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산업용 배기가스를 이용한 가스 하이드레이트로부터의 천연가스 생산 연구

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Study of Producing Natural Gas From Gas Hydrate With Industrial Flue Gas

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Abstract : There have been many methods for producing natural gas from gas hydrate reservoirs in permafrost and sea floor sediments. It is well knownthat the depressurization should be a best option for Class 1 gas hydrate deposit, which is composed of tow layers: hydrate bearing layer and an underlying free gas. However many of gas hydrate reservoirs in sea floor sediments are classified as Class 2 that is composed of gas hydrate layer and mobile water, and Class 3 that is a single gas hydrate layer. The most appropriate production methods among the present methods such as thermal stimulation, inhibitor injection, and controlled oxidation are still under development with considering the gas hydrate reservoir characteristics. In East Sea of Korea, it is presumed that the thick fractured shale deposits could be Class 2 or 3, which is similar to the gas hydrate discovered offshore India. Therefore it is needed to evaluate the possible production methods for economic production of natural gas from gas hydrate reservoir. Here we would like to present the production of natural gas from gas hydrate deposit in East Sea with industrial flue gases from steel company, refineries, and other sources. The existing industrial complex in Gyeongbuk province is not far from gas hydrate reservoir of East Sea, thus the carbon dioxide in flue gas could be used to replace methane in gas hydrate. This approach is attractive due to the suggestion of natural gas productionby use of industrial flue gas, which contribute to the reduction of carbon dioxide emission in industrial complex. As a feasibility study, we did the NMR experiments to study the replacement reaction of carbon dioxide with methane in gas hydrate cages. The in-situ NMR measurement suggeststhat 42% of methane in hydrate cages have been replaced by carbon dioxide and nitrogen in preliminary test. Further studies are presented to evaluate the replacement ratio of methane hydrate at corresponding flue gas concentration.

1. Introduction

Gas hydrates are nonstoichiometric crystalline compounds that belong to the inclusion group known as clathrates. They are formed when guest molecules are incorporated in host cages formed by water molecules through hydrogen bonding. Low molecular weight gas molecules such as methane, nitrogen, and carbon dioxide are captured into these cages. The huge amount of natural gas has been founded in marine sediments and permafrost region since late 1970s. Kvenvolden suggest that $21*10^{15}$ m^3 is a consensus value for the volume of natural gas resource stored in the form of gas hydrate. This value is approximately 50 times greater that the world conventional gas endowment, and makes naturally occurring gas hydrate a future energy resource.

November 2007, Ulleung Basin Gas Hydrate Expedition (UBGH 1) successfully explored and recovered gas hydrate bearing sediments at three different locations in East Sea of Korea. The dominant sediments form the three locations were siliceous and calcareousclays and gas hydrate was detected at all three

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sites as pore filling material withinthe layers. Quantification of gas hydrate from porewater freshening analysis showed that gas hydrate sand layers contained an average of 30% gas hydrate by pore volume. Methane was the predominant gas within core voids as well as in gas hydrate at all three sites, while ethane was 0.3 or less of most gas samples. It is estimated that the deposit contains about 600 million m^3 of natural gas and could meet the country's gas needs for about 30 years.

Recently it is no secret that the current global warming and climate change is induced by anthropogenic CO_2 and argent action if required to reduce CO_2 emissions and to stabilize the concentration of atmospheric CO_2. These proposals include strong CO_2 in various geologic formations, chemically transforming CO_2 into thermodynamically stable minerals, and injecting CO_2 into deep sea sediments. The only economic uses of the CO_2 that have thus far been discussed in detail are geological sequestration for enhanced oil and gas recovery, and the use of the CO_2 as an industrial consumable. Considerable attention has been given to offsetting the cost of CO_2 sequestration into deep sea sediments and these efforts have been bridged to gas hydrate deposits from the idea of replacing methane in hydrate cages by CO_2 as suggested by Ohgaki et al. This concept involves injecting CO_2 into gas hydrate bearing sediment, which isthen allowed to equilibriate with methane hydrate along the hydrate equilibrium boundary suggesting beneficial aspect of additional methane gas recovery.

Intense investigations concerning the effect of external factors such as injection depth and initial droplet size of liquid CO_2 have been carried out to realize the injection process as a part of Carbon Capture and Sequestration (CCS). Hirohama et al. suggested that the driving force for methane and CO_2 replacement seems to be the fugacity difference between fluid and hydrate phase. Komai et al. and Ota et al. studied these processes, however all of these studies were conducted in bulk conditions. Kinetics of replacement was investigated by Uchida et al. and Lee et al. Sivaraman studied the effect of CO_2 on methane recovery in presence of porous media with the test pressure below the CO_2 saturation pressure. McGrail et al. suggested the injection of micro-emulsion with CO_2 into methane hydrate deposits for providing a low grade heat source. Park et al represent that the 85% methane recovery rate could be achieved by the direct use of N_2 and CO_2 gas mixture, which is well known post-combustion flue gas. Because the injection of CO_2 require the processing of industrial flue gas to produce high purity of CO_2 gas, the direct injection of $N_2$and CO_2 gas mixture could reduce the sequestration cost by removing complex CO_2 processing plant.

The Uleung basin bearing huge amount of gas hydrate is located at 135km from Pohang City of Gyeongbuk province,in which steel plant and refinery plant are emitting large quantities of flue gas having various concentration of CO_2. As an ongoing work from our previous results, here we reports a preliminary results on the methane hydrate replacement by various sources of CO_2 from industry and represents the microscopic measurement to address the structural characteristics during the replacement reaction.

2. Experiments

Methane and CO_2 with a minimum purity of 0.9999 mole fraction, $N_2$and CO_2 gas mixture of desired concentration is supplied by World Gas Co. Water is supplied by Sigma-Aldrich Chemicals Co. with a purity of 0.991 mole fraction. Silica gel of nominal pore diameter 15~20 nm was purchased from Silicycle (Canada) and the properties of silica gel were measured on a Micromeritics ASAP 2000 pore size analyzer.

The reaction of methane hydrate with N_2 and CO_2 gas mixturewas monitored with a Bruker 400 MHz solid sate NMR spectrometer having a specially designed static high pressure probe built around a 7 mm O.D. ZrO_2 cell, which is connected to a gas handling system. Methane hydrate was formed in silica gel pores (pore size 15~20 nm) at 270 K and 140 bar for one day. The temperature was controlled using a Bruker BVT 3000 temperature control unit during the experiments. After confirming the formation of methane hydrate, methane gas was completely vacuumed and N_2 and CO_2 gas mixture was charged to 100 bar with gas handling system. ^1H NMR spectra was monitored to follow the replacement reaction and calculate the amount of methane replaced by $N_2$and CO_2 gas mixture. In addition, the replacement reaction was followed by measuring the ^{13}C NMR signal to observe the change of methane amount in cages of hydrate structure as a function of time. Silica gel was first dried at 373 K for 24 h before water sorption. Then, pore saturated silica gel was prepared by placing the dried material in a desiccator containing degassed and distilled water, evacuating the desiccator, and allowing it to stand more than five days. The total amount of sorbed water in the silica gel pores was confirmed by measuring the mass of silica gel before and after saturation and was found to be almost identical with the pore volume in each silica gel. The composition of gas phase and dissociated gas from hydrate phase were measured to investigate the replacement ratio in porous media using gas chromatograph, which is used to be compared with NMR spectroscopic results.

The experiment began by charging the reaction cell with about 25 cm^3 of silica gel containing pore water. After the reaction cell was pressurized to the desired pressure with methane, the cell was cooled slowly to 274 K. When the pressure reduction due to hydrate formation reached a steady-state, the cell was remainedfor at least one day in order to minimize unreacted water phase. Then the methane was discharged completely and N_2 and CO_2 gas mixture of desired composition was introduced to 100 bar. In this study, the flue gas from steel company was considered as possible CO_2 source as it contains CO_2 concentration of 20 ~ 40 mol%. Here we used 20 mol% of CO_2 and 40 mol% of CO_2 gas mixture balanced with

N_2. The reaction cell stayed for at leat two days, then the composition of gas and hydrate phase were measured. For composition measurements of gas released from hydrate, a sampling valve with a loop volume of 1μL was installed and connected to a gas chromatograph on-line, which was previously calibrated for CO_2 and N_2. The evolving gases were analyzed several times by a gas chromatograph attached directly to the reactioncell to eliminate possible errors that might arise during the sampling procedure and to confirm the reproducibility of the data.

3. Results and Discussion

Both methane and CO_2form structure I hydrate, as do mixtures of these gases. When the gas mixtures form structure I, there is preferential partitioning of methane and CO_2 between the gas and the hydrate phases because CO_2 has preference for the large cage in the hydrate. In our previous work, we carried out the investigation of the distribution of methane over the cages of structure I for hydrate samples prepared from gas mixtures of methane and CO_2. Fig. 1 shows the ratio of methane in large to small cages at corresponding concentration of vapor phase. It is noted that for ^{13}C NMR spectra of pure methane hydrate the ratio of methane in large to small cages, $A_{L,CH4}/A_{S,CH4}$, is 3.69 so that the small cage is occupied to a smaller degree than the larger cage. With increasing CO_2 in the gas mixture, the ratio declines steadily and reaches0.23 for very dilute methane gas mixture. This indicatesthat there is a limit to the degree of substitution that one can expect under equilibrium conditions even when the gas composition approaches 100% CO_2. When methane hydrate is exposed to gas mixture of methane and CO_2, the ratio of methane in hydrate cages shows different occupancies at corresponding gas mixture of methane and CO_2. As the concentration of CO_2 is increased in gas mixture that is exposed to methane hydrate, the ratio of methane in hydrate cages declines, although the value is almost identical until 40mol% CO_2 and balanced methane gas mixture. When the concentration of CO_2 is increased to 60mol% in gas mixture, the ratio declines to 3.20 and reaches 2.54 for 100mol% CO_2, which indicates the replacement reaction mainly occurred in large cages of structure I. The measurement of hydrate phase after dissociation suggests that the concentration of CO_2 is only 4.2mol% for 40mol% CO2 and balanced CH4 gas mixture, increased to 56.6mol% for 100mol% CO_2, which confirmed the NMR spectroscopic results as the replacement reaction only occurs after the concentration of CO_2 is increased more than 40 mol%. These results indicate that there is limit CO_2concentration of vapor phase to induce the replacement reaction if methane hydrate contact with methane and CO2 gas mixture.

However, when methane hydrate is exposed to N_2 and CO_2 gas mixture it shows different replacement reaction characteristics. Fig. 2 shows ^1H NMR spectra as a function of time when methane hydrate is exposed to 20mol% CO_2 and balanced N_2 gas mixture. It is likely that the methane is replaced and the amount of methane in hydrate cages decreased steadily. When running the experiment for 65 hrs, it is confirmed that 42% of methane is replaced. These resultssuggest that methane in hydrate cages could be replaced when it exposed to N_2 and CO_2 gas mixture although the concentration of CO_2 isas low as 20mol%. Fig. 2 also suggests that the replacement reaction is fast at earlier stage as 25% of methane is replaced until 17hrs and slowly reaches 42% for last 48hrs. In order to follow the change of methane in hydrate cages, ^{13}C NMR spectra have been measured during the replacement reaction, as showed in Fig. 2. It showed only methane molecules in hydrate cages, full range spectrum gives also CO_2 in large cages of structure I after 65hrs of replacement reaction. It is not confirmed that CO_2 molecules is occupied in small cages of structure I because the chemical shift of CO_2in gas phase and small cages of hydrate is almost identical. The results indicate that 36% of methane in small cages is replaced while 31% of methane in large cages is replaced during 17hrs. It is well matched with ^1H NMR results as the amount of replaced methane is 25% during 17hrs. The number of replaced methane indicates that the methane in small cages is replaced more than those in large cages. However in structure I the large cages outnumber the small cages by a factor of three, thus the amount of replaced methane should be much larger in large cages than small cages.

The above spectroscopic results indicates that the methane in hydrate cages is replaced, the question is aroused what gas molecules are react with methane in hydrate cages. ^{13}C NMR spectroscopic result suggests that CO_2 molecules occupy large cages by replacing methane molecules, but it did not give the clue the nitrogen as replacement reactant. In orderto investigate the fate of nitrogen during the replacement reaction, we used macroscopic approach for measuring vapor and hydrate phase concentration after the replacement reaction. We put methane hydrate contact with CO_2 and N_2 gas mixture for at least 60hrs, then measure the gas composition of both vapor and hydrate phase. The composition of hydrate phase is concluded by measuring gas composition dissociated from hydrate phase. Fig 4 shows the vapor and hydrate phase composition when methane hydrate is contact with 20mol% CO_2 and N_2gas mixture for 60hrs at 274K and 100bar. Fig. 3 (a) shows the vapor phase composition contacting with hydrate phase. The initial composition is 20mol% of CO_2 and 80mol% of N_2, however after 60hrs of replacement reaction, the CO_2 and N_2decreased to 10.7 and 69.1mol%, respectively. It is noted that the methane is detected as 20mol%, which is considered evolved from hydrate phase due to replacement reaction. Fig. 3 (b) gives the composition of hydrate phase as the methane is 51.9mol% and the N_2 and $CO_2$are 23.6, 24.5mol%, respectively. It is interesting that the amount of N_2 and $CO_2$is almost identical in hydrate phase, which implies that both N_2 and CO_2molecules participate in

replacement reaction. These results represent that when the N_2 and CO_2gas mixture contact with methane hydrate, both gas molecules replaced methane in hydrate cages and occupy small and large cages of structure I hydrate. It is noted that from Fig. 2 and 3, the hydrate structure did not change and N_2 and CO_2 molecules did not form separate structure II hydrate that is known to be formed from pure N_2molecules. Increase of CO_2 in gas mixture also increase the amount of methane in gas phase as it shows 27 mol% of methane in vapor phase. Moreover the amount of CO_2 in hydrate phase increased to 36.5 mol%, which indicates that the CO_2 might have more capability of replacement reaction than N_2molecules. Remaining methane is 49mol% in hydrate phase, and 51mol% of methane is replaced by both N_2 and CO_2 molecules.

4. 결 론

Here we report the replacement reaction of methane hydrate by N_2 and CO_2 gas mixture at similar conditions of marine sediment. At least three days are needed to replace 42 mol% of methane in hydrate as monitored by ^{1}H NMR spectroscopy, and the reaction is more focused on large cages of structure I as it showed in ^{13}C NMR measurements. Macroscopic measurements also suggest similar replacement reaction as ~50mol% of methane is replaced by $N_2$and CO_2 molecules. It is noted that the more CO_2 in vapour phase induce more CO_2 in hydrate phase suggesting that CO_2 might have more capability of replacing methane in hydrate cages than N_2. These experimental results could be good start point to establish CO_2 capture and sequestration into methane hydrate deposits in East Sea of Korea. High purity of CO_2 gas should be favourableto sequestration and recovery of methane from hydrate reservoir, but experiments also shows that expensive CO_2capture and processing facility could be avoided by direct injection of industrial flue gas, especially from Iron and Steel Company.

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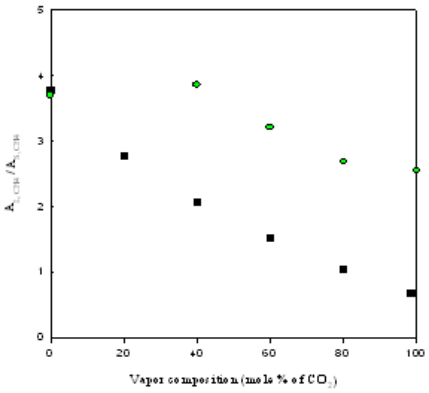

Fig. 1. Ratio of methane in hydrate cages at corresponding gas composition. (■) equilibrium ratio, (●) after replacement.

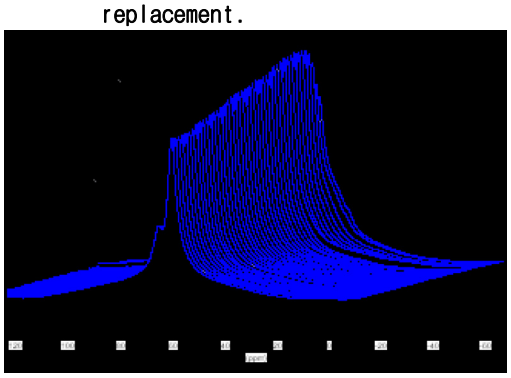

Fig. 2. ^{1}H NMR spectra at 273K and 100bar when methane hydrate exposed to N_2 and CO_2 gas mixture (20mol% CO_2).

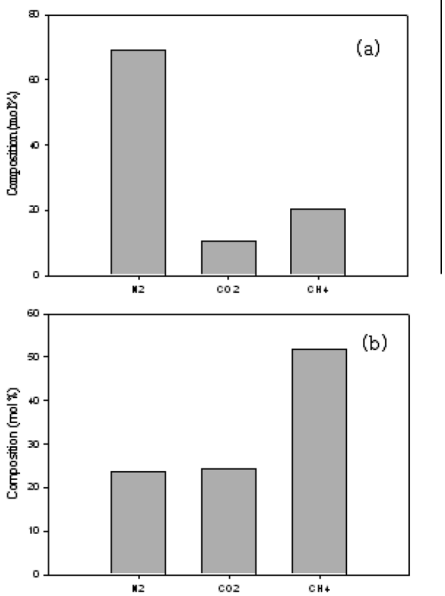

Fig. 3. Vapor and hydrate phase composition after 60hr of replacement with 20 mol% CO_2 and N_2 gas mixture. (a) vapor phase, (b) hydrate phase.