

Reformation and Replacement of CO₂ and CH₄ Gas Hydrates

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INTRODUCTION

Large amounts of gas hydrates, clathrate compounds of water and gases formed under high pressure and low temperature, are found in marine sediments and permafrost. To extract methane gas from its reservoir in a practical method, it is necessary to obtain fundamental information on the mechanism underlying the formation and dissociation of gas hydrates and their properties, including kinetics and crystal growth. We have proposed an advanced method of gas hydrate production, by which methane gas is extracted from the reservoir by replacing methane with carbon dioxide at the molecular level. This method would be feasible to achieve the sequestration of carbon dioxide into the sediments. The main purposes of this research are to elucidate the mechanism underlying hydrate reformation and replacement and accumulate practical data for completing the original concept of the proposed method. We have carried out experiments on the dynamics on reformation and replacement of gas hydrates using an apparatus consisting of a high pressure vessel and a Raman spectroscopy. In this paper we present the experimental results concerning the behavior of gas hydrate reformation and replacement, and some discussion on the dynamics and the mechanism of gas hydrate formation.

EXPERIMENTAL

The experimental apparatus, in which the formation and replacement of gas hydrate could be observed, was designed and constructed, so that the several conditions of pressure, temperature and concentration of gases could be precisely controlled. Fig.1 illustrates the schematic diagram of the apparatus and measuring system used in the experiment. The pressure cell, made of stainless steel with a 3.2 ml internal volume, can be used at a pressure condition of up to 20 MPa. It contains a glass window for observing Raman scattering of monochromatic lights, a thermoelectric temperature control module, and some nozzles for the introduction of gas and liquid components. The pressure cell is installed on a constant temperature plate filled with a cooling agent methanol, where the temperature can be controlled with an accuracy of ± 0.1 K. It is equipped with transducers for detecting and controlling pressures with an accuracy of ± 0.05 MPa. The observation system of the Raman spectroscopy and a CCD camera are mounted in the apparatus as shown in Fig.2.

As a preliminary experiment, samples of CH₄ gas hydrate were synthesized from fine ice crystals and pressurized CH₄ gas, and stored as solid-phase pellets under extremely low temperature. The procedures of the experiment on reformation and replacement of gas hydrates are as follows. A pellet of CH₄ gas hydrate sample with a volume of 0.8 ml is placed into the pressure cell at a low temperature (< 253 K), and remaining volume of the pressure cell is filled with pressurized CO₂ gas. The internal pressure and flow rate of the gas can be adjusted using a fluid supplier system. The flow rate of CO₂ is set to approximately 5 ml/min. The reformation of CO₂ gas hydrate is observed during the changes in temperature of entire system. CH₄ gas hydrate no longer exists in this condition. The experiment on replacement is conducted under the conditions where both CO₂ and CH₄ gas hydrates can exist in the solid phase. An optical cell and the Raman spectroscopy system are installed on the glass window for detecting the nucleation and change of component of the hydrate structure. The gas components are analyzed by gas chromatography.

RESULTS AND DISCUSSION

a) Reformation of CO₂ and CH₄ gas hydrates

There are many differences of formation properties between CO₂ and CH₄ gas hydrates, such as the phase equilibrium and the formation rate. Fig.3 shows the pressure-temperature relationship of formation obtained at the first run of CO₂ and CH₄ gas hydrates. A first run is a situation of nonequilibrium formation without any gas hydrate nuclei in dissolved solution. The upper curve represents the relationship between nonequilibrium formation temperature T_f and pressure P_f , the lower curve, that between dissociation temperature T_d and pressure P_d . The center curve corresponds to the three-phase equilibrium estimated using the thermodynamic theoretical approach (Sloan). It can be seen that the relation between $P_f(P_d)$ and $T_f(T_d)$ is approximately linear in a semilog plot. In addition, it was found that the formation relation greatly differs from the theoretical data of phase equilibrium. The differential temperatures between nonequilibrium

formation and dissociation for CO₂ gas hydrate were slightly higher than those for CH₄ gas hydrate. At the second and third runs, reformation of gas hydrates occurred under conditions of higher temperatures and/or lower pressures than those at the first run. However, a supercooling temperature higher than 1.5 K was necessary for gas hydrate reformation in the case of CO₂. These properties may reveal interesting phenomena concerning the mechanism of gas hydrate nucleation under nonequilibrium conditions.

b) Solid-phase formation of CH₄ gas hydrate samples

CH₄ gas hydrate samples were synthesized in the solid phase for the replacement experiment using fine grains of ice crystal (average diameter: 0.1 mm) and the solution in which CH₄ gas hydrates were dissociated at a temperature slightly higher than the equilibrium temperature. It took a relatively short time to achieve nucleation of gas hydrate using the dissociated solution. When the temperature was set 2.0 K lower than the equilibrium temperature, the reformation of CH₄ gas hydrate could be achieved within 24 hours. Fig.4 shows the result of Raman spectroscopic analysis for CH₄ gas hydrate obtained using the procedure. A sharp Raman shift appears around 2905/2915 cm⁻¹, indicating the existence of Type-I CH₄ gas hydrates. According to a more precise analysis, the hydration number of the obtained samples was in the range of 6.4 to 6.0, that is, the ratio of occupancy in small cages can be estimated to be approximately 85-95 percent.

c) Formation rate of CO₂ gas hydrate in quasi-liquid phase

The formation rate of CO₂ gas hydrate was measured in situ observation using Raman spectroscopy; results are shown in Fig.1. The nucleation of gas hydrate was initiated from fine ice crystals under a temperature lower than 273 K. After setting ice crystals into the pressure cell, CO₂ gas was introduced to maintain the pressure inside the cell at 1.6 MPa. Fig.5 illustrates the trend of the Raman shifts obtained from 10 minutes to 2170 minutes after nucleation. Four Raman shift peaks were observed, in which peaks of around 1276 cm⁻¹ and 1381 cm⁻¹ are due to the existence of guest in the CO₂ gas hydrate structure. It was found in Fig.5 that the values of peak strength increase with time after the nucleation of gas hydrate. As the peak strength closely corresponds to the numbers of molecules in the structure, the formation rate of gas hydrate can be estimated from the peak strength. Fig.6 shows the formation rates of CO₂ gas hydrate obtained at temperatures from 254.5K to 274.5K. The formation rates of gas hydrate changed greatly with temperature, especially in the range between 269 K and 275 K. This suggests that the existence of quasi-liquid phase water, a type of slightly melting ice, plays an important role in promoting formation of gas hydrate at the gas-solid interface. Based on the behavior of CO₂ formation, the optional temperature for the replacement process was set around 273-275 K.

d) Replacement of CO₂ and CH₄ gas hydrates in solid phase

The replacement experiment on CO₂ and CH₄ gas hydrates was carried out using a bulk scale testing apparatus. Samples of CH₄ gas hydrate were synthesized in the solid phase from fine ice crystals and the dissociated solution. A preliminary process was performed under the conditions mentioned in the experimental procedure. During the process of replacement, the pressure of CO₂ was 2.0 MPa and the temperature was 274 ± 0.5 K. Fig.7 illustrates the Raman shifts obtained from the replaced hydrate sample observed 1 hour following CO₂ introduction. Two typical peaks appeared in the Raman spectra, 2905/2915 cm⁻¹ for CH₄ hydrate and around 1275/1380 cm⁻¹ for CO₂ hydrate. This means that both CH₄ and CO₂ gas hydrates coexist in the structure of the replaced hydrate sample. Based on quantitative analysis, the ratio of occupancy for CO₂ / CH₄ gas hydrates in the replaced hydrate sample were 40 and 45 percent, respectively. The portion of CO₂ gas hydrate in the sample increased with time. Fig.8 shows the trend of CO₂ / CH₄ components in the solid hydrate after CO₂ introduction as a function of time. The data were obtained from in situ observation and the analysis of peak strength of Raman shifts. This result indicates that the replacement of guest elements in solid gas hydrates could be achieved within a short period of 12 hours, if the pressure and temperature are precisely controlled in the pressure cell. It is also considered that a period of 2 hours is sufficient for nucleation of CO₂ hydrate at the surface of sample, and then crystal growth proceeds as a result of CO₂ transport into the solid hydrate. Because the transport of CO₂ gas should be fast in porous media, the in situ replacement of CO₂ gas hydrate may be used for the extraction of gas hydrates from their reservoirs. More systematic researches are necessary to elucidate the phenomenon underlying gas hydrate replacement.

CONCLUSIONS

Experimental studies on the dynamics and behavior of reformation and replacement of gas hydrates was carried out using a specially designed apparatus. It was shown that reformation of gas hydrates easily occurred in the quasi-solid structure when the dissociated solution is used. The rate of reformation of CO₂ gas hydrate was observed by Raman spectroscopy. The results of the bulk scale experiment showed that replacement of CO₂ gas hydrate could be achieved within a period of 12 hours in pure samples of CH₄ gas hydrate that had been synthesized as solid crystal, if

the pressure and temperature are precisely controlled in the pressure cell. The replacement of guest elements in CO_2 and CH_4 gas hydrates may be quite innovative from both aspects, the extraction of gas hydrates and sequestration of CO_2 , to maintain the global environment and stability of marine sediments.

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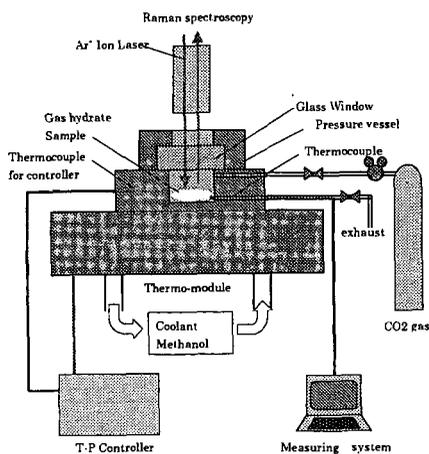


Fig.1 Schematic diagram of the experimental setup for gas hydrate formation.

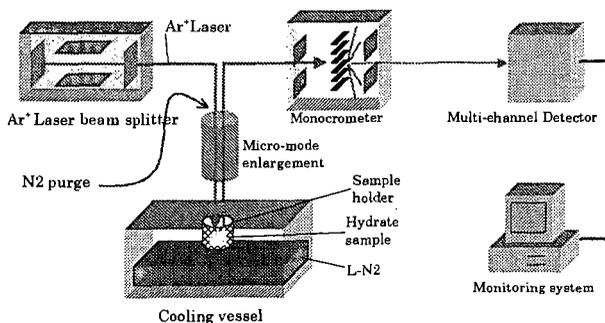


Fig.2 Raman spectroscopy apparatus for observing gas hydrate structure and component.

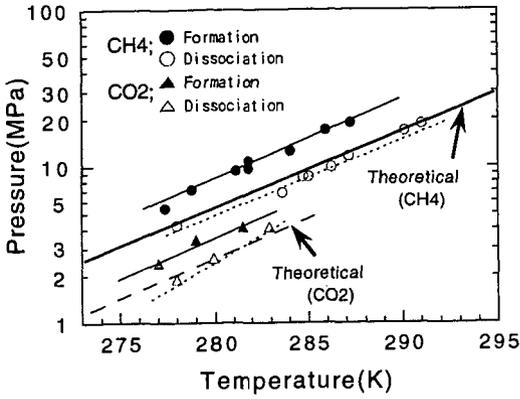


Fig.3 The relations of formation/dissociation P and T for CO₂ and CH₄ gas hydrates.

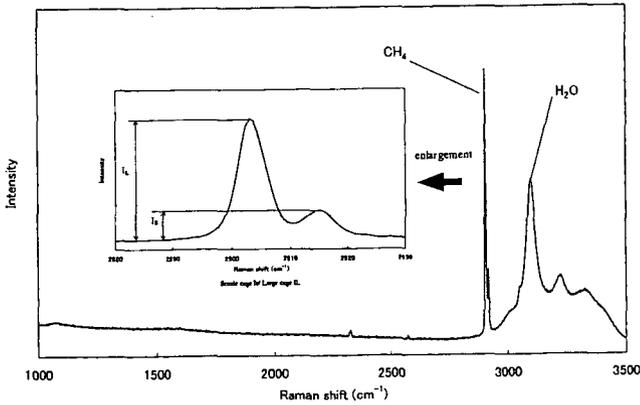


Fig.4 Raman shift for a sample of CH₄ gas hydrate made from ice crystals

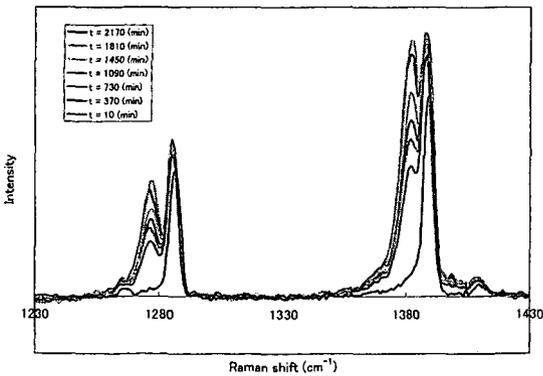


Fig.5 Changes in Raman shifts observed for CO₂ gas hydrate formation.

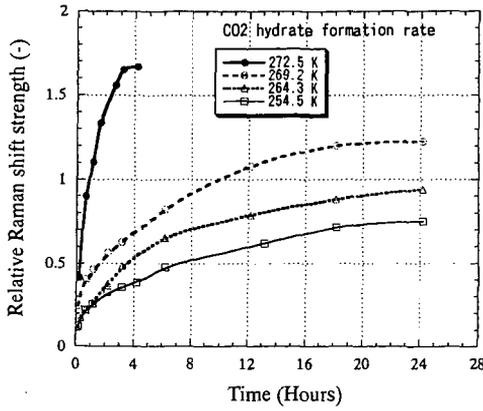


Fig.6 The trend curves of the formation rate of CO₂ gas hydrate under different temperatures.

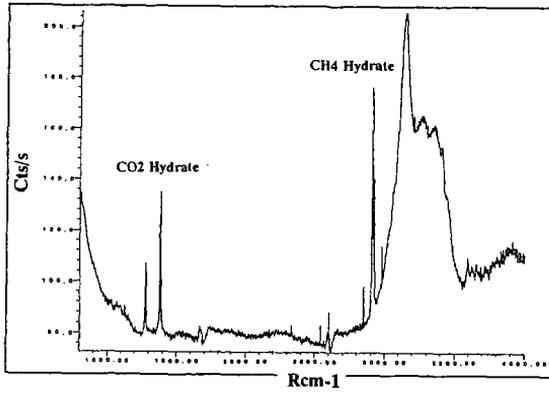


Fig.7 Raman shift for a sample of replacement from CH₄ to CO₂ gas hydrates.

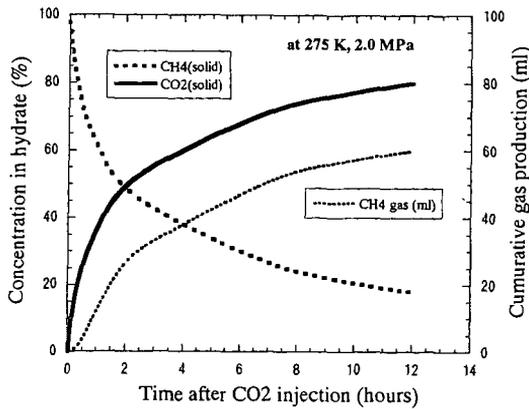


Fig.8 The trend curves of CO₂ and CH₄ components in replaced gas hydrate sample and the cumulative CH₄ production.