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Natural gas storage and transportation within gas hydrate of smaller particle: Size dependence of self-preservation phenomenon of natural gas hydrate

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HIGHLIGHTS

- Larger particles of NGH allowed a larger fraction of gas hydrate to be preserved.
- Dense NGHs over 0.50 mm could keep natural gases for 14 days at 253 K and 1 atm.
- Ice films on self-preserved NGHs over 1.0 mm had an equivalent thickness.

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ABSTRACT

In this study, the preservation ability of natural gas hydrate (NGH) with different particle size from 0.50 mm to 30 mm was investigated. It is known that natural gas preservation does not occur when NGHs are in powder form and their size is under several tens of micrometers, while the dense bulk NGH was preserved after the initial rapid dissociation. It is important to investigate the required size of NGH particle for self-preservation to occur when NGH is used as a storage media of natural gases. Despite the difference in particle size, the experimental results herein revealed that the NGH sample was enveloped by an ice film caused by the initial rapid dissociation. The thickness of the ice film grown during the initial rapid dissociation was almost the same and did not depend on the particle size of NGH being over 1.0 mm and higher than that of methane hydrate. The thickness of the ice film necessary for the self-preservation of NGH may be the reason why powder NGH does not show the self-preservation phenomenon. However, we revealed that NGH particles with diameters of more than 0.50 mm were preserved for two weeks.

1. Introduction

Due to the expansion of the worldwide demand for natural gas, production of natural gas from not only conventional gas fields but also unconventional gas fields, such as shale gas, is increasing. Therefore, ocean transportation of natural gas or liquefied natural gas (LNG) is the key for further development of the use of natural gas. Natural gas hydrate (NGH) is one of the clathrate compounds formed from water and natural gases, such as CH_4, C_2H_6, C_3H_8, C_4H_{10}, etc., with natural compositions. NGH is a candidate for a new media for natural gas storage and transportation because it can contain about 170 times as much natural gas in the form of gas hydrate (Gudmundsson and Borrehaug, 1996; Sloan, 2003).

It is known that gas hydrates are usually stable under high pressures and at low temperatures. Some gas hydrates keep gases under atmospheric pressure and just below the melting point of ice though the surroundings are outside thermodynamically stable temperature and pressure conditions; this is called the self-preservation phenomenon (Yakushev and Istomin, 1992). It has been reported that CH_4 and CO_2 hydrates show the preservation phenomenon (Stern et al., 2001; Kuhs et al., 2004; Shimada et al., 2005; Falenty and Kuhs, 2009). Additionally, the preservation phenomenon of these hydrates correlate to their size, that is, larger particles of CH_4 or CO_2 hydrates exhibit better stability

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(Takeya et al., 2005; Sun et al., 2011). Meanwhile, CH_4 hydrate particles packed well with hydrate crystals showed better stability independently from particle sizes (Nakoryakov and Misyura, 2013), and it has been suggested that the thicknesses of ice films enveloping CH_4 hydrate were independent from particle size when the particle size was at least several hundreds of micrometers (Stoporev et al., 2014).

On the other hand, C_2H_6 and C_3H_8 hydrates do not show the preservation phenomenon, and a mixture of C_2H_6 or C_3H_8 with CH_4 reduces the preservation ability of CH_4 hydrate (Stern et al., 2003; Takeya and Ripmeester, 2008, 2010). When the $CH_4+C_2H_6+C_3H_8$ hydrate system was formed from water with surfactant (Zhang and Rogers, 2008), the hydrate particles were compacted on the metal surfaces to minimize internal void spaces, and the consolidated hydrate mass exhibited high stability at atmospheric pressure and 268 K. Recently, we have found that mechanically packed dense NGH pellets without any additives can also be preserved for three weeks when stored at 253 K under atmospheric pressure, while powdered NGH did not show the preservation phenomenon (Takeya et al., 2012). These facts call into question the effect of particle size on gas hydrate stability and whether smaller NGH particles (less than several tens of mm in diameter) can be preserved in the same way as CH_4 hydrates.

Here, NGH particles from 0.50 mm to 30 mm stored at 253 K, which is outside their thermodynamically stable zone, were examined. The change of NGH particles depending on particle size under atmospheric air conditions was investigated over two weeks at 253 K. We report our findings on how the particle size of NGH affects its dissociation.

2. Experimental section

2.1. Sample preparation

A cylindrical NGH pellet φ33 mm in diameter was formed by means of a semi-batch system with a reactor and one directional pelletizing machine. The system was pressurized to 4.6 MPa with methane gas, and then a gas mixture of 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}) was supplied and pressurized up to 5.5 MPa. The pressure was kept at 5.5 MPa during the formation process by supplying the gas mixture intermittently. NGH slurry was formed at 281 K, and then the slurry was dewatered and pelletized into a φ33 mm cylindrical mass. Then, the system was cooled to 253 K and depressurized to atmospheric pressure to obtain the NGH pellet. The NGH pellet was divided into two parts. The part for the measurements of initial NGH properties was kept under liquefied nitrogen immediately after the NGH pellet was obtained. The other part was kept at 253 K, and the storage test was started as soon as possible.

2.2. Measurements of initial NGH properties by GC, PXRD, and phase contrast X-ray imaging

Part of the NGH pellet was arranged for the initial property measurements using gas chromatography (GC), powder X-ray diffraction (PXRD), and phase contrast X-ray CT by means of a diffraction enhanced imaging (DEI) technique.

A portion of the NGH pellet was dissociated, and the gases from the NGH sample were collected after the initial rapid hydrate dissociation to obtain the correct gas composition in the sample by means of GC (Micro GC CP4900, Varian, Walnut Creek, CA). The other portion was ground into powder in an atmosphere of vapor from liquefied nitrogen at a temperature lower than 100 K to avoid NGH dissociation. PXRD measurement was performed at 123 K in the $\theta/2\theta$ step scan mode with a step width of 0.02° over a 2θ range of 6–60° using CuKα radiation and parallel beam optics (40 kV, 40 mA; Ultima III, Rigaku, Japan). Rietveld analysis using the RIETAN-FP program (Izumi and Momma, 2007) was conducted to analyze unit cell parameters of hydrate crystal, mass fraction of ice, and NGH using the same method as our earlier study (Takeya et al., 2012). Internal imaging of the NGH pellet sample was demonstrated by DEI to visualize the distribution of NGH coexisting with ice formed due to residual water or NGH dissociation

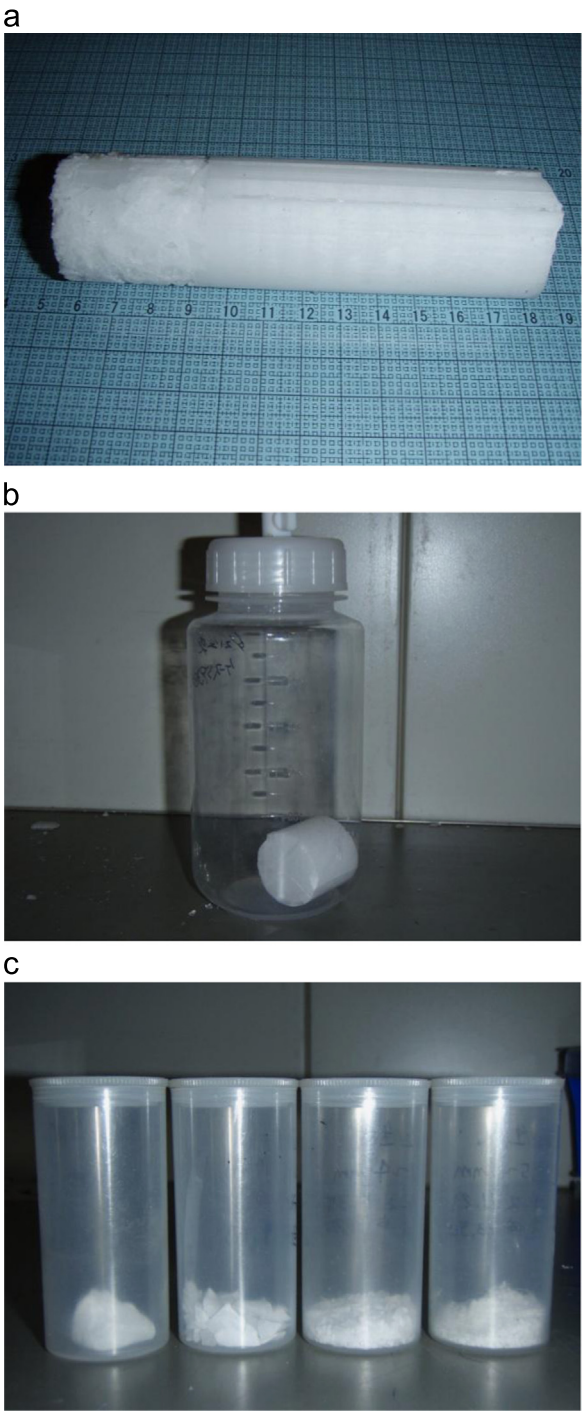

Fig. 1. Pellet and particle samples of NGH for storage test. (a) Side view of cylindrical NGH pellet that has just come out from the hydrate formation system. About quarter of left part of pellet was porous because this part was only cohered not pelletized. (b) Largest sample of $\varphi 33 \times 30$ mm^2 for storage test. (c) Samples of NGH particles smaller than 20 mm for storage test. Diameters of particles were 10–20, 4.0–6.7, 1.0–4.0, and 0.50–1.0 mm from left to right.