Formation and dissociation studies for optimizing the uptake of methane by methane hydrates

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Abstract

Characteristics such as temperature and pressure profiles for methane hydrate formation and dissociation in pure water, simulated seawater, and water–surfactant systems have been established. A hysteresis effect has been observed for repeated formation–dissociation cycles of the same methane–water system. In an attempt to maximize the uptake of methane during methane hydrate formation, the addition of sodium dodecyl sulfate provided methane uptake of over 97% of the theoretical maximum uptake. Additional surfactants were tested for their ability to enhance the uptake of methane for hydrate formation. Successful demonstration of efficient methane storage using hydrate formation enhanced by addition of surfactants could provide a safe, low-cost alternative method for storage of natural gas at remote locations.
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1. Introduction

Gas hydrates were first observed in the laboratory in 1810 [1]. It was not until nearly 150 years later that they were observed in nature. Hydrates can occur in permafrost, sediment where gas exists under moderate to high pressure and low temperatures, and offshore beneath deep water. Hydrates are a problem in the oil and gas production industry because they can form in the well or pipelines, thereby blocking the flow of fuel. Estimates by the US Geological Survey project that world hydrate deposits contain approximately 2×10^4 trillion m^3 of methane [2]. Estimates of methane hydrate deposits off the coast of the US is approximately 9×10^3 trillion m^3 of methane with an additional 17 trillion m^3 of methane in the permafrost on the north slope of Alaska [2]. Access to even a small percentage of this vast fuel resource would provide hundreds of years' worth of additional natural gas resources. Much research continues to

be performed on accessing the fuel in these deposits, with focuses ranging from mining techniques to use and conversion methods.

In addition to representing a vast amount of fuel resources that remain to be accessed, the physical characteristics of methane hydrates offer other interesting and potentially valuable alternatives to current methods for storage and access to methane fuel. Methane hydrates represent the maximum amount of methane gas that can be contained in water. In fact, previous studies have shown that the solubility of methane in water is a limiting factor for some chemical processing methods for conversion of methane [3,4]. The theoretical maximum uptake of methane as a hydrate is 180 volumes of methane at standard temperature and pressure (STP). In practice, laboratory experiments on natural systems have struggled to achieve even 30% of this theoretical maximum. One promising method for maximizing the uptake of methane by hydrate formation is the addition of surfactants to the system [5–7].

Some conventional methods of storing natural gas for future use include liquified natural gas (LNG), or pumping the gas into salt caverns or depleted gas reservoirs. The natural gas can then be accessed when needed by pumping it back out of the well. The main drawback to liquification of the gas is that the process is expensive and energy demanding, costing as much as 25% of the gas volume used in liquification and transport. A problem with storage of the gas in depleted wells is that the location of the wells is often not adjacent to where the gas is needed. The storage of natural gas in a hydrate structure may be a promising technology for those remote locations that do not have a used gas well in close proximity. In order for this option to be competitive, it must be shown that the hydrate is able to store large volumes of methane, and that the formation stability is appropriate for addressing safety concerns. It also must be a cost-effective technique in order to be a viable storage option. It has been stated that the ability to perform multiple cycles of hydrate formation–storage–dissociation and subsequent release of the gas may allow gas storage as methane hydrate to compete with the conventional methods of gas storage. On a cost-per-volume basis, figures of 4, 14, and 54 cycles per year would be required for gas hydrate storage to compete with LNG, salt caverns, and depleted reservoir, respectively, making gas hydrate storage particularly appropriate for frequent demands of stored gas rather than long term bulk storage [6].

Another proposed use of gas hydrates is in the maritime transportation of associated gases from offshore oil production sites, or to remote locations where pipeline transport is not practical [8–10]. Typically, these associated gases are flared, which is becoming an increasing concern from both an environmental and an economic standpoint. In fact, the ability to utilize these gases may dictate whether oil developments proceed because of the need to find economically feasible methods for disposal or use of the associated gas. Collection and transportation as a gas hydrate may be an effective method of using these gases.

It has been determined that hydrate formation in pure water–natural gas systems suffers from inadequate storage capacity and rate of formation to be competitive as a storage option, but the addition of a surfactant to the system provides many benefits [5–7]. Using surfactants leads to a 700-fold increase in the rate of formation, and the amount of methane absorbed approaches the theoretical limit (86% with sodium dodecyl sulfate (SDS)). Previous studies on the use of additives for inhibition of hydrate growth or prevention of agglomeration in the natural gas industry have determined that the mechanism of formation is altered by the presence of the additives [11–14]. These additives, such as ethylene glycol and electrolytes, alter the surface properties at the methane–water interface so that methane uptake may be more favorable. The physical characteristics of formation with surfactant force the hydrates outward toward the cell walls, exposing fresh surface at the water–gas interface [5–7]. These studies used SDS as the surfactant, at concentrations ranging from 0.240 to 0.284 kg/m^3.

While the addition of SDS has enhanced the formation characteristics of gas hydrate systems, it may be helpful to investigate the ability of other surfactants, or other experimental parameters for additional beneficial properties of hydrate formation and dissociation. This work will evaluate the storage capability of methane hydrates formed with a variety of surfactants, and will investigate formation and dissociation characteristics as well. It will also attempt to establish important parameters for maximizing the amount of methane that can be taken up as a hydrate, and elucidate other important parameters that affect the stability, formation, and dissociation of the methane hydrate to further evaluate its use as a viable storage methodology for natural gas usage.

2. Experimental

All experiments were conducted in a high-pressure view cell. The cell, diagrams of which are shown in Fig. 1, is constructed of 316 stainless steel with 6.35 cm (2.5 in.) o.d. and is 27.4 cm (11 in.) in length. The internal volume of the cell is approximately 40 ml. The cell is fitted with two machined endcaps, one of which contains a sapphire window to allow for observation of the contents of the cell using a CCD camera. The cell is fitted with ports to accommodate the fill gas inlet and reaction product outlet,

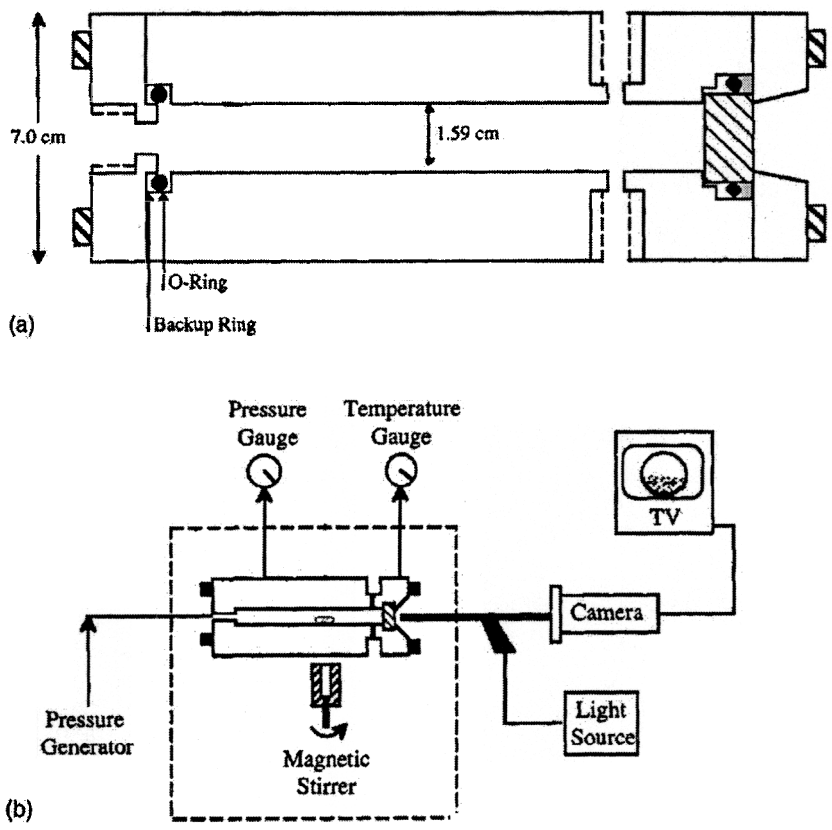

Fig. 1. (a) Diagram of the high-pressure view cell used in the hydrate formation studies. (b) Diagram of the entire experimental apparatus as used for formation and dissociation studies.

a pressure transducer to monitor the internal pressure of the gas inside the cell, and a thermocouple that terminates inside the cavity of the cell to monitor the temperature of the liquid–hydrate mixture. While the working pressure of the cell is rated at 220 MPa (32,000 psig), all experiments were conducted at 13.8 MPa (2000 psig) or less. The temperature of the cell is controlled by the flow of a glycol–water solution from an external circulating temperature bath through a coil of 0.64 cm (0.25 in.) copper tubing that is wrapped around the outside of the cell. Several layers of insulating material are wrapped around the cell to help maintain constant temperature.

2.1. General hydrate formation procedure

A typical experiment involves filling the cell with approximately 20 ml (±0.1 ml) of double-distilled water. A Teflon®-coated stir bar is also placed inside the cell. The endcaps are placed on the cell and tightened to specifications. An external magnetic stirrer is used to obtain a high degree of vortex mixing inside the cell. The cell is connected to the gas manifold and purged several times with methane. Following the purge procedure, the cell is charged with methane at pressures of 8.3–10.3 MPa (1200–1500 psig). Using the external circulating temperature bath, the temperature of the water in the cell is gradually lowered until formation of the methane hydrate is observed. After formation of the hydrate, the temperature of the cell is lowered to approximately −10 °C and held constant as the unabsorbed methane is released from the cell. The cell is then allowed to warm slowly to room temperature, which causes the hydrate to release its absorbed methane gas. The uptake of methane is determined based on the maximum pressure built up by the released methane inside the cell.

2.2. Multiple hydrate formations

Multiple hydrate formation experiments were conducted using the following solutions: 30 ml of distilled–deionized water, and 30 ml of simulated seawater (made by dissolving 26.8 g of sodium chloride and 5.3 g of magnesium chloride in 1 l of distilled–deionized water). The cell was connected to the reactor manifold and charged with methane as described above. The temperature of the cell was reduced to 5 °C and held constant until the methane hydrate formed. After formation of the methane hydrate, the temperature of the cell was increased to 15 °C. This increase in temperature forced the methane hydrate to dissociate, as observed through the cell's view port and by the return of the cell pressure to the initial pressure prior to hydrate formation. To reform the methane hydrate, the temperature of the cell was reduced to 5 °C. This formation–dissociation procedure was repeated several times.

2.3. Maximized methane uptake experiments

The experiments to determine maximum uptake of methane by the hydrate were conducted by adding 10 ml of the distilled–deionized water and surfactant mixture (SDS added at a concentration of 0.224 kg/m^3), adding the Teflon®-coated stir bar, and sealing the cell, all as described above. The cell was connected to a modified gas manifold containing two single-stage high-pressure regulators in series and was purged several times with methane. Following the last purge, the valves connecting the cell to the manifold remained opened, and the regulators were set to deliver methane at 9.7 MPa (1400 psig). This allowed the experiment to proceed at a constant head pressure of 9.7 MPa (1400 psig) even as methane was taken up during the formation of the hydrate. Again, an external magnetic stirrer was used to obtain a high

degree of vortex mixing inside the cell. Temperature of the water in the cell was lowered until formation of the methane hydrate was observed. Following formation of the hydrate, the temperature of the cell was lowered to approximately −10 °C to minimize the dissociation of the hydrate in the subsequent depressurization step. After several hours at −10 °C, the cell was isolated from the manifold and the unabsorbed methane was released, bringing the head pressure to a minimum. After release of the head pressure, the cell was re-sealed and warmed to room temperature. Methane uptake was determined based on the amount of pressure that built up inside the cell due to outgassing of the hydrate.

2.4. Performance comparison among different surfactants

Using conditions of continuous stirring and constant methane headspace pressure, the following surfactants were tested to determine the magnitude of increasing the methane uptake: dodecyl trimethyl ammonium chloride, dodecylamine, dodecylamine HCl, sodium lauric acid, sodium oleate, Superfloc 16®, Superfloc 84®. To maintain consistency for the comparison studies, all surfactants were added at the same concentration range of 0.200–0.230 kg/m^3. It is important to note that all surfactants used in this study were compared at the same concentration level. This concentration level corresponds to the critical micellar concentration (CMC) of SDS under temperature and pressure conditions during hydrate formation, as shown in previous works [5,7]. A volume of 10.0 ml of double-distilled water and surfactant was added to the system. Procedures identical to the maximum uptake experiments with SDS were followed. The amount of methane absorbed by each system was determined and the results compared based on percentage of theoretical maximum uptake for methane hydrate formations.

3. Results and discussion

3.1. Hydrate formation and dissociation

Our first experiments were to study the formation and dissociation of methane hydrates in binary (methane–water) systems. Fig. 2 shows a typical pressure–temperature profile for this process. During the initial stages of cooling, the pressure inside the cell mirrors that which would be predicted from the

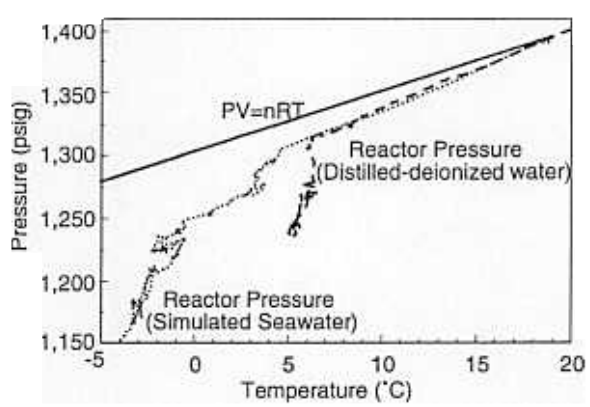

Fig. 2. Pressure–temperature profile for the formation of a methane hydrate from double-distilled water and simulated seawater.

ideal gas law. However, as the hydrate begins to form, a sharp decrease in the cell pressure is observed, indicating that methane is being absorbed from the headspace. Formation begins at a temperature of about 5.5 °C for the distilled–deionized water system, which is appropriate for the pressure and temperature conditions of hydrate formation predicted by the hydrate equilibrium stability diagram where hydrate exists at or below 12 °C at this pressure [15]. Addition of salts to the system, in the form of NaCl and $MgCl_2$ at a net salt concentration of 3.2%, lowers the formation temperature by approximately 2 °C. Visually, the initial hydrate formation appears as ice crystals suspended in the water. As formation of the hydrate continues, the hydrate begins to agglomerate, forming a slush. As additional hydrate is formed inside the cell, the slush is transformed into a solid mass. Even after formation of the solid mass, over time the hydrate incorporates more of the free methane into the crystal structure. Upon warming, the hydrate dissociates with evolution of methane.

3.2. Multiple hydrate formations

We were interested in investigating the potential existence of a "memory effect" for multiple formations of methane hydrates. We have observed in our laboratory that after the initial formation of a hydrate with a given reactant system, and dissociation of the hydrate to release methane back into the headspace, subsequently decreasing the temperature can reform the methane hydrate. Moreover, the second formation of hydrate occurs more quickly, and seemingly at slightly higher temperatures, than the original formation. This is shown in Fig. 3. Note that the elapsed time required for hydrate formation to begin, as determined by the initial steep reduction in pressure of the system, is notably faster during the second formation (1 h as opposed to 4 h). The third and forth formation of the hydrate occur at times slightly less than the second formation. This decrease in formation time may be due to microscopic hydrate crystals that are still present in the solution, even at 15 °C. These crystals would act as seeds for future formations [16]. The formation of methane hydrates in simulated seawater followed the same physical changes as that observed for hydrate formed in pure water. In investigating this phenomenon further, we found that when the hydrate is dissociated by warming to slightly higher temperatures (25 °C), this memory effect is not

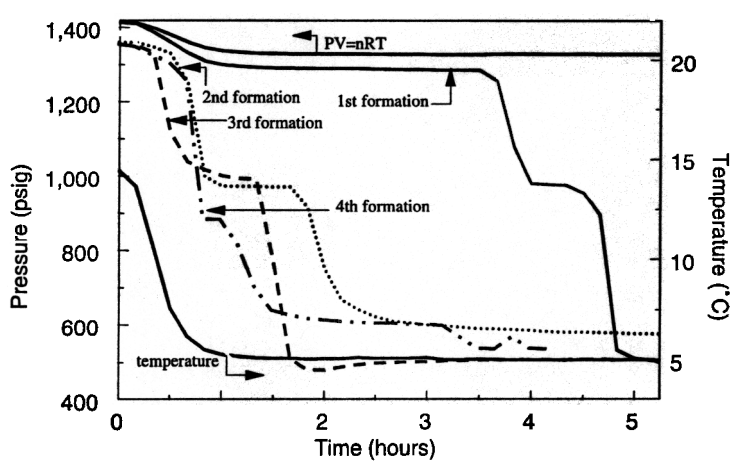

Fig. 3. Temperature and pressure data as a function of time for repeated formations of methane hydrates using the same binary (methane–water) reactants.

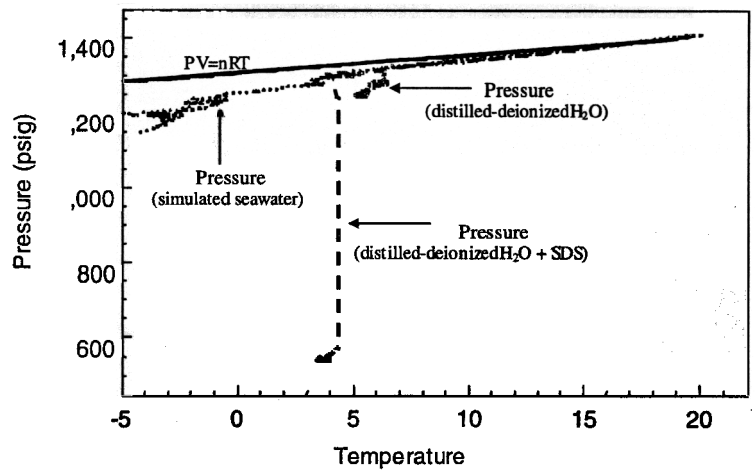

Fig. 4. Pressure as a function of temperature for the formation of a methane hydrate in double-distilled water, simulated seawater, and water with 0.224 kg/m^3 SDS added.

observed (data not shown). The higher temperature may dissociate even the microscopic crystals that could be responsible for the effect.

3.3. Maximizing methane uptake

Formation of methane hydrates in double-distilled water, simulated seawater and double-distilled with a surfactant added is shown in Fig. 4. The data for the double-distilled water and simulated seawater formations is identical to Fig. 2, except for the scale required to accommodate the uptake by the water–surfactant system. As is shown in the figure, methane uptake by both double-distilled and simulated seawater is ~1.4 MPa (200 psig). Also of note is that the onset of hydrate formation in the simulated seawater occurs approximately 2 °C lower than that of the double-distilled water. When surfactant is added to the water, methane uptake by the hydrate increases to ~5.6 MPa (800 psig), which is over a four-fold increase compared to hydrates formed without surfactant. The increase observed in the uptake of methane when the surfactant is present can be explained by examining the processes that occur during hydrate formation. Since methane hydrate is less dense than water, hydrates form on the surface of the water. Even with stirring, enough hydrate will form to essentially cover the water–gas interface with a thin layer of methane hydrate. This severely limits the absorption of additional methane, as it must diffuse through the hydrate layer in order to encounter free water. When the surfactant is present, the hydrate formed is forced to the edges of the surface of the stainless steel cell, allowing significantly more contact between the methane and the surface of the free water. Access to free water allows the concentration of methane in the water to increase continuously, enhancing the amount of hydrate formation.

In order to determine the maximum amount of methane that the water–surfactant system could have taken up during hydrate formation, we formed methane hydrate in the water–surfactant system with a constant supply of methane in the headspace. The results are shown in Fig. 5. During this experiment, the hydrate was formed under a constant head pressure of 9.7 MPa (1400 psig), with formation beginning at approximately 3.5 °C. Once uptake of methane appeared to have ended, the temperature of the cell

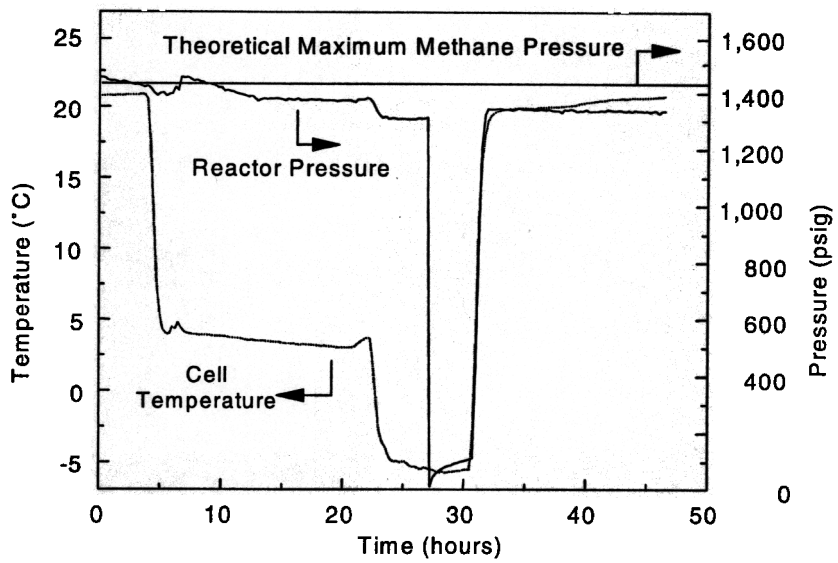

Fig. 5. Pressure and temperature profile as a function of time for the formation of a methane hydrate with 0.224 kg/m^3 surfactant added, with a constant headspace pressure of 9.7 MPa (1400 psig).

was further decreased to ≤ -5 °C, in order to preserve the hydrate during the subsequent depressurization of the unabsorbed methane inside the cell. Following depressurization at ≤ -5 °C, the cell was warmed to room temperature, accompanied by an increase in cell pressure due to methane outgassing from the melting hydrate. As Fig. 5 shows, the cell pressure reached approximately 1350 psig. Our calculations indicate that the hydrate formed by this method contained over 96% of the maximum theoretical amount of methane.

For percent uptake calculations, the maximum theoretical uptake for the methane hydrates was calculated, assuming that the hydrates being formed in our experiments were type I structures. The theoretical ratio of 5.75 mol water to 1 mol methane per volume of methane hydrate predicts that from a 15 ml volume (0.833 mol) of water, 0.145 mol of methane can be absorbed. Next, the experimental amount of methane absorbed was calculated. Using the final pressure that is reached inside the cell after outgassing of the hydrate, the amount of methane that was absorbed was calculated. This value must be corrected for deviation from ideal conditions using the compressibility factor (z), which ranges from 0.8 to 1, depending on experimental conditions [17]. This compressibility factor is used to convert the experimental pressure to an ideal pressure, because experimental conditions such as internal pressure make it seem like less gas was released from the hydrate. Without taking this compressibility into account, the calculated results would be biased low, as more methane would have been taken up than the experimental pressures portray.

Based on the results of the uptake studies using SDS, it was determined that maximum uptake was demonstrated under conditions where a constant methane headspace pressure was used, and the reaction mixture was stirred. Therefore, subsequent methane hydrate formation experiments to evaluate the effectiveness of different surfactants were performed using constant headspace pressure and stirring. Under these conditions, the following surfactants were evaluated: dodecyl trimethyl ammonium chloride, dodecylamine, dodecylamine HCl, sodium lauric acid, sodium oleate, Superfloc 16®, and Superfloc 84®, all added at similar concentrations in the range of 0.205–0.220 kg/m^3. The results of the uptake evaluations

Table 1
Surfactants tested for ability to maximize the uptake of methane in methane hydrate formations

Surfactant	Pressure following dissociation (psig)	Compressibility factor (z)[a]	Percent uptake
Dodecyl trimethyl ammonium chloride	140	0.9824	13.9
Sodium dodecyl sulfate	1440	0.8206	97.3
Dodecylamine	100	0.9877	9.9
Dodecylamine HCl	120	0.9850	11.9
Sodium lauric acid	715	0.9058	77.4
Sodium oleate	655	0.9139	70.5
Superfloc 16®	195	0.9756	19.6
Superfloc 84®	200	0.9754	20.1

[a] Values for compressibility factor taken from [17].

are shown in Table 1. As the data demonstrates, the largest amount of methane absorbed in our study was for the SDS–water system. Uptake for this system surpassed 97% of the theoretical maximum uptake of methane during methane hydrate formation.

4. Conclusions

Methane hydrates have been produced using a high-pressure view cell in our laboratory. The temperature and pressure profiles for hydrate formation for several different starting pressures of methane, as well as different aqueous media, have been determined. It appears that maximum methane uptake by any given system occurs when the reactants are continuously stirred, and when the methane pressure to the system is maintained during uptake and hydrate formation. We have observed that subsequent formations of methane hydrate occur more rapidly than the initial formation of hydrate with a given reactant system. This observation may provide a synergistic advantage when determining the number of cycles required for gas hydrate storage to compete on a cost basis with conventional gas storage methods. The addition of the surfactant SDS increases the uptake of methane during formation of the hydrate. The amount of methane uptake obtained using the surfactant has reached greater than 97% of the theoretical limit. Of the suite of surfactants studied, it appears that SDS may be the most appropriate surfactant to use for maximizing methane uptake for storage of methane as methane hydrate.

5. Disclaimer

Reference in this report to any specific commercial product, process, or service is to facilitate understanding and does not necessarily imply its endorsement or favoring by the US Department of Energy.

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