Crystal Growth Behavior of Clathrate Hydrate in Flowing Liquid Water Saturated with Natural Gas

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ABSTRACT

This paper reports the visual observation on the growth and formation of clathrate hydrate crystals in the stream of flowing liquid water presaturated with simulated natural gas: methane + ethane + propane gas mixture. The composition of the methane + ethane + propane gas mixtures were 90:7:3 and 98.5:1.4:0.1 in molar ratio. The morphology (the geometric configuration of crystal such as crystal size or shape) of natural gas hydrate crystals grown in liquid water stream varied depending on the system's subcooling temperature. The subcooling temperature is defined as the difference between equilibrium temperature of the hydrate and experimental temperature. At subcooling temperature larger than 6.0 K, the crystals grew from the porous pipe surface into the bulk of liquid water in both gas mixture systems. At a lower subcooling condition, polygonal flat plate crystals were observed. At ~9.0 K to ~12.0 K, the crystal morphology enters the transition phase, where the polygonal flat plate crystals started to change into dendritic crystals with increase in subcooling. When the subcooling temperature is greater than 12.0 K, polygonal crystals were completely replaced by the dendritic crystals.

These conclusions enable us to estimate the hydrate morphologies corresponding to the marine sediment condition. The natural gas hydrate would grow and fill up the pore spaces, which later affect the geomechanical stability of the marine sediment.

INTRODUCTION

Clathrate hydrates are crystalline solid that are composed of hydrogen-bonded water molecules called "host" and other molecule called "guest" are enclosed in the cages of hydrogen-bonded water molecules. There are three major structures of clathrate hydrate; structure I, structure II and structure H which varies depending on the guest substances[1]. Clathrate hydrates have several unique properties such as high gas storage capacity, guest substance selectivity and large formation/dissociation heat. Therefore, hydrate-based technologies such as transportation and storage of natural gas[2] and hydrogen[3,4], sequestration of carbon dioxide[5] and development of highly efficient heat pump/refrigeration systems[6] utilizing the heat for hydrate formation/dissociation have been proposed. Various clathrate hydrates are being investigated for the development of these hydrate-based technologies.

In the deep marine sediments, natural gas hydrates are formed at low temperature and high pressure conditions. Natural gas hydrates grow in the pore space of sedimentary particles. Existence of natural gas hydrate could affect the mechanical properties of marine sediments[7-9]. The understanding on the mechanism of formation and growth of natural gas hydrates is important not only to deal with industrial issues. Previous studies[9-15] have revealed that the crystal morphology (the geometric configuration of crystal such as crystal size or shape) of hydrate crystals growing in liquid water, presaturated with guest substances, depended on the strength of driving force. Watanabe et al.[14] reported the crystal growth behavior and crystal morphologies of natural gas hydrate in batch system. However, the elucidation on morphology of hydrate crystals grown into liquid water presaturated with guest gas is fragmentary due to the limited number of previous studies. Aifaa et al.[16] observed formation and growth of methane hydrate crystals in the system with continuous supply of methane. They reported that the particle size of methane hydrate observed in methane continuous supply system is larger than that in batch system. Although there are differences between crystal structure of natural gas hydrate and crystal structure of methane hydrate, guest gas' continuous supply has effects for crystal growth of natural gas hydrates.

Since natural gases are unlimitedly provided from natural gas field in the deep marine sediment, we have to investigate crystal growth behavior in the continuous guest supply system. The concentration of natural gas in the bulk water was kept constant by the flowing liquid water in the continuous guest supply system. The crystal morphology and crystal growth behavior of natural gas hydrate in the continuous guest supply system may be different from those in the batch system. Therefore, we conducted experiments to reveal the crystal growth behavior of natural gas hydrate in a system with continuous natural gas supply. The results were analyzed to understand how mass transfer of guest molecules affects the crystal morphology. The continuous supply of dissolved natural gas tested in this study is relevant to the hydrate growth condition in the marine sediment as the abundant amount of natural gas would serve as unlimited supply for hydrate crystal growth. The effect of existence of natural gas hydrate on deep marine sediment will be discussed based on the results observed in this study.

EXPERIMENTAL PROCEDURE

The sample fluids used in the experiment to form a hydrate were liquid water, which was distilled and deionized beforehand using laboratory water distiller (Yamato Scientific Co., Ltd., model WG222), and two gas mixtures of methane, ethane and propane of following compositions in molar ratio: (1) 90% methane, 7% ethane, 3% propane; (2) 98.5% methane, 1.4% ethane, 0.1 % propane. The experimental setup that was used for the hydrate crystal
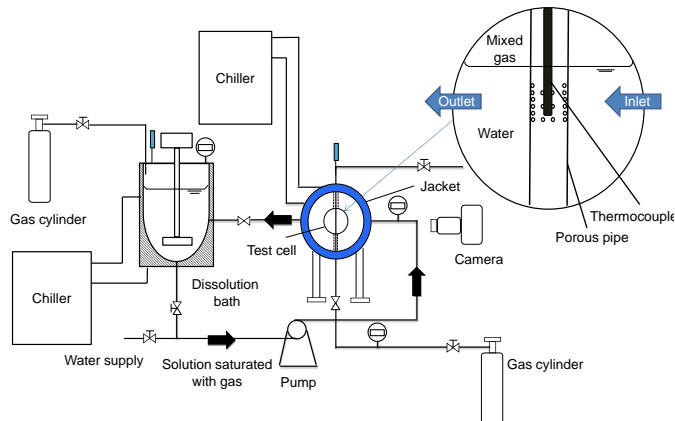

Figure 1 Schematic diagram of the experimental apparatus.
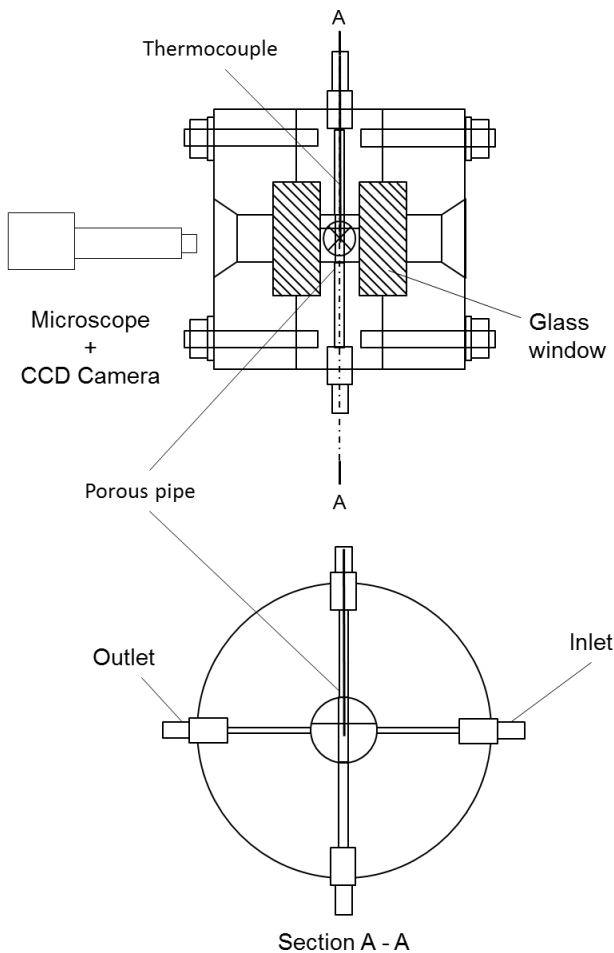

Figure 2. Cross-section of the hydrate formation reactor.

growth study is presented schematically in Figure 1 while Figure 2 illustrates the close up image of the hydrate formation reactor. The experimental setup mainly consists of a 206 cm^3 capacity dissolution bath which is equipped with a stirring device, a plunger pump and a hydrate formation reactor. These parts were connected to form a cycle as shown in Figure 1 and mixed gas saturated aqueous solution is circulated in this cycle. The hydrate formation reactor was made of a stainless steel cylinder with a pair of flange-type glass windows. The inner space of the reactor was 25 mm in diameter and 20 mm in axial length. The temperature inside the reactor, experimental temperature (T_{ex}), was controlled by circulating temperature-controlled ethylene glycol solution through a brass jacket covering the reactor while the pressure inside the reactor, P, was controlled by supplying the sample gas from a gas cylinder through a pressure-regulating valve. A porous pipe was inserted inside the reactor and the sample gas was injected into the pipe in order to enhance the hydrate crystal nucleation as shown in Figure 3. The purpose of the porous pipe was to form the hydrate and maintain the growth of crystal in flowing water. The reactor was the test section where the hydrate is formed and the observation was conducted. A thermocouple (ϕ1.0 mm, Ichimura Metal Co., Ltd.) was inserted into the porous pipe and T_{ex} was measured within the ±0.2 K uncertainty. Meanwhile, P was measured by a strain-gauge pressure transducer within the uncertainty of ±0.05 MPa. The temperature and pressure inside the dissolution bath were also measured using these instruments.

The necessary quantity of deionized water was injected into the system (~220 cm^3) and then simulated natural gas was injected in excess. The air in the experiment system was replaced with the mixed gas by repeating the pressurization of the system with mixed gas and evacuating it from the system. P was then set at a prescribed level. The stirrer in the dissolution bath was set on and the mixture in the system was maintained at constant conditions for 1-2 days to let the natural gas saturated in the water. Temperature in the dissolution bath was set 1-2 K higher than Equilibrium Temperature (T_{eq}) of mixed gas hydrate corresponding to P, while the temperature in the reactor, T_{ex} was first set to about 264 K to form hydrate (and also ice) and then raised to a temperature 3-4 K higher than T_{eq}.
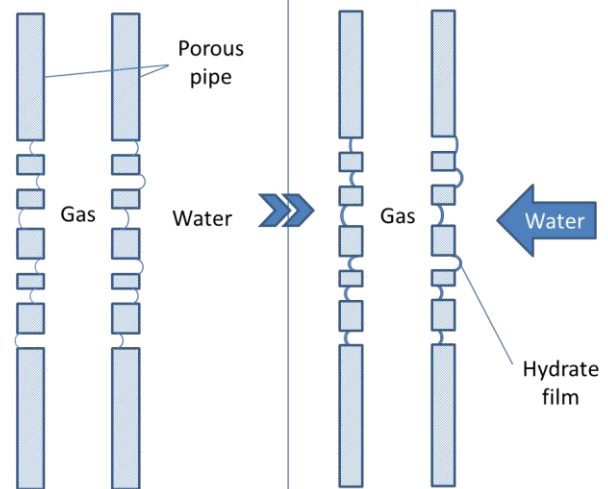

Figure 3 Gas-liquid interface formed by the porous pipe.

These were done to first avoid the hydrate formation in the dissolution bath and second, exert the memory effect to the mixture in the reactor as it can shorten the induction time for the hydrate reformation. After the dissociation of the formed hydrate was visually confirmed, T_{ex} was then reduced to a temperature lower than T_{eq} by about 4-12 K in order to observe the hydrate crystals formation and growth in the reactor. The plunger pump was started up when the hydrate formation in the reactor was visually confirmed and the saturated mixed gas aqueous solution was circulated throughout the system with the flow rate about 1.5 cm³/min.

The formation and growth of hydrate crystals were observed and recorded per one minute using CMOS camera (Fortissimo Corp., model CMOS130-USB2) and a microscope (Edmund Optics Co., Ltd.). The system's subcooling temperature ΔT_{sub} is defined as the index of the driving force for the crystal growth which is used throughout this study. ΔT_{sub} is the difference between the system temperature T_{ex} and the equilibrium temperature T_{eq} corresponds to the prescribed pressure P. T_{eq} was calculated with CSMGem[17].

RESULT AND DISCUSSION

Crystal growth behavior of Hydrate in Flowing Liquid Water Saturated with Methane + Ethane + Propane Gas Mixture.

The experiments were conducted at several degrees of system subcooling in the range from 4 K to 13 K. The nucleation of natural gas hydrate crystals initially occurred at the random point of interface between mixed gas and liquid water. Then a hydrate film grew into intervene between the mixed gas and liquid water. Subsequently the hydrate crystals grew in liquid water phase. In this system, these crystals had two patterns of
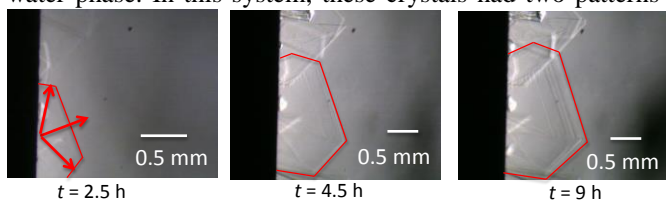

Figure 4 typical sequence of hydrate formation and growth observed in the liquid water and methane + ethane + propane gas mixture with composition of 98.5:1.4.0.1, ΔT_{sub} = 6.4 K. Arrows in this figure indicate typical growth direction of polygonal crystals.
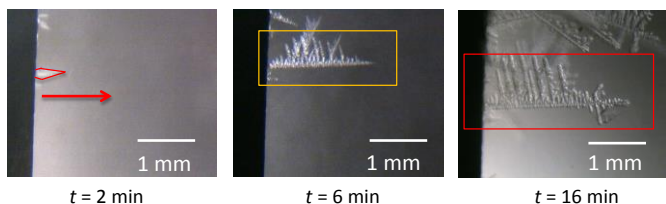

Figure 5 typical sequence of hydrate formation and growth observed in the liquid water and methane + ethane + propane gas mixture with composition of 98.5:1.4.0.1, ΔT_{sub} = 9.1 K. Arrow in this figure indicates typical growth direction of dendritic crystals.

growth. One of them was that the hydrate crystals grew directly from the porous pipe surface. The hydrate crystals grew from the hydrate film into liquid water bulk in almost all previous studies. However, hydrate crystals in this system grew directly from the surface of the porous pipe because the pipe creates a mixed gas-liquid water interface which is a preferable condition for nucleation of hydrate crystals. The other one was that the floating crystals formed in the liquid water bulk which grew after attached to the pipe or to the nearby crystals. These processes of hydrate formation and growth were commonly observed in all experimental systems. Figure 4 and 5 show a typical sequence of hydrate formation and growth observed in the liquid water and methane + ethane + propane gas mixture with composition of 98.5:1.4.0.1 and ΔT_{sub} = 6.4 K, 9.1 K respectively. The hydrate crystals nucleate at the surface of the porous pipe and then grew into the flowing water. The size of hydrate crystals increased with the time lapse in both subcooling conditions. However, the morphology of natural gas hydrate vary depending on the subcooling. At ΔT_{sub} = 8.9 K, we observed that hydrate crystals at the mixed gas-liquid water interface grew into a thin hydrate film that covered interface within several seconds. After the complete coverage of interface, polygonal flat plate hydrate crystals grew in the water stream. 9 hours after the formation of hydrate, the crystals had grown to approximately 2.1 mm in axial length. At ΔT_{sub} = 11.4 K, the interface between mixed gas and liquid water was similarly covered with in several seconds. The needlelike crystal grew toward the flow and then also other needlelike crystals grew from sides of first one. Eventually, the dendritic crystals were observed in the liquid water phase. Only 16 minutes after the formation of hydrate, the longest side of dendritic crystal reached approximately 2.6 mm.

The Comparison between Results of Continuous Guest Supply System and Those of Batch System.

Comparison of crystals observed in the present study with previous observations conducted by Watanabe et al.[14] and Kodama & Ohmura[15] were shown in Figure 6. Sample gas used were methane + ethane + propane mixture gas with composition of 98.5:1.4.0.1 and 90:7:3 and arranged using ΔT_{sub}.

The general tendency in crystal morphology that changes from polygonal to dendritic with increase in subcooling is observed in all systems. When the subcooling temperature is larger than 12 K, only dendritic crystals grew from the surface of the porous pipe into flowing water. At subcooling temperature approximately 9.0 K to 12.0 K, the crystal morphology enters the transition phase, where the polygonal flat plate crystals and dendritic crystals coexisted together. Some of them grew into liquid water as needle like crystals. Afterwards flat plate crystals were generated at the side of needlelike crystals. When the subcooling temperature was lower than 9 K, polygonal flat plate crystals were observed. At this point, no new findings on crystal shape change due to the increase in ΔT_{sub} which represents the driving force for crystal growth was obtained as in the previous literatures[14,15] In addition, hydrate crystals formed in continuous supply system show no noticeable difference with the previous studies in term of hydrate crystals shape. With regard to the limit condition for

crystal growth, when subcooling temperature was below 6.0 K, there was no crystal growth at liquid water phase in batch systems. On the other hand, hydrate crystal growth was observed in the continuous guest supply system, when the subcooling temperature is lower than 6.0 K. This difference on the limit condition of crystal growth is ascribed to retention of the driving force for the crystal growth by continuous supplying of guest substances. Based on these results, we can predict existence of natural gas hydrate in the nature more precisely. Natural gas hydrates may exist in the area that was previously considered to be absent.

In terms of crystal growth time, the crystal growth into liquid water continue at most 1 hour in the batch system[14,15]. However, the hydrate crystals kept growing for over several hours in the continuous guest supply system. As the clathrate hydrate grew, the concentration of guest substances in the water phase gradually decreased in the batch system[14,15]. As a result, quantity of guest substances were not enough for crystal growth. In the continuous guest supply system, supply of guest saturated water prevented the decrease in concentration of guest substances in the bulk water phase. Consequently, the crystal growth time is longer in the continuous guest supply system.

The marine sediments where natural gas hydrates exist are mainly composed of sands. Since the particle size of sands is about several tens of μm to a few mm, the pore spaces of marine sediments are several millimeter at most. The hydrate crystals grown in this study are large enough to fill the pore space in the marine sediments. In addition, the crystal growth time in the nature would continue much longer than that in this study. This suggests that natural gas hydrates affect the geomechanical property of marine sediments by growing and filling the pore spaces.

CONCLUSION

Visual observations on the clathrate hydrate crystals formation and growth in flowing liquid water presaturated with natural gas were conducted. The composition of the methane + ethane + propane gas mixtures were 90:7:3 and 98.5:1.4:0.1 in molar ratio. The morphology of natural gas hydrate crystals varied depending on subcooling. At subcooling temperature larger than 6.0 K, the crystals grew from the porous pipe surface into the bulk of liquid water in both of the gas mixture systems. At a lower subcooling condition, polygonal flat plate crystals were observed. At ~9.0 K to ~12.0 K, the crystal morphology enters the transition phase, where the polygonal flat plate crystals started to change into dendritic crystals with increase in subcooling. When the subcooling temperature is greater than 12.0 K, polygonal crystals were completely replaced by the dendritic crystals. The hydrate crystals observed in this study have the same characterisitics of crystal morphology with hydrate crystals observed in the previous studies. However, crystals formed in flowing liquid water grew longer than that in the quiescent system. That is because the concentration of natural gas was kept for longer time by the continuous supply of water presaturated with natural gas. These conclusions enable us to estimate the hydrate morphologies corresponding to the marine sediment condition. The natural gas hydrate would grow and fill up the pore spaces, which later would affect the geomechanical stability of the marine sediments.
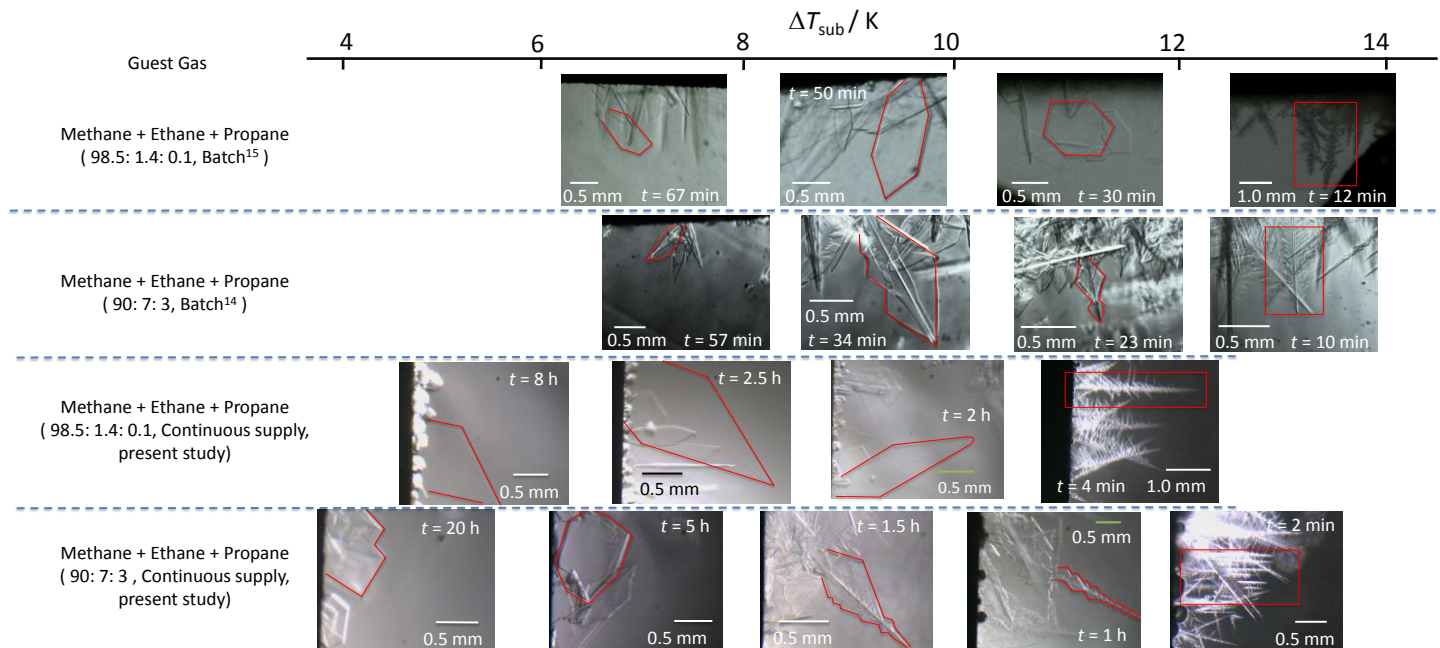

Figure 6 Variation in hydrate crystal morphology depending on ΔT_{sub}

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