Title	Clathrate hydrates useful for natural gas storage and CO2 extraction : effective utilization of materials that are similar to but are not ice
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Introducing
Researchers

Featured in this issue is Associate Professor Ryo Ohmura,
who tackles new technological development in the energy field by utilizing clathrate hydrates.

Clathrate hydrates useful for natural gas storage and CO_2 extraction

Effective utilization of materials that are similar to but are not ice

Clathrate hydrates have a cage-like structure made of water molecules in which a substance other than water has been sealed and crystallized. Substances that can be sealed in the cage structure include hydrophobic gases such as methane, nitrogen, and carbon dioxide (CO_2). While clathrate hydration is a focus of attention as an effective gas solidification technology, many mysteries still remain as to its principles and mechanism. Keio University's Faculty of Science and Technology boasts one of the world-leading achievements in the study of clathrate hydrate application technology. Associate Professor Ryo Ohmura, the person who spearheads this research activity, explained what clathrate hydrates are like.

Water molecules form a cage in which a guest substance stays.

Dr. Ohmura explains the characteristics of its structure: "Clathrate hydrate is a crystal of orderly arranged water molecules. Though it resembles ice in appearance, it differs from ice in the way water molecules are arranged. Unlike ice, in which water molecules are closely arranged leaving no space between them, clathrate hydrate features a polyhedron cage structure made of water molecules. The cage structure takes in a non-water guest substance and is then crystallized."

Imagine the traditional "Kagome-kagome" game of Japanese children and it will easily explain the clathrate hydrate structure. In the center of a circle is a tagger bending his or her body with eyes closed. The surrounding children, tanking each other's hands, are compared to water molecules. The tagger is not left out of the game but is surrounded at a distance from the others. The tagger can neither get hand-in-hand with the others nor is allowed to get out of the circle. The guest substance in clathrate hydrate is something like the tagger in the "Kagome-kagome" game.

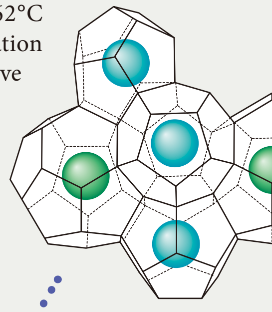
It solidifies a hydrophobic gas and enables its efficient storage and transport

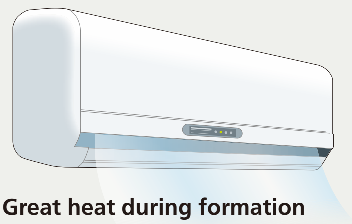
Clathrate hydrates with such characteristics also exist in the natural world. Methane hydrate, recently in focus of attention as a promising natural resource, is a kind of clathrate hydrate with its guest substance being methane molecules.

Similar to ice, methane hydrate is attracting attention as a medium capable of storing methane gas at a high density. Mr. Ohmura addresses the research project of taking advantage of such excellent storage capacity of clathrate hydrates for energy utilization of natural gas.

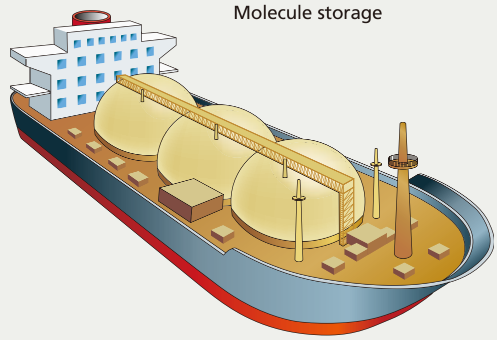
"Methane hydrate is a crystal containing water and methane molecules at a ratio of 46 to 8. Methane hydrate's storage capacity is 170 times greater in volume than that of methane gas. I came up with the idea of sealing natural gas as a guest substance. This marked the beginning of my study of natural gas hydrates. This research endeavor has come to the stage just before commercialization or engineering practice. The foremost merit of natural gas hydration is its ease of temperature management. Normally, natural gas is stored and transported as liquefied natural gas (LNG) after being cooled down to −162°C or less. By making it into the hydrate form, natural gas can be compressed to 1/170 in volume at a temperature of only −20°C. Though the volume of natural gas hydrate increases 3.5 times greater than that of LNG, it eliminates extra maintenance and management costs associated with cooling it to the cryogenic temperature of −162°C or less, making methane hydration highly promising as an alternative technology."

Since hydration enables





Great heat during formation and decomposition
Hydrate heat pump
Hydrate heat accumulation



High gas-holding capacity
Ability to hold 60 to 200 times more gas
Energy storage
Molecule storage

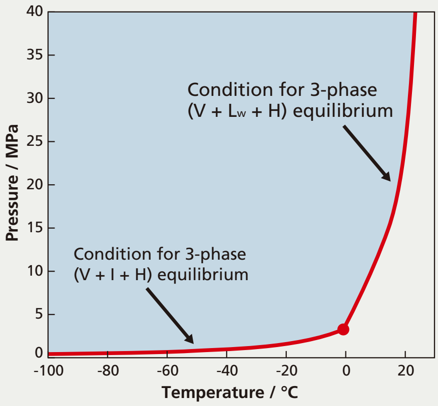
Fig.1 Application technologies that make the most of clathrate hydrate's physical characteristics
Highly efficient use and handling of clathrate hydrates becomes possible by incorporating their superb physical characteristics (greater gas storage capacity and greater decomposition heat) peculiar to clathrate hydrates into existing technologies and systems. Examples of application include natural gas storage and transport technology, carbon dioxide separation and extraction technology, and application to high-efficiency heat pumps. As future possibilities, innovative technologies, such as a hydrate engine, are also being conceived.

a guest substance to be stored at the molecular level, its application for the storage of hard-to-store or dangerous substances is being examined positively.

"Ozone (O_3) that exhibits superb bactericidal actions is a very unstable substance. In principle, ozone cannot be stored as is since its molecules react to each other and turn into more stable oxygen ($2O_3 \rightarrow 3O_2$). Once hydrated, however, it can be separated and preserved in the molecular form, thus enabling storage over a period of long time," he remarks.

Fig.2 Conditions required for methane hydrate formation

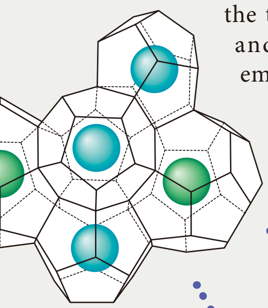
Methane hydrate can be formed only when methane, water molecules, and temperature and pressure conditions become complete. The graph on the right shows the relationship between temperatures and pressures. When the temperature is low, the required pressure is low accordingly. But a higher pressure is required as the temperature rises. However, the low temperature and pressure required for control remain within a controllable range. Thus, ease of handling is another characteristic of methane hydrate. These physical characteristics can be seen commonly among all clathrate hydrates.

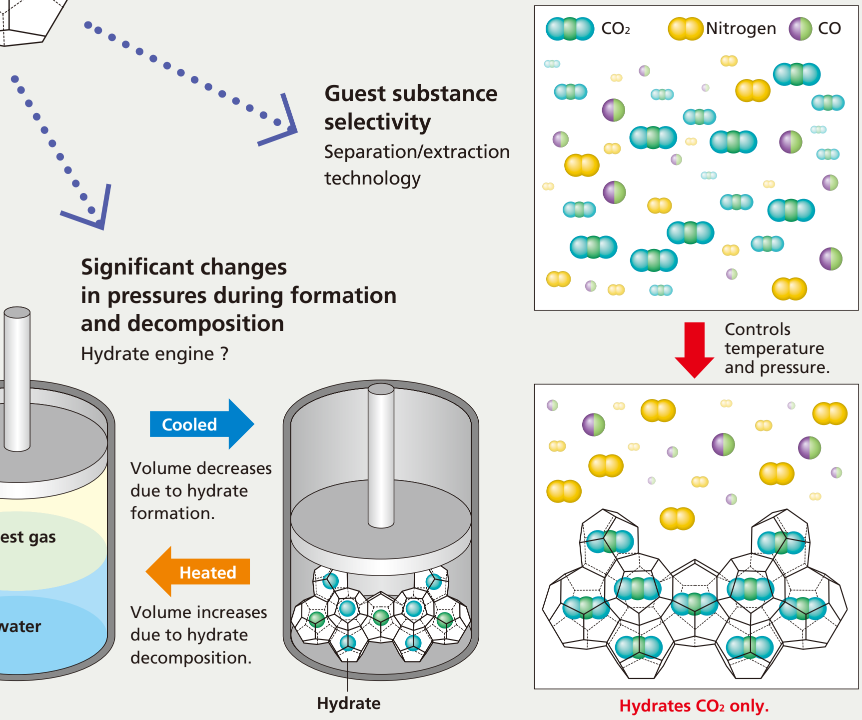


Can extract a specified substance and is promising as a CO_2 removal technology.

Clathrate hydrate cannot be formed by simply mixing water and a guest substance together. The formation of clathrate hydrate requires conditions of low temperature and high pressure. However, such conditions vary according to the guest substance in question. For example, at the temperature of 0°C, methane can be hydrated under 26 atmospheres (approx. 2.6 MPa), while carbon dioxide (CO_2) and nitrogen require 12 atmospheres and over 150 atmospheres, respectively.

"By taking advantage of such differences in hydrate-forming conditions, it is possible to hydrate particular guest substances selectively. Attracting attention as an application of this is the technology for CO_2 separation and removal from exhaust gas emitted by thermal power plants. It is an attempt to selectively solidify CO_2 only. In this process, exhaust gas, which consists of carbon dioxide and nitrogen, is given an optimum condition for hydration by having it react with water. Currently, the amine process* is used commonly as a CO_2 removal technology, but it involves the necessity to handle amine, a dangerous substance. Contrary to the amine process, the removal process, based on hydration of CO_2, uses water only, making it a highly promising process as an alternative to the amine process."





Also expected as a highly efficient thermal storage medium substituting for ice thermal storage

As clathrate hydrate is formed, its water molecules turn into a solid ice-like state, which can be controlled at a temperature range of between 5°C and 15°C. The creation of an efficient thermal energy storage medium for cooling can be expected as an application of this physical characteristic.

"Currently, most large buildings employ an ice thermal-energy storage system for their air-conditioning, which uses nighttime power to make ice and uses its cold air as the air-conditioning thermal source. From an efficiency viewpoint, however, it is pointed out that the thermal source of 0°C is too low since a thermal source temperature of approximately 10°C is optimum for producing cool air of 15°C needed to maintain the room temperature of 28°C. In fact, as much as 40% power conservation can be expected if the thermal source temperature is raised to 10°C. With hydrate thermal storage, it is possible to create a thermal source of approximately 10°C by controlling the guest substance and pressure – a thermal storage system far surpassing the efficiency of conventional ice thermal storage systems."

As Dr. Ohmura puts it, however, hydrate thermal-energy storage is not without problems. To realize practical application of clathrate hydrates, not only must the safety of guest substances be verified beforehand, but also the technology's principles and mechanism must be brought to light, the knowledge of which should be shared by many researchers and opinion leaders.

"As the stage of practical application of this technology approaches, now is the time for us to devote ourselves to basic studies. As a person in the academic world and as a leading researcher in this field, I think we now have to approach the clathrate hydrate phenomenon from a broader perspective, not biased for a particular engineering field," he concluded.

Studies of clathrate hydrates are steadily in progress.

(Reporter & text writer: Kaoru Watanabe)

* One of the CO_2 separation/removal methods. As an absorbent liquid, it uses an alkanolamine solution, the molecular structure of which incorporates an amino group that causes a combination reaction with carbon dioxide. The problem of cost reductions for absorbent liquid renewal still remains unsolved. Amine shows strong alkalescence, which requires utmost care for handling.