

## Distinctive Dissociation of Methane Hydrate Coexisting with NaCl Aqueous Solution

Methane hydrate pellets including up to 2.7 wt% NaCl were formed artificially and subjected to a storage test at 253 K under ambient pressure. The dissociation process of the pellets during storage was investigated using phase contrast X-ray computed tomography. It was revealed that the dissociation rate of methane hydrate pellets containing NaCl accelerated in proportion to the NaCl concentration. In addition, dissociating spots were scattered all over the pellets in contrast to pure methane hydrate. These experimental results suggest that the formation of NaCl aqueous solution promote the dissociation of methane hydrate pellets even below the ice point.

Methane hydrate is attracting public attention as a potential natural gas resource. Methane hydrate spontaneously forms under the ocean floor, which satisfies the conditions of low temperature and high pressure, when methane comes in contact with water [1]. The dissociation of methane hydrate is suppressed under atmospheric pressure and just below the ice point, though the conditions are well outside the equilibrium region. This is known as the self-preservation phenomenon [2]. Self-preserved methane hydrate generally dissociates from its surface to the inside with the dissociated parts converting into ice, which suppresses the diffusion of methane gas [3, 4]. The phenomenon is complicated because it depends on many factors such as ice film [3, 4], electrolytes, and so on [5, 6]. Moreover, electrolytes also affect the phase equilibria of methane hydrate; electrolytes shift the equilibrium to higher pressure and lower temperature [1]. Thus, electrolytes affect both the formation and dissociation of methane hydrate. In this study, the dissociation of methane hydrate pellets coexisting with sodium chloride (NaCl) was investigated during storage at 253 K and ambient pressure. Dissociation areas inside the samples were visualized by phase contrast X-ray imaging to determine the dissociation mechanism [7].

Methane hydrate pellets ( $\phi 33$  mm  $\times$  30 mm) including 0.5 wt% NaCl and 2.7 wt% NaCl were formed at

273–277 K under 5.5 MPa, and stored at 253 K under atmospheric pressure for over seven days. Weight loss attributed to the release of methane gas from dissociating methane hydrate during storage was observed for estimation of residual gas fractions in the samples.

Phase contrast X-ray computed tomography (CT) using the diffraction-enhanced imaging (DEI) method was applied to obtain tomographs of the methane hydrate samples [8, 9]. The samples were immersed in methyl acetate at  $188 \text{ K} \pm 1 \text{ K}$  throughout measurement to eliminate artifacts caused by the outer surface of the samples. The samples were irradiated by monochromatic synchrotron X-rays with the energy of 35 keV. An X-ray CT using the DEI method was carried out with a spatial resolution of 0.040 mm [8] and density resolution of  $\sim 0.01 \text{ g/cm}^3$  [10].

Figure 1 shows residual gas fractions of the methane hydrate samples with storage time. The sample containing 0.5 wt% NaCl had dissociated by only 3% in gas fraction after storage for seven days at 253 K. On the contrary, the residual gas fraction of the sample containing 2.7 wt% NaCl dissociated by nearly half in the same time. It was thus revealed that the dissociation rate of the methane hydrate pellets at 253 K under atmospheric pressure depended greatly on the NaCl concentration.

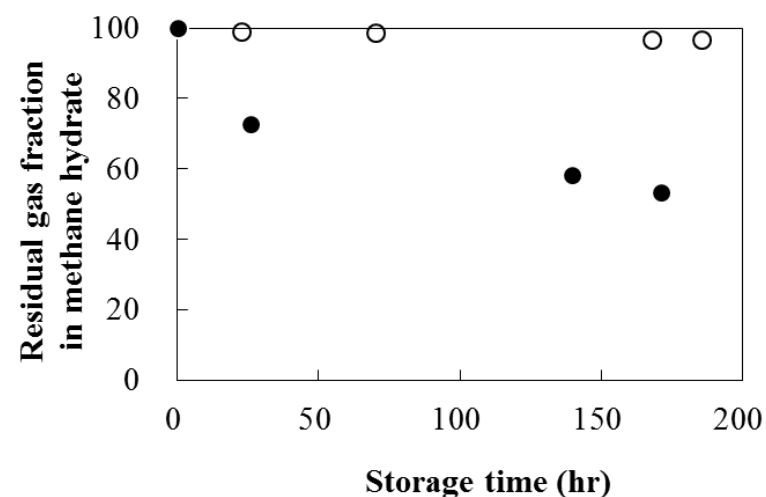


Figure 1: Reduction of gas content in the methane hydrate samples of  $\phi 33$  mm  $\times$  30 mm. Open and solid circles show residual gas fractions remaining in the methane hydrate samples with 0.5 wt% NaCl and 2.7 wt% NaCl, respectively. The error bars fall within the plotted points.

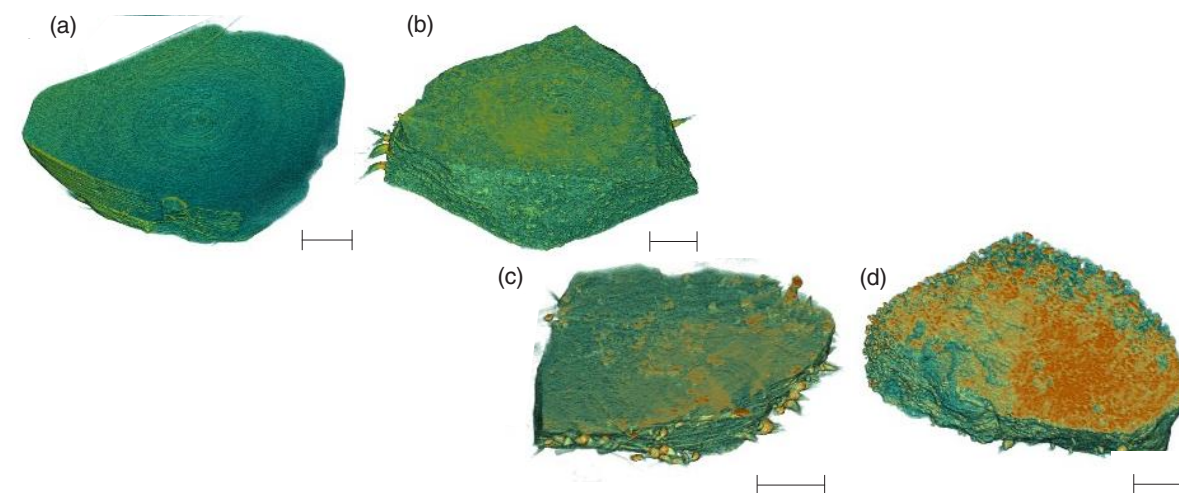


Figure 2: 3D images of methane hydrate: (a) just-formed methane hydrate with 0.5 wt% NaCl, (b) methane hydrate with 0.5 wt% NaCl after seven days' storage, (c) just-formed methane hydrate with 2.7 wt% NaCl, and (d) methane hydrate with 2.7 wt% NaCl after seven days' storage. Scale bars show 2 mm length.

Figure 2 shows 3D images of the methane hydrate samples obtained from phase contrast X-ray CT using the DEI method. Color gradation corresponds to density; bluish color indicates heavier material, and orange color indicates lighter material. The blue and orange regions roughly correspond to methane hydrate ( $0.934 \text{ g/cm}^3$  at 193 K [8]), and hexagonal ice ( $0.927 \text{ g/cm}^3$  at 193 K [8]), respectively. The methane hydrate containing 0.5 wt% NaCl had a uniform texture without dissociated parts at first (Fig. 2a). After seven days at 253 K, particles indicating lower hydrate concentration resulting from dissociation spread throughout the sample (Fig. 2b). On the other hand, the methane hydrate containing 2.7 wt% NaCl was studded with areas of lower hydrate concentration even after it had just formed (Fig. 2c). Almost all of the sample turned to ice after seven days of storage at 253 K (Fig. 2d). This indicated that methane hydrate including NaCl dissociates from inside areas, though methane hydrate formed without additives dissociates from its outer surface to the inside while ice forms mainly on the methane hydrate surface as layers [11].

NaCl concentrations in local parts of the methane hydrate pellets were extremely high, because NaCl was excluded from methane hydrate crystals and accumulated at the grain boundaries. The eutectic point of the water and NaCl system was 23.3 wt% NaCl at 252 K [12]. Therefore, methane hydrate pellets including NaCl might coexist with an aqueous solution of NaCl during storage at 253 K, even though this was lower than the ice point. Accordingly, suppression of gas diffusion by ice as the self-preservation phenomenon cannot be expected.

Consequently, the NaCl concentration was one of the most influential factors for the dissociation of methane hydrate because the presence of NaCl led to coexistence with aqueous solution which promoted the dissociation even below the ice point. Additionally, the phase contrast X-ray CT images showed that the meth-

ane hydrate pellets containing NaCl had many dissociation sites, indicating that dissociations occurred not only on the surface but also inside the pellets.

### REFERENCES

- [1] E. D. Sloan and C. A. Koh, *Clathrate Hydrates of Natural Gases*, third ed., (CRC Press, Florida, 2007). 1.
- [2] V. S. Yakushev and V. A. Istomin, "Gas-Hydrates Self-Preservation Effect" in *Physics and Chemistry of Ice* edited by N. Maeno and T. Hondo (Hokkaido Univ. Press, 1992). 136.
- [3] W. Shimada, S. Takeya, Y. Kamata, T. Uchida, J. Nagao, T. Ebinuma and H. Narita, *J. Phys. Chem. B* **109**, 5802 (2005).
- [4] S. Takeya and J. A. Ripmeester, *Chem. Phys. Chem.* **11**, 70 (2010).
- [5] H. Sato, T. Tsuji, T. Nakamura, K. Uesugi, T. Kinoshita, M. Takahashi, H. Mimachi, T. Iwasaki and K. Ohgaki, *Int. J. Chem. Eng.* 843274 (2009).
- [6] H. Sato, H. Sakamoto, S. Ogino, H. Mimachi, T. Kinoshita, T. Iwasaki, K. Sano and K. Ohgaki, *Chem. Eng. Sci.* **91**, 86 (2013).
- [7] H. Mimachi, S. Takeya, Y. Gotoh, A. Yoneyama, K. Hyodo, T. Takeda and T. Murayama, *Fluid Phase Equilibria* **413**, 22 (2016).
- [8] S. Takeya, A. Yoneyama, K. Ueda, K. Hyodo, T. Takeda, H. Mimachi, M. Takahashi, T. Iwasaki, K. Sano, H. Yamawaki and Y. Gotoh, *J. Phys. Chem. C* **115**, 16193 (2011).
- [9] S. Takeya, K. Honda, Y. Gotoh, A. Yoneyama, K. Ueda, A. Miyamoto, T. Hondoh, A. Hori, D. Sun, R. Ohmura and K. Hyodo, T. Takeda, *J. Synchrotron Radiat.* **19**, 1038 (2012).
- [10] A. Yoneyama, J. Wu, K. Hyodo and T. Takeda, *Med. Phys.* **35**, 4724 (2008).
- [11] S. Takeya, A. Yoneyama, K. Ueda, K. Hyodo, T. Takeda, H. Mimachi, M. Takahashi, T. Iwasaki, K. Sano, H. Yamawaki and Y. Gotoh, *J. Phys. Chem. C* **115**, 16193 (2011).
- [12] J. Timmermans, "The Physico-Chemical Constants of Binary Systems in Concentrated Solutions VOL. 3", (Interscience Publishers, Inc., New York, 1960.) 308.

### BEAMLINE

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