

## Stability and Phase Change Properties of Methane Hydrate (Abstract of the Final Report)

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### 1. Introduction

Methane hydrate is a crystalline solid compound formed by hydrogen-bonded water molecules configured into cages, each of which holds one methane molecule. Methane-hydrate crystals have been reported to naturally occur in sediments in sub sea and permafrost areas, which are considered to be the source of primary deposits of carbon in the Earth's crust. If in the future, the earth's climate becomes warmer as predicted, methane hydrate crystals present at shallow depths in the permafrost zone could dissociate due to the increase in temperature, thereby possibly releasing a considerable amount of methane gas into the atmosphere. Researchers in Russia have also discovered the presence of methane hydrate in the shallow layers of the permafrost where the overburden pressure was lower than the phase equilibrium condition. The methane hydrate in shallow layers of permafrost would be much more susceptible to the release of methane gas due to climate change than the methane hydrate in the deep ocean and in permafrost sediment layers. In order to investigate the relationship between the methane hydrate in permafrost areas and global climate change, the stability and phase change properties of methane hydrate should be studied.

### 2. Research Objectives

Given the high latent heat of methane hydrate, any heat transfer process is a very important rate-controlling step during its formation and dissociation. In both deep sea sediments and permafrost areas, methane hydrate exists in the pore spaces of the sediments along with water/ice and gases. As the thermal conductivity of ice ( $2.2\text{W/m}\cdot\text{K}$ ) is four times greater than that of water ( $0.56\text{W/m}\cdot\text{K}$ ) at a temperature of  $0^\circ\text{C}$ , the methane hydrate in the permafrost regions would be more sensitive to changes in temperature and/or overburden pressure due to climate change than the methane hydrate in deep sea sediments. In fiscal year of 2006, to examine the stability of the methane hydrate in permafrost regions, thermal conductivity measurements on the frozen soil was performed, in consideration of the occurrence of ice.

The solid-state  $^{13}\text{C}$  NMR method using Cross Polarization and Magic Angle Spinning (CP-MAS) technique seems to be useful for determination of crystallographic structure and cage occupancies on gas hydrates containing a wide variety of hydrocarbon since hydro-

carbon molecules in different cages can be distinguished each other, where CP is one of the signal enhancement techniques in solid-state NMR. The  $^{13}\text{C}$  NMR measurements have been mainly carried out at 193-253K in the studies already reported. The signal intensities increase with a decrease in the measurement temperature. In the present study, CP-MAS  $^{13}\text{C}$  NMR measurements on the  $\text{CH}_4+\text{C}_2\text{H}_6$  mixed hydrate system are carried out at lower temperatures than 183K to demonstrate the effectiveness of CP-MAS  $^{13}\text{C}$  NMR method for the determination of the crystallographic structure and the quantitative estimation of the cage occupancies of the guest molecules in mixed gas hydrate with  $\text{CH}_4$  and  $\text{C}_2\text{H}_6$ . In addition, our aim in the present study is also to show the effectiveness of the CP-MAS  $^{13}\text{C}$  NMR technique as a measuring method for the decomposition process of gas hydrates at low temperatures.

### 3. Research Methods

#### (1) Thermal conductivity of frozen soil

The following experimental method was used to measure the thermal conductivity of frozen soil. In order to prepare a homogeneously wet sand mixture, ice particles were sieved to sizes of 0.5mm or less and mixed with quartz sand in a cold room at a temperature of 258K before they were melted at a temperature of 283K. The quartz sand had an average particle size of 0.212mm and a real density of  $2.670\text{g/cm}^3$  (Toyoura standard sand). Water content was controlled between 4.7% and 19.0%. The wet sand was densely packed into an acrylic cylinder with an inner diameter of 65mm and a length of 140 mm, and frozen in the cold room. The frozen sand was cut into a specimen measuring  $100\text{mm}\times 50\text{mm}\times 30\text{mm}$  using an electric cutter. Microscopic observation indicated that the sand was strongly cemented by ice using this method. The porosity of the specimen was between 41.2% and 42.5% and its ice saturation was between 20.0% and 79.4%. A weakly cemented frozen sand specimen was also prepared by mixing the quartz sand with very fine ice particles measuring 0.106mm or less, produced by spraying water in the cold room. The porosity of this specimen was between 54.0% and 64.0% and its ice saturation was between 14.1% and 19.8%. Microscopic observation revealed that fine ice particles were present in the pore spaces of the specimen. A water saturated clay specimen was also prepared using a mixture of 70% Kaolinite and 30% Chlorite. The porosity this specimen was 51.4%.

Thermal conductivity measurements were conducted using a thermal conductivity meter (Type QTM-500 by Kyoto Electronics Manufacturing Co., Ltd.) by the hot wire method.

#### (2) Studies on structure of gas-hydrates by $^{13}\text{C}$ -NMR method

Pure  $\text{CH}_4$  and  $\text{C}_2\text{H}_6$  hydrates were prepared from water (or ice particles) and the corresponding gas. The  $\text{CH}_4+\text{C}_2\text{H}_6$  mixed gas hydrates were prepared in the same way using the gas mixtures with desired compositions. The gas compositions were analyzed by gas chromatography. The hydrate samples were recovered from the vessel at liquid  $\text{N}_2$  temperature. A small portion of the sample was decomposed in a small vessel to analyze the dissociated gases from the mixed gas hydrate samples by gas chromatography. The  $^{13}\text{C}$  NMR spectra of hydrate samples were measured by the NMR spectrometer (JEOL model JNM-AL400, 100 MHz) equipped with the probe for solid sample (JEOL model SH40T6). The measurements were performed at temperatures ranging from 123 to 203K using cooled dry  $\text{N}_2$  gas. The hydrate samples were introduced into a zirconia sample tube (JEOL; diameter: 6mm, length: 22mm) in liquid  $\text{N}_2$ .

### 4. Results and Discussion

#### (1) Thermal conductivity of frozen soil

The sand containing no ice exhibited a thermal conductivity of  $0.242\text{W/m}\cdot\text{K}$  at a tem-

perature of 267.5K. The thermal conductivity of the specimen with strong cementation between ice and sand increased with increased ice saturation. Conversely, the specimen with an ice saturation of 74.9% exhibited a thermal conductivity of 4.01W/m·K, which was seventeen times larger than the thermal conductivity of sand containing no ice. The thermal conductivity of the specimen with weak cementation between sand and ice was less than that of the specimen with a strong cementation and exhibited only a slight dependence on the ice saturation. This experiment demonstrated that the thermal conductivity of frozen sand depends on the occurrence of ice in its pore spaces as well as the degree of ice saturation. In particular, the cementation between ice and sand strongly increases the thermal conductivity. The water-saturated clay had a thermal conductivity of 2.938W/m·K, which is less than the thermal conductivity of the frozen sand with the strong cementation between ice and sand.

The experimental results were compared with the thermal conductivity values obtained from thermal conductivity models (Fig.1). Using these models, the thermal conductivity of frozen sand was calculated from the individual thermal conductivities of its components, that is, the sand particles, ice and air. In these models, the three components were arranged either in series or in parallel for the heat flow and were referred to as the series and parallel models, respectively. The calculations were performed by assuming the thermal conductivities of ice and water to be 2.302W/m·K and 0.0241W/m·K, respectively. The thermal conductivity of sand particles were assumed to be between 5W/m·K and 6W/m·K, using the value for the quartzite sand.

The results of the series model revealed that thermal conductivity exhibited only a slight dependence on the degree of ice saturation, with the values of the specimen containing no ice and the specimen with weak cementation between sand and ice being approximately similar. Given the limited contact among sand particles in these specimens, the conduction of heat exhibited marked thermal resistance required for the series model. Although the thermal conductivity of the specimen with strong cementation was similar to that predicted by the series model under conditions of low ice saturation, the parallel model was adequate for estimating thermal conductivity at high ice saturations. Given that the extent of heat bridges composed of ice between sand particles increased with an increase in ice saturation, the parallel model with low thermal resistance was adequate for estimating thermal conductivity at high ice saturations. These results suggest that the mechanism of the thermal conductivity of the frozen specimens is dependent upon the occurrence of ice in the pore spaces.

## (2) Studies on structure of gas-hydrates by $^{13}\text{C}$ -NMR method

CP-MAS  $^{13}\text{C}$ -NMR spectra of gas hydrate samples have been commonly observed at higher temperatures than 193K due to the instrumental assurance. We have tried to observe the spectra at lower temperatures than 193K, since the NMR signal intensities of  $\text{CH}_4$  hydrate decreased in accordance with the decomposition of it even at 193K. After some improvements of the cooling system for the NMR probe, we have finally succeeded to observe CP-MAS  $^{13}\text{C}$ -NMR spectra on gas hydrates at 123K. At temperatures lower than 163K, the decomposition of gas hydrate was remarkably suppressed.

Measurements of CP-MAS  $^{13}\text{C}$ -NMR spectra were carried out on  $\text{CH}_4+\text{C}_2\text{H}_6$  mixed gas hydrates. The changes in the NMR chemical shift values on  $\text{CH}_4$  and  $\text{C}_2\text{H}_6$  clearly corresponded to the structural changes in the hydrate structure. Namely, the structural changes from structure I to structure II and then to structure I with an increase in  $\text{C}_2\text{H}_6$  concentration were observed by  $^{13}\text{C}$  NMR technique.

It is possible to estimate gas composition from  $^{13}\text{C}$  NMR signal intensities on  $\text{CH}_4$  and  $\text{C}_2\text{H}_6$  in the case of the mixed gas hydrates with  $\text{CH}_4+\text{C}_2\text{H}_6$ . The concentration of  $\text{C}_2\text{H}_6$  by

$^{13}\text{C}$  NMR (denoted by  $y_{\text{E(NMR)}}$ ) is evaluated by the following equation.

$$y_{\text{E(NMR)}} = (1/2)A_{\text{E}} / \{A_{\text{M}} + (1/2)A_{\text{E}}\}$$

In the equation,  $A_{\text{M}}$  and  $A_{\text{E}}$  represent the peak areas for  $\text{CH}_4$  and  $\text{C}_2\text{H}_6$ , respectively. The  $\text{C}_2\text{H}_6$  concentrations estimated from CP-MAS  $^{13}\text{C}$  NMR spectra at 163 K on eight mixed gas hydrates ( $y_{\text{E(NMR)}}$ ) are compared with those estimated by gas chromatography ( $y_{\text{E(GC)}}$ ). As shown in Fig.1, the plots between  $y_{\text{E(NMR)}}$  and  $y_{\text{E(GC)}}$  showed a good co-relation between them. The agreement between  $y_{\text{E(NMR)}}$  and  $y_{\text{E(GC)}}$  indicates that fractions of  $\text{CH}_4$  and  $\text{C}_2\text{H}_6$  in the mixed gas hydrates can be directly determined from the CP  $^{13}\text{C}$  NMR data.

Changes in the peak intensities for  $\text{CH}_4$  and  $\text{C}_2\text{H}_6$  on the mixed hydrate samples, which contain both structures of sI and sII, with decomposition time were measured at various temperatures in the range of 208-163K. Results are shown in Fig.2(1)-(4). At 163K, almost no appreciable changes in peak intensities were observed. In the case of the decomposition at 198K and 203K, the decomposition rate on sII was observed to be almost the same with that of sI, whereas the former was observed to be much faster than the later at 208K.

In the present study, CP-MAS  $^{13}\text{C}$  NMR spectra on the  $\text{CH}_4 + \text{C}_2\text{H}_6$  mixed hydrates were observed at the super-cold condition (123-203K). It is very valuable for the measurements of CP-MAS  $^{13}\text{C}$  NMR spectra at lower temperatures, since the signal intensities are much enhanced at such low temperatures. Although further experiments would be required for the detail discussion on the decomposition process of the mixed gas hydrates, measurements at 208 K showed different decomposition process of sII from that of sI. Namely, at 208 K, the decomposition rate of sI was observed to be faster than that on sII.

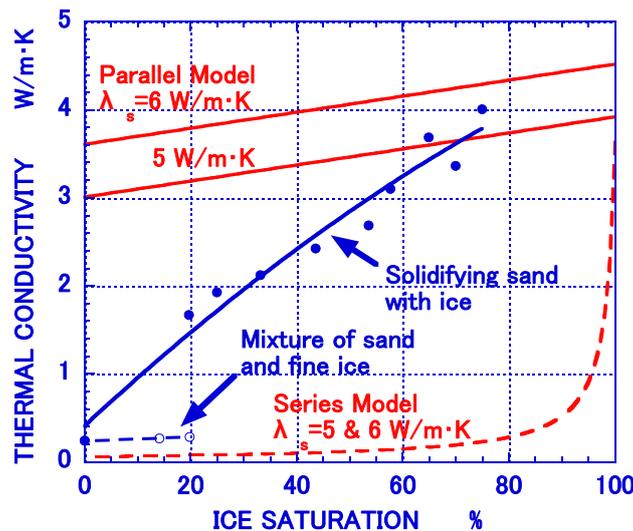


Fig.1 Comparison of thermal conductivity models of frozen sand with experimental results

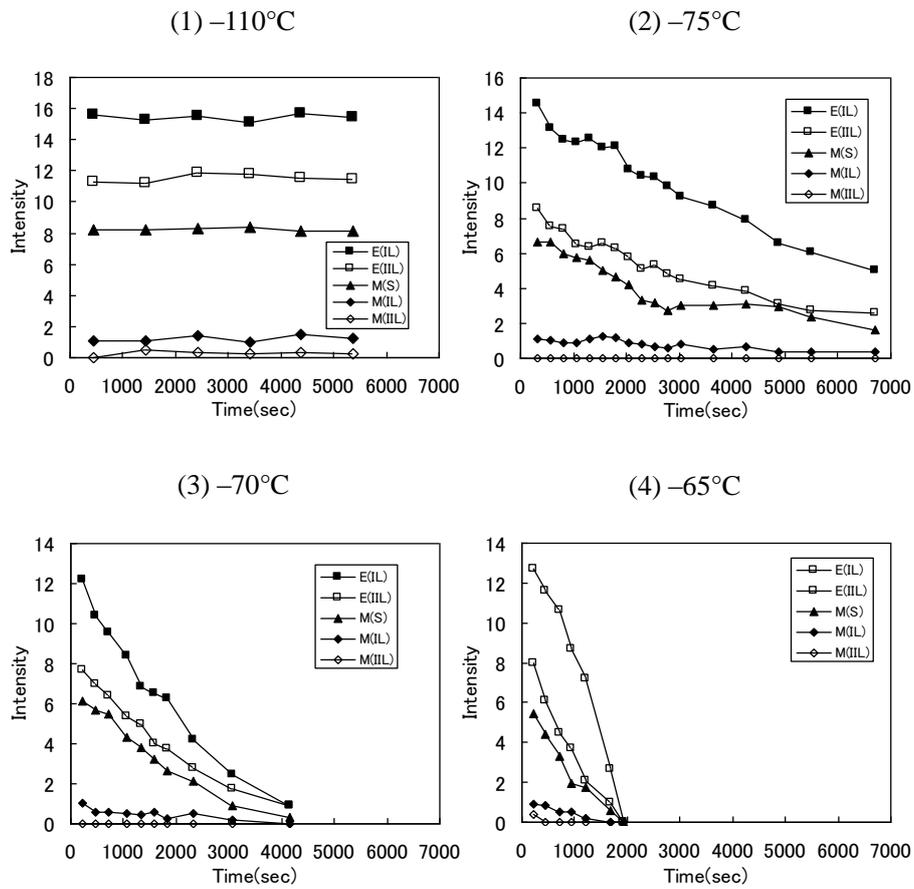


Fig.2 Decomposition process of the  $\text{CH}_4 + \text{C}_2\text{H}_6$  gas hydrates containing both structures of I and II at different temperatures