Storage Performance and Structural Characteristics of Natural Gas Hydrate

Natural gas hydrate (NGH) pellets are one candidate for a natural gas storage and transportation medium due to their high gas density and much easier storage method compared to liquefied natural gas (LNG) and compressed natural gas (CNG). More than 80% of natural gas stored within NGH pellets with different particle sizes from 0.50 mm to 30 mm was maintained for two weeks at 253 K under ambient pressure. The internal texture of the NGH pellets was investigated using phase contrast X-ray CT by diffraction enhanced imaging (DEI), revealing that the outer surface of the pellet was covered with an ice film and NGH was well preserved inside.

The production of natural gas from both conventional and unconventional fields is increasing because of the expanding worldwide demand for natural gas. Therefore, energy transportation systems have diversified not only to pipelines and LNG, but also new means such as gas to liquids (GTL), natural gas liquids (NGL), natural gas hydrate (NGH) [1-6]. NGH is a clathrate crystal that consists of water and natural gases such as CH_4, C_2H_6, and C_3H_8, with natural compositions. NGHs are usually stable at high pressure and low temperature, and can contain natural gas of approximately 170 times their own volume. It is known that CH_4 and CO_2 hydrates are preserved just below the freezing point of water under atmospheric pressure, though the conditions are outside the thermodynamically stable zone of CH_4 and CO_2 hydrates [7-11]; this is called the self-preservation phenomenon [7]. The surfaces of self-preserved CH_4 and CO_2 hydrates are covered with ice [9-12], so the distribution of ice film is thought to be important for the preservation of gas hydrate. NGH also shows the self-preservation phenomenon below the ice point. Especially, NGH in the form of pellets is well preserved under the conditions of 253 K and atmospheric pressure while powdered NGH does not show the preservation phenomenon [13]. In this study, we focused on how the small size of NGH pellets showed the self-preservation phenomenon, and then phase contrast X-ray computed tomography by diffraction enhanced imaging (DEI) measurements were carried out to prove that the original surface of the NGH pellet was covered with ice [14].

NGH pellets containing simulated natural gas (89.8% CH_4, 5.6% C_2H_6, 3.1% C_3H_8, 0.6% iso-C_4H_{10}, 0.8% n-C_4H_{10}, and under 0.1% iso-C_5H_{12}) were formed using a semi-batch system [13], and then they were divided into φ33 × 30, 10–20, 4.0–6.7, 1.0–4.0, and 0.50–1.0 mm. The mass fraction of NGH was 75 wt%, and that of ice was 25 wt% for the sample of φ33 × 30 mm. The others were 72 wt% for 10–20 mm, 59 wt% for 4.0–6.7 mm, 34 wt% for 1.0–4.0 mm, and 19 wt% for 0.50–1.0 mm (Fig. 1). The pellets were stored for two weeks at 253 K under ambient pressure to investigate their storage performance. After two weeks, the mass fraction of each NGH was 74 wt%, 67 wt%, 57 wt%, 32 wt%, and 16 wt% in descending order. In other words, the ratios of weight loss between the initial and final mass fraction of NGH in the storage test were 0.76 wt%, 6.9 wt%, 3.3 wt%, 6.7 wt%, and 17 wt% from largest to smallest. This result showed that smaller NGH samples had lower NGH fractions at the start of the storage test and were likely to dissociate during the storage period. This is because the smaller NGH particles have larger specific surface areas. Thus, larger particles of over approximately 10 mm in diameter of NGH pellets are more favorable than smaller ones from the viewpoint of gas storage.

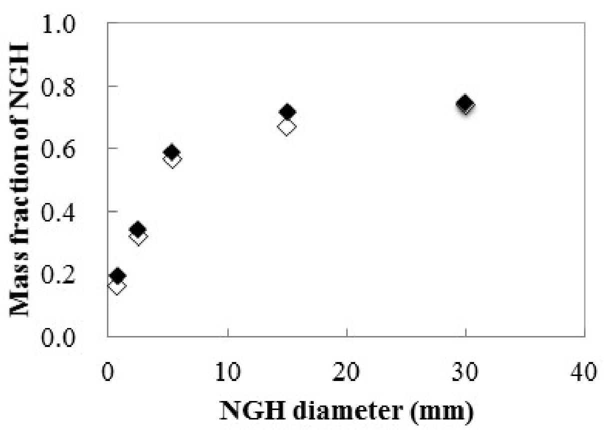

Figure 1: Change of mass fraction of NGH for each diameter. Solid diamonds represent starting mass fraction of NGH and open diamonds represent that of NGH after two weeks' storage.

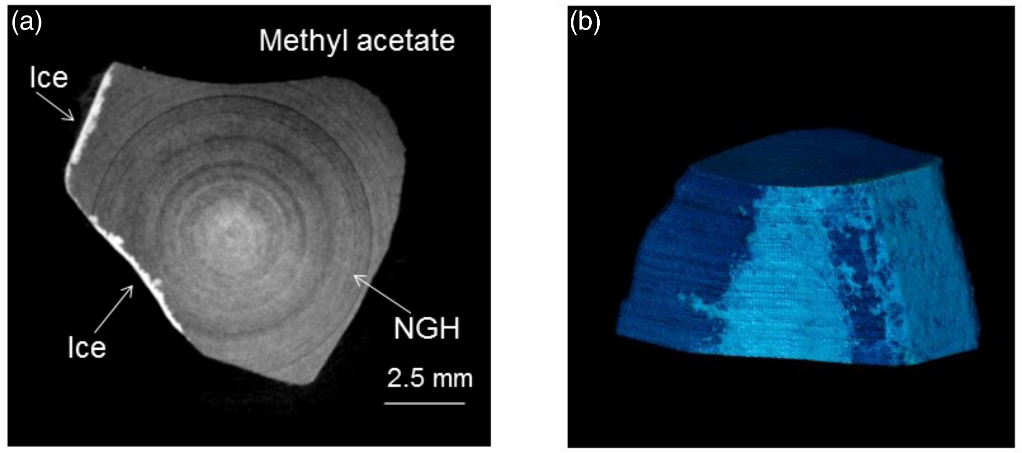

Figure 2: Cross-section image (a) and 3D image (b) of NGH particle with ice film obtained from DEI. Ring patterns in the cross-section image are artifact of X-ray CT imaging.

Non-destructive measurement by DEI was performed on the NGH pellets to visualize the internal distribution of NGH and ice with a spatial resolution of 0.040 mm. A 35-keV monochromatic synchrotron X-ray at a vertical wiggler beam was irradiated to an NGH pellet that was immersed in methyl acetate at 193 K ± 1 K to eliminate artifacts caused by the outer surface of the pellet [12, 13]. Phase map images were obtained by detecting the X-ray beam that diffracted after passing through the sample using the analyzer crystal. The sample was scanned at 11 positions with the scanning time of one second for each position, and the number of projections was 500. An internal image of the NGH pellet is shown in Fig. 2. The difference in density of the NGH pellet is reflected in the gray scale [Fig. 2(a)]. The white region shows ice whose density was lower than that of the surroundings, and the gray and black areas were NGH and methyl acetate, respectively. The observed result showed that only some part of the surface was covered with ice film [Fig. 2(b)]. But this is due to that the sample was shaved at a temperature below 150 K, a condition which suppressed NGH dissociation, to suitable size for the DEI measurement. Considering the good storage performance as shown in Fig.1 and its similarity with CH_4 hydrates, the NGH pellet in common state was undoubtedly thought to be fully covered with ice film. An ice film with a thickness of approximately 0.30 mm was observed on the pellet, and the inside of the pellet was dense with NGH without ice grains or pore spaces. Consequently, the formed NGH pellet that maintained natural gases under mild storage conditions was proved to be stabilized by the surface thin ice film.

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H. Mimachi[1], S. Takeya[2], A. Yoneyama[3], K. Hyodo[4], T. Takeda[5], Y. Gotoh[2], and T. Murayama[1] ([1]Mitsui Engineering and Shipbuilding Co. Ltd., [2]AIST, [3]Hitachi Ltd., [4]KEK-IMSS-PF, [5]Kitasato Univ.)