

## Dissociation Behavior of Hydrate Core Sample Using Thermodynamic Inhibitor

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**The dissociation behavior of an artificial hydrate core sample in an inhibitor aqueous solution (methanol aqueous solution) was investigated experimentally. A newly constructed experimental setup equipped with a core holder was used to investigate the dissociation behavior of the hydrate core sample under conditions similar to those below the seafloor. It was observed that an inhibitor that changes the hydrate stability condition is effective in accelerating the hydrate dissociation rate. In addition, it was observed that the temperature of the solution from the outlet of the core changes continuously, while the outlet temperature does not change in the case of pure water. This result suggests that the inhibitor concentration around the hydrate surface changes continuously.**

### INTRODUCTION

Natural gas hydrates are crystalline compounds that can contain a large amount of natural gas (Sloan, 1998). Owing to recent seismic exploration and geological research, it is widely known that the natural gas hydrate that exists in sediment constitutes a large natural gas resource expected to be a future energy source (Makogon, 1981; Brooks et al., 1986; Kvenvolden, 1988; Kvenvolden et al., 1993; Okuda, 1993; Gornitz and Fung, 1994; Sassen, 2001). To make the recovery of natural gas from hydrates commercially viable, hydrates must be dissociated in situ. The inhibitor injection method is thought to be one of the effective dissociation methods, as well as depressurization and thermal stimulation. However, there is only limited information about dissociation kinetics in inhibitors, while there exist substantial phase equilibrium data.

In our previous study, the dissociation behavior of the pure methane hydrate (MH) in an inhibitor (ethylene glycol aqueous solution) was investigated using a pellet-type MH sample (Kawamura et al., 2003a, b). The results suggested that the dissociation rate was increased by ethylene glycol. Observations also suggested that water generated from the MH dissociation prevented MH from further contacting the inhibitor. Thus, the concentration of the inhibitor changed around the MH surface resulted in slower dissociation than expected from the initial concentration (Kawamura et al., 2003a).

In this study, the dissociation behavior of a pure MH pellet in a methanol aqueous solution was investigated as a first step. Methanol is a widely known thermodynamic inhibitor of clathrate

hydrate, and there exist substantial phase equilibrium data (Davidson et al., 1981; Ng and Robinson, 1985; Robinson and Ng, 1986). Fig. 1 shows the 3-phase diagram of MH with methanol obtained by the thermodynamic calculation developed by Yoon et al. (2002).

In addition, experiments were conducted to simulate the dissociation behavior of actual MH sediment using an artificial MH core sample by injecting an ethanol aqueous solution. A newly constructed experimental setup equipped with a core holder was used to investigate the dissociation behavior of an MH core sample under conditions similar to those below the seafloor. A warm inhibitor aqueous solution was injected through the core sample. The heat supplied by the solution contributed to the dissociation of MH. The experiment was carried out varying the temperature and concentration of the inhibitor. The relationship between these parameters and the dissociation behavior was obtained.

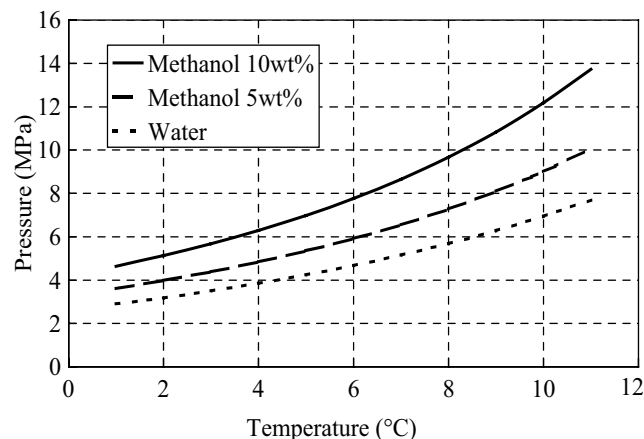


Fig. 1 Three-phase diagram of methane-water-hydrate system with methanol (Yoon et al., 2002)

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