Microscopic and Macroscopic Observations of CH4 Hydrate Production by N2-CO\textsubscript{2} Gas Injection

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Gas hydrates are typical water-based crystalline materials in which guest molecules such as CH4, N2, and CO\textsubscript{2} are captured in host water cavities constructed by the hydrogen-bonded networks of icy-materials. Gas hydrates are considered one of the most promising unconventional energy resources due to a huge amount of natural gas in the form of natural gas hydrates. As the demand for energy resources increases, the utilization of CH4 hydrate as a new energy resource has been extensively studied, and thus; depressurization, thermal stimulation, and CH4 – CO\textsubscript{2} replacement techniques have been designed to extract CH4 gas from CH4 hydrate deposits. Among these techniques, the replacement technique is recognized as a promising option for solving key issues in energy and environmental fields, providing the dual functions of CH4 production and CO\textsubscript{2} sequestration.

Based on these considerations, the kinetics of CH4 replacement with CO\textsubscript{2} and N2 gas in CH4 hydrate has been studied by microscopic and macroscopic approaches. In-situ 1H and 13C NMR spectroscopy (Microscopic approach) has been used to monitor the replacement patterns occurring in CH4 hydrate. The replacement process was monitored by in situ 1H NMR spectra, where about 42 mol % of the CH4 in the hydrate cages was replaced in 65 h. Large amounts of free water were not observed during the replacement process, indicating a spontaneous replacement reaction upon exposing CH4 hydrate to CO\textsubscript{2} and N2 gas mixture. From in situ 13C NMR spectra, we confirmed that the replacement ratio was slightly higher in small cages, but due to the composition of structure I hydrate, the amount of CH4 evolved from the large cages was larger than that of the small cages.

A long cylindrical high-pressure reactor (Macroscopic approach) was designed to demonstrate the recovery of CH4 from CH4 hydrate bearing sediments, and the injection rate of the gas mixture was controlled to monitor the amount of recovered CH4 from CH4 hydrates. The recovery efficiency of CH4 gas from CH4 hydrates is in inverse proportion to the flow rate of the CO\textsubscript{2} and N2 gas mixture. CH4 hydrates were synthesized by using two different sediments, having particle size distributions of 75 to 150 \textmu m and 45 to 90 \textmu m with the same porosity, and the recovery efficiency of CH4 from CH4 hydrates was also monitored. We confirmed that there is no significant difference in the replacement characteristics by using these two different sediments. Horizontal and vertical flows of the CO\textsubscript{2} and N2 gas mixture were applied to monitor the effect of flow direction on replacement characteristics and we also confirmed that a similar amount of CH4 was recovered in horizontal and vertical flows of the CO\textsubscript{2} and N2 gas mixture at the same flow rate.