# EXPERIMENTAL STUDY OF ENHANCED GAS RECOVERY FROM GAS HYDRATE BEARING SEDIMENTS BY INHIBITOR AND STEAM INJECTION METHODS

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### ABSTRACT

The inhibitor and steam injection methods have been examined using a laboratory-prepared methane hydrate bearing sediment. New experimental apparatuses have been designed and constructed. In the case of inhibitor injection, the measurement of gas production vs. time suggested that the inhibitor increased dissociation rate. Core temperature decreased upon the inhibitor injection, in contrast to that in the case of pure water injection. The observed pressure differentials between the inlet and outlet of the core sample suggest that the inhibitor effectively prevented the hydrate reformation within the dissociation coupled. In the case of steam injection coupled with depressurization, it can be seen that the effect of steam (or hot water) injection was clear in the later stage of dissociation, compared with that in the case of depressurization alone. The inner (core) temperature change indicates that the coupling of the center of the sample. However, it starts from an upstream region and continues downstream steadily in the case of steam (hot water) injection alone.

Keywords: natural gas, hydrate, exploitation, core sample, inhibitor, steam, dissociation

## INTRODUCTION

Owing to recent seismic exploration and geological research, it is widely known that natural gas hydrates exist in geological formations, constituting a potentially large natural gas resource for the future [1-7]. To make the recovery of natural gas from hydrates commercially viable,

hydrates must be dissociated in-situ. The inhibitor injection method is thought to be an effective method of forcing gas hydrate dissociation, apart from depressurization and thermal stimulation. However, there is only limited information on dissociation kinetics in the presence of hydrate inhibitors, although substantial phase equilibrium

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data are available [8-10]. Meanwhile, the steam injection method is practical for heavy oil recovery from oil sand and is recognized to be commercially viable [11-15].

In this study, the inhibitor and steam injection methods for methane hydrate (MH) bearing sediments have been examined and discussed. New experimental apparatuses have been designed and constructed. Using these apparatuses, inhibitor and steam were successfully injected into artificial methane hydrate bearing sediments that were simulated on a laboratory scale.

#### EXPERIMENTAL

### Inhibitor injection

The schematic of the experimental setup is shown in Figure 1. It was equipped with a core holder and a custom-designed temperature control system. An artificial MH core sample was wrapped with a flexible rubber sleeve and pressurized with fluid to simulate an in-situ formation pressure of 15 MPa. A thermal jacket enables temperature control from -50 °C to 100 °C. The jacket was divided into 7 sections, with each section employing a 3-way valve to select the cooling or heating medium. This system ensured that the thermal gradient of fluid adjacent to the core was very close to that of the core sample itself. In other words, the heat flow through the core sample can be considered essentially one-dimensional, neglecting radial heat loss. The core sample was 50 mm in diameter and 500 mm in length. Gas and liquid can be injected into the core sample at specified pressures, temperatures and flow rates. The MH core samples used in this work were laboratory-prepared artificial samples. An artificial MH bearing sediment was prepared using Toyoura sand, which is mainly composed of SiO<sub>2</sub>, and the average grain diameter is approximately 200 µm. An artificial MH bearing sediment had a low porosity of approximately 0.37 and a MH saturation within approximately 40-45 % [16, 17]. The T-P conditions were set to the MH equilibrium conditions (~13 °C, ~10 MPa) to stand by for gas hydrate dissociation. An aqueous methanol (MeOH) solution (10 wt %), NaCl solution (3 wt%) or pure water was injected into the MH core sample to initiate dissociation at a given temperature (20 °C or 40 °C) and a flow rate of 5 ml/min. During the dissociation, the core temperatures within the upstream and downstream portions of the sample should vary and a temperature gradient should be established. Accordingly, the temperature along each section of the outer jacket was controlled to correspond to the localized core temperature. The amount of gas produced was determined, and the temperatures of the fluid at the inlet and outlet were measured. The inner temperatures of the core were measured by 5 thermocouples located 50 mm, 150 mm, 250 mm, 350 mm and 450 mm from the top of the core. Also, the outer temperatures of the core (temperatures of high-pressure fluid around the core) were measured by 5 thermocouples located at the same axial positions to the inner thermocouples



Figure 1 Schematic illustration of experimental apparatus equipped with long core holder for inhibitor injection.

#### **Steam injection**

The schematic of the experimental apparatus used for steam injection is shown in Figure 2. This apparatus was designed to make steam injection for the MH core sample possible. The steam generator can inject steam at a maximum temperature of 300 °C and a maximum rate of 10 ml/min in liquid conversion. The high-pressure reactor is column-shaped and constructed with an outer tube made of stainless steel (SUS 316) and an inner tube made of zirconium. It is designed to minimize lengthwise thermal conduction through the tubes to achieve accurate thermal control. It also has jackets for thermal control from 0 °C to 300 °C. The jackets consist of 10 pieces from the top to the bottom of the reactor, and each piece has heaters to control a wide temperature range. The artificial MH bearing sediment had a diameter of 50 mm and a length of 500 mm. It had a low porosity of approximately 0.37 and a MH saturation of approximately 40 % [16, 17]. The T-P conditions were set to the MH equilibrium conditions (~13 °C, ~10 MPa) to stand by for dissociation reaction. Steam was prepared at 250 °C. Outlet pressure was decreased to a given pressure using a backpressure regulator. Just after the depressurization, steam was injected into the MH core. Injection rate was set at 5 ml/min in liquid conversion. During dissociation, core temperatures within the upstream and downstream portions of the sample should vary and a temperature gradient should be established. Accordingly, the temperature along each section of the outer jacket was controlled to correspond to the localized core temperature. The amount of gas produced was determined and the temperatures of the fluid at the inlet and outlet were measured. The inner temperatures of the core were measured by 10 thermocouples located 25 mm, 75 mm, 125 mm, 175 mm, 225 mm, 275 mm, 325 mm, 375 mm, 425 mm and 475 mm from the top of the core. Also, the temperatures of the outer jackets were measured by 10 thermocouples located at same axial positions to the inner thermocouples.

## **RESULTS AND DISCUSSION**

#### **Inhibitor injection**

a) Gas production behavior during dissociation Pure water, aqueous MeOH solution (10 wt%) and aqueous NaCl solution (3 wt%) were injected into the artificial MH bearing sediments. The temperature of injected fluid was set at 40 °C in each case. A plot of cumulative gas production vs. time is shown in Figure 3. The total gas production behavior can be divided into three stages. The first was the replacement of the remaining gas with the injected solution in the pore space, the second was the gas production by hydrate dissociation and the third was steady state and gas release by resetting atmospheric pressure. It is clear that the cumulative gas productions of MeOH and NaCl proceeded more rapidly than those in the case of pure water, suggesting that these solutions are more effective for dissociation than warm water alone. Accordingly, in case of MeOH and NaCl injections, gas production terminated earlier than that in the case of pure water injection.



Figure 2 Schematic illustration of experimental apparatus equipped with steam generator for steam injection.

## b) Temperature profile

The temperature profile during dissociation by the injection of pure water (MeOH 0 wt %) is shown in Figure 4. The data indicate that outer temperatures closely follow the interior core temperature changes, while showing similar trends. This result suggests that the system for controlling thermal gradients works well; therefore, it is reasonable to consider that one-dimensional heat flow is essentially achieved (neglecting radial heat loss). As shown in Figure 4, inlet water temperature increased to 40 °C just after the start of the experiment, dissociating the MH in the upstream portion of the core sample. When the MH in the area around the 50 mm thermocouple was completely dissociated, the temperature at 50 mm began to increase. MH dissociation progressed from upstream to downstream, with temperature increases at the 150 mm thermocouple, and subsequently at the 250 mm thermocouple. The temperatures at downstream successive thermocouples increased continuously until the whole system stabilized near 40 °C, indicating that the all MH was completely dissociated. It is also clear that as dissociation progressed within the sample, the upstream core temperatures were equal to the initial fluid temperature and that the downstream temperatures were maintained at the initial (equilibrium) temperature. This sequence suggests a steady progress from the inlet to the outlet.

An aqueous methanol solution (MeOH 10 wt%) was injected into an artificial MH bearing sediment at 40 °C. The core temperature data obtained are shown in Figure 5. As was the case with pure water injection, the outer (jacket) temperature closely tracked changes tin core (inner) temperature, with both temperatures showing similar trends. The temperature increases observed were also similar to those observed in the case of pure water. That is, when the MH in the vicinity of the 50 mm thermocouple was completely dissociated, the temperature at 50 mm began to increase, followed by increase in the temperature at 150 mm and subsequently at 250 mm, and so on. The increases in downstream temperatures progressed continuously until the whole system stabilized at 40 °C, indicating that all the MH in the sample was completely dissociated. Note that downstream temperatures were not maintained at the initial temperature, but decreased from the initial temperature to a certain temperature just after the dissociation was started.

After reaching the minimum temperature, it slowly increased. The minimum temperatures were approximately 8-9 °C. In the case of NaCl injection, a temperature-changing phenomenon was also observed as shown in Figure 6. It can be considered that this temperature-changing phenomenon downstream was caused by the coupling effect of the change in equilibrium temperature and the change in injected inhibitor concentration as discussed in our previous work [18]. It was speculated that this phenomenon was caused by the water produced from MH dissociation. That is, the produced water diluted the injected inhibitor solution in the immediate area of hydrate dissociation, limiting the contact between the remaining hydrate and the more concentrated inhibitor. It can be suggested that this phenomenon should occur in an actual MH reservoir.



Figure 3 Gas production behaviors for inhibitor and pure water injections at 40  $^{\circ}$ C.



Figure 4 Temperature profile for pure water injection at 40 °C.



Figure 5 Temperature profile for MeOH 10wt% injection at 40 °C.



Figure 6 Temperature profile for 3wt% NaCl injection at 40 °C.

c) Pressure differentials during dissociation

The pressure differentials between the inlet and the outlet for each case are shown in Figure 7. In the case of water injection at 40 °C, the pressure differential increased substantially just after the start of injection. This may indicate inconsistent injection rates or interrupted injection during the course of the experiment. It is considered that the large pressure differential may have been caused by MH recrystallization. The methane gas generated by MH dissociation (and or any residual gas remaining in the pore space) was transported from an upstream region downstream by the injected water. It is reasonable that this gas-water mixture may have formed additional MH in the downstream portion of the sample in areas where T-P conditions still favoured thermodynamically stable MH [16, 17]. In this case, some portion of the transported methane may have recrystallized to MH while the remainder was exhausted to the outside. In the case of pure water injection at 20 °C, a large pressure differential was also observed, but there was no indication of intermittent or interrupted fluid injection, and the pressure differential decreased smoothly over time. In the case of MeOH or NaCl injection, the trends of the pressure differential were similar at each injection temperature, and maximum pressure drops (approximately 0.5 MPa) were much smaller than that in the case of water injection. This suggests that MeOH and NaCl effectively prevented the reformation of MH in downstream portions of the core sample, and contributed to the maintenance of relatively high sample permeability.



#### **Steam injection**

a) Gas production behavior during dissociation MH was dissociated coupling effect of both steam injection and depressurization. A plot of cumulative gas production vs. time is shown in Figure 8. The generated steam (250 °C) was injected into an artificial MH bearing sediment just after depressurization to 3 and 5 (or 10) MPa. At 10 MPa, pressure was maintained at the initial pressure during dissociation. It was assumed that injected water was in liquid phase in the core, since the vapor pressure of water at 250 °C is estimated to be approximately 4 MPa. At 5MPa, it was assumed that injected water was in the border at the vapor and liquid phases. At 3 MPa, it could be assumed that water was injected in the vapor phase. It was clear that the cumulative gas production at 3 MPa proceeded more rapidly than that at 5 MPa, suggesting that depressurization promotes dissociation effectively. Interestingly, no gas release by resetting to atmospheric pressure was observed in at of 3 and 5 MPa. The case of depressurization (5 MPa) alone is also shown in Figure 8. In this case, gas release was observed at 50 min. It can be seen that the effect of steam (or hot water) injection is clear in a later stage of dissociation.



Figure 8 Gas production behaviors for steam (hot water) injection.



Figure 9 Temperature profile for depressurization (3MPa) and steam injection (250°C).

#### b) Temperature profile

The temperature profile during dissociation by the coupling of depressurization (3MPa) and steam injection is shown in Figure 9. Steam temperature was kept constant at 250 °C. Inner (core)

temperatures decreased from the initial temperature to a certain temperatures just after the depressurization. After reaching the minimum temperature, it increased to 250 °C. The minimum temperatures were approximately 0-2 °C, which correspond to the equilibrium temperature of MH at 3 MPa. No such temperature decrease was observed in the steam (hot water) injection alone. Also, temperature increases started from both upstream and downstream regions. However, it started from an upstream region and continued downstream steadily in the case of steam (hot water) injection alone. This indicates that the coupling of depressurization and steam injection induces MH dissociation from both upstream and downstream to the center of sample.

## CONCLUSION

The dissociation behavior of an artificial MH bearing sediment by the injection of an aqueous methanol solution or steam was investigated using newly developed experimental apparatuses. In the case of inhibitor injection, note that downstream sample temperatures were not maintained at the initial temperature, but decreased somewhat immediately following the initiation of MH dissociation. It can be speculated that this downstream temperature change is due to the coupling effect of the temperature of dissociation and the changes in inhibitor concentration at MH surfaces. It is clear that the cumulative gas production during the injection of inhibitors was consistently greater than that during pure water injection, suggesting more rapid MH dissociation using inhibitors by water alone. The pressure drop between the inlet and outlet for inhibitors injection were much smaller than that in the case of water injection, suggesting that inhibitors effectively prevented MH reformation and contributed to the maintenance of high permeability.

In the case of steam injection coupling with depressurization, it was clear that the cumulative gas production at 3 MPa proceeded more rapidly that 5 MPa, suggesting than at that depressurization promotes the dissociation effectively. It can be seen that the effect of steam (or hot water) injection was clear in a later stage of dissociation, compared with that in the case of depressurization alone. Inner (core) temperatures decreased from the initial temperature to a certain temperature that corresponds to the equilibrium temperature at experimental pressure just after the depressurization. Then, temperature increases start from both the upstream and downstream regions. This indicates that the coupling of depressurization and steam injection induces MH dissociation from both upstream and downstream to the center of sample. However, it starts from an upstream region and continues downstream steadily in the case of steam (hot water) injection alone.

## ACKNOWLEDGMENT

The authors thank Mr. Y. Tsukada, Ms. C. Hirayama and Ms. M Miyata for carrying out the experimental work. This research was conducted with financial support of MH21 research consortium.

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