FORMATION – DISSOCIATION BEHAVIOR
OF METHANE HYDRATE
IN BENTONITE OR KAOLIN SUSPENSION

Taro Kawamura*, Takeshi Tetsu, Takuya Tsubaki and Yoshitaka Yamamoto
Methane Hydrate Research Center,
National Institute of Advanced Industrial Science and Technology,
Tsukuba, Ibaraki, 305-0035
JAPAN

ABSTRACT
Natural gas hydrate existing in geological formations constitutes a potentially large natural gas resource for the future. Hydrate formation in a gas line is a critical problem for economical and safe gas production from the natural gas hydrate reservoir. Since hydrate bearing sediment contains considerable amount of clay and salinity, the formation-dissociation behavior of gas hydrate in such condition is required information. In this study, methane hydrate formation-dissociation behavior in bentonite or kaolin suspension with or without NaCl was experimentally investigated. Raman spectroscopic analysis determined the crystal structures of clathrate hydrates formed from clay suspensions were sI. It also indicated that the small cavity occupancies of hydrate formed from calcium bentonite and kaolin smaller than that of pure MH or hydrate formed from sodium bentonite. Vapor pressure measurement and obtained equilibrium condition indicated the clay comportments do not affect significantly to the equilibrium condition up to the concentration range of 1 wt%. It can be speculated that the equilibrium condition of NaCl 20 wt% - clay 10 wt% suspension may shift to that of NaCl 20 wt% solution considering to their vapor pressure.

Keywords: natural gas hydrates, gas recovery, bentonite, kaolin, Raman spectroscopy, vapor pressure, equilibrium

INTRODUCTION
Recent seismic exploration and geological research have revealed that natural gas hydrate, which exists in the sediment, constitutes a large natural gas resource and is expected to be an energy source in the future [1-8]. Depressurization has been found to be the most desirable dissociation method to recover natural gas from the hydrate bearing sediments by the Research Consortium for Methane Hydrate Resources in Japan (MH21 Research Consortium) [9]. Figure 1 shows an example of gas production scheme. The system consists of some facilities shown in figure 1. And there is a concern that some interruptions for gas production will occur, i.e. plugging by hydrate reformation in the facilities. Accordingly, both technical and fundamental investigations for the flow assurance are highly demanded for safety and economical operation. Since it is known that the methane hydrate (MH) bearing sediments around Japan form an alternate strata of sand and clay, clay particle i.e. bentonite or kaolin will exist in dissociated fluids of MH bearing sediments. Therefore, it is expected that the MH formation-
dissociation will occur under the existence of such clay particle. The authors had investigated the formation-dissociation behaviors of MH in bentonite or bentonite-NaCl suspension [10]. It was speculated that bentonite affect not thermodynamically but kinetically on hydrate formation-dissociation reaction within some concentration region.

In this study, Raman spectroscopic analysis is conducted to investigate the property of formed hydrate from bentonite or kaolin suspension. Vapor pressures of these suspensions, which are related to hydrate equilibrium conditions, are also obtained. Finally, phase equilibrium properties of hydrate in clay suspensions are presented.

**EXPERIMENTAL**

**Materials**
The bentonite used in this work was sodium base and calcium base bentonite supplied by Kunimine Industries Co. Ltd. The kaolin was supplied by Sanyo Clay Co. Ltd. The methane gas was research-grade with purity of 99.9 %. The pure water was ion exchanged distilled water. The NaCl has a purity of more than 99.5 % supplied by Sigma-Aldrich Co.

**Raman spectroscopic analysis**
For Raman spectroscopic analysis, Laser Raman microprobe spectrometer (Jobin Yvon Ramanor HR-320) with a single monochromator and a CCD detector was used. The resolution of the Raman system is ±1 cm⁻¹. The wavelength of the Ar⁺ laser was set at 514.5 nm with a beam spot diameter of 10 µm. The sodium base bentonite, calcium base bentonite or kaolin and pure water were mixed with the concentration of 1.0 wt%. The prepared suspensions were pressurized by methane at the pressure of approximately 6 MPa and the temperature of 5.5 °C to form clathrate hydrate. After formation, the hydrate was sampled and measured by Raman at atmospheric pressure and the temperature condition of −100 °C to prevent dissociation.

**Determination of vapor pressure of suspension**
The experimental apparatus used to determine the vapor pressure was shown in figure 2 [11]. The reactor made from PFA has inner volume of 250 ml. Nitrogen gas was continuously injected into the suspensions or aqueous solutions in the reactor for 300 min with flow rate of 300 ml/min. Extracted vapor was divided into water and dry nitrogen by the cold trap. The vapor pressure of water can be determined by the amount of extracted nitrogen and trapped water. The suspensions and aqueous solutions used in this work were pure water, NaCl 20 wt% aqueous solution, clay suspensions and NaCl 20 wt% - clay mixed suspensions. Concentrations of clay were 1 or 10 wt%. Temperature was ranged from 5 to 20 °C.

**Determination of phase equilibrium condition**
An experimental apparatus used in this work is a high-pressure reactor having inner volume of 200 ml and maximum pressure of 20 MPa. It is equipped with a gas inlet, outlet, a thermistor, a pressure-gauge, and an agitator to accelerate and homogenize the reaction. Temperature of the reactor can be controlled from −15 °C to 40 °C by a temperature controlled bath. The accuracy of the thermistor and the pressure-gauge are ±0.04 °C and ±0.04 MPa respectively.

The suspensions used in this work were clay suspension, NaCl 3 wt% - clay mixed suspensions
and pure water. Concentrations of clay were 1 wt%. Each liquid were injected into the reactor. The vapor of the reactor was purged by methane gas and the temperature was kept constant. The inner pressure was increased by methane, and then the temperature was decreased to hydrate formation temperature. After the confirmation of formation, the temperature was increased 0.1 °C step. Each temperature was kept approximately 12 hours and the pressure was determined.

RESULT and DISCUSSION

Raman spectroscopic analysis

The Raman spectra of clathrate hydrate formed from each suspension is shown in figure 3. Also, the Raman spectra of pure methane hydrate (structure I), methane-THF binary hydrate (structure II) and methane vapor are shown in figure 4 as a reference. In figure 4 the spectra at 2904 cm$^{-1}$ and 2916 cm$^{-1}$ can be identified as methane in large 16-hedral cavity and small 12-hedral cavity respectively [12]. As clearly shown in figure 4, in the case of sI hydrate, the ratio of the area of these spectra is approximately 3:1. On the other hand, in the case of sII, the spectrum at 2916 cm$^{-1}$ (small cavity) is distinguished while no spectrum is shown at 2904 cm$^{-1}$ (large cavity), since most of large 16-hedral cavities are occupied by THF molecules. Even though all of large cavities are occupied by methane molecules, the area ratio increases up to 1:2 considering to the ratio of large / small cavity in sII. In case of clathrate hydrates formed from clay suspensions, accordingly, these crystal structures can be determined as sI, since the ratio of spectra area of large / small is approximately 3:1 as shown in figure 3.

The obtained spectra from the clathrate hydrates formed from clay suspensions are deconvoluted by Voigt function to estimate each spectrum area. By using the obtained the spectrum area of methane in large cavity $A_L$ and that in small cavity $A_S$, cage occupancy of small cavity and large cavity are estimated by following statistical thermodynamic equation [12-16].

$$\frac{A_L}{A_S} = \frac{6\theta_L}{2\theta_S}$$  \hspace{1cm} (2)

where, $\Delta \mu_{W(h)}$ is chemical potential difference between water and ice, $\Delta \mu_{W(h0)}$ is chemical potential difference between empty hydrate and ice (1297 J mol$^{-1}$), $R$ is gas constant (8.31 J K$^{-1}$ mol$^{-1}$) and $T$ is absolute temperature. The hydration number $n$ can be estimate using following equation considering the number of large and small cavities and water molecules in unit cell of sI.

$$n = \frac{46}{6\theta + 2\theta}$$  \hspace{1cm} (3)
The estimated cavity occupancies and hydration numbers are listed in table 1. The large cavity occupancies of hydrates formed from clay suspensions are ranged from 0.969 to 0.977, which are comparable value to that of pure MH. However, the small cavity occupancies of hydrate formed from calcium bentonite and kaolin are 0.792 and 0.794 respectively, which are approximately 10 % smaller than that of pure MH or hydrate formed from sodium bentonite. Also hydration numbers of hydrate formed from calcium bentonite and kaolin show larger value than that of pure MH or hydrate formed from sodium bentonite. Further investigation should be needed for confirmation the phenomenon, however, it is probable that some component in calcium bentonite or kaolin may occupy the small cavities or interaction between methane and them (or water) may affect.

<table>
<thead>
<tr>
<th>Structure</th>
<th>Cavity occupancy</th>
<th>Hydration Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water (calculated)</td>
<td>sI 0.900/0.980</td>
<td>5.99</td>
</tr>
<tr>
<td>1%Sodium Ben.</td>
<td>sI 0.912/0.969</td>
<td>6.02</td>
</tr>
<tr>
<td>1%Calcium Ben.</td>
<td>sI 0.792/0.977</td>
<td>6.18</td>
</tr>
<tr>
<td>1%Kao.</td>
<td>sI 0.794/0.977</td>
<td>6.17</td>
</tr>
</tbody>
</table>

Table 1. Crystal structures, cavity occupancies and hydration numbers of clathrate hydrates formed from clay suspensions.

**Determination of vapor pressure**

Figure 5 shows the vapor pressures of water obtained from pure water and NaCl 20 wt% aqueous solution. It is clear that they increase as the temperature becomes high. At each temperature, the vapor pressure of NaCl 20 wt% aqueous solution is approximately 14 % smaller than that of pure water. Since the vapor pressure reflect the water activity of solution or suspension, the difference of vapor pressure means the shift of the equilibrium condition of clathrate hydrate in each liquid. According to the CSMGem, the equilibrium pressure at 10 °C in NaCl 20 wt% aqueous solution is 31.1 MPa, while that in pure water is 7.0 MPa [17, 18]. In this measurement, 14% smaller vapor pressures of NaCl 20 wt% aqueous solution corresponds to the shift of equilibrium pressure compared to pure water.

Figure 6 shows the vapor pressure of each suspension or solution at 20 °C. In the case of clay suspension without NaCl, the values are almost similar to that of pure water. In the case of NaCl - sodium bentonite and NaCl - calcium bentonite, the vapor pressures become small as the concentrations of clay become high. For NaCl 20 wt% - sodium bentonite 10 wt% suspension and NaCl 20 wt% - calcium bentonite 10 wt% suspension, the vapor pressures are rather smaller than that of NaCl 20 wt% solution. It suggests the equilibrium pressures in these suspensions become high compared to that in NaCl 20 wt% solution. For NaCl 20 wt% - calcium bentonite 1 wt% suspension, the vapor pressure shows larger value than NaCl 20 wt% solution, while the vapor pressure of NaCl 20 wt% - sodium bentonite 1 wt% suspension is almost
same to NaCl 20 wt% solution. It may caused by the exchangeable cations in each clay. In the case of NaCl - kaolin suspension, no concentration dependency are shown for their vapor pressure. It is known that the some amount of water molecules in bentonite suspension are caught by bentonite as interlayer water or adsorbed on the bentonite surface, whereas kaolin has little interlayer and/or adsorbed water. It can be speculated that the inactiveness of kaolin results is the no concentration dependency.

Determination of phase equilibrium condition

Figure 7 shows temperature-pressure diagram of MH equilibrium condition obtained in this experiment. Solid line and broken line represent equilibrium T-P condition of MH in pure water and NaCl 3 wt% aqueous solution calculated by CSMGem, respectively [17]. In the case of pure water, experimental values agree well with calculated equilibrium curve, demonstrating the soundness of this experimental apparatus and procedure. For 1 wt% sodium bentonite suspension and 1 wt% kaolin suspension, it is clear that the experimental results show similar values to that of pure water. This result is consistent with the result of vapor pressure; the difference between pure water and clay suspension was small. And it can be speculated that the difference of small cavity occupancy, which was detected by Raman measurement, have small affect on the thermodynamic equilibrium condition.

When NaCl is added in liquid phase, the dissociation pressure shifts to higher pressure and lower temperature compared to pure water, because of its thermal inhibition effect [18]. NaCl can change the water activity in liquid phase to change the equilibrium T-P condition. In the case of NaCl 3 wt% - sodium bentonite 1 wt% suspension, NaCl 3 wt% - calcium bentonite 1 wt% suspension and NaCl 3 wt% - kaolin 1 wt% suspension, the experimental values were found to be similar to that of NaCl 3 wt% aqueous solution. It indicates that their clay comportments do not affect significantly to ionization degree of NaCl within this concentration range. Actually, the changes of the vapor pressure by 1 wt% clay were small as mentioned above, which is consistent with the results of equilibrium data. Accordingly, it is possible that the equilibrium condition of NaCl 20 wt% - clay 10 wt% suspension may shift to that of NaCl 20 wt% solution considering to their vapor pressure.

Figure 7 Three-phase equilibrium condition of MH in each solution or suspension

CONCLUSION

From Raman spectroscopic analysis, the crystal structures of clathrate hydrates formed from clay suspensions can be determined as sI. The large cavity occupancies of hydrates formed from clay suspensions are ranged from 0.969 to 0.977, which are comparable value to that of pure MH. However, the small cavity occupancies of hydrate formed from calcium bentonite and kaolin are 0.792 and 0.794 respectively, which are approximately 10 % smaller than that of pure MH or hydrate formed from sodium bentonite.

Vapor pressures of these suspensions, which are related to hydrate equilibrium conditions, are determined. It suggests that equilibrium T-P condition in clay suspension without NaCl does not shift within the concentration region of 1 to 10 wt%. In the case of NaCl - sodium bentonite and NaCl - calcium bentonite, the vapor pressures become small as the concentrations of clay become high. For NaCl 20 wt% - sodium bentonite 10 wt% suspensions and NaCl 20 wt% - calcium bentonite 10 wt% suspensions, the vapor pressures are rather smaller than that of NaCl 20 wt% solution.

Obtained equilibrium condition indicated the clay comportments do not affect significantly to the equilibrium condition up to the concentration range of 1 wt%, which is consistent with the results of vapor pressure. It can be speculated that the equilibrium condition of NaCl 20 wt% - clay 10 wt% suspension may shift to that of NaCl 20 wt% solution considering to their vapor pressure.

ACKNOWLEDGEMENT

The authors thank Ms. M. Ohtake and Ms. M. Miyata for carrying out the experimental work.

REFERENCES