

# Investigation of self-preservation of argon hydrate by measuring specific surface area

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Self-preservation occurs during the dissociation of gas hydrate and drastically decreases speed of dissociation at around 253K and under atmospheric pressure in the case of methane hydrate. Takeya and Ripmeester (2008) revealed that not only methane but also nitrogen, oxygen, argon, and CO<sub>2</sub> hydrates showed the same self-preservation effect. This phenomena is explained that (1) gas hydrate dissociates below the ice point, (2) ice remains on the surface of crystals, (3) ice layer forms and covers on the surface of hydrate and prevent from further dissociation. We developed a device for measuring specific surface area of snow particles (Hachikubo *et al.*, 2014), and it is also available for gas hydrate crystals. Because self-preservation phenomena depends on temperature, we investigated the change of specific surface area of argon hydrate samples in their dissociation process under various temperature conditions.

Fine ice balls (diameter: 0.108-0.180 mm) were formed in liquid nitrogen using water spray and sieved in a cold room (temperature: 255 K). 3 g of ice balls were put into a pressure cell (volume: 30 mL) and measured their specific surface area. After that, argon was introduced and hydrate crystals formed at 273.2 K. Temperature of the samples were controlled at 226K, 243K, 254K, and 263K, and then the residual gases in the pressure cell were quickly removed. The internal pressure decreased to the atmospheric pressure and the samples started to dissociate. Dissociation times were controlled as 1 minute, 10 minutes, and 100 minutes, and after that the samples were fixed at the temperature of liquid nitrogen and we measured their specific surface area. Their dissociation rate were estimated from weight data of gas and water. Specific surface area of the original fine ice balls and (pure) argon hydrate samples were also measured.

Ice balls were expected to change completely into “hydrate balls” , however, more fine and irregular grains of argon hydrate were observed using an optical microscope Specific surface area of original ice balls was  $71 \pm 5$  [m<sup>2</sup> kg<sup>-1</sup>], and that of argon hydrate increased to 119 [m<sup>2</sup> kg<sup>-1</sup>]. When the dissociation period was 1 minute, more than 90% of hydrate still remained at 226-263 K. The rate of dissociation at 254 K was fastest in the case of 10 minutes dissociation (65% of hydrate remained), but about 80% of hydrate sample remained at 263 K. The specific surface area was around 120 [m<sup>2</sup> kg<sup>-1</sup>] after 10 minutes at 263 K, indicating that the condition of surface was not changed at 263 K. On the other hand, the specific surface area increased to 279 [m<sup>2</sup> kg<sup>-1</sup>] at 226 K after 10 minutes. Therefore, these results indicate that the self-preservation effect appeared at 263 K and kept the surface of crystals smooth rather than the case at 226 K.

## References

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