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## **Research Methane Hydrate Meta-stable Property for Application to Natural Gas Storage and Transportation**

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### **Abstract**

Gas hydrates are group ice-like crystalline compounds, which form through a combination of water and suitably sized guest molecules under low temperature and high pressure conditions. The important properties of hydrate are very high gas to solid ratio, 1m<sup>3</sup> of hydrate may contain up to 175m<sup>3</sup> of gas (at standard condition). When the conditions change, the methanhydrate can dissociate to methane and water. Hydrate meta-stable (self-preservation) property has been reported by some researchers in recent years. If we can utilize the property economically in addition to its high-density gas containing property, it is possible to store and transport stranded natural gas at higher temperature and lower pressure compared to the conventional liquid natural gas method. The authors conducted laboratory experiments of methane hydrate dissociation in order to examine its potential for application to natural gas storage and transportation. As the result, relatively extremely slow dissociation was confirmed within temperature range between -7.5°C and -3°C. These results seem to be very promising for practical application of self preservation property to natural gas storage and transportation.

### **1. Introduction**

Gas hydrates are ice-like crystalline materials that contain water and gases with small molecules, which were first observed in the laboratory in 1810. It was not until nearly 150 years later that they were observed in nature. Gas hydrates are inclusion compounds composed of water cages that trap guest molecules. It is estimated that over 99% of the guest content is methane. Gas hydrate can form naturally on Earth or as a result of made conditions. Naturally occurring gas hydrate in sediments (permafrost regions and subsea sediments) can be a potential natural gas resource. Natural gas hydrates offer a largely unexploited means of energy recovery and transportation and they could play a significant role in past and future climate changes. One volume of hydrate could release 150 to 180 volumes natural gas at standard conditions.

Hydrate technology development has focused on using gas to market to convert gas to solid to transport natural gas to market as low cost solution to managing associated gas in regions lacking in gas infrastructure and/or market. There could be possibilities for natural gas hydrate fir transport of natural as form Trinidad to the Caribbean islands at volumes much less than those normally considered for LNG, but still commercial to the whole transport chain from producer to consumer.

Compared to alternative technologies such as LNG and gas to liquids, gas to a solid hydrates conversion is relatively simple, low cost and does not require complex processes or extremes of pressure or temperature. It can be small-scale, modular and particularly appropriate for offshore associated gas applications. Put simply, the hydrate production concept amounts to assign water to natural gas and stirring. However, a comprehensive understanding of hydrate behavior is necessary to design the technology for transoceanic gas transportation.

At least two different gas hydrate crystalline structures are known, each of which is a clathrate crystalline structure. A clathrate hydrate unit crystal of structure I includes two tetrakaidecahedron cavities and six dodecahedron cavities for every 46 water molecules. A clathrate hydrate unit crystal of structure II includes 8 large hexakaidecahedron cavities and 16 dodecahedron cavities for every 136 water under pressure in these cavities. For example, it has been determined that natural gas hydrates can contain as much as 180 standard cubic feet of gas per cubic foot of the solid natural as hydrates.

Early on, gas hydrates were considered an industrial nuisance. Petroleum and natural gas production facilities often are located cold environments, where the product is located in deep underground or underwater wells. When tapping these wells, all of the necessary conditions and ingredients are present for producing gas hydrate. i.e., light hydrocarbon gases and water are present, the drilling and transmission pipes and equipment when an oil or natural gas well was tapped. Because gas hydrates are solid materials that do not readily flow in concentrated slurries or in solid form, when spontaneously produced in oil or natural gas production, they tend to clog the equipment, pipes, and channels in the production and transmission system. These disadvantageous properties of gas hydrates spawned much research into methods for inhibiting hydrate formation and eliminating this nuisance.

Because of the relatively high volume of gas that potentially can be stored in gas hydrates, however, eventually researchers began to look at this “nuisance” as a possible method for safely and cost effectively storing and/or transporting gases.

The hydrate dissociates when its temperature increases to above the temperature of hydrate formation at a special pressure, or when the system pressure decreases to below the pressure of hydrate formation at a specified temperature. The dissociation rate, which depends on the temperature-pressure (T-P) conditions and other environmental conditions, is an essential parameter to evaluate the gas recovery from hydrate layer.

In this study, the dissociation behavior of gas hydrates was investigated, since it was reported that the gas compositions of naturally occurring natural gas hydrate contained most is methane. The mixed gas hydrates used in this work were artificially prepared using the binary gas mixture of methane–propane and the ternary gas mixture of methane–ethane–propane. The crystal structures and the guest compositions of these hydrates are clearly identified by using Raman spectroscopy and gas chromatography. The obtained information contributed to evaluating the parameters that were needed for model calculations. These samples were shaped into uniform pellets and dissociated under isothermal isobaric conditions. The elapsed times from the start of dissociation to complete disappearance of the pellet were determined. Comparing to the analytical model, the characteristic dissociation kinetics of the mixed gas hydrates that contain propane was discussed.

## 2. Experimental

The authors conducted laboratory experiments of gas hydrates formation at high pressure and hydrate dissociation at atmospheric pressure in order to examine its Meta-stable Property for application to natural gas storage and transportation

### 2.1 Experimental apparatus

The main part of the experimental setup (Fig.1) contains a titanium alloy high-pressure reactor (60MPa) with a length of 0.43 meters, an internal diameter of 0.16 meters and an internal volume of about 850 cm<sup>3</sup>. The hydrate samples were formed and were dissociated in the reactor. The reactor was placed in an air bath whose temperature was regulated by refrigerator. A pressure transducer was used to measure the system pressure in the reactor that is monitored by a pressure transducer (accuracy of 0.02MPa), and the temperature distribution in an axial direction of the reactor was measured by a PRT to an accuracy of 0.1°C. A mechanical stirrer that is fixed to the drill bit with adjustable rotation speed is used to agitate the test fluids. This temperature, pressure and torque data were transmitted into a personal computer through a recorder collection and controlled board and were recorded in a data file simultaneously and continuously. The temperature and pressure were recorded in 30s time intervals by using an in-house software.

### 2.2 Experimental procedure

The reactor was filled with water at room temperature and after evacuation it was charged with gas methane at pressure up to 55MPa. Hydrates were formed by decreasing the temperature down to 0.5 °C at a cooling rate of 4.5 °C/h. the system was then kept at this temperature until the pressure in the reactor reached a steady-state condition. The system was left for about 24hours, and gas hydrate was formed. The bath temperature was decreased to -5°C again and the reactor was re-pressurized with methane gas. After equilibrium of the system, the bath temperature was increased to just above the freezing point again. Hydrates begin to reform, and the system was again left for another 24 hours. After the above pressurization-formation process of a 24 hours cycle was repeated until the reactor was re-pressurized with gas and system pressure keep the stable for more than 24 hours. It was confirmed that conversion from water in to hydrate reached greater than 90% in every sample. Once the whole interface is covered with the hydrate film, the free water is no longer in contact with the gas and hydrate formation is almost stopped. In this work, in order to increase the rate of hydrate formation and the amount of water converted into hydrate (or equivalently the amount of hydrate formed) we added 0.02 wt% of SDS to water.

### 3. Results and discussion

#### 3.1 Peculiarities of hydrate formation with SDS

The hydrate formation experiments were conducted at 0 °C with methane and pure water or SDS aqueous solution. The measured pressure profiles were depicted in Fig. 2 and fig. 3. The results of the experiments showed that the formation rate of gas consumed increases with the concentration of SDS in aqueous solution. Surfactants do not promote the formation of hydrates but either accelerate their onset or modify them to increase the agglomeration tendency. The SDS concentration was carried from experiment to experiment over the range up to 500ppm. At a concentration as high as 300ppm or above, we noted that during the induction time before the inception of the hydrate formation, that solution forming a pool in the test chamber was no longer clear but lightly opaque and that fine precipitate particles were sparsely sprinkled over the bottom of the chamber.

It is clear that the formation rate and the quantity of gas consumed increases with the concentration of SDS in aqueous solution; the highest formation rate reaches at 500 ppm. The fact is that the presence of SDS increases the formation rate and storage capacity. The results of both the pressure drop and the partition coefficient of ethylene between hydrate phase and vapor phase were increased remarkably by adding SDS to water. Theoretically, as a kinetic promoter, SDS cannot dramatically influence the initial hydrate formation conditions thermodynamically because its concentration is very small. However, when large quantity of hydrate is formed, SDS might have effect on the water-hydrate equilibrium behavior. At first, as it has been widely proved, the presence of SDS increases the fraction of water converted into hydrate. For the closed systems concerned in this work, the increase of the quantity of the hydrate phase will certainly increase the pressure drop and influence the partitions of gas components between water and hydrate. Secondly, with the proceeding of hydrate formation, SDS will be condensed in the residual aqueous solution and its concentration might become high enough to influence phase equilibrium conditions. Thirdly, when with the presence of SDS in water, a large number of SDS micelles with gas molecules solubilized in them are formed in solution. Each micelle may become a nucleation center. Therefore, unlike the formation of hydrate from pure water occurs only in the gas/water interface, a number of small hydrate particles forms subsurface of the bulk water. When hydrate particles move above the surface of water, the SDS molecules might be adsorbed to the surface of hydrate particles with their hydrocarbon tail towards gas phase. The adsorption of SDS molecules in the surface of hydrate particles will lower the surface free energy and resist the agglomeration among the hydrate particles. Hence, hydrate formed from SDS aqueous solution is in the form of fine powder as has been observed. There are sufficient spaces among the hydrate particles to guarantee a perfect gas/hydrate contact and make vapor-hydrate equilibrium could be established more easily and the composition of hydrate phase is more uniform. On the contrary, when without the presence of SDS, hydrate formation rate is very low and the formed hydrate is in the form of bigger block. Because the composition of gas phase changes with the proceeding of hydrate formation, the composition of hydrate formed will also change with time. As the diffusion of gas molecules among the cavities of hydrate is very difficult, the composition of the hydrate block might not be uniform. Additionally, as ethylene molecules could be solubilized in SDS micelles more easily than methane molecules, ethylene molecules may be enclosed into the hydrate lattice preferentially. That might be one reason why the presence of SDS can increase the partition coefficient of ethylene between hydrate and vapor. It is of significance that adding SDS can increase both hydrate formation rate and partition coefficient of ethylene between hydrate and vapor (Zhang, 2005).

The experiment, the temperature and pressure during hydrate dissociation were set at its non-equilibrium condition, i.e. between -7.5°C and 0°C, and at atmospheric pressure (0.1MPa), in order to confirm self-preservation effect of hydrate. The test section was depressurized along the following lines. After hydrate formation, the bath temperature was first decreased to a desired temperature, and the system was left for one hour until the hydrate sample in the reactor reached equilibrium condition. Next, both sides of the reactor were opened little by little and the system pressure was decreased gradually until it reached somewhat above an equilibrium pressure of methane hydrate corresponding to the sample temperature. After that, the system was depressurized very rapidly and the hydrate sample began to dissociate. The typical depressurization procedure is shown in Figure 3. The reasons for depressurizing the system at such two stages are as follows.

- (1) Hydrate dissociation start can be caught rather correctly, since the evolved gas is measured soon after the sample is brought to non-equilibrium condition.
- (2) Sample temperature drop due to Joule-Thomson cooling can be reduced by minimizing rapid the depressurization of the system.

### 3.2 Correlation between hydrate dissociation and time

It was observed that hydrate sample dissociation was most rapid at the dissociation start, and subsequently decreased exponentially in every test. correlation between hydratedissociation and time from dissociation start at atmospheric pressure and at -5 C with ice particle size for hydrate formation varied between 250 micrometers and 1,180 micrometers. Most experimental data for each test were on a linear line in log-log plot. It was likely that some data were dispersing near the origin since those data include more errors due to relatively rapider dissociation just after dissociation start.

Hydrate dissociation within 24 hours after dissociation start ranged from 17% to 35%. As the results of a minimum dissociation data extrapolation in the present work, the period at which all samples finished dissociating was estimated to be approximately 120 days. This result seemed to be very promising for practical application of self-preservation property to natural gas storage and transportation.

### 3.3 Correlation between hydrate dissociation and temperature

In order to examine the self-preservation effect of formed NG hydrate, the produced hydrate is weighed and transferred to the fridge immediately and kept at low temperature. The self-preservation and weight loss is determined gravimetrically by regularly controlling the product weight with time. Figure 4 presents the self-preservation effect of NG hydrate produced with pure water. It should be noted that for this test, the produced hydrate were initially kept at -25 °C for 98 hrs and then the fridge temperature was changed to -15 °C for another 255 hrs and then -10 °C for 60 hrs and -8 °C for another 300 more hours. As can be seen from the figure, the NG hydrates became stable (i.e., did not lose weight) very quickly at enough low temperature (i.e., under freezing point of water). It shows that the NG hydrate has significant self-preservation effect enabling it to be transported at atmospheric pressure and feasible low temperature. As explained and can be seen from the figure, changing the temperature to higher temperatures (ofcourse lower than freezing point of water) does not have any negative impact on its self-preservation effect.

Figure 5 shows the self-preservation effect of NG hydrate produced with 1 mass% TBAB. For this test again, the produced hydrate were initially kept at -15 °C for 230 hrs and then the fridge temperature was changed to -10 °C for 75 hrs and then -8 °C for another 290 more hours. The same temperature influence and self-preservation effect as previous test with pure water was observed.

The main differences between NG hydrates with and without TBAB were: 1) With TBAB the hydrate has more gas content and there is more gas consumption while hydrate formation, this could be attributed to change in gas solubility in the presence of TBAB and also kinetic change in formation rate of hydrate in the presence of TBAB, 2) The hydrate formed with TBAB is less stable in room temperature and its tendency to dissociate is very high. It shows the comparison between the self-preservation effects of NG hydrate with and without TBAB.

In general, for practical cases, the hydrate production rig should be placed in a cool room, in order to prevent/minimise hydrate dissociation while transferring the produced hydrates from the reactor and the produced hydrate should be immediately transferred to low temperature conditions. It can be concluded that, as a guideline for NG hydrate production, the produced hydrate should be kept at low temperature around -20 °C for first instance (8-10 hours) and then it can be transferred to higher temperature conditions around -5 to -8 °C without any hydrate dissociation occurs.

## 4. Conclusions

An extensive literature review with critical evaluation was conducted on comparison of various alternative methods including hydrate technology for natural gas storage and transportation, as well as various gas hydrate production techniques.

A new method of dry gas hydrate production in the presence of excess gas was studied. The method was applied in production of dry natural gas.

It can be concluded that NG hydrate can be preserved and transported at atmospheric pressure. Moreover, the rate of hydrate formation can be improved in the presence of Ammonium salts such as TBAB. It is speculated that TBAB changes the gas solubility in aqueous phase and/or the kinetic of hydrate formation.

Storage and transportation temperature in the case of Gudmundsson et al. is -20 C ~ -10 C, and -5 C in our case. Needless to say, our concept is superior to theirs from a viewpoint of energy loss so far as the temperature is concerned.

## 5. Acknowledgments

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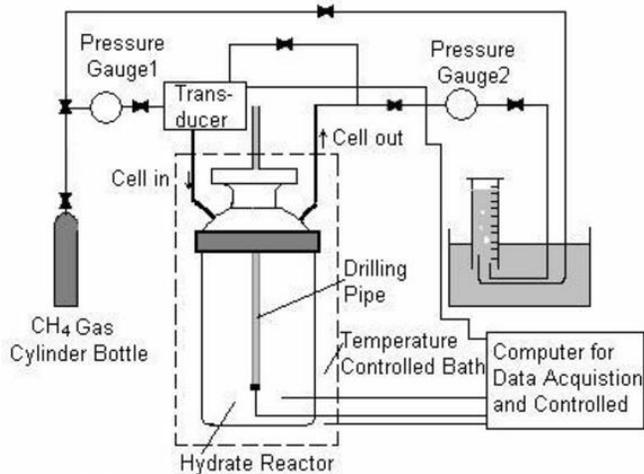


Fig.1 Schematic of Experimental Apparatus

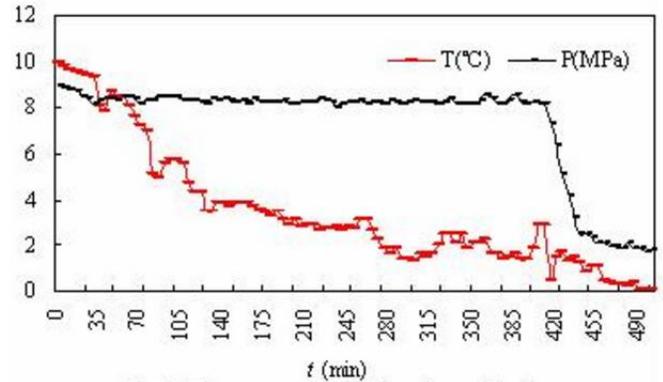


Fig.2 The temperature changing of hydrate formation with gas and water

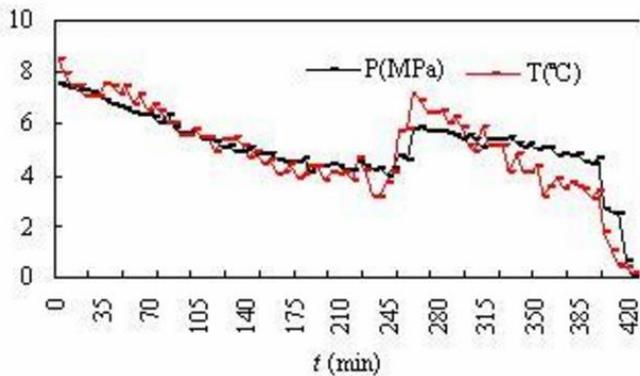


Fig.3 Temperature changing of hydrate formation with SDS in aqueous solution

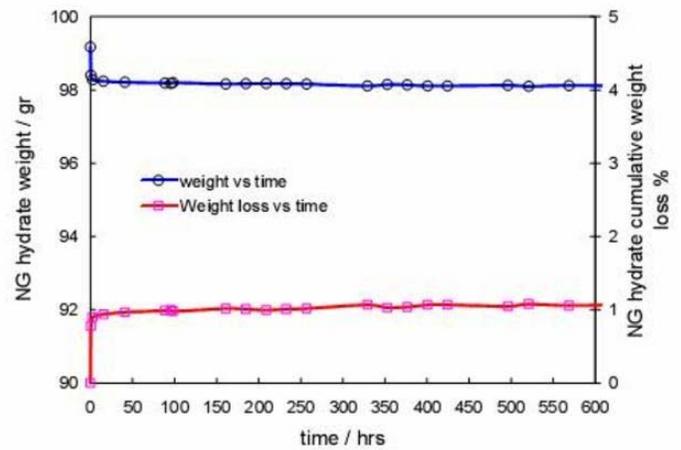


Fig.4 Stability of NG hydrate produced with pure water versus time.

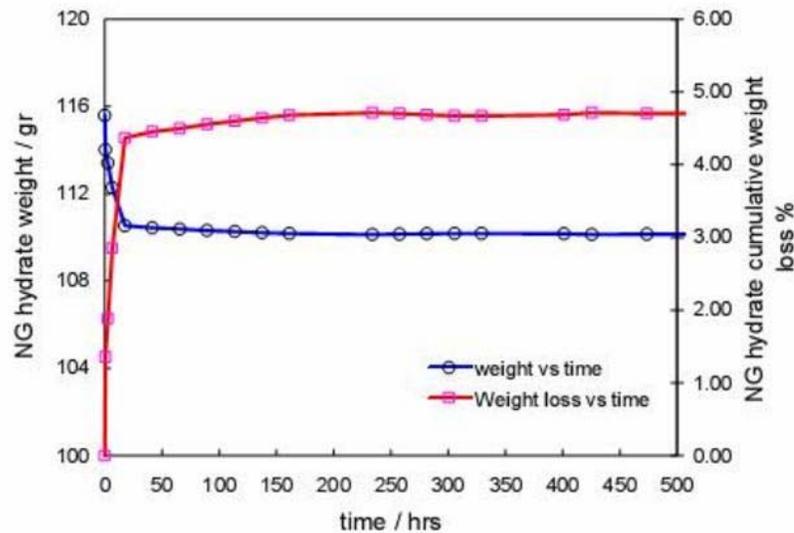


Fig.5 Stability of NG hydrate produced with 1 mass% TBAB aqueous solution versus time.