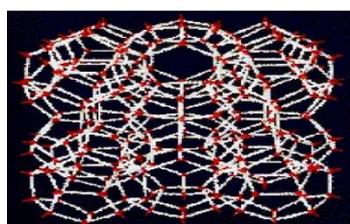
Original Research

## Investigating the Unknown Abilities of Natural Gas Hydrates

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### GRAPHICAL ABSTRACT



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### ABSTRACT

The high capacity of gas hydrate in natural gas storage makes it attractive for the storage and transportation of the natural gas and other gases as a competitor to liquefaction and condensation methods. Since the 1960s, when gas hydrate was introduced as a disturbing factor in gas pipelines, the idea of natural gas transfer by hydrate has been on the minds of many scientists. As the hydrate transport temperature is higher than the liquefied natural gas (LNG) the transport temperature and gaseous hydrate can be easily transported. Therefore, the technology of building hydraulic vessels will be much less complex compared with that of the LNG vessels, and hydrogen production facilities, which can be designed much easier than LNG facilities. But the main problem is the smaller volume of gas transferred. Each cubic meter of hydrate contains 175 cubic meters of gas. However, in LNG technology, the volume reduction reaches one hundred percent, and this issue is very important in the economics of gas transmission projects, especially long distances. Nevertheless, there is still great hope that hydrate will be used as a completely economical solution for gas transmission. In this regard, British Petroleum, in collaboration with other scientific centers such as the University of Gwasen, is building a small industrial unit that can produce 100 kg of hydrate per day.

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## Introduction

The discovery of large amounts of gas hydrates in the northern slopes of Alaska and down the southeastern Gulf of the United States reinforces the idea that gas hydrates are a very important source of energy in the future. However, very important technical issues need to be addressed first [1-4].

Gas hydrates can be introduced as an important source of energy in the world. Gas hydrates are naturally in the form of crystalline materials, consisting of water and gas [5-9].

In hydrates, a solid network of water molecules. Gas is stored in a cage-like structure. Gas hydrates are found mostly in the frozen and polar regions and under the sea in sedimentary layers. While methane, propane, and other gases can be trapped in the structure of our cage, they are much more likely to form methane hydrates [10-14].

The amount of methane trapped in gas hydrates is very high, and the estimate is more speculative. It ranges from 100,000 to 270,000,000 trillion cubic feet. It seems that the amount of gas in the world's hydrate reserves is much higher compared with that of the volume of other energy sources, although so far it is about the availability and production of these hydrates [15-19].

The primary goal of research on the gas hydrates is to assess the geological parameters that control the formation of gas hydrates [16]. Under the suitable temperature and pressure conditions, gas hydrates usually form a primary crystalline structure. Each cell unit

of structure 1 hydrate gas consists of 46 water molecules that form two small empty spaces and 6 large spaces. Gaseous hydrate structures can only accommodate small gas molecules, such as methane and ethane, with a molecular diameter of less than 2.5 angstroms [17-20].

And 8 are large binary hexagonal voids formed by 136 water molecules. The structure of 2 gas hydrates may contain gases with molecular dimensions in the range of 5.9 to 6.9 angstroms such as propane and isobutane. Under the standard temperature and pressure (STP) conditions, one volume of methane saturated hydrate (structure 1) contains more than 164 volumes of methane gas. Due to this huge gas storage capacity, these hydrates are important sources of natural gas. At the macroscopic level, many of the mechanical properties of gas hydrates are like ice [21-24]. Because hydrates contain at least 85% water on a molecular basis. Most interesting are the properties of the gas hydrate equilibrium phase, which are mostly controlled by the proportion of the guest gas molecules inside the water hydrate cages. For example, adding propane to a pure methane hydrate changes the structure of the hydrate [25-27].

## Gaseous Hydrates of Frozen and Polar Regions

Gas hydrates appear to exist in the western Siberia and are thought to be present in other Arctic regions of northern Russia, such as the Tyman-Pachura state, the eastern Siberian and northeastern Siberian cratons, and the Kamchatka region [26-28].

Gas is also available in the Arctic North Alaska and North American states. Indirect evidence of well drilling in these areas has revealed the presence of the gas hydrates in the northern slopes of Alaska and confirms the possibility of multiple layers of gas hydrates in the Prudhoe Bay area and the Coparuc River oil fields. In one-fifth of the wells drilled in the Maknazi Delta area, the presence of gas hydrates has been confirmed, and an examination of the wells of the Arctic Islands shows that in the polar-regions, gas hydrates are present at depths of 130 to 2000 meters [29-31].

### **Marine gas Hydrates**

The presence of the gas hydrates in marine areas is mainly the result of the abnormal seismic reflection coming from within the boundary specific zone of gas hydrates [32-34].

These reflections are mainly called terminal excitation reflection or BSR. BSRs have been mapped at depths of 100 to 1100 meters above sea level. Gas hydrates have been found in the sedimentary layers of the Gulf of Mexico, the offshore section of the Eel River Basin in California, the Black Sea, the Caspian Sea, and the Okhotsk Sea. Further subsoil depths have been discovered in the southeastern United States, the Black Kidge in the Gulf of Mexico, the Cascade Basin near Oregon, the Central American Canal, the Peruvian Sea, and in eastern and western Japan [35-38].

### **Evaluation of gas hydrate sources**

#### **Gas production from gas hydrates**

Proposed methods for recovering gas from hydrates usually involve separating or melting gas hydrates by the following methods:

- 1) Heat the tank to the temperature of hydrate formation
- 2) Reducing the tank pressure below the hydrate balance
- 3) Inject an inhibitor such as methanol or glycol into the tank to reduce hydrate stabilization conditions [39-41].

At present, however, the recovery of gas from hydrates is not delayed because hydrates are commonly distributed in rough polar-regions and deep-sea areas. It has been shown that gas can be produced in sufficient quantities from hydrates to convert gas hydrates into a technically recyclable resource, although the high cost of these advanced gas recycling techniques prevents recycling [42-44].

The use of gas hydrate inhibitors to produce gas from hydrates is physically possible, however, the use of large volumes of chemicals such as methanol has a high economic and environmental cost. The most cost-effective method is the decompression scheme. The Messoyakha gas field in the northern part of the western Siberian Basin is often used as an example of hydrocarbon gas production. All geological information has been used to confirm the presence of gas hydrates in the upper part of the basin [45-48].

The history of gas production from hydrates in this area shows that gas hydrates are an immediate source of natural gas production and production can be started and maintained by conventional methods. Long-term

production from the Messoyakha gas hydrate section is accessible with a simple de-pressure relief program [46]. It is attributed to the release of free gas from segregated hydrates. About 36 percent (about 183 billion cubic feet) of gas has been extracted from this area so far, although some researchers believe that the gas produced was not from hydrates. In 1996, a geological and seismic survey was conducted on the continents of northeastern and southeastern Japan [47].

According to the study, about 1,800 trillion cubic feet of gas were stored in the gas hydrates of the Nakai area. India, like Japan, has begun several research studies on the presence and possibility of recycling gas from gas hydrates in the country due to the high cost of importing LNG [48].

### **Investigation of gas transfer through gas hydrate technology (Gts) and comparison with transfer**

Natural gas cannot be stored or transported in the initial conditions of extraction, because in addition to corrosion, due to its physical properties, it needs to provide high pressures or very low temperatures in order to increase its bulk density [49].

There are a number of ways to export gas from the fields to consumer markets, including:

- Pipeline
- Liquefied natural gas (LNG)
- Gas - Liquid (GtL)
- Conversion of Cases to Consumer Goods (GtC)

- Generation of electricity using gas in power generation and transmission by cable (GtW)
- Compressed natural gas (CNG)
- Conversion of gas to hydrated solids (GtS or NGH)

The cost of gas transmission per unit of energy is much higher compared to crude oil due to its pressure-volume behavior. The natural gas transmission economy depends on the annual volume and transmission distance. Currently, pipelines are used for onshore transmission at high volumes and distances of less than 1000 km. Gas-to-liquid (LNG) conversion is used for sea transfers and distances of more than 1000 km. Other tubeless transmission technologies are suitable for different volumes and distances [50].

Due to the existing capabilities of technology to transport gas over long distances, the LNG method of liquefied natural gas as an economical method has been able to solve the difficulty of transporting gas in large quantities. However, selling small volumes of LNG is still not cost-effective. Experts say that the conversion of gas into liquid products (GTL) is also a good way to transport gas to distant markets. Because they believe that although technology (GtL) has not yet been widely used in countries with gas, transporting liquid products to consumer markets is much easier and less expensive than the LNG conversion method [50-52].

In addition, gas-liquid products can be easily sold in the consumer market; however, due to the specific type of the LNG demand that

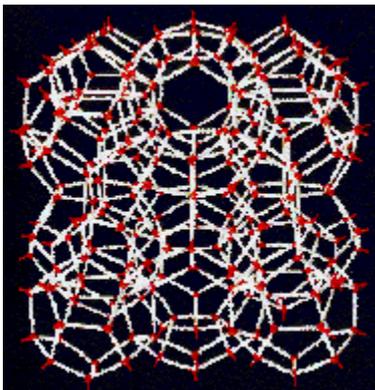
requires special receiving facilities, the sale of LNG is always more difficult. Due to the high cost of transportation natural gas in any of the above technologies, research to find other solutions is always ongoing. In this regard, in addition to LNG and GTL technology, hydrate and CNG technologies may also be able to be a suitable and inexpensive solution for transmission. Gas to be raised [53].

### Natural Gas Hydrate (NGH), Tubeless Gas Transmission

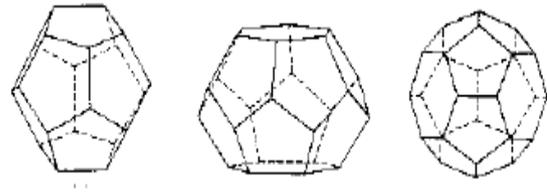
Natural gas hydration occurs when the conditions for crystal formation are met. Conditions for hydrate formation are:

- 1) Suitable pressure and temperature
- 2) The presence of water molecules
- 3) Existence of gas molecules

As the hydrogen bonds of the water molecules approach each other, polygons are created that have empty spaces and trap the gas molecules.

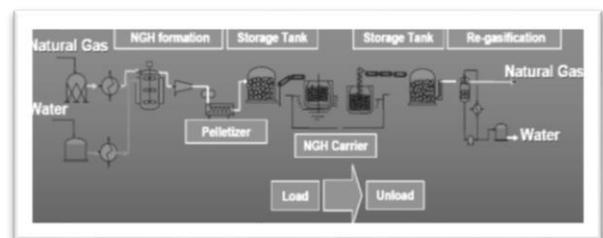


**Figure 1.** One of the hydrate structures  $\text{CO}_2$

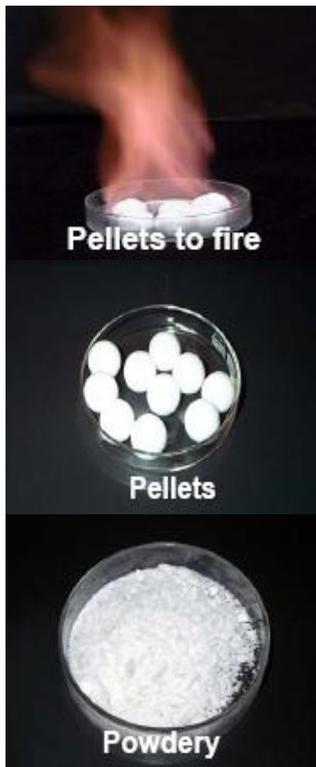


**Figure 2.** Examples of hydrate configurations

Methane hydrate is stable at 1 atmospheric pressure up to  $-80^\circ \text{C}$ . Hydrates at atmospheric pressure are rarely separated at temperatures above  $70\text{-}50^\circ \text{K}$ . This property is called self-protective hydrates. This property makes NGH capable of It is necessary to transfer water at pressures and temperatures below the freezing point. Gas transfer costs are also reduced for this reason. The transfer of natural gas in the form of NGH is one of the new concepts in transfer technologies. The production of NGH as well as its transfer is simpler than the process of liquefaction of natural gas (LNG). NGH is a tubeless transmission technology for transporting low to medium annual volumes at appropriate intervals. Studies show that gas transport in the form of crystalline hydrates is more beneficial for maritime transport.

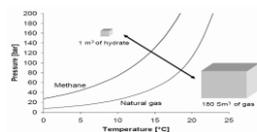


**Figure 3.** Scheme of marine natural gas transmission chain by NGH pellets



**Figure 4.** Different forms of natural gas hydrates

Because hydrate transport temperatures are higher than LNG transport temperatures, gaseous hydrates can be easily transported. From LNG facilities can be designed. Figure (4) shows the pressure curves of methane and natural gas. According to studies, each cubic meter of hydrate contains 180-150 cubic meters of gas. LNG technology reduces the volume by one hundred percent and in CNG to one hundredth, and this is very important in the economics of gas transmission projects, especially over long distances.



**Figure 5.** Pressure-temperature curve for methane and natural gas (NGH = Natural Gas + Water)

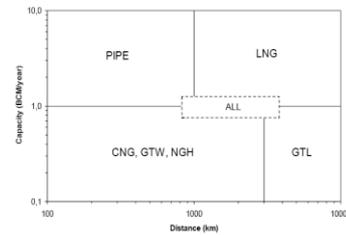
In 1995, studies were conducted to investigate the costs of using NGH on one of the Barents Sea gas fields in Norway. For this purpose, seawater at 5 ° C was used as a desiccant. Two LNG chains And NGH were compared at similar capacities (4.1 BCM per year) and 3,500 nautical miles (6,475 km). The results are shown in Table (3). On this basis, NGH fixed costs were about 24% lower than LNG.

### Discussion

The LNG technology is economically only available on large-scale scientific projects and the standard cost of production should be limited to 4 BCM. For the small to medium gas fields, hydrate and CNG technology is more suitable than the gas liquefaction. The growth of industry in LNG technology is one of its important values, while CNG and NGH are still considered as new technologies and have not grown. Hydrate technologies are now widely used in the United Kingdom and Norway. Countries such as Japan are also designing related processes. CNG technology, or compressed natural gas, is capable of transporting natural gas over long distances. CNG can be stored on special vessels and then transported to the intended destinations. Although the CNG carrier cannot transfer the gas to the loaded quantities on the LNG vessels, Re-gasification in CNG technology is easier and much less expensive than LNG. Gas storage in CNG ships is in the form of gas storage in pipes with a tolerance of 3000 - 1500 psi and a diameter of 18 to 36 inches. These pipes, which are installed horizontally

and vertically in the ship, have the ability to store large amounts of gas. To reduce the potential hazards, the temperature of these pipes is maintained at  $-20^{\circ}\text{C}$ . Due to the high pressure of CNG in tubular tanks, the high probability of explosion risk is one of the main problems of not implementing the widespread use of CNG technology in the field. Today, the use of new techniques in the construction of CNG ships means using 6-inch diameter pipes. So they would better be installed in large spools inside the ship. However, atmospheric processes are always considered in terms of safety and no costs associated with providing more pressure. The cost of the GtL and GtC units as well as the raw materials required in them (eg bauxite, silica, and limestone) is very high. Research on these two industries is still ongoing. Pipe lines as one of the common methods of transmission the pressure of pipelines is usually 1100-700 psig, which depends on the material and life of the pipeline. The cost of installing pipelines is about US \$ 1-5 per mile. In the design of onshore pipelines, all available routes should be in terms of distance and its effects on the investment and operating costs of the project, the natural condition and the salaries paid to the landowners along the route were compared with each other and finally chose the most economical route for gas transmission. Regarding the offshore routes using existing technologies, today it is possible to install pipelines to a depth of more than 2000 m above sea level. But the increase in technical risk is usually less inclined among

the financiers of gas transmission projects to invest Such schemes (compared to onshore pipeline schemes) are attractive. This can be considered as one of the economic reasons for the superiority of NGH over pipelines on sea routes. Affected by the pipeline. Figure (6) shows the capacity-distance curve for transmission methods.



**Figure 6.** Production capacity-distance curve

## Conclusion

Gas hydrates can block gas pipelines as they can form at temperatures above the ice formation temperature. This is an issue that has been addressed, and led to the regulation of water in the natural gas being transported. Many scientists have conducted extensive research on the effect of inhibitors on hydrate formation. In this case, many chloride salts such as Ca, Na and K were considered. Methanol gradually became the most common inhibitor. Since the discovery of the South Pars gas reservoir and the increase in Iran's proven natural gas reserves, the Iranian government has expanded its efforts to increase natural gas exports. According to the latest statistics available in 2004, more than 502 billion cubic meters of gas is piped by countries. Producer has shifted to consuming countries. This represents 74% of total global gas trade this

year. Using simpler and less expensive technologies can reduce the cost and increase the profits for countries with such technologies. NGH seems to be the simplest and least expensive option that can be transferred in the right conditions.

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