## Research on Sea-Borne Transportation of Natural Gas by Means of Gas Hydrate Pellets --- Study on Self-Preservation Property of Gas Hydrate Pellets ---

## by

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## Abstract

For the purpose of sea-borne transportation of stranded natural gas in the new form of gas hydrate, we examined experimentally several thermal properties of methane hydrate pellets (MHP) in bulk, which had been made by using methane hydrate production and pelletization trial machines for the research of high-speed mass production of natural gas hydrate pellets.

(1) Temperature Influence on Self-Preservation Property of MHP in Bulk

In order to examine correlation between temperature and self-preservation property of MHP in bulk during navigation, we designed and manufactured the experimental apparatus with which we could control the temperature of 50 pellets within approximately 0.1°C of fixed temperature, and conducted MHP's dissociation experiments at atmospheric pressure with the fixed temperature varied between -25°C and -5°C. As a result, we confirmed that the self-preservation property of MHP in bulk at atmospheric pressure reached its peak at around -20°C in the present experiments. The results coincided qualitatively with those of the experiments for single pellet which had been conducted independently by Mitsui Engineering & Shipbuilding Co., Ltd. and Osaka University.

(2) Compressive Load Influence on Self-Preservation Property of MHP in Bulk

In order to verify whether or not the self-preservation property of MHP in bulk at sea is maintained at atmospheric pressure with either the influence of its own weight or that of the acceleration owing to ship motion and gravity, we examined dissociation behaviors of MHP in bulk with either static or repetitious compressive load weighted. As a result, we came to the following conclusions.

- (a) The influence of the static compressive load on MHP's dissociation is not significant, compared to that of absolute temperature. From the viewpoint of sea-borne transportation, therefore, it is reasonable to suppose that MHP's dissociation rate does not increase by significant degree owing to its own weight in ship cargo holds.
- (b) The influence of the repetitious compressive load on MHP's dissociation is not significant in the case of no more than 10,000 times of repetition number. On the other hand, we observed significant influence of 100,000 times of the repetitious load on MHP's dissociation. Taking that the data were obtained for a special condition into account, however, we may well conclude that the compressive load (owing to both ship's own weight and its motion during ordinary navigation) which acts on ship cargo does not have significant influence on MHP's dissociation.

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#### **1. Introduction**

## 1.1 Gas Hydrate and Self-Preservation Property 1.1.1 Structure of Gas Hydrate

Gas hydrate has three-dimensional structure, in which gas molecules are contained (enclathrated) in spherical cages formed by water molecules through hydrogen bonds, as illustrated in Figure 1.1, and Figure 1.2. Here, water and gas molecules are termed 'host' and 'guest' molecules, respectively  $^{1)}$ .



Figure 1.1 Instance 1 of Gas Hydrate Structure (Guest Molecule: Methane)



Figure 1.2 Instance 2 of Gas Hydrate Structure (Guest Molecule: Methane)

Thus far, it is known that gas hydrate structure is classified into three models of structure I (hereafter, s-I), structure II (hereafter, s-II), and structure H (hereafter, s-H) according to the type of enclathrated gas molecule. As shown in Figure 1.3, s-I and s-II are composed by the combination of two types of polyhedrons among three types of cages, namely, pentagonal dodecahedron ( $5^{12}6^4$ ). In addition, it has been verified by <sup>13</sup>C nuclear magnetic resonance (<sup>13</sup>C-NMR) that there is s-H, which is composed of three types of polyhedron ( $5^{12}6^4$ ), irregular dodecahedron ( $4^35^66^3$ ), and icosahedron ( $5^{12}6^8$ )) <sup>2</sup>.



Figure 1.3 Three-Dimensional Structure of Gas Hydrate (s-I and s-II)

As shown in Table 1.1, the gas molecule which can be enclathrated in each type of cage is diverse according to its molecular weight. Of the natural gas components which form simple hydrate, nitrogen, propane and iso-butane are known to form s-II. Methane, ethane, carbon dioxide, and hydrogen sulfide all form s-I as simple hydrate <sup>1)</sup>.

Table 1.1	Guest	Molecule	and	Hydrate	Structure
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Gas Molecule	Guest Diameter (Å)	Hydrate Structure
Argon (Ar)	3.8	s-II
Krypton (Kr)	4.0	s-II
Nitrogen (N2)	4.1	s-II
Oxygen (O2)	4.2	s-II
Methane (CH4)	4.36	s-I
Hydrogen Sulfide (H2S)	4.58	s-I
Carbon Dioxide (CO2)	5.12	s-I
Ethane (C2H6)	5.5	s-I
Propane (C3H8)	5.8	s-II
Iso-butane (i-C4H10)	6.5	s-II

For such multi-component hydrate as natural gas, a considerable number of researches have been recently carried out into their phase equilibrium and structure, and it has been reported that the hydrate structure changes according to the ratio of components  $^{3)-5)}$ . For instance, although either methane or ethane forms s-I, the half-and-half mixed gas of them forms s-II hydrate. Also, the natural gas mixtures containing propane and iso-butane usually form s-II hydrate, since the larger molecules of propane and

iso-butane only fit into the larger cage of s-II  $(5^{12}6^4)^{-1}$ .

Gas hydrate is generally formed at comparatively high pressure or low temperature. For instance, methane hydrate at 0°C remains stable (does not dissociate) above approximately 2.7MPa, and methane hydrate at atmospheric pressure remains stable below approximately  $-80^{\circ}C^{-1}$ ). Figure 1.4 shows the pressure-temperature phase diagram of methane hydrate.



Figure 1.4 Instance of Pressure-Temperature Phase Diagram (Guest Molecule: Methane)

Theoretical stoichiometry of methane hydrate, which forms s-I hydrate, is CH4•5.75H2O, as calculated from 46 water molecules and 8 methane molecules which are contained in their unit structure. Here, the ratio (5.75) of the number of water molecules to that of gas molecules is termed 'hydrate number.' Namely, approximately 0.220m<sup>3</sup> of methane (normal state) is contained in 1kg of water. Also, approximately 174m<sup>3</sup> of methane is contained in 1m<sup>3</sup> of methane hydrate, since the specific gravity of methane hydrate is approximately 0.92. Incidentally, it has been assumed that 'genuine' hydrate number is roughly equal to 6.2 with all hydrate synthesis conditions, in the case of methane hydrate which is synthesized from methane and water <sup>6)</sup>, where 'genuine' means that adherent water is deducted from the hydrate number.

## 1.1.2 Self-Preservation Property of Gas Hydrate

Since the peculiar meta-stability of methane hydrate was reported by Yakushev et al. <sup>7)</sup> in 1992, the research on self-preservation property of gas hydrate has been advanced by degrees. Of them, some principle researches are surveyed as follows.

Yakushev et al.<sup>7)</sup> conducted methane hydrate dissociation experiments at atmospheric pressure by using several samples in different conditions. They observed various dissociation behaviors and preservation periods, namely the periods when hydrate samples last without dissociation, according to humidity, surface / mass ratio in hydrate samples, temperature, light radiation, etc. The preservation periods of some samples ranged from several months to a few years. They suggested that such the self-preservation property of hydrate occurs because thin ice films, impermeable to gas molecules, form on hydrate surfaces during depressurization and interrupt further dissociation of hydrate.

Gudmundsson et al. <sup>8)</sup> synthesized mixed-gas hydrate at pressures from 2MPa to 6MPa and at temperatures from  $0^{\circ}$ C to  $20^{\circ}$ C, from a 92:5:3 methane:ethane:propane mixture, which should form s-II hydrate that is stable to much warmer temperature and lower pressure than s-I methane hydrate. The amount of the water converted to hydrate was 27% to 44% in these experiments. Temperature was decreased adiabatically to  $-18^{\circ}$ C at high pressure, and hydrate samples were kept frozen in a freezer for 24 hours. They examined meta-stability of the hydrate after rapid depressurization to atmospheric pressure, confirming that the samples remained meta-stable at  $-18^{\circ}$ C,  $-10^{\circ}$ C and  $-5^{\circ}$ C at atmospheric pressure and dissociated only slightly in 7 days to 10 days.

Stern et al. 9) conducted the thorough experiments on dissociation regions of methane hydrate at atmospheric pressure over the temperature range from -78°C to 17°C. They indicated that there are three distinct dissociation behaviors when the hydrate was removed from its stable field by rapid depressurization. Of them, the regime between -31°C and -2°C has an anomalously slow dissociation rate of hydrate. At the temperature of -5°C, the dissociation percentages within 24 hours and 1 month after dissociation start time were 7% and 50% respectively (confirmed as shown in Stern et al.<sup>10)</sup> ), which were the best results of self-preservation. In the latest study of Stern et al.<sup>10</sup>, they confirmed that s-II methane-ethane (91:9 mol%) hydrate showed no comparable preservation behaviors at atmospheric pressure, and that the self-preservation of methane hydrate was improved by elevated pressure (2MPa). Furthermore, they stated that it is highly probable that ice 'shielding' effects provided by partial dissociation along hydrate grain surfaces are not a primary mechanism for the anomalous preservation behavior observed in rapidly depressurized samples, in the light of scanning electron microscope (SEM) imaging of hydrate sample materials and their experimental results on both s-I and s-II gas hydrate.

With regard to the mechanism of the self-preservation property of gas hydrate, some ideas have been proposed thus far, but the details of the mechanism are still poorly understood.

## **1.2 Application of Self-Preservation Property to** Natural Gas Sea-Borne Transportation

An idea of applying the self-preservation property of gas hydrate to natural gas transportation was first suggested by Gudmundsson et al. <sup>11)</sup> in 1996.

Gudmundsson et al.<sup>11)</sup> examined the natural gas transportation by hydrate from an economical viewpoint on the basis of their experimental results. They compared a natural gas hydrate (hereafter, NGH) transportation chain (including production plant, hydrate carriers and re-gasification plant) to an equivalent conventional liquefied natural gas (hereafter, LNG) transportation chain, on the assumption of natural gas transportation of 3,500,000,000m<sup>3</sup> over 5,500km. As a result, the capital cost of the NGH chain was estimated to be 24% lower than that of the equivalent LNG chain. In the latest study of Gudmundsson et al.<sup>12</sup>, an NGH slurry (mixture of natural gas hydrate and crude oil) process was also examined, using a floating production storage and offloading (hereafter, FPSO) vessels for stranded natural gas utilization.

In the 21st century, also in Japan, several researches on application of gas hydrate to natural gas transportation have been conducted zealously by private shipbuilding companies and national institutes. It is assumed that such the lively research activities in Japan were motivated by the following Japanese energy situation and backgrounds.

(a) Japan has never had abundant indigenous natural resources, so has imported virtually almost all of its energy supplies for a long time. For instances, its domestic oil and natural gas production are only 0.25% and 3.0% of its consumption, respectively. Since the exhaust gas of combusted methane is relatively clean, compared to conventional fossil fuels such as coal and oil, the natural gas consumption in Japan is expected to rise in the future. According to the government forecast of long-term energy supply and demand, the natural gas consumption in the year 2015 will reach approximately 1.75 times as much as that in the year 1997 in Japan <sup>13</sup>.

(b) Although a great deal of natural gas is globally transported through pipelines from gas field to consumer market, almost all of the natural gas consumed in Japan is liquefied at a low temperature below  $-160^{\circ}$ C, and is stored / transported by LNG carriers. However, the transportation by LNG requires substantial energy consumption in the gas liquefaction process <sup>14)</sup>. If the self-preservation property of gas hydrate can be utilized economically in addition to its high-density gas containing property, it is possible to store and transport stranded natural gas at higher temperature, compared to the conventional LNG method. Also, this new method has potential not only for the prevention of energy loss owing to liquefaction, but also for the reduction of equipment costs for liquefaction and storage.

Shirota et al. <sup>15)</sup> examined experimentally the influence of dissociation temperature on the dissociation of pure methane hydrate between -7.5°C and 0°C. They obtained relatively extremely slow dissociation data within the temperature range between -7.5°C and -3°C, which coincided with the results by Stern et al. 9) qualitatively but differed from them quantitatively. They also estimated the period at which all samples would finish dissociating at approximately 120 days, and concluded that the estimate seemed to be very promising for practical application the of self-preservation property to natural gas storage and transportation.

Iwasaki et al. <sup>16)</sup> of Mitsubishi Heavy Industries, Ltd. (hereafter, MHI) designed a conceptual framework of NGH commercial production part with natural gas sea-borne transportation in mind. Kimura et al. <sup>17)</sup> examined both screw press and centrifugal filtration among existing dewatering methods, and verified that the former was superior to the latter in terms of dewatering performance.

Takaoki et al. 18) and Nakajima et al. 19) stated that 'pellet' is the most suitable and feasible form for natural gas sea-borne transportation from viewpoints transportation efficiency, loading-unloading of efficiency, and cargo warranty, among the possible various forms of NGH such as powder, slurry, pellet, and block. The former manufactured methane hydrate production / pelletization machines by way of trial for the research of high-speed mass production of natural gas hydrate pellets (hereafter, NGHP) in Mitsui Engineering & Shipbuilding Co., Ltd. (hereafter, MES), and confirmed that compressing mechanically hydrate powder into pellet improved its self-preservation property.

This study is an extension of the researches <sup>18)-19)</sup> and corresponds to a portion of the results obtained in a three-year joint research of the

MES, Osaka University, and National Maritime Research Institute (hereafter, NMRI) on sea-borne transportation of natural gas by means of gas hydrate pellets, which has been carried out as the Program for Promoting Fundamental Transport Technology Research by the Japan Railway Construction, Transport and Technology Agency (hereafter, JRTT). Figure 1.5 and Figure 1.6 show our concept of natural gas sea-borne transportation using gas hydrate and the outline of the allotted share of each institute in the joint research, respectively. As known from Figure 1.5, the aim of our research is to transport efficiently natural gas in the form of pellet at around -20°C and at atmospheric pressure.

In this paper, we deal with influence of both temperature and compressive load on self-preservation property of gas hydrate pellets in bulk.



Figure 1.5 Our Concept of Natural Gas Sea-borne Transportation Using Gas Hydrate



Figure 1.6 Outline of Allotted Share of Each Institute in Joint Research

## 1.3 Gas Hydrate Pellets Used in Experiments

Natural gas is composed of many components such as methane, ethane, propane, and nitrogen. Although the composition of natural gas is diverse according to gas field, the main component (> 90%) is methane. Also, there is a possibility that the dissociation phenomenon of hydrate which is made from plural kinds of guest molecules is too complicated. From these viewpoints, in the present work were used the hydrate which had been made from only methane instead of natural gas.

With the intention of obtaining consistent experimental results in three institutes, all the methane hydrate pellets (hereafter, MHP) used as sample in the joint research were made by the MES, using methane hydrate production and pelletization trial machines for the research of high-speed mass production of NGHP. Therefore, it should be noted that the properties of pellets may change in future.

Methane hydrate powder was synthesized in bubbling / mixing methods from water and pure methane gas (99.99% purity) at 5.2MPa to 5.4MPa and at 2°C to 3°C equal to the temperature lower by several degrees than the methane-water equilibrium temperature corresponding to the pressure. After the synthesis and cooling processes, hydrate powder was taken out and formed into MHP by a mechanical compressor at atmospheric pressure and at approximately -20°C. No extra heat and no ice were added during the pelletization process. Then, it is supposed that hydrate dissociation partly started and the pellet was a mixture of methane hydrate and ice. The thermal history of hydrate powder / pellets was not controlled thoroughly, since the machine was developed for the main purpose of NGHP high-speed mass production. After manufactured by the MES, the MHP were conveyed to the NMRI in a stable state (at low temperature with liquid nitrogen) by using a Dewar vessel or a cooler box within a day.

The diameter and weight of one MHP were roughly 0.02m and 0.003kg, respectively. Figure 1.7 shows the appearances of the MHP used in our experiments.



Figure 1.7 Appearances of Methane Hydrate Pellets Used in Experiments

## 2. Study on Temperature Influence on Self-Preservation Property of Gas Hydrate Pellets in Bulk

## 2.1 Aim of Experiments

When we intend to transport natural gas at sea utilizing self-preservation property of gas hydrate, one of the most important and interesting questions is; 'At how much temperature should we keep pellets in bulk in cargo holds in order to prevent them from as much as possible?' dissociating Although Stern et al.<sup>9)</sup> have examined details with regard to correlation between pure methane hydrate and temperature, the self-preservation property of 'pelletized' hydrate has not been examined yet.

Stern et al. <sup>9)</sup> stated that the self-preservation property (dissociation rate) of methane hydrate at atmospheric pressure varies extremely sensitively according to absolute temperature, especially around at -5°C. So, in this study, we designed and manufactured the experimental apparatus with which we could control the temperature of 50 pellets within approximately 0.1°C of fixed temperature, and conducted MHP's self-preservation property experiments with the fixed temperature varied between -25°C and -5°C. The aim of the present study is to examine correlation between temperature and the self-preservation property of MHP in bulk at atmospheric pressure, and to make clear the optimum temperature for the sea-borne transportation of NGHP.

# 2.2 Experimental Apparatus2.2.1 Whole Experimental Apparatus

The schematic view of whole experimental apparatus for the self-preservation property experiment of MHP in bulk is shown in Figure 2.1. We can conduct the model experiments of pellets in bulk in ship cargo holds at atmospheric pressure by using this experimental apparatus.

The temperature of pellets in the gastight chamber can be controlled accurately with the chamber submerged in the temperature-controlled bath. The gas cylinder bottle is used to set the atmosphere inside chamber for a gas-filled condition before the self-preservation property experiment, by supplying the chamber with methane through the gas pre-cooler.

The gas evolved during the experiment is collected directly from the end of pipes, and the gas volume is measured manually by the inverted cylinder.



Figure 2.1 Schematic View of Whole Experimental Apparatus for Self-Preservation Property Experiment of MHP in Bulk

#### 2.2.2 Gastight Chamber for Hydrate Pellets

In this study, an exclusive gastight chamber for hydrate pellets was designed and manufactured. Figure 2.2 shows the schematic of the gastight chamber for hydrate pellets.



Figure 2.2 Schematic of Gastight Chamber for Hydrate Pellets

The chamber is made of stainless steel, and its interior is cylindrical in shape with 80mm in internal diameter and 100mm in height. The net volume of chamber is approximately 500cm<sup>3</sup>. Both the temperature distribution and the temperature change inside the chamber can be monitored continuously by three multi-purpose type K thermocouples.

The spiral stainless steel tubes around the chamber are equivalent to the above-mentioned gas pre-cooler, through which the methane from the gas cylinder bottle is cooled in order to prevent the gas from giving unnecessary heat to the pellets in the chamber before the experiment.

The opening of the chamber is sealed by using both an O-ring and a chain-type quick coupling,

which warrant that the coolant in the temperature-controlled bath does not go into the chamber. In our experiments, we should submerge the chamber in the temperature-controlled bath as soon as possible after loading the pellets in the chamber. The quick coupling is just suitable for our experiments, since it reduces the installation time.

During the experiments, only one pipe (the rightmost one in Figure 2.2) is kept open to the outside. Consequently, all the gas that is evolved owing to the dissociation of pellets is released to the cylinder for gas measurement.

## 2.2.3 Temperature-Controlled Bath

In this study, we use a temperature-controlled bath in order to control the temperature of the gastight chamber for hydrate pellets with high accuracy. The temperature control accuracy of bath is  $\pm 0.01^{\circ}C \sim 0.02^{\circ}C$ . Ethanol / water solution (53%) is selected as coolant for the bath. The concentration of the solution is decided in order that the solution does not freeze for the possible temperature range in our experiments (-25°C to 10°C). Figure 2.3 shows the photograph of the gastight chamber submerged in the temperature-controlled bath.



Figure 2.3 Appearances of Gastight Chamber Submerged in Temperature-Controlled Bath

## 2.2.4 System for Measurement of Temperature Data

The temperatures monitored automatically in the experiments are a bath temperature and three temperatures inside the gastight chamber for hydrate pellets.

The bath temperature is monitored by a built-in panel of the temperature-controlled bath (see above Figure 2.3). Of the temperatures inside the

chamber, one data is transferred to a monitor panel for real-time monitor. The others are directly acquired by a data logger of the latest model, and are continuously recorded by a general-purpose computer every one minute. The software attached to the data logger is used for help to data acquisition / recording. Figure 2.4 shows the photograph of the measurement system of the temperature data.



Figure 2.4 Appearances of System for Measurement of Temperature Data (Left: General-Purpose Computer, Center: Temperature Monitor Panel, Right: Data Logger)

## 2.2.5 System for Measurement of Evolved Gas Volume

After the gas evolved in the experiments is transferred from the chamber through a vinyl tube, the gas volume is measured continuously and manually by displacement of the water filled with an inverted graduated cylinder. At the same time, the temperature in the bucket is measured by a digital thermometer. The data is used to calculate the amount (mole) of evolved gas. Figure 2.5 shows the photograph of the measurement system of evolved gas volume.



Figure 2.5 Appearances of System for Measurement of Evolved Gas Volume

### 2.2.6 Main Laboratory and Cold Room

The experiments are conducted in both a main laboratory and a cold room in the NMRI. The temperature-controlled bath and the measurement system of the temperature data and the evolved gas volume are located in the main laboratory. The cold room is used only when the pellets are taken out on a tray and the sampled ones are weighed and enclosed into the gastight chamber (see Chapter 3.1.2.3 with regard to the cold room).

#### 2.2.7 Container for Conveyance of Sample Pellets

In order to convey the sample pellets in a stable state from the MES to the NMRI, a Dewar vessel with enough liquid nitrogen is used in the experiments. It was confirmed that both the temperature inside the cooler box and that of sample pellets were kept below -100°C during the conveyance.

#### 2.3 Experimental Conditions

In the experiments, we use 50 pellets in order to conduct the trial experiments of pellets in bulk in ship cargo holds. During the experiment, each pellet in the chamber is expected to contact one another at random. Here, we use the pellets which have been conveyed to the NMRI in a stable state (at below -100°C with liquid nitrogen) in a Dewar vessel, after manufactured by the MES (see Chapter 1.3 with regard to the details of the pellets). The temperature of the sample pellets is fixed every 5°C between -25°C and -5°C in order to include the target temperature for NGHP sea-borne transportation. The pressure of the sample pellets is kept at atmospheric pressure by opening the chamber to the outside through the vinyl tube. The period of the temperature-controlled experiment is fixed at 2 weeks, assuming a sea-borne transportation from natural gas fields in southeastern Asia to Japan. Principle experimental conditions are shown in Table 2.1.

Table 2.1 Experimental Conditions for Self-PreservationProperty Experiment of MHP in Bulk

Number of Pellets	50
Temperature	-25°C, -20°C, -15°C, -10°C, -5°C
Pressure	0.1MPa (Atmospheric Pressure)
Period of Temperature-controlled Experiment	336 hours (2 weeks)

#### 2.4 Experimental Method and Procedure

A chain of experimental procedure for the self-preservation property experiment of MHP in bulk is summarized as follows.

- The temperature of the temperature-controlled bath is fixed at an intended one (-25°C∼-5°C).
- (2) The pressure in the main laboratory and the temperature of the water in the bucket for the gas volume measurement are measured / recorded.
- (3) Pure methane (99.99% purity) is brought into both the pipe laying and the gastight chamber in order to set up their inside atmosphere a gas-filled condition.
- (4) In the cold room whose temperature has been kept lower by roughly 5°C than the fixed (namely, -30°C~-10°C), pellets in a Dewar vessel at below -100°C with liquid nitrogen are taken out on a stainless steel tray. Then, the pellets are left for a period of time in order to be warmed up to the room temperature.
- (5) In the same room, 50 pellets are sampled from among the ones on the tray, and are weighed. Without delay, the pellets are enclosed in the gastight chamber that has been pre-cooled at the same temperature as the room.
- (6) Separately from (5), 15 pellets are sampled from among the remainder on the tray, and are weighed likewise. Afterward, as control experiments, the 'pre-test gas content' of the pellets is estimated and the 'pre-test hydrate ratio' of them is calculated, based on a simple estimate method by utilizing buoyant force difference owing to air (see Appendix B. with regard to the 'simple estimate method', and see Chapter 2.5 with regard to the 'hydrate ratio').
- (7) After quickly transferred from the cold room to the main laboratory, the chamber is submerged into the temperature-control bath. The thermocouples are connected to the measurement system, and relevant pipes are joined together.
- (8) The inside temperature of the chamber reaches the intended one after a while (It took 1.5 to 2 hours in the present experiments). The time when the inside temperature gets equal to the fixed one is regarded as 'measurement start time.'
- (9) The volume of the gas evolved owing to hydrate dissociation is measured continuously from the measurement start time during the period of the

temperature-controlled experiment. Here, the gas volume divided by its collection period is regarded as 'dissociation rate.' The amount (mole) of the evolved gas is calculated by both trapezoidal integral of the dissociation rate measured at respective time and Pen-Robinson equation of state for real gas <sup>20</sup>).

- (10) After the period of the temperature-controlled experiment, the bath temperature is increased to +4°C in order to completely dissociate all the pellets in the chamber. Then, all the gas evolved from the pellets is collected / measured, and the amount (mole) of gas is calculated in the same way as (9).
- (11) From both the volume of the gas evolved during the period of the temperature-controlled experiment (9) and that of the gas evolved after the experiment (10), the initial gas content of the sample pellets is estimated. Also, the initial hydrate ratio of the sample pellets is estimated from the weight of the sample pellets measured in (5) and the estimated initial gas content.
- (12) The accuracy in the experiment is verified by comparing the initial hydrate ratios estimated in(6) and (11) by two different methods.

### **2.5 Experimental Results**

Table 2.2 shows the results of the self-preservation experiments of MHP in bulk for 5 fixed temperatures.

Table 2.2 Changes of MHP's Hydrate Ratio and Hydrate Dissociation Ratio during Experiment

Experiment No.	1	2	3	4	5	
Temperature	[°C]	-25	-20	-15	-10	-5
MHP's Initial Weight (50 Pellets)	[g]	146.5	148.9	146.3	146.2	146.7
Period of Temperature-Controlled Experiment	[hour]		3.	36		72
Pre-Test Hydrate Ratio (A')	[%]	75.8	77.0	80.3	82.9	81.9
Initial Hydrate Ratio at Measurement Start Time (A)	[%]	71.6	74.4	77.6	75.9	75.6
Hydrate Ratio 24 Hours from Measurement Start Time (B)	[%]	69.4	73.7	75.9	72.0	39.8
Final Hydrate Ratio (C)	[%]	53.4	68.8	67.5	64.4	6.8
Change of Hydrate Ratio (C-A)	[%]	-18.2	-5.6	-10.1	-11.5	-68.8
Hydrate Dissociation Ratio 24 Hours from Measurement Start Time (A-B)/A	[%]	3.0	1.0	2.2	5.0	47.4
Hydrate Dissociation Ratio during Temperature-Controlled Experiment (A-C)/A	[%]	25.3	7.5	13.0	15.1	91.0

In Table 2.2, 'hydrate ratio' and 'hydrate dissociation ratio' are defined as

(Hydrate ratio) = (Gas volume actually contained

in sample pellets) / (Gas volume theoretically capable of being contained in sample pellets)

and

(Hydrate dissociation ratio) = (Gas volume already evolved (=dissociated) from sample pellets) / (Gas volume actually contained in sample pellets at measurement start time).

At the fixed temperature  $-5^{\circ}$ C, the temperature-controlled experiment was finished earlier than we had planned, since almost all the sample pellets dissociated in 3 days (72 hours). In the series of experiments, it was assured that the fluctuations of fixed temperature were kept within  $\pm 0.1^{\circ}$ C.

Next, shown in Figure 2.6 and Figure 2.7 were the changes of the MHP's hydrate ratio and the hydrate dissociation ratio during the temperature-controlled experiments, respectively.



Figure 2.6 Changes of MHP's Hydrate Ratio during Experiment



Figure 2.7 Changes of MHP's Hydrate Dissociation Ratio during Experiment

Finally, shown in Figure 2.8 is the correlation between temperature and MHP's hydrate dissociation ratio for 24 hours from the measurement start time.



Figure 2.8 Correlation between Temperature and MHP's Hydrate Dissociation Ratio for 24 Hours from Dissociation Start

#### 2.6 Discussion

## 2.6.1 Discussion on Estimate of Initial Hydrate Ratio of Sample Pellets

As mentioned above, in this study, the initial hydrate ratio of the sample pellets at the measurement start time (A in Table 2.2) was estimated from the volume of the gas evolved during the period of the temperature-controlled experiment, that of the gas evolved after the experiment, and the weight of the sample pellets. Also, the pre-test hydrate ratio of the sample pellets (A' in Table 2.2) was estimated, based on the simple estimate method.

We see from Table 2.2 that A' exceeds A in all the experiments, and the disparity of both data was 2.6%~7.0%. It is reasonable to suppose that we see such the disparity for the following reasons.

- (1) The sample pellets started dissociating gradually during the period (roughly 15 minutes) when they were taken out on the tray, were enclosed in the gastight chamber and were transferred from the cold room to the main laboratory.
- (2) After submerged into the temperature-control bath, the chamber and the sample pellets received a considerable quantity of heat for 1.5 to 2 hours until their temperature got equal to the fixed one. The dissociation of the sample pellets progressed owing to the heat input.

In the present experiments, it was confirmed that the self-preservation of the pellets was extremely sensitive to the heat input. Especially, we observed that the sample pellets dissociated rather rapidly for 1.5 to 2 hours just before the measurement start time. It is assumed that the reason (2) participates in the disparity in A and A', of the above possible reasons.

The initial hydrate ratio of the sample pellets

at the measurement start time ranged from 71.6% to 77.6%, and the initial weight of the sample pellets ranged from 0.146kg to 0.149kg. Namely, every experiment was conducted by using the pellets which had almost the same initial hydrate ratio and weight.

## 2.6.2 Discussion on Changes of Hydrate Ratio and Hydrate Dissociation Ratio of Sample Pellets

We see from Figure 2.6 and Figure 2.7 that the dissociation rate of the sample pellets became smaller monotonously as the fixed temperature decreased between  $-5^{\circ}$ C and  $-20^{\circ}$ C. At the fixed temperature of  $-25^{\circ}$ C, however, the sample pellets dissociated more rapidly than the case of  $-20^{\circ}$ C. Namely, we confirmed that the self-preservation property of MHP in bulk at atmospheric pressure reached its peak at around  $-20^{\circ}$ C in the present experiments.

The qualitative property for the temperature between  $-5^{\circ}$ C and  $-20^{\circ}$ C coincided with the data in our preliminary experiments <sup>21)</sup>, although there was some disparity in quantity between these two. In the joint research (see Figure 1.5), the self-preservation property experiments for single pellet were conducted independently by the MES and Osaka University. And, all the results coincided qualitatively with one another, in the respect that the self-preservation property of MHP in bulk at atmospheric pressure reached its peak at around  $-20^{\circ}$ C.

The results in this study indicate that there is a temperature regime in which methane hydrate dissociates more rapidly at atmospheric pressure as the temperature decreases, as seen in Figure 2.8. The existence of such the regime had been already confirmed and reported by Stern et al.<sup>9)</sup>. However, their data indicate that there is a regime in which methane hydrate dissociates extremely slowly at around  $-5^{\circ}$ C, and are quite different from our data from a quantitative viewpoint. It should be noted that there are the following differences in both the experiments in experimental conditions, when we compare the experimental data.

(1) Difference in manufacturing method of hydrate samples: The hydrate samples made by Stern et al.<sup>9)</sup> were synthesized very slowly from small ice particles (180μm~250μm) and methane at 12MPa and at 17°C, whereas ours were synthesized in bubbling / mixing methods from water and methane at 5.2MPa to 5.4MPa and at 2°C to 3°C. There is a possibility that such the difference in manufacturing method of the samples has some influence upon the hydrate particle size and the self-preservation property.

- (2) Difference in thermal history of samples: Our samples were kept in a Dewar vessel at below -100°C with liquid nitrogen after synthesized at 2°C to 3°C and pelletized at -20°C. Furthermore afterward, they received a considerable quantity of heat in the temperature-controlled bath. Namely, our samples underwent heat input / output several times before the experiments, whereas the samples made by Stern et al. <sup>9</sup>) were not regarded to undergo such the drastic heat input / output.
- (3) Influence of pelletization process: The samples made by Stern et al. <sup>9)</sup> did undergo no pelletization process, whereas ours were formed from hydrate powder into pellets by a mechanical compressor. Takaoki et al. <sup>18)</sup> reported that the pelletization process improved the self-preservation property.
- (4) Difference in initial hydrate ratio of the hydrate samples: The initial hydrate ratio of the samples made by Stern et al. 9) was almost 100%, whereas that of ours was in the 70% to 80% range. Our sample is assumed as 'mixture of ice and hydrate.' In some hypotheses on the mechanism of the self-preservation property of gas hydrate, participation of 'ice film' in the mechanism is referred to, and there is no denying the possibility that the ice content of gas hydrate has some influence upon the self-preservation property.

It is assumed that these differences are the conditions greatly related to the self-preservation property of gas hydrate. In order to elucidate the mechanism of the self-preservation property, it is necessary to conduct the minute researches from the above-mentioned viewpoints in the future.

- 3. Study on Compressive Load Influence on Self-Preservation Property of Gas Hydrate Pellets in Bulk
- 3.1 Static Compressive Load Influence on Self-Preservation Property of Gas Hydrate Pellets in Bulk

#### 3.1.1 Aim of Experiments

Although there seems to be little agreement as to the mechanism of the self-preservation property of

gas hydrate, one hypothesis is that 'thin ice films, impermeable to gas molecules, are formed on hydrate surfaces owing to hydrate dissociation and interrupt further dissociation of hydrate.' Leaving aside the question of whether or not the hypothesis is a principal factor in the mechanism, on the assumption that the ice films have some influence on the self-preservation property, the self-preservation of pellets is supposed to change when the ice films are cracked.

Since the particles of the cargo stowed in ship holds are under compressed condition resulted from their weight and acceleration owing to ship motion and gravity, there is a possibility that the experimental results with no load are inapplicable to the self-preservation of MHP in ship cargo holds. From the viewpoint, in this study, we examined dissociation behaviors of MHP in bulk with static compressive load weighted, after the example of aggregate destructive test in the field of soil mechanics. The aim of the present study is to verify whether or not the self-preservation property of MHP in bulk at sea is maintained with the influence of its own weight at atmospheric pressure.

## 3.1.2 Experimental Apparatus 3.1.2.1 Apparatus for Static Compressive Loading Experiment

Figure 3.1 and Figure 3.2 show the photograph and the schematic view of experimental apparatus for static compressive loading experiment of MHP in bulk, respectively.



Figure 3.1 Appearances of Experimental Apparatus for Static Loading Experiment



Figure 3.2 Schematic of Experimental Apparatus for Static Loading Experiment

The apparatus consists of 4 molds, 4 loading disks, 4 guide frames, 20 loading weights, and 2 supports. Two molds and 2 guide frames are installed in a support, as seen in Figure 3.2.



Figure 3.3 Appearances of Cylindrical Mold for Hydrate Pellets (Left: Cylindrical Mold, Center: Loading Disk, Right: Cylindrical Lid)



Figure 3.4 Conceptual Schematic of Static Loading Experiment

The mold is cylindrical in shape with 0.1m of the inner diameter with a cylindrical lid, as seen in Figure 3.3. As loading weight, used are lead ingots with 50kgf of weight each. The apparatus has the mechanism that the loading disk in the mold is loaded with the weights of both guide frame and loading weight through the guide frame, by jacking up and down the loading weights. We can load roughly 1,000cm<sup>3</sup> of the sample pellets in the cylindrical mold with the weight up to 485kgf. Figure 3.4 shows the conceptual schematic of the static loading experiment.

## 3.1.2.2 System for Estimate of Gas Content of Sample Pellets

In the experiments, general-purpose electronic scales, with which we can measure up to 1mg, are used in order to estimate the gas content of the sample pellets. For collection of the gas evolved from the sample pellets, polyethylene bags impermeable to water / gas are used. See Appendix B. with regard to the detailed method of calculating the gas content of pellets. Figure 3.5 shows the photograph of the polyethylene bag and the electronic scale for measurement of the gas content of sample pellets.



Figure 3.5 Polyethylene Bag and Electronic Scale for Measurement of Gas Content

#### 3.1.2.3 Cold Room

The experiments are conducted in a cold room in the NMRI. The room is 6m long, 6m wide and 4.5m high. The inside temperature of the cold room can be fixed / controlled within the range of  $-60^{\circ}C^{\sim}0^{\circ}C$ . Since the cold room is closed tightly for insulation, a methane gas detector, which functions even at low temperature, is installed on the room for security during experiments.

## 3.1.2.4 Container for Conveyance of Sample Pellets

A Tupperware, a thermal-insulating material, and a cooler box are used in order to convey the sample pellets in a stable state from the MES to the NMRI. The sample pellets in the Tupperware are again enclosed in the cooler box, after enclosed in the thermal-insulating material. A small amount of dry ice is added between the thermal-insulating material and the cooler box in order to keep the temperature of the pellets at low temperature. Although tried to measure the temperature inside the cooler box during the conveyance of the sample pellets for reference, we did only confirm that the temperature inside the cooler box were kept below the temperature inside the cooler box were kept below

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The load which would be acted on the actual ship cargo holds should be estimated before experiments. We estimated the maximum load from both the essential items of the ship which was assumed in our project (dead weight: 100,000,000kg, cargo density: 700kg/m<sup>3</sup>, depth of hold: 20m) and the guidance formulae for acceleration components owing to ship's motion of International Gas Carrier code <sup>22)</sup> (hereafter, IGC code) (see Appendix A. with regard to the calculation of the maximum load).

In the experiments, 2 series (8 sets) of static compressive loading experiments are conducted for 5 kinds of compressive loads, as shown in Table 3.1. The maximum static load in Table 3.1 roughly corresponds to the load estimated in Appendix A. Also, the pressure in Table 3.1 is calculated by dividing the static load by the contact area of the loading disk. The period of the static loading experiments is fixed at 5 days.

Table 3.1 Static Load Conditions

14.152	<i>1</i> 9 <b>.</b> 901	<del>1</del> 8.7£	00°E	56 <b>.</b> 0E2	15.76	E0.E1	00 <b>.</b> E	[हृष्म]	Pressure
EE'58I	£ <del>1</del> .28	16.06	04.2	<i>1</i> 6. <del>1</del> 81	88.62	10.44	04.2	[រុនិរុ]	Static Load (Total)
7-4	£-7	<b>z-</b> z	1-7	1-t	£-1	<b>7-I</b>	1-1	Experiment No.	

Unlike the above-mentioned self-preservation

property experiments, it is very difficult to decide the temperature of the sample pellets by measuring it directly in the present experiments, since the sample volume is considerably much. In the present experiments, therefore, the temperature of the cold room is assumed equal to that of the sample pellets by leaving

the pellets in the temperature-fixed room for one day. The temperature of the cold room is fixed at  $-20^{\circ}$ C. Here, it should be noted that the temperature in the cold room is uneven according to place within roughly  $1^{\circ}$ C. Figure 3.6 shows the change of the room temperature recorder monitored by an all-purpose temperature recorder during the static loading experiment. The average temperatures during the first and second series of temperatures of temperatures during the first and second series of temperatures were approximately  $-22.4^{\circ}$ C and  $-20.5^{\circ}$ C.

Compared Time (day) Participation -20 Compar

Figure 3.6 Change of Room Temperature during Static Loading Experiment

## 3.1.4 Experimental Procedure

respectively.

A chain of experimental procedure for the static compressive loading experiment of MHP in bulk is summarized as follows.

- (1) The temperature of the cold room is fixed at a desired one (- $20^{\circ}$ C).
- (2) After taken out from the cooler box, sample pellets in the Tupperware are left in the cold room for one day. As a result, the temperature of

the sample pellets is assumed equal to -20°C.

- (3) All the pellets are taken out on a stainless steel tray. After 4 groups of pellets in the inner mold are made by sampling from among those on the tray, the groups are separately weighed.
- (4) Of the 4 groups of pellets in the inner mold, 1 group is left with no load for the fixed period (5 days), after enclosed in the outer mold (for control experiment).
- (5) Of the 4 groups of pellets in the inner mold, the remaining 3 groups are fixed in the experimental apparatus for the static compressive loading experiment, after enclosed in the outer mold. These groups are left with the separate fixed load for the fixed period.
- (6) After the fixed period, the period when the fixed load was weighed is recorded, and all the groups are taken out from the outer mold and are

separately weighed again.

(7) After the sample pellets are taken out from the inner mold, the gas content of the pellets is separately estimated (see Appendix B. with regard to the estimate method of the gas content of the sample pellets).

### **3.1.5 Experimental Results**

We conducted 2 series of static loading experiments of MHP in bulk. Table 3.2 shows the changes of MHP's weight in the present experiments.

Table 3.2 Changes of MHP's Weight during Static Loading Experiment

Experiment No. (Series - Set)		1-1	1-2	1-3	1-4	2-1	2-2	2-3	2-4
Loading Period	[hour]	121.0	121.3	121.6	121.9	120.0	120.0	120.0	120.0
Initial Weight of Sample	[g]	363.13	362.06	373.40	369.11	351.87	357.78	345.68	353.26
Final Weight of Sample	[g]	361.41	360.33	371.59	367.09	350.04	355.93	343.87	351.23
Weight Change of Sample	[g]	-1.72	-1.73	-1.81	-2.02	-1.83	-1.85	-1.81	-2.03
Weight Change Ratio of Sample	[%]	-0.47	-0.48	-0.48	-0.55	-0.52	-0.52	-0.52	-0.57

Next, Table 3.3 shows the changes of MHP's hydrate ratio during the static loading experiments, which were found on the basis of the estimate method in Appendix B. The change of hydrate ratio in Table 3.3 means the difference between the initial hydrate ratio and the final hydrate ratio. The gas content of MHP could not be measured because of any troubles during the measurement in the experiment number 1-2, 2-3, and 2-4.

Table 3.3 Changes of MHP's Hydrate Ratio in Static Loading Experiment

Experiment No. (Series - Set	1-1	1-3	1-4	2-1	2-2		
MHP's Weight before Dissociation	[g]	360.44	370.84	365.95	349.45	353.96	
MHP's Weight after Dissociation (without Buoyancy Correction)	[g]	307.31	316.96	313.65	296.24	300.35	
Temperature	[K]	298.5			288.9		
Initial Gas Content By Percentage	[%]	8.626	8.519	8.445	8.939	8.890	
Final Gas Content By Percentage	[%]	8.190	8.073	7.941	8.461	8.416	
Initial Hydrate Ratio	[%]	64.42	63.62	63.07	66.75	66.39	
Final Hydrate Ratio	[%]	61.17	60.29	59.31	63.19	62.85	
Change of Hydrate Ratio	[point]	-3.25	-3.33	-3.76	-3.56	-3.54	

Finally, Figure 3.7 shows the correlation between the MHP's weight change and the static loading. Assuming that the MHP's initial hydrate ratio in the same series is roughly uniform in Table 3.3, we can obtain the initial hydrate ratio as the average, as seen in Figure 3.7.



Figure 3.7 Results of Static Loading Experiment

In the experiments, some pellets were crushed owing to compressive loading. Also, some pellets adhered to the inside of the mold or lid. Figure 3.8 and Figure 3.9 show the appearance of the sample pellets in the molds after the 2nd series of experiments and that of sample pellets, which were taken out on the tray after the experiment number 2-4 (the static load is the maximum), respectively.



Figure 3.8 Appearances of Samples (MHP in Mold) after Static Loading Experiment



Figure 3.9 Appearances of MHP after Static Loading Experiment (Experiment Number 2-4)

## 3.1.6 Discussion

We see from Figure 3.7 that there seems to be no significant difference among the MHP's weight change ratios for the different static loads. Also, according to the preliminary self-preservation experiments of MHP by Nakajima et al. 19) and the self-preservation property experiments of MHP in bulk (see Chapter 2), the decrease of MHP's hydrate ratio at atmospheric pressure becomes smaller clearly, as the temperature decreases from -5°C to -20°C. The above-mentioned experimental results suggest that the influence of the static load on MHP's dissociation is not significant, compared to that of absolute temperature. From the viewpoint of sea-borne transportation, it is reasonable to suppose that MHP's dissociation rate does not increase by significant degree (several percents, for instance) owing to its own weight (static load) in ship cargo holds.

Although we can see some pellets crushed owing to compressive loading in Figure 3.8 and Figure 3.9, the phenomenon might have been caused by an excessive load acted locally on the MHP in the mold. Therefore, we can not discuss whether NGHP is crushed or not owing to load at sea, based on only the present results.

## 3.2 Repetitious Compressive Load Influence on Self-Preservation Property of Gas Hydrate Pellets in Bulk

#### 3.2.1 Aim of Experiments

From the viewpoint mentioned in Chapter 3.1.1, in this study, we next examined dissociation behaviors of MHP in bulk with repetitious compressive load weighted. The aim of the present study is to verify whether or not the self-preservation property of MHP in bulk at sea is maintained with the influence of acceleration owing to ship motion and gravity at atmospheric pressure.

#### **3.2.2 Experimental Apparatus**

# 3.2.2.1 Apparatus for Repetitious Compressive Loading Experiment

Figure 3.10 and Figure 3.11 show the photograph and the schematic view of experimental apparatus for repetitious compressive loading experiment of MHP in bulk, respectively.



Figure 3.10 Appearances of Experimental Apparatus for Repetitious Loading Experiment



Figure 3.11 Schematic of Experimental Apparatus for Repetitious Loading Experiment

#### 3.2.2.2 Other Systems and Apparatus

The same system as the static loading experiment is applied to estimate the gas content of the sample pellets (see Chapter 3.1.2.2). So are the cylindrical molds for hydrate pellets, the cold room, and the container for the conveyance of sample pellets (see Chapter 3.1.2.1, Chapter 3.1.2.3, and Chapter 3.1.2.4).

Figure 3.12 shows the conceptual schematic of the repetitious loading experiment. The basic principle of the repetitious loading experiment is the same as that of the static loading experiment with the exception of adding cyclic load to sample pellets.



Figure 3.12 Conceptual Schematic for Repetitious Loading Experiment

## 3.2.3 Experimental Conditions

The static compressive load by the guide frame and the loading weights are fixed at 103kgf (corresponding to the pressure of approximately 129kPa) in the repetitious loading experiments.

The amplitude and frequency of vibration are fixed at 20mm and 2.0Hz, respectively (corresponding to the set vertical acceleration (cyclic loading) of approximately 0.32G in the present experiments). We here decide the frequency of vibration moderately in order to prevent the apparatus from resonance. The set vertical acceleration (0.32G) is supposed to be large enough to simulate the acceleration which is acted regularly on the ship cargo at sea. Figure 3.13 shows the typical change of acceleration monitored in the repetitious loading experiments



Figure 3.13 Typical Change of Acceleration in Repetitious Loading Experiment

The temperature of the cold room is fixed at -20°C in the repetitious loading experiments, also. Figure 3.14 shows the typical change of the room temperature monitored in the same way as the static loading experiments.



Figure 3.14 Typical Change of Cold Room in Repetitious Loading Experiment

Assuming that the period of sea-borne transportation and the wave period are equal to 7 days and 8 seconds respectively, we obtain 75,600 times of the load repetition number. Therefore, the maximum load repetition number is decided at above 100,000 times (corresponding to the maximum loading period of above 13.9 hours) in the present experiments. The load repetition number is varied exponentially between 1,000 and 100,000.

## 3.2.4 Experimental Procedure

A chain of experimental procedure for the repetitious compressive loading experiment of MHP in bulk is summarized as follows.

- (1) The temperature of the cold room is fixed at a desired one (-20°C).
- (2) After taken out from the cooler box, the sample pellets in the Tupperware are left in the cold room for one day. As a result, the temperature of sample pellets is assumed equal to -20°C.
- (3) All the pellets are taken out on a stainless steel tray. After 2 groups of pellets in the inner mold are made by sampling from among those on the tray, the groups are separately weighed.
- (4) Of the 2 groups of pellets in the inner mold, 1 group is left with no load for the fixed period, after enclosed in the outer mold (for control experiment).
- (5) Of the 2 groups of pellets in the inner mold, the remaining 1 group is fixed in the experimental apparatus for the repetitious compressive loading experiment, after enclosed in the outer mold. Then, the intended vertical acceleration is added to the group.
- (6) After (5), the period when the acceleration was added to the group is recorded. Then, all the groups are taken out from the outer mold and are

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separately weighed again.

(7) After the sample pellets are taken out from the inner mold, the gas content of the pellets is separately estimated (see Appendix B. with regard to the estimate method of the gas content of the sample pellets).

### **3.2.5 Experimental Results**

We conducted 5 series of repetitious loading experiments of MHP in bulk. Table 3.4 shows the changes of MHP's hydrate ratio in the present experiments. Also, Figure 3.15 shows the correlation between the decrease of MHP's hydrate ratio and elapsed time.

Table 3.4 Changes of MHP's Hydrate Ratio inRepetitious Loading Experiment

Experiment No.			1	:	2		3		4		5
Compressive Load	[kgf]	103.0					10	2.5			
Pressure	[kPa]	129					12	28			
Loading Period	[hour]	15.1 15.5		2.8		1.2		15.2			
Load Repetition Number	[]	105	0	105	0	104	0	10 <sup>3</sup>	0	10 <sup>3</sup>	0
Initial Hydrate Ratio	[%]	74	.23	73	.69	69	.04	67	.19	70	.19
Final Hydrate Ratio	[%]	72.46	73.40	71.60	72.82	68.71	68.90	67.07	67.13	69.77	69.84
Change of Hydrate Ratio	[point]	-1.77	-0.83	-2.09	-0.87	-0.33	-0.14	-0.12	-0.06	-0.42	-0.35



Figure 3.15 Results of Repetitious Loading Experiment

## 3.2.6 Discussion

A glance at the data for 100,000 times of repetition number and 15 hours of elapsed time in Figure 3.15, will reveal that there is a significant difference between the decreases of MHP's hydrate ratio and those in the control experiments. The result of these experiments leads to the presumption that such the repetitious load can have some influence significantly on the dissociation of MHP in bulk in ship cargo holds.

In the present experiments, 130kPa of the static compressive load is equivalent to the pressure which acts on the bottom of ship hold owing to the weight of the cargo whose specific gravity in bulk and depth are 0.7 and 20m, respectively.

Now, 0.32G of the vertical acceleration corresponds to the value in the case of navigation in considerably stormy weather. On the assumption that the wave period is equal to 8 seconds, 100,000 times of the repetition number corresponds to the case of 9-day navigation in such the stormy weather, which is extremely uncommon for such large ship as the 10,000DWT-class NGHP carrier. Also, we see from Figure 3.15 that the influence of the repetitious compressive load (vertical acceleration) on MHP's dissociation is not significant in the case of no more than 1-day navigation in stormy weather (corresponding to 10,000 times of the repetition number). Since it is hardly conceivable that the NGHP carrier suffers stormy weather for days on end under way generally, we may well conclude that the self-preservation property of MHP in bulk is not aggravated significantly owing to both its own weight and ship motion during ordinary navigation.

As one reason why the repetitious load has some influence on MHP's dissociation, it is supposed that the load could cause ice films on the pellets to be fissured or could contribute development of the fissures in the films. However, we can not discuss that point definitely at the present stage, since there is no accepted view of the mechanism of the self-preservation property.

The results of the present experiments will serve as a reference when the mechanism of the self-preservation of methane hydrate (pellets) is discussed. Needless to say, our results should be studied in detail with other studies and experimental data.

## 4. Conclusions and Recommendations for Future Works

The following conclusions have been made;

(1) We designed and manufactured the experimental apparatus with which we could control the temperature of 50 pellets within approximately 0.1°C of fixed temperature, and examined correlation between temperature and self-preservation property of MHP in bulk at atmospheric pressure. As a result, we confirmed that the self-preservation property of MHP in bulk at atmospheric pressure reached its peak at around  $-20^{\circ}$ C in the present experiments. The results coincided qualitatively with those of the experiments for single pellet which had been conducted independently by the MES and Osaka University.

- (2) We examined dissociation behaviors of MHP in bulk with static compressive load weighted in verify whether or not order to the self-preservation property of MHP in bulk at sea is maintained with the influence of its own weight at atmospheric pressure. Also, we examined dissociation behaviors of MHP in bulk with repetitious compressive load weighted in order to verify whether or not the self-preservation property of MHP in bulk at sea is maintained with the influence of acceleration owing to ship motion and gravity. As a result, we came to the following conclusions.
  - (a) The influence of the static compressive load on MHP's dissociation is not significant, compared to that of absolute temperature. From the viewpoint of sea-borne transportation, therefore, it is reasonable to suppose that MHP's dissociation rate does not increase by significant degree owing to its own weight in ship cargo holds.
  - influence of the The repetitious (b) compressive load (0.32G) on MHP's dissociation is not significant in the case of no more than 10,000 times of repetition number. On the other hand, we observed significant influence of 100,000 times of the repetitious load on MHP's dissociation. Taking that the data were obtained for a special condition into account, however, we may well conclude that the compressive load (owing to both ship's own weight and its motion during ordinary navigation) which acts on ship cargo does not have significant influence MHP's on dissociation.

In the joint research, besides the above-mentioned studies, we examined experimentally MHP's thermo-physical properties and estimated both temperature distribution inside cargo hold of NGHP carrier and the volume of gas evolution during ordinary navigation by numerical simulation. We summarize those results as follows.

- (3) We examined experimentally MHP's thermal conductivity and specific heat with a view to fixing input data for heat transfer analysis, since there were not enough references to thermo-physical properties of methane hydrate. The MHP's thermal conductivity was measured by Guarded Hot Plate (GHP) method with the fixed temperature varied between -40°C and -10°C in the following two cases.
  - (a) Only 20mm-diameter MHP (corresponding to low filling ratio)
  - (b) Mixture of 5mm-diameter and 20mm-diameter MHP (corresponding to high filling ratio)

As a result, the MHP's thermal conductivity in the case of (b) was twice to 3 times as large as that in the case of (a). It may safely be said that augmentation of contact area among pellets owing to improvement of filling ratio caused the increase in thermal conductivity. Also, the specific heat of single MHP was measured by Differential Scanning Calorimetry (DSC) with the fixed temperature varied between -33°C and -13°C. Then, all experiments were conducted at high pressure in order to avoid the sample MHP from dissociating. As a result, the specific heat of single MHP increased according to increase of temperature, and the measured data (1.73J/(gK) to 1.96J/(gK)) were close on the reference ones<sup>23)</sup>. It was assumed that the specific heat of our sample MHP is almost equal to that of pure methane hydrate.

(4) We proposed several models for heat transfer analysis by using the hydrate dissociation model which had been proposed from Osaka University. Then, we conducted numerical analyses on the basis of those models by using our laboratory data of thermo-physical properties as input data, in order to estimate both the temperature distribution inside cargo hold of NGHP carrier and the volume of gas evolution during ordinary navigation. Our computer code has been already improved and used in the MES for design of NGHP carrier, for instance, in order to select suitable thermal insulating materials.

The results obtained in (1), (2), and (3) will

serve as precious data by which we have a right understanding of the properties of both NGHP and common hydrate. However, we would suggest that much more empirical data will need to be forthcoming from the viewpoint of realization of NGHP carrier. As mentioned above, we should conduct 'actual-scale' bulk experiments in the next stage.

Furthermore, early establishment of safety requirements and technical criteria, and test standards of all sorts for assessment of cargo property, will have the key to realize NGHP carrier smoothly in the not-too-distant future.

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#### (Appendix A.) Estimate of Load Acted on Ship Cargo

The components of acceleration owing to ship's motions corresponding to a probability level of  $10^{-8}$  in the North Atlantic are given as guidance in the IGC code <sup>22)</sup>. The guidance formulae are used to estimate the maximum probable accelerations of ship with a length exceeding 50m for 20 years. Therefore, the estimated load here corresponds to the maximum load which is acted on cargo holds during long-term navigation.

The vertical acceleration  $a_z$  and the transverse acceleration  $a_y$  are defined as

$$a_{z} = \pm a_{0} \sqrt{1 + \left(5.3 - \frac{45}{L_{0}}\right)^{2} \left(\frac{x}{L_{0}} + 0.05\right)^{2} \left(\frac{0.6}{C_{B}}\right)^{1.5}}$$
$$a_{y} = \pm a_{0} \sqrt{0.6 + 2.5 \left(\frac{x}{L_{0}} + 0.05\right)^{2} + K \left(1 + 0.6K \frac{z}{B}\right)^{2}}$$
$$a_{0} = 0.2 \frac{S}{\sqrt{L_{0}}} + \frac{34 - \frac{600}{L_{0}}}{L_{0}} \quad , K = 1.$$

 $\sqrt{L_0}$   $L_0$  By supposing the essential items of ship as

where:

seen in Table App.-A.1, these accelerations are obtained as seen in Table App.-A.2.

When we assume an acceleration ellipse now, the product of acceleration by the measure of cargo hold in the acceleration's direction becomes the maximum, in the case where the acceleration acts vertically downward. Therefore, the maximum compressive load which acts on the cargo can be decided by multiplying the depth of cargo hold, the vertically downward acceleration (1.588G=1G+0.588G for x=+100m), and the density of cargo in bulk together. On the assumption that the depth of cargo hold and the density of cargo in bulk are equal to 20m and  $700kg/m^3$  respectively, the maximum compressive load is calculated approximately 220kPa.

Table App.-A.1 List of Ship Essential Items forCalculation of Acceleration

Supposed Essential Item	Remarks		
<i>L</i> <sub>0</sub> =275 [m]	Length of Ship		
$C_B = 0.8$	<b>Block</b> Coefficient		
<i>B</i> = 46 [m]	Greatest Molded Breadth of Ship		
<i>x</i> = -100, -50, 0, 50, 100 [m]	Longitudinal Distance from Amidships to Center of Gravity of Cargo Hold (x is positive forward of amidships)		
z=-5 [m]	Vertical Distance from Waterline to Center of Gravity of Cargo Hold (z is positive above waterline)		
S = 15 [knots]	Service Speed		

Table App.-A.2 Calculation Results of Acceleration

<i>x</i> [m]	<i>az</i> [G]	<i>ay</i> [G]
-100	0.486	0.389
-50	0.338	0.365
0	0.303	0.361
+50	0.411	0.376
+100	0.588	0.409

## (Appendix B.) Estimate Method of Gas Content of Sample Pellets

Although the gas content of pellets can be estimated by dissociating all the pellets at normal temperature and by measuring the evolved gas volume in principle, then we should evade water evaporation. Therefore, we estimated the gas content of the sample pellets by utilizing buoyant force difference owing to air in the static / repetitious loading experiments and partly in the self-preservation property experiments. The following is the estimate method.

Firstly, the sample pellets are enclosed in an impermeable bag and are weighed at low temperature. Next, all the pellets are dissociated into water and gas at normal temperature, and the water and gas are weighed. From the above weight difference, buoyant force difference is found. Furthermore, the gas content of the pellets is found from the density of solid part of MHP, the density of methane gas, and the density of water. In analysis, both the gas content of MHP, which means the gas rate in MHP on a weight basis, and the hydrate ratio of MHP are found, assuming that MHP is a mixture of hydrate and ice. In order to find the hydrate ratio, it was assumed that the hydrate number of methane hydrate part in MHP is equal to the theoretical one (5.75) (see Chapter 1.1.1 with regard to the 'hydrate number'). The molecular weight of methane hydrate with the hydrate number is equal to 119.63032, as shown in Table App.-B.1. Therefore, for 100% of hydrate ratio, the gas content of MHP is equal to the molecular weight of methane divided by the molecular weight of methane hydrate; namely 13.41%. The hydrate ratio of MHP can be found by dividing the gas content of MHP by 13.41%.

Table App.-B.1 Molecular Weight of s-I Methane Hydrate

Atomic Weight of Hydrogen (H)	1.00794
Atomic Weight of Carbon (C)	12.01070
Atomic Weight of Oxygen (O)	15.99940
Molecular Weight of Water (H2O)	18.01528
Molecular Weight of Methane (CH4)	16.04246
Molecular Weight of Methane Hydrate (s-I) (CH4 · 5.75H2O)	119.63032

The technique for calculating the gas content of the pellets is as follows. The solid density of the samples is assumed constant irrespective of hydrate ratio. The state of the samples at the time of measuring the sample weight and that of the samples at the time of measuring water / gas, are hereafter called 'state 1,' and 'state 2.' The gas content is defined as

$$\alpha = \frac{W_G}{W_S} \,. \tag{App.-B.1}$$

The buoyant force acting on the air in the bag is negligible here, since it is zero when there is no difference in the air density inside and outside the bag. Then, The weights measured in the state 1 and state 2; namely  $W^1$  and  $W^2$ , are given as

$$W^1 = W_S - BF^1 \tag{App.-B.2}$$

$$W^2 = W_W + W_G - BF^2$$
. (App.-B.3)

Since the buoyant force acting on the bag is negligible here,  $BF^1$  and  $BF^2$  are equivalent to the buoyant forces acting on the sample in the state 1 and 2, respectively. The buoyant forces; namely  $BF^1$  and  $BF^2$ , are given as

$$BF^1 = \gamma_A^1 \cdot V_S \tag{App.-B.4}$$

$$BF^2 = \gamma_A^2 \cdot (V_W + V_G^2).$$
 (App.-B.5)

Assuming the solid density of the samples constant, the following formulae are obtained from (App.-B.2) and (App.-B.4).

$$W^{1} = W_{S} - \gamma_{A}^{1} \cdot \frac{W_{S}}{\gamma_{S}}$$
(App.-B.6)

$$W_{S} = \frac{W^{1}}{\left(1 - \frac{\gamma_{A}^{1}}{\gamma_{S}}\right)}$$
(App.-B.7)

The weight in the bag does not change, since the bag is sealed. Therefore, the following formula is obtained.

$$W_S = W^2 + BF^2 \qquad (App.-B.8)$$

The following formulae are obtained from (App.-B.1), (App.-B.5), and (App.-B.8).

$$W_{S} - W^{2} = \gamma_{A}^{2} \cdot \left(V_{W} + V_{G}^{2}\right) \quad (App.-B.9)$$
$$W_{S} - W^{2} = \gamma_{A}^{2} \cdot V_{W} + \gamma_{A}^{2} \cdot V_{G}^{2}$$
$$= \gamma_{A}^{2} \cdot \frac{W_{W}}{\gamma_{W}} + \gamma_{A}^{2} \cdot \frac{W_{G}}{\gamma_{G}^{2}}$$
$$= \gamma_{A}^{2} \cdot \frac{W_{S} \cdot (1 - \alpha)}{\gamma_{W}} + \gamma_{A}^{2} \cdot \frac{W_{S} \cdot \alpha}{\gamma_{G}^{2}}$$
$$(App.-B.10)$$

$$W_{S} \cdot \left(1 - \frac{\gamma_{A}^{2}}{\gamma_{W}}\right) - W^{2} = \alpha \cdot \gamma_{A}^{2} \cdot W_{S} \cdot \left(\frac{1}{\gamma_{G}^{2}} - \frac{1}{\gamma_{W}}\right)$$
(App.-B.11)

$$\alpha = \frac{W_{S} \cdot \left(1 - \frac{\gamma_{A}^{2}}{\gamma_{W}}\right) - W^{2}}{\gamma_{A}^{2} \cdot W_{S} \cdot \left(\frac{1}{\gamma_{G}^{2}} - \frac{1}{\gamma_{W}}\right)} \qquad (App.-B.12)$$

The gas content of the pellets can calculated from (App.-B.12).

## Nomenclature

 $a_0$  = dimensionless basic acceleration

- $a_y$  = maximum dimensionless transverse acceleration
- $a_z$  = maximum dimensionless vertical acceleration
- B = greatest molded breadth of ship
- $BF^1$  = buoyant force owing to air in the state 1

 $BF^2$  = buoyant force owing to air in the state 2

 $C_B =$  block coefficient

K = coefficient for loading condition and hull form  $L_{\theta} =$  length of ship

- S = service speed
- $V_G^2$  = volume of methane in the state 2
- $V_s$  = volume of mixture of hydrate and ice (solid part
  - of MHP)
- $V_W$  = volume of water
- $W^1$  = weight in the state 1
- $W^2$  = weight in the state 2
- $W_G$  = weight of methane
- $W_s$  = weight of mixture of hydrate and ice (solid part of MHP)
- $W_W$  = weight of water
- x = longitudinal distance from amidships to center of gravity of cargo hold (positive forward of amidships)
- *z* = vertical distance from waterline to center of gravity of cargo hold (positive above waterline)
- $\alpha$  = gas content
- $\gamma_A^{\ 1}$  = specific weight of air in the state 1
- $\gamma_A^2$  = specific weight of air in the state 2
- $\gamma_G^2$  = specific weight of methane in the state 2
- ys = specific weight of mixture of hydrate and ice
   (solid part of MHP)
- $\gamma_W$  = specific weight of water