

## CO<sub>2</sub> Sequestration on Various Structures of Natural Gas Hydrate Layer for Effective Recovery of CH<sub>4</sub> Gas

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**Key words** : natural gas hydrate, methane, carbon dioxide, replacement, recovery

**Abstract** : On the continental margins and in permafrost regions, natural gas, which has been expected to replace petroleum energy, exists in solid hydrate form. World hydrate reserves including natural gas are estimated at about twice as much as the energy contained in total fossil fuel reserves. Because of its vast quantities, the efficient recovery of natural gas from natural gas hydrate becomes the most important factor on evaluating the economic feasibility in the sense of commercialization. It has been noted that carbon dioxide, one of the well-known green house gases, possibly can be stored in the ocean floor as a carbon dioxide hydrate. If the natural gas hydrate could be converted into carbon dioxide hydrate, natural gas hydrate deposits would serve as energy sources as well as carbon dioxide storage sites in the deep ocean sediments. In this study, we first attempted to examine the real swapping phenomenon occurring between guest molecules and various structures of gas hydrate through spectroscopic identification such as NMR spectroscopy.

### Nomenclature

sI : structure I  
sII : structure II

### subscrip

sI<sub>S</sub> : small cage of sI  
sI<sub>L</sub> : large cage of sI  
sII<sub>S</sub> : small cage of sII  
sII<sub>L</sub> : large cage of sII

## 1. Introduction

The natural gas hydrates are deposited on the continental margin and its permafrost regions and scattered all over the world<sup>1)</sup>. The total amount of natural gas hydrate over the world is estimated about twice as much as the energy contained in fossil fuel reserves<sup>2)</sup>. For efficient recovery of CH<sub>4</sub> hydrates deposited at various conditions, several strategies such as thermal treatment, depressurization and inhibitor addition into the hydrate layer have been proposed. However, all these methods are based on making CH<sub>4</sub> hydrate decomposed by external stimulation and might lead to trigger catastrophic slope failures<sup>3)</sup>. Further, if CH<sub>4</sub> hydrate decomposes rapidly, it is also possible that the released CH<sub>4</sub> from the hydrate can be transferred to the air and significantly accelerate the greenhouse effect<sup>4)</sup>. It needs to be thus recognized that the present natural gas

production technologies have their own inherent limitations to be really adopted for the effective recovery of natural gas hydrates and thus the safest and economically feasible means should be developed with a full consideration of environmental impacts. Recently, the replacement of CH<sub>4</sub> hydrate with CO<sub>2</sub> has been suggested as an alternative option for recovering CH<sub>4</sub> gas. This swapping process between two gaseous guests is considered to be a favorable way as a long-term storage of CO<sub>2</sub> and enables the ocean floor to remain stabilized even after recovering the CH<sub>4</sub> gas because CH<sub>4</sub> hydrate maintains the same crystalline structure directly after its replacement with CO<sub>2</sub>. Here, we have further extended our investigations to cover the occurrence of CO<sub>2</sub> replacement phenomena on sII hydrate which seems to actually and potentially exist in the seabed. We present an interesting conclusion reached by inducing structure transition. The microscopic analysis was attempted to examine the real swapping phenomena occurring between CO<sub>2</sub> guest molecules and sII hydrate through spectroscopic identification such as solid-state Nuclear Magnetic Resonance (NMR) spectrometer.

## 2. Experimental Procedure

CO<sub>2</sub>, and CH<sub>4</sub> + C<sub>2</sub>H<sub>6</sub> (90 mol% CH<sub>4</sub> and 10 mol% C<sub>2</sub>H<sub>6</sub>) mixed gas were used. The hydrate samples were prepared in a mechanically stirred reactor having the

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volume of 300 cm<sup>3</sup> and formed from finely pulverized ice particles crushed in a mortar and pestle. The reactor, which maintained a constant temperature of 274.15 K, was filled with powdered ice particles and then pressurized with gases to a higher pressure than the corresponding three-phase equilibrium pressure at the same temperature. After making CH<sub>4</sub> + C<sub>2</sub>H<sub>6</sub> hydrate(sII) with a mechanically stirred high-pressure reactor, these hydrate sample were move to another high-pressure reactor to experience the replacement with pure CO<sub>2</sub>.

### 3. Results

In the present work, replacement of the mixed CH<sub>4</sub> + C<sub>2</sub>H<sub>6</sub> hydrate with CO<sub>2</sub> was performed in order to investigate the swapping phenomena on sII CH<sub>4</sub> hydrate. Fig. 1 shows the <sup>13</sup>C HPDEC MAS NMR spectra of mixed CH<sub>4</sub> + C<sub>2</sub>H<sub>6</sub> hydrates that are replaced with CO<sub>2</sub> molecules. Three peaks representing CH<sub>4</sub> in sII<sub>S</sub>, CH<sub>4</sub> in sII<sub>L</sub>, and C<sub>2</sub>H<sub>6</sub> in sII<sub>L</sub> appeared at chemical shifts of -3.95, -7.7, and 6.4 ppm, respectively. Interestingly, during the swapping process, the external guest CO<sub>2</sub> molecules attack both small and large cages for better occupancy, which causes the structure transition of sII to sI to continuously proceed. Within 24 hours the sII peaks almost disappeared and instead only a very small amount of CH<sub>4</sub> in sI<sub>S</sub> and sI<sub>L</sub>, and C<sub>2</sub>H<sub>6</sub> in sI<sub>L</sub> was detected at chemical shifts of -4.0, -6.1, and 7.7 ppm, respectively<sup>5)</sup>. From a structural viewpoint, it is speculated that the hydrate lattices are slightly adjusted to accommodate the three guests of CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, and CO<sub>2</sub> in highly stabilized hydrate networks.

The CH<sub>4</sub> recovery rate was checked by the gas chromatography analysis and the results are shown in Fig. 2. During the swapping process, the CH<sub>4</sub> and C<sub>2</sub>H<sub>6</sub> molecules in hydrate phase continuously decrease until reaching the recovery rate of 92% for CH<sub>4</sub> and 99% for C<sub>2</sub>H<sub>6</sub>. Both the NMR and GC results imply that most of CH<sub>4</sub> molecules in sI<sub>L</sub> as well as sI<sub>S</sub> were displaced by CO<sub>2</sub> molecules. The externally approaching CO<sub>2</sub> guests attack and occupy most of the sII<sub>S</sub> and sII<sub>L</sub> cages accompanying structure transition of sII to sI.

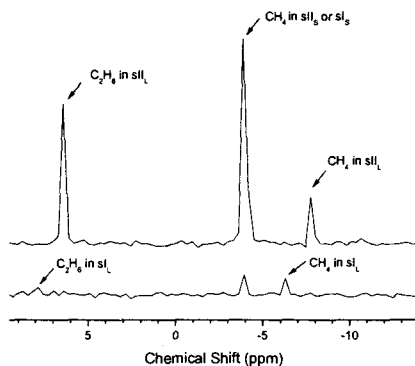


Fig. 1 <sup>13</sup>C MAS HPDEC NMR spectrum

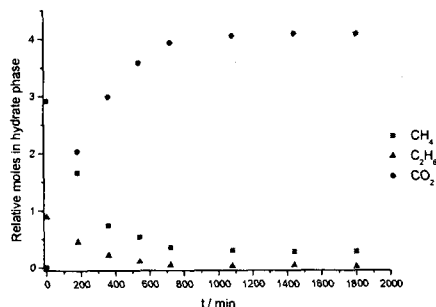


Fig. 2 Guest molecules in hydrate phase

### 4. Conclusion

During swapping the sII CH<sub>4</sub> hydrate structurally transforms to sI, which causes CH<sub>4</sub> molecules in sII<sub>S</sub> to spontaneously be released through a continuous reduction of small cage sites. The utilization of this natural swapping phenomenon might greatly contribute to realizing both ocean storage of CO<sub>2</sub> and CH<sub>4</sub> recovery from marine deposits in a large scale.

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