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# Dissociation Behavior of Hydrate Core Sample Using Thermodynamic Inhibitor—Part 2: Experimental Investigation Using Long Core Samples

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**The dissociation behavior of a laboratory-made methane hydrate core sample following injection of an inhibitor (aqueous methanol solution) has been investigated using a specially developed experimental setup. The core holder utilized in this work is 5 times greater in length than the one previously employed. A warm aqueous methanol solution was injected into core samples, which simulate natural gas hydrate sediment under the seafloor. Core temperature decreased upon injection of the inhibitor, in contrast to the case of pure water injection. Measurement of gas yields versus time suggests that the inhibitor increased dissociation rates. The observed pressure differentials between inlet and outlet of the core sample suggest that the inhibitor effectively prevented the reformation of hydrate within the dissociating core sample.**

## INTRODUCTION

Natural gas hydrates are crystalline compounds that can contain large amounts of natural gas (Sloan, 1998). Owing to recent seismic exploration and geological research, it is widely known that natural gas hydrate exists in geological formations (mainly unconsolidated sediment) and constitutes a potentially large natural gas resource for the future (Makogon, 1981; Brooks et al., 1986; Kvenvolden, 1988; Kvenvolden et al., 1993; Okuda, 1993; Gornitz and Fung, 1994; Sassen, 2001). To make recovery of natural gas from hydrates commercially viable, hydrates must be dissociated in situ. The inhibitor injection method is thought to be an effective method for forcing gas hydrate dissociation, apart from depressurization and thermal stimulation. While there is only limited information about dissociation kinetics in the presence of hydrate inhibitors, substantial phase equilibrium data are available (Davidson et al., 1981; Ng and Robinson, 1985; Robinson and Ng, 1986).

In our previous study, an experimental setup featuring a small core holder was successfully used to investigate the dissociation behavior of a methane hydrate (MH) core sample under simulated sub-seafloor conditions. Results indicated that the presence of an inhibitor (methanol) effectively accelerated the rate of hydrate dissociation. Additionally, it was observed that the temperature of solution at the outlet of the core holder changed continuously, while outlet temperature remained constant in the case where only pure water was present. This result also suggested that the concentration of inhibitor in contact with the hydrate surface changed continuously (Kawamura et al., 2006). In this study, a new experimental setup has been developed to enable the extension of the core holder to 5 times its previous length. A warm aqueous methanol solution was injected through the artificial core samples, which simulate natural gas hydrate sediment under the seafloor. The experiments were designed to reveal specific dissociation behaviors that could not be detected by the previous experiments.

## EXPERIMENTAL

### Apparatus

Fig. 1 shows a schematic of the experimental setup equipped with core holder and temperature control system. An artificial MH core sample was wrapped with a flexible rubber sleeve, and end-caps were installed on both ends of the core. High-pressure fluid is injected into the core sample to simulate in situ formation pressures up to 30 MPa. A thermal jacket enables temperature control from −50°C to 100°C. The jacket was divided into 7 sections, with each section employing a 3-way valve to select the cooling or heating medium. Lateral fins around the core sleeve prevented heat flow by convection of the high-pressure fluid. This system ensured that the thermal gradient of fluid adjacent to the core was very close to that of the core sample itself. In other words, the heat flow through the core sample can be considered to be essentially 1-dimensional, neglecting radial heat loss. The diameter of the core sample was 50 mm, while the length was extended by a factor of 5 to 500 mm (compared to 10 mm in the previous work). Gas and liquid (i.e. aqueous methanol solution or water) can be injected into the core sample at specified pressure, temperature and flow rates.

### Procedure

MH core samples used in this work were laboratory-made artificial samples. A sand column was prepared using Toyoura sand, which is mainly composed of $SiO_2$ and whose average grain diameter is approximately 200 $\mu$m. Toyoura sand was packed in the rubber sleeve with a low porosity of approximately 0.37. In this state, the pore space was filled with pure water. After setting the sand column into a thermal jacket, it was pressurized by high-pressure fluid at 15 MPa, simulating earth pressure. Research-grade methane gas (99.9%) was injected into the sand column to exhaust free water so as to form an irreducible water saturation

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