ВЕСТНИК ИНЖЕНЕРНОЙ ШКОЛЫ ДВФУ. 2013. № 4 (17)

ТЕПЛОЭНЕРГЕТИКА И ЭНЕРГОСБЕРЕЖЕНИЕ

УДК 548.562+665

Masayoshi Kobiyama

MASAYOSHI KOBIYAMA – professor, Muroran Institute of Technology, Muroran, Japan.
E-mail: jrc98@mmm.muroran-it.ac.jp

GENERATION OF GAS HYDRATE USING FRESH SNOW

Hydrate is formed when hydrogen bonds in water molecules have a basket-like structure. The central volume of hydrate is comparatively vast, vacuumated and can be filled with gas molecules. A technical problem arises when solid water (water and ice) interacts: as the speed of the formation of hydrate is too slow, the quantity of guest gas absorbed by the hydrate is not sufficient. To solve the problem, the authors attempted to use snow as a host hydrate: the contact surface of snow with guest gas is much larger as compared with ordinary ice, the capacity of snow to absorb gas being much higher than that of ice. We used propane for guest gas filling hydrate. It has been proved that fresh snow absorbs gas much better (70 per cent) than other kinds of ice do.

Key words: hydrate, gas, ice, fresh snow, experimental result, efficiencies.

Получение газогидратов с использованием свежего снега. Масаёси KOBIYAMA – профессор, Институт технологий города Муроран, г. Муроран, Хоккайдо, Япония.

Гидрат образуется, когда водородные связи в молекулах воды имеют структуру в виде ячеек. Центральный объем гидрата сравнительно велик, вакуумирован и может быть заполнен молекулами газа. Существует техническая проблема при взаимодействии твердой фазы воды (льда) и газа: так как скорость образования гидрата слишком мала, количество газа, которое всасывается в гидрат, недостаточно. Для решения этой проблемы авторы предприняли попытку использовать снег как принимающий гидрат: контактная поверхность снега с газом значительно больше по сравнению с обычным льдом, к тому же способность снега принимать газ намного выше, чем у льда. В качестве газа, заполняющего гидрат, был использован пропан. Исследовалось семь видов твердой фазы воды. В работе доказано, что эффективность поглощения газа свежим снегом (70%) выше, чем других видов льда.

Ключевые слова: гидрат, газ, лед, свежий снег, экспериментальный результат, эффективность.

Preface

A hydrate is formed when the water molecules are connected by the hydrogen bond as a basket-like structure. The central void of the hydrate is comparatively wide and can be filled with small gas molecules. The interaction force between the host water molecules and the guest gas molecules is weak. The temperature and pressure to which change of formation and dissociation of a hydrate takes place are different by the structure of a hydrate and by the kind of gas molecule. The phase equilibrium curves of various gases, such as nitrogen, methane, carbon dioxide, propane gas, and hydrogen sulfide is clarified. As methods to form the hydrate, it has been used to contact with host freezing water and guest gas, or host ice and guest gas. There was a technical problem in the combination of solid water, that is, ice and gas. That is, the speed of formation of hydrate was too slow, and then the quantity of the guest gas absorbed in the hydrate was not sufficient.

In this study, as one method of solving this problem, the authors attempt to use snow as host solid ice because a contact surface of snow with guest gas is very wide as compared with usual ice, and snow has excellent breath ability than ice. In addition, if the combination of this host and a guest is practical, we can expect to utilize the rich snow resources more widely and effectively. And as the phase equilibrium conditions of forming the hydrate are different by the kind of guest, we can use this characteristic to separate and to concentrate the small amount of guest gas contained in the air. To develop this type easy separation and concentration of gas component is also the future purpose of this study of hydrate formation with the snow as host water.

In this paper, a propane gas was used as the guest gas because the conditions of temperature and pressure to form the gas hydrate are comparatively easy. From the experimental results with various samples of snow and ice which were made under different conditions, it is cleared that the hydrate forming process with fresh snow was most suitable because 70% of guest gas, that is propane gas, was absorbed and this value is near the limit of gas hydrate formation.

Experimental Equipment and Method

An experimental equipment is shown in Fig. 1.This is a simple equipment consisted with a hydrate formation cell, a pre-cooler, a propane gas reservoir, a vacuum pump, pressure and temperature sensors, some connecting pipes and a insulating box with cooler. It is not necessary to possess a refrigerator to absorb the thermal energy as to phase change from liquid water to solid ice.

A propane gas is used as the guest gas. 7 kinds of ice are used for host water, that is, ice made from distilled water frozen at –10 and -20 ^{o}C , sintering ice made from –10 ^{o}C of distilled water and set for 24-hour in a freezer of –8 ^{o}C, town and snowmelt waters frozen at –10 ^{o}C, and fresh and granular snows. These ice samples are made into small fragments by a slicer, and 15g of them are compressed into density of 0.73 g/cm^3.

After setting an ice sample in the hydrate formation cell cooled -8 ^{o}C, all air in the equipment is purged by the vacuum pump. Propane gas is charged into the pre-cooler under not liquefy condition. At the time the gas is cooled -8 ^{o}C, a valve connected to formation cell is opened and propane gas is poured into the cell to the pressure of 0.12 MPa. The experiments are held for 72 hours without any operation.

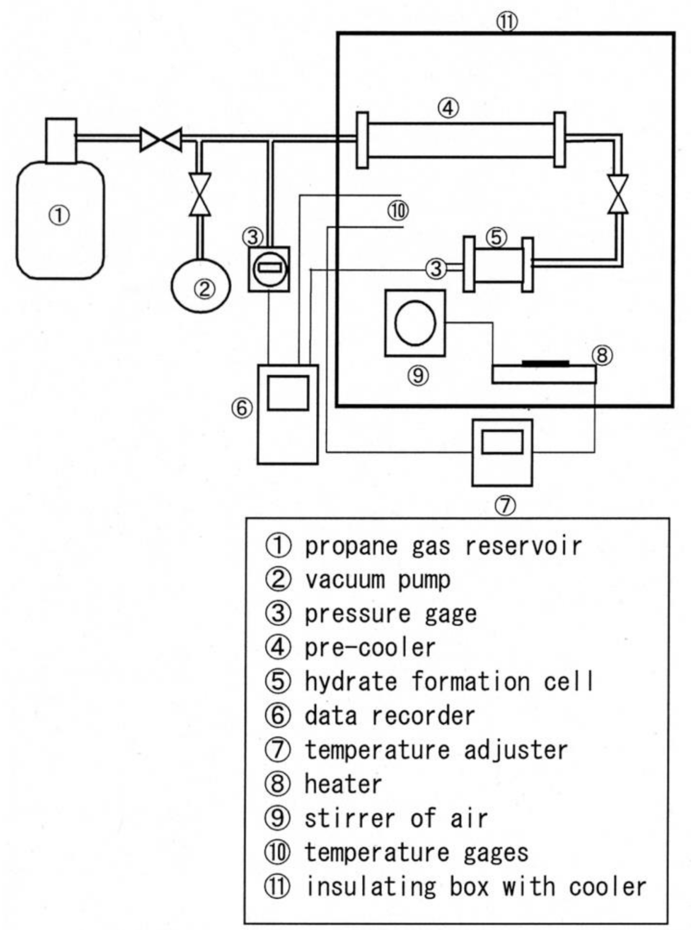


Fig. 1. Experimental equipment

Equations for Experiment

Theoretical Absorption of Propane Gas

Theoretical absorption of propane gas into hydrate Q_{th} [Ml/g], that is, clathrate quantity, can be calculated by the following molecular formula of a propane-gas hydrate:

C_3H_8 17 H_2O. (1)

It is cleared that from this equation:

$C_3H_8 : H_2O$ = 1 mol : 17 mol = 73.21 ml : 1 g. (2)

That is, 73.21ml of propane gas can be absorbed in 1g of water ice (= Q_{th}).

Equations for Amount of Absorption

From the experimental results, the amount of absorbed guest gas in the host ice Q [ml] can be calculated as follows:

$$Q = (M_A RT_N / P_N) \times 10^6 \text{ [ml]}, \quad (3)$$

where

$M_A = M_1 - M_2$ [kg],

$M_1 = P_1 V / RT$ [kg],

$M_2 = P_2 V / RT$ [kg]

and

M_1 : amount of initial gas [kg],

M_2 : amount of final gas[kg],

P_1 : initial gas pressure[Pa],

P_2 : final gas pressure[Pa],

V : volume of formation cell $=1.53\times10^{-3}$ [m^3],

R : gas constant = 0.1887 [KJ/kgK],

T : setting temperature=265.15[K],

P_N : atmospheric pressure $=1.013\times10^5$ [Pa],

T_N : temperature (0 °C) =273.15 [K].

The amount of absorbed gas per unit mass Q_m [ml/g] can be calculated as follows:

$$Q_m = Q / m, \quad (4)$$

where m : mass of ice samples = 15[g].

The ratio of the actual amount of gas absorption as the hydrate to the amount of theoretical gas absorption is defined as follows and call it as absorption efficiency η_{ab} [%].

$$\eta_{ab} = Q_m / Q_{th} \times 100. \quad (5)$$

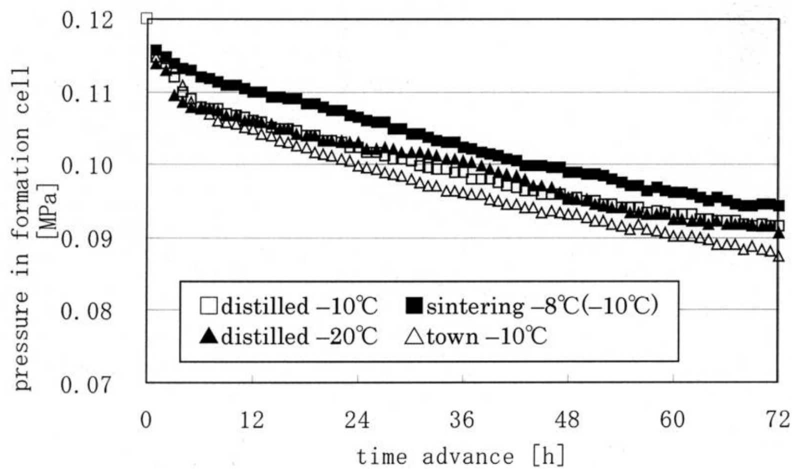
In usually, the value of absorption efficiency η_{ab} is said to be 70–80%.

Experimental Results

Trajectories of the pressure in the hydrate formation cell by the holding time advance are shown in Fig. 2. In the early period of holding, from 0 to 5 hours, the changes of pressure are rapidly because there are the wider contact surfaces of ice not to be hydrated. After these early period, the pressure declines become slow and approach some values.

Absorption efficiencies η_{ab} are shown in Fig. 3. η_{ab} of the fresh snow is higher than those of the other ices and is higher value of 70%. However η_{ab} of granular snow is low slightly because of sintering for long time, the values of η_{ab} are the almost same order except the case of the fresh snow host with the wider contacting surface area with guest and the higher gas breath ability.

a



b

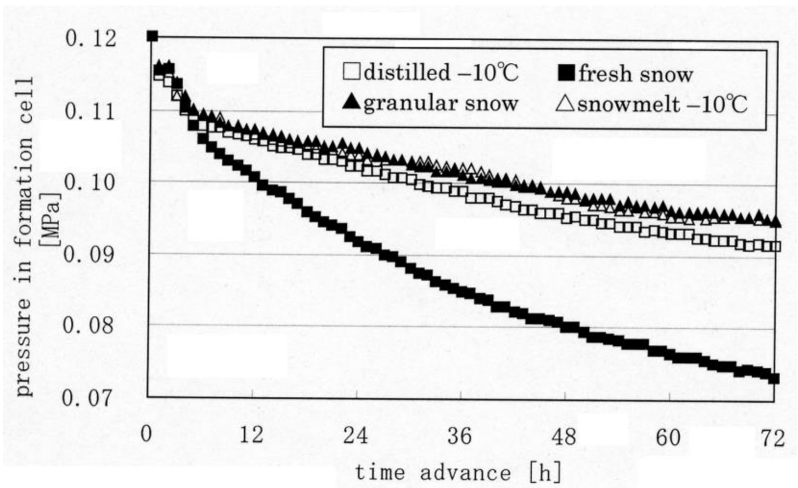


Fig. 2. a, b – Trajectories of pressure in formation cell

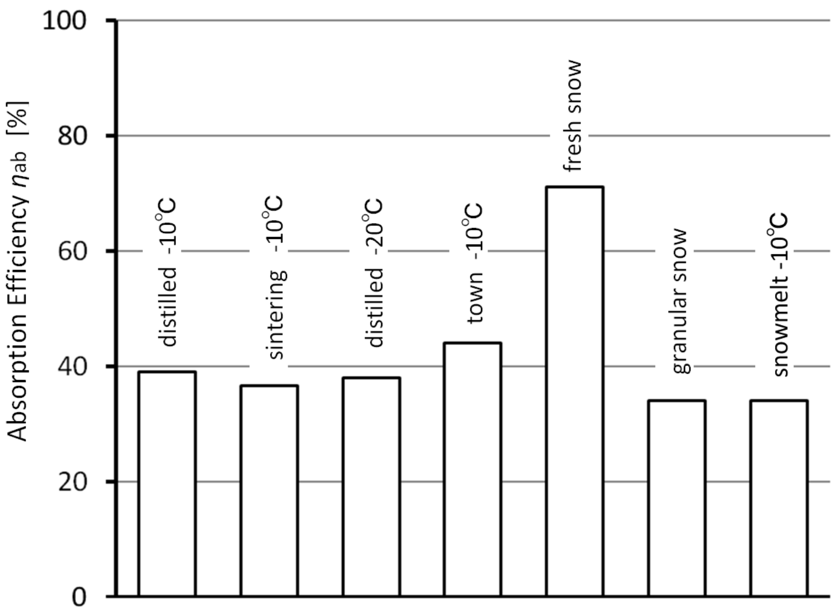


Fig. 3. Absorption efficiency

Fig. 4. Burning Snow i.e., Propane Gas Hydrate made from Fresh Snow

Conclusions

From this experimental study with simple equipment, it is cleared that the absorption efficiencies of the fresh snow is higher than those of the other types of ice, and is higher value of 70% which is near the limit of gas hydrate formation. When we make the gas hydrate by the combination of guest gas and solid water host, it is most suitable to use fresh snow.

We have been studying on the utilization of natural snow. In the field of gas hydrate, it is cleared the possibility of snow resources use. So to speak, we get "*Burning Snow*" (see Fig. 4).