

メタンハイドレート自己保存効果発現時の比表面積の測定

Measurement of specific surface area of methane hydrate under self-preservation

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Self-preservation effect occurs in the dissociation process of methane hydrate and drastically decreases speed of dissociation at around 253K and under atmospheric pressure. This phenomena is explained that ice layer forms and covers on the surface of hydrate. Recently, microstructural change of methane hydrate was observed using a scanning electron microscopy and the freeze-fracture replica method (Fujimoto and Sugahara, 2017). On the other hand, a device for measuring specific surface area of snow particles has been developed (Hachikubo *et al.*, 2014), and it is available for methane hydrate. We report the change of specific surface area of methane hydrate samples in their dissociation process.

Small ice balls (diameter: 0.5-1.0mm) were formed in liquid nitrogen using water spray and sieved in a cold room (temperature: 255K). 0.5g of ice balls were put into a pressure cell (volume: 30mL) and measured their specific surface area. After that, methane gas was introduced and methane hydrate formed at 273.2K for more than five days to ensure that ice balls were completely changed to “hydrate balls”. Eight samples were prepared, and the gas in the pressure cells were quickly removed. The internal pressure decreased to the atmospheric pressure, and the samples started to dissociate at 243.2K, 248.2K, 253.2K, 258.2K, 263.2K, 268.2K, and 272.2K using a temperature-controlled liquid bath, and at 223.2K in a cold room. We measured rate of dissociation for 10 minutes and their specific surface area.

Specific surface area of original ice balls was 8.2 [m² kg⁻¹], and this value is located between the theoretical value of 6.5 [m² kg⁻¹] (diameter: 1.0mm) and 13.1 [m² kg⁻¹] (diameter: 0.5mm). The rate of dissociation at 223.2K was fastest, and more than 80% of sample dissociated in 10 minutes. On the contrary, about 97% of the samples survived at 272.2K and 268.2K, and about 85% of the samples survived at 248.2K and 243.2K. These results indicate that the self-preservation phenomena tend to effective at higher temperature. Specific surface area of the original methane hydrate sample was 23.3 [m² kg⁻¹], and those of samples from 243.2K to 272.2K increased to 28.0-40.2 [m² kg⁻¹]. Specific surface area of the sample at 223.2K increased to 73.4 [m² kg⁻¹], suggesting that major part of methane hydrate dissociated and the rest ice particles had large surface area.

Reference

Fujimoto A, Sugahara T (2017) Scanning electron microscopic studies on the methane hydrate decomposition using the freeze-fracture replica method. Bull Glaciol Res 35: 39-45

Hachikubo A, Yamaguchi S, Arakawa H, Tanikawa T, Hori M, Sugiura K, Matoba S, Niwano M, Kuchiki K, Aoki T (2014) Effects of temperature and grain type on time variation of snow specific surface area. Bull Glaciol Res 32: 47-53

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