Effect of Clay Particle for Methane Hydrate Formation - Dissociation Behavior

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ABSTRACT

Formation / dissociation behavior of clathrate hydrate in bentonite or kaolin suspension with or without sodium chloride was experimentally investigated for safe gas production from the natural gas hydrate reservoir. Raman spectroscopic analysis is conducted to investigate the property of formed hydrate from bentonite or kaolin suspension. Vapor pressures of water of these suspensions, which are related to hydrate equilibrium conditions, are also determined. The crystal structures of clathrate hydrates formed from clay suspensions can be determined as sI. However, the small cavity occupancies of hydrate formed from calcium bentonite and kaolin are 0.792 and 0.794 respectively, which are approximately 10 % smaller than that of pure MH or hydrate formed from sodium bentonite. Obtained vapor pressure suggests that equilibrium T-P condition in clay suspension without NaCl does not shift within the concentration region of 1 to 10 wt%. However, for NaCl 20 wt% - sodium bentonite 10 wt% suspension and NaCl 20 wt% - calcium bentonite 10 wt% suspension, the vapor pressures are rather smaller than that of NaCl 20 wt% solution. It suggests the equilibrium pressures in these suspensions become high compared to that in NaCl 20 wt% solution.

KEY WORDS: Natural gas; Hydrate; Exploitation; Clay; Inhibitor; Raman spectroscopy.

INTRODUCTION

Natural gas hydrates are crystalline compounds that can contain a large amount of natural gas (Sloan and Koh, 2008). Owing to recent seismic exploration and geological research, it is widely known that natural gas hydrate that exists in the sediment constitutes a large natural gas resource and is expected to be an energy source in the future (Makogon, 1981; Brooks et al., 1986; Kvenvolden, 1988; Kvenvolden et al., 1993; Okuda, 1993; Gornitz and Fung, 1994; Sassen, 2001; Fujii, 2008). Natural gas hydrate will be dissociated mainly by the depressurization in the geologica formation for commercial gas recovery. Fig. 1 shows an example of gas production scheme. The system consists of some facilities shown in fig. 1. And there is a concern that some interruptions for gas production will occur, i.e. plugging by hydrate formation in the facilities. Accordingly, both technical and fundamental investigations for the flow assurance are highly demanded for safety and economical operation. Since it is known that the methane hydrate (MH) bearing sediments around Japan form an alternate strata of sand and clay, clay particle i.e. bentonite and kaolin will exist in dissociated fluids of MH bearing sediments. Therefore, it is expected that the MH formation-dissociation will occur under the existence of such clay particle. The authors had investigated the formation / dissociation behaviors of MH in bentonite or bentonite - NaCl suspension (Kawamura et al., 2010). It was speculated that bentonite affect not thermodynamically but kinetically on hydrate formation / dissociation reaction within some concentration region. In this study, Raman spectroscopic analysis is conducted to investigate the property of formed hydrate from bentonite or kaolin suspension. Vapor pressures of these suspensions, which are related to hydrate equilibrium conditions, are also obtained.