# Clathrate-Hydrate Formation by Water Spraying onto a Porous Metal Plate Exuding a Hydrophobic Liquid Coolant

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*A novel technique for producing a clathrate hydrate from a gaseous guest substance was devised and experimentally tested. This technique employs a horizontally oriented spray nozzle and a vertically oriented porous metal plate placed in opposition to each other in a guest-gas phase. Water is sprayed onto the plate while a precooled hydrophobic liquid coolant is seeping out of the plate to form a continuous film flowing down the plate surface. The coolant film is expected to sweep the heat released by hydrate formation away from the plate surface and, at the same time, to prevent the hydrate crystals from agglomerating on the surface thereby hindering the successive contact of the water spray with the coolant. A series of experiments has been performed to reveal the behavior of hydrate formation in the above scheme of guest-gas/water/coolant contact operations.* © 2009 American Institute of Chemical Engineers *AIChE J*, 55: 1056–1064, 2009

*Keywords: clathrate hydrate, gas hydrate, hydrate formation, natural gas storage, energy storage*

## Introduction

Technologies for using clathrate hydrates (abbreviated hydrates hereafter) as the media for storing and/or transporting natural gas, separating particular species from gas mixtures, or storing and conveying cool energy in air-conditioning systems are currently under development. One of the major hurdles to materializing such new technologies for industrial use lies in establishing hydrate-formation technology (including the design of the hydrate-forming reactors and their operational scheme) which ensures a sufficiently high-rate hydrate production per unit reactor volume and also compatibility with the scaling up of the reactors from a laboratory scale to a bench scale, a pilot-plant scale, and finally a commercial-plant scale. Concerning the hydrate production for natural gas storage, for example, various types of hydrate-forming reactors have been proposed and, though mostly on a laboratory scale, actually tested.[1] A few of them have been subjected to bench-scale or pilot-plant-scale examinations.[2–4] Nevertheless, we are still far from the stage of constructing a general guideline for the selection of a specific type of hydrate-forming reactors suitable for each application with given hydrate-forming conditions that may include the chemical species of the given *guest substance* (the substance that provides hydrate crystals with guest molecules), the pressure and temperature conditions, the required rate of hydrate formation, the spatial scale of hydrate-forming equipment, etc. Instead, we are still seeking new hydrate-forming technologies that may yield higher hydrate-forming performance and cost-effectiveness compared with those reported so far. In this article, we present a novel version of the water-spraying type hydrate-forming scheme, which we expect to be applicable to hydrate-formation from gaseous guest substances such as natural gas or biogases.

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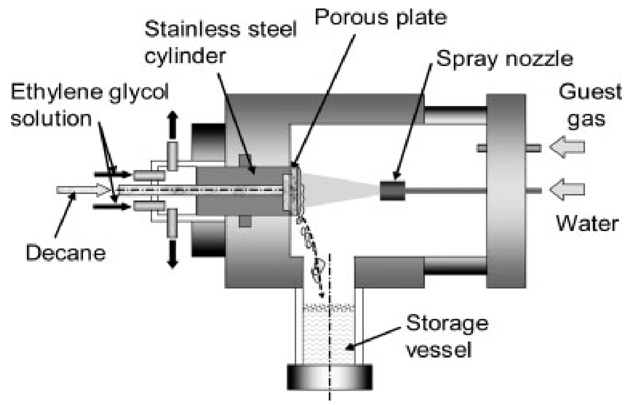

**Figure 1. Schematic of the internal structure of the spray chamber integrated with an assembly for exuding a hydrophobic coolant (decane) through a porous plate confronting a spray nozzle.**

As already pointed out elsewhere,[1] there are two conditions that need to be satisfied to produce a high rate of hydrate formation: (1) a good mixing of the guest substance (e.g., natural gas) and water, and (2) an effective cooling for removing the heat released by the hydrate formation. The water spraying into a guest-gas phase meets condition (1) well. Moreover, the water spraying scheme is favorable for scaling up the reactors. If the scale-up is done by simply multiplying the spray nozzles to be set in array inside each reactor, we can easily estimate the hydrate-forming performance of a reactor of any size based on the performance data obtained with a laboratory-scale reactor equipped with a single nozzle. On the other hand, the water spraying technique does not necessarily meet condition (2). In fact, this technique is apt to suffer from insufficiency of the performance of heat discharge from the reactors.[1] In our preceding article,[5] we briefly reviewed the devices previously contrived for discharging heat from water-spraying type reactors and presented an experimental examination of a new heat-discharge device. In this article, we report a part of our continuing efforts devoted to improving the above device.

The study that we describe in this article originated from an idea of water spraying onto a cooled metal-block surface exposed to a hydrate-forming gas inside a reactor so that the heat released by hydrate formation on the surface may be directly removed by the heat conduction through the metal block. This idea was first tested by Fukumoto et al.,[6] then examined in more detail by Matsuda et al.[5] Either of these studies used a horizontally oriented cylindrical copper or brass block with its front surface extruding into a spray chamber charged with HFC-32 ($CH_2F_2$), a structure-I hydrate forming gas, while its backside was steadily chilled. Water was sprayed onto the front surface of the block from a flat-spray nozzle with its axis set horizontal. Observing the hydrate formation on the brass block surface and, at the same time, measuring the heat flow rate through the block, Matsuda et al.[5] found that the rate of hydrate formation was significantly increased by the use of conductive cooling via the brass block in addition to a conventional cooling device, i.e., water circulation through an external loop incorporating a heat exchanger, without overly intensifying the latter cooling at the risk of loop obstruction due to internal hydrate formation. On the other hand, Matsuda et al.[5] recognized two technical problems yet-to-be solved: (a) the plugging of the spray nozzle by hydrate formation on the nozzle tip due to water mist drifting back from the metal block surface, and (b) the growth of a wet but sticky hydrate layer on the metal block surface, hindering the heat flow into the block. To cope with these problems, particularly problem (b), we attempted to replace the solid metal block with a porous plate through which a hydrophobic liquid coolant substantially precooled is seeping out so that sprayed water droplets fall on a coolant film flowing down the plate surface. Hydrate crystals formed within the area of the porous plate surface are expected to be carried away by the coolant film, instead of piling up on the plate surface. The heat released by the hydrate formation will be dissipated into the coolant film and advected away out of the area of the porous plate surface. A series of experiments has been performed to examine the above idea of heat discharge from the hydrate formation sites, using HFC-32 as the guest gas and decane as the liquid coolant. The obtained results are, as demonstrated later in this article, rather favorable for the idea. We can expect that, using the liquid-coolant seeping technique, problem (b) will be practically eliminated and, at the same time, problem (a) will become less serious.

## Description of Experiments

### *Experimental apparatus*

The experimental apparatus described by Matsuda et al.[5] was used again, with two modifications having been made in its major portion, i.e., the spray chamber used as the hydrate-forming reactor. The structure of the spray chamber thus modified is schematically illustrated in Figure 1, while the layout of the entire experimental system is illustrated in Figure 2. The modifications made in the spray chamber were the replacement of the spray nozzle and that of the cylindrical

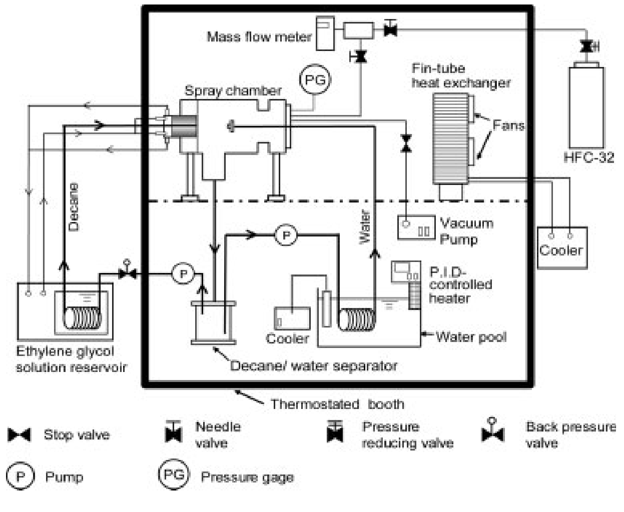

**Figure 2. Experimental system layout.**

block which was inserted into the chamber so that its front surface was to be exposed to the HFC-32 gas and the water spray during hydrate-forming experiments. These modifications are explained below in some detail.

The spray nozzle to be incorporated in the spray chamber is required to function at a rather low water flow rate (~50 $cm^3$/min) and to have a geometrically smooth front face such that water droplets hardly grow on the face, as the result of accumulation of water mist globules from the surrounding gas phase, which may turn into hydrate agglomerates and hinder the nozzle from stably spraying. Neither Fukumoto et al.[6] nor Matsuda et al.[5] could find a full-cone spray nozzle that met the above requirements; hence they employed a hollow-cone spray nozzle[6] or a flat-fan spray nozzle[5,6] that seemed to meet the requirements. Because we found a full-cone spray nozzle (model MW145 manufactured by BETE Fog Nozzle, Greenfield, MA) that functions at a flow rate of ~50 $cm^3$/min and has a flat front face flush with the spray outlet, we decided to use it throughout our experiments.

The assembly for exuding a hydrophobic coolant, decane, into the spray chamber was fabricated so as to be interchangeable with the solid brass-block assembly used in the previous study.[5] The core portion of the former assembly was machined from a SUS316 stainless steel block into a 49-mm dia. solid cylinder with a 5-mm dia. hole perforated along its centerline. This hole opened into a circular cavity, 44 mm in dia. and 11 mm in depth, machined on the front side of the cylinder. A 4-mm thick and 49-mm dia. sintered SUS316 plate was welded onto the cavity so that the coolant supplied through the hole to the cavity was allowed to flow out of the cylinder only through the micro-perforations in the plate. The cavity was equipped with a thermocouple well (not illustrated in Figure 1) to allow the temperature measurement of the coolant just before its seeping into the spray chamber. On the rear side of the cylinder, the hole on the centerline was connected to a stainless-steel coolant-supply tube, which extended through a cylindrical vessel entirely covering the rear of the cylinder. A temperature-controlled secondary coolant (an aqueous ethylene glycol solution) could be circulated through this vessel to prevent the primary coolant, decane, from being heated while flowing into and through the cylinder.

Despite the above modifications having been made, the internal geometry of the spray chamber was completely the same as that in the previous study. That is, the central space in the chamber was 80-mm wide, 112.7-mm high and 160-mm deep. This space held the porous plate for exuding decane and the spray nozzle, which were set on a common horizontal axis leaving a 50-mm distance between them. A cylindrical Pyrex vessel, 65.4-mm ID and 100-mm high, hanging from the bottom of the central space was used to store the hydrate and the two liquids (decane and water) falling down from the surface of the porous plate. Only the liquids were allowed to flow out of the vessel through a port on the flange-type stainless-steel bottom plate of the vessel. The spray chamber was enclosed, together with some auxiliary portions of the apparatus, in a booth temperature-controlled at 10 ± 2°C.

The experimental system layout illustrated in Figure 2 is different from that in the previous study[5] only in the installation of a decane circulation loop, in addition to the water circulation loop, which is outlined here. The two liquids, decane and water, drained out of the Pyrex hydrate/liquid storage vessel were poured into a separator, a 700-$cm^3$ vessel made of a Pyrex cylinder and stainless-steel flange-type lids, to be separated into the two layers due to the density difference between them. With the aid of a nonpulsating double-plunger pump (Nihon Seimitsu Kagaku, model NP-LX-310), the decane was sucked from the upper layer in the separator and pumped to a heat exchanger, then to the stainless-steel cylinder inserted to the spray chamber. The heat exchanger was made of a helical stainless-steel tube immersed in a pool of an ethylene glycol solution which was temperature-controlled by an immersion cooler and a PID-controlled heater + stirrer unit. The ethylene glycol solution temperature-controlled here was also circulated in a loop passing through the cooling vessel covering the rear of the stainless-steel cylinder inserted into the spray chamber. The water (to be more exact, the water-rich liquid) forming the bottom layer in the separator was sucked out by another plunger pump of the same type and sent back to the spray nozzle via a helical tube heat exchanger immersed in a water pool, which was temperature-controlled just in the same way as in the ethylene glycol solution pool installed in the decane circulation loop.

There was no change from our previous study[5] in the rest of the experimental system, the details of which was described by Matsuda et al.[5] In short, a high-pressure HFC-32 cylinder was connected to the spray chamber via a pressure-reducing valve and a mass-flow meter (STEC SEF-V111DM + FI-1000) so that HFC-32 gas could be supplied to the spray chamber to compensate for the loss of the gas due to hydrate formation and thereby maintain the pressure inside the chamber almost constant. The mass-flow meter indicated $\dot{V}_g$, the volume flow rate of HFC-32 [converted to the normal temperature−pressure condition (NTP), i.e., 0°C and 0.1013 MPa] into the spray chamber, with an uncertainty of ±0.08 $cm^3$/s. The pressure $p$ inside the spray chamber was measured by a strain-gauge pressure transducer (Valcom model VPMC-D-A) with an uncertainty of ±1.5 kPa.

### *Procedure of hydrate-forming experiments*

In this study, we performed two groups of experiments. The first group was to exclusively examine the effect of the alteration of the spray nozzle from the flat-fan type to the full-cone type, using the same brass block that we used in the previous study,[5] instead of the decane-exuding assembly described above, together with the full-cone spray nozzle. Every experiment in this group was performed, completely following the procedure that Matsuda et al.[5] described. The second group used the decane-exuding assembly and the full-cone spray nozzle to investigate the effect of the precooled liquid coolant instead of the cooled metal block. The experimental procedure used in the second group is outlined below.

Each experimental run was commenced by evacuating the spray chamber, the water and decane circulation loops, and the HFC-32 gas supply line between the pressure reducing valve and the spray chamber. Deionized and distilled water in the amount of 300 $cm^3$ and also decane

(99% certified purity, supplied by Sigma-Aldrich) in the amount of 400 $\text{cm}^3$ were then sucked into the separator, which was the only vessel incorporated both in the water and decane circulation loops. HFC-32 (99.9 % certified purity, supplied by Asahi Glass) was supplied into the chamber so that the pressure in the chamber was increased to the prescribed level, 0.400 MPa. The supply of HFC-32 was continued to compensate for the dissolution of HFC-32 into the water and decane in the separator, thereby maintaining the pressure $p$ in the chamber at about 0.40 MPa. The temperature in the bath of ethylene glycol solution in which the heat exchanger on the decane circulation loop was immersed was controlled at a prescribed level (in the range from −8.8 to 5.0°C), while the flow rate of decane, $\dot{V}_{\text{hc}}$, was controlled at 0.417, 0.833, or 1.583 $\text{cm}^3/\text{s}$ (25, 50, or 95 $\text{cm}^3/\text{min}$), so that the temperature at which decane seeped out of the porous plate, $T_{\text{hc}}$, was held at a desired level (−8.0, −4.0, 0.5, or 5.0°C). The temperature in the water bath in which the heat exchanger on the water circulation loop was immersed was controlled at 6.5°C. Because of the thermal design of the heat exchanger and of the insulation of the water-supply line from the heat exchanger to the spray nozzle,[5] we can safely assume that the temperature $T_{\text{w}}$ at which the water was sprayed was practically the same as that in the water bath, i.e., $T_{\text{w}} = 6.5°\text{C}$, when the rate of water circulation, $\dot{V}_{\text{w}}$, was adjusted to 0.833 $\text{cm}^3/\text{s}$ (50 $\text{cm}^3/\text{min}$). After starting the circulation of decane and water, the rate of HFC-32 supply into the spray chamber, $\dot{V}_{\text{g}}$, was measured at every 30 s. At the same time, the inside of the chamber was continuously video-recorded to observe the behavior of formation and accumulation of the hydrate inside the chamber.

### Thermodynamic conditions

The pressure inside the spray chamber, $p$, was initially adjusted within ± 3 kPa about the target level, 0.400 MPa. Once the hydrate formation started, $p$ tended to decrease by 7 kPa at most, then gradually recovered toward its initial level. Because of such a minute pressure variation throughout the present experiments, we evaluated the phase-equilibrium temperature and some physical properties of the materials (water, decane and the hydrate) exclusively at the nominal pressure level, $p = 0.400$ MPa, in processing the experimental results. The $p$ values indicated in the captions of some figures shown later represent the initial pressures just before the inception of hydrate formation in the respective experimental runs.

Because decane is neither molecularly involved in the hydrate formation from HFC-32 nor more than slightly soluble in water and has very small vapor pressures in the temperature range set in the present experiments,[7] we can assume that the four-phase (gas + water-rich liquid + decane-rich liquid + hydrate) equilibrium $p-T$ relation in the ternary (HFC-32 + water + decane) system is identical with the three-phase (gas + water-rich liquid + hydrate) equilibrium $p-T$ relation in the binary (HFC-32 + water) system. Thus, the phase-equilibrium temperature $T_{\text{eq}}$ and the heat of hydrate dissociation (on the guest-substance mole basis) $\tilde{h}_{\text{hg}}$ corresponding to the system pressure, $p = 0.400$ MPa, are evaluated to be 8.3°C and 67.09 kJ/mol, respectively (see the Appendix in Ref. 5).

### Operational parameters relevant to heat discharge

In the second group of hydrate-forming experiments, the apparatus was set so as to be equipped with two channels for discharging the heat released by the hydrate formation; i.e., the water circulation loop and the decane circulation loop each incorporating an external heat exchanger. The latter channel was substituted for the backside-cooled brass block used in our previous study.[5] The capacity of heat discharge through each channel is evaluated below.

The maximum rate at which heat could possibly be discharged via the water circulation loop, $\dot{Q}_{\text{w,max}}$, is evaluated as follows[1,5]:

$$\dot{Q}_{\text{w,max}} = \dot{V}_{\text{w}} \rho_{\text{w}} c_{\text{p,w}} \, \Delta T_{\text{sub,w}} \tag{1}$$

where $\dot{V}_{\text{w}}$, $\rho_{\text{w}}$ and $c_{\text{p,w}}$ are the volume flow rate (=0.833 $\text{cm}^3/\text{s}$), the mass density and the specific heat capacity, respectively, of the circulating water, and $\Delta T_{\text{sub,w}}$ is the degree of subcooling of sprayed water defined as $T_{\text{eq}}-T_{\text{w}}$. Analogously, the maximum rate at which heat could be discharged via the decane circulation loop, $\dot{Q}_{\text{hc,max}}$, is evaluated as follows[1,5]:

$$\dot{Q}_{\text{hc,max}} = \dot{V}_{\text{hc}} \, \rho_{\text{hc}} \, c_{\text{p,hc}} \, \Delta T_{\text{sub,hc}} \tag{2}$$

where $\dot{V}_{\text{hc}}$, $\rho_{\text{hc}}$ and $c_{\text{p,hc}}$ are the volume flow rate (=0.417 −1.583 $\text{cm}^3/\text{s}$), the mass density and the specific heat capacity, respectively, of the circulating decane, and $\Delta T_{\text{sub, hc}}$ is the degree of subcooling of sprayed water defined as by $T_{\text{eq}}-T_{\text{hc}}$. The maximum of the total rate of heat discharge, $\dot{Q}_{\text{max}}$, is given by

$$\dot{Q}_{\text{max}} = \dot{Q}_{\text{w,max}} + \dot{Q}_{\text{hc,max}} \tag{3}$$

If a hydrate were continuously formed at such a rate as to release heat at the rate just balancing $\dot{Q}_{\text{max}}$, the HFC-32 gas inside the spray chamber would be consumed at the following rate (the gas volume at NTP per unit time):

$$\dot{V}_{\text{g,max}} = \tilde{v}_g(\dot{Q}_{\text{max}}/\tilde{h}_{\text{hg}}) \tag{4}$$

where $\tilde{v}_{\text{g}}$ is the molar volume of HFC-32 at NTP. We later compare $\dot{V}_{\text{g}}$, the observed rate of HFC-32 gas supply into the spray chamber for compensating the gas consumption due to hydrate formation, to $\dot{V}_{\text{g,max}}$ to evaluate the efficiency of the dual heat-discharge channels prepared in the present experimental system.

In the first group of experiments, a backside-cooled solid brass block was used just the same as in our previous study.[5] In this case, the second channel for heat discharge is, as detailed by Matsuda et al.,[5] composed of the heat conduction through the block and the convective heat transfer to the aqueous coolant (27.4 mass % ethylene glycol solution) impinging onto the backside surface of the block. The subcooling of the coolant, $\Delta T_{\text{sub,c}} \equiv T_{\text{eq}}-T_{\text{c}}$, is considered to be the driving force for the heat discharge through the block, where $T_{\text{c}}$ denotes the temperature of the incoming coolant.

Table 1. Operational Conditions and Results of Experiments Using a Backside-Cooled Solid Brass Block

| Run No. | $T_c$ (°C) | $\Delta T_{sub,c}$ (K) | $\tau$ (s) | $V_{gt}$ (cm$^3$ NTP) | $\dot{V}_{g,av}$ (cm$^3$/s NTP) |
|---|---|---|---|---|---|
| 1 | 0.5 | 7.8 | 960 | 2274 | 2.37 |
| 2 | 0.5 | 7.8 | 1350 | 2823 | 2.09 |
| 3 | 5.0 | 3.3 | 1710 | 2921 | 1.71 |
| 4 | 5.0 | 3.3 | 1470 | 2080 | 1.41 |

## Results and Discussion

### *Specifications of experiments*

The operating conditions common to all of the 17 experimental runs performed in this study are: the system pressure $p = 0.400 \pm 0.003$ MPa, the water-spray temperature $T_w = 6.5$°C ($\Delta T_{sub,w} = 1.8$ K), and the water flow rate $\dot{V}_w = 0.833$ cm$^3$/s. As already stated in the preceding section, these runs are divided into two groups—the first group in which the cooled solid brass block was used and the second group in which the decane-exuding assembly was used. For each of the four runs in the first group, the temperature and the subcooling of the ethylene glycol solution used to cool the backside of the brass block are indicated in Table 1, together with some experimental data to which we will later refer. For each of the residual 13 runs in the second group, the temperature, the subcooling and the flow rate of decane are indicated, together with relevant experimental data, in Table 2.

### *Qualitative observations*

Figure 3 shows two typical sequences of hydrate formation—one observed in an experiment using the brass block and the other observed in a different experiment using the decane-exuding assembly. Each sequence shows the time evolution of the wet hydrate agglomerated on the surface (and its periphery) of the solid brass block or the porous stainless-steel plate exuding decane. Despite the replacement of the flat-spray nozzle used in the previous study[5] by the full-cone nozzle, the behavior of such hydrate-agglomerate growth observed with the solid brass block in this study was little different from that in the previous study.[5] For example, one will find that sequence (a) exhibited in Figure 3 in this article is quite similar to sequence (b) in Figure 3 in the previous article by Matsuda et al.,[5] which was obtained at $\Delta T_{sub,w}$ and $\Delta T_{sub,c}$ conditions similar to those relevant to the former sequence. Either of these sequences indicate that a hydrate agglomerate grew on the peripheral area of the brass block surface, taking the form of an annular bank. Hydrate crystals newly formed on the brass block surface were instantaneously swept by a radial water-film flow to the "bank," then slid down along it toward the bottom of the surface. The major portion of the hydrate crystals thus supplied to the bottom part of the block surface flowed down together with residual water into the hydrate/liquid storage vessel below the central space of the spray chamber (Figure 2), whereas the rest was left on the bottom part of the hydrate bank, resulting in the continuous growth of the bank.

The behavior of hydrate-agglomerate growth on the porous plate exuding decane was appreciably different from that described above. Although a hydrate agglomerate formed a bank over the major latitudinal portion of the circular periphery of the porous plate, the bank grew less at lower positions on the plate surface and was vanishing over the bottom portion located in the path of the decane/water/hydrate mixture flowing down, and away from, the plate surface. Evidently, the decane exuding through the plate effectively functioned as a carrier of instantaneously formed hydrate crystals for removing them away from the plate surface. The formation of the hydrate bank on the periphery of the porous plate surface except for its bottom portion is mostly ascribable to a lower flux (flow rate per unit area) of decane exuding through the peripheral area of the plate, compared with the flux over the core area, which was inevitable due to the internal structure of the decane-exuding assembly composed of the stainless-steel cylinder and the porous plate. The formation of such hydrate banks could possibly be prevented, if we used a sufficiently large porous plate with which the sprayed water would hardly impinge on its peripheral area. Although we could not actually use such a large porous plate because of the dimensional limitations of our spray chamber, the above possibility is of potential importance in planning industrial-scale hydrate-forming reactors based on the same conceptual design as that of the apparatus used in this study.

Another important finding by our visual observation is concerned with the formation of a water mist filling the gas phase inside the spray chamber. As reported by Matsuda et al.,[5] a dense mist of water was generated by the impingement of the water spray onto the brass block surface. The outer surface of the spray nozzle was readily wetted by the mist drifting back from the brass block surface, resulting in

Table 2. Operational Conditions and Results of Experiments Using a Decane-exuding Assembly

| Run No. | $T_{hc}$ (°C) | $\Delta T_{sub,hc}$ (K) | $\dot{V}_{hc}$ (cm$^3$/s) | $\tau$ (s) | $V_{gt}$ (cm$^3$ NTP) | $\dot{V}_{g,av}$ (cm$^3$/s NTP) |
|---|---|---|---|---|---|---|
| 5 | 0.5 | 7.8 | 0.417 | 2130 | 4821 | 2.26 |
| 6 | 0.5 | 7.8 | 0.417 | 1350 | 3192 | 2.36 |
| 7 | 0.5 | 7.8 | 0.833 | 2100 | 5906 | 2.81 |
| 8 | 0.5 | 7.8 | 0.833 | 1500 | 4261 | 2.84 |
| 9 | 0.5 | 7.8 | 1.583 | 1140 | 3283 | 2.88 |
| 10 | 0.5 | 7.8 | 1.583 | 1470 | 4082 | 2.78 |
| 11 | 0.5 | 7.8 | 1.583 | 930 | 2844 | 3.06 |
| 12 | 5.0 | 3.3 | 0.833 | 1830 | 3825 | 2.09 |
| 13 | 5.0 | 3.3 | 0.833 | 2400 | 5214 | 2.17 |
| 14 | −4.0 | 12.3 | 0.833 | 1410 | 4628 | 3.28 |
| 15 | −4.0 | 12.3 | 0.833 | 1200 | 3847 | 3.21 |
| 16 | −8.0 | 16.3 | 0.833 | 1230 | 4381 | 3.56 |
| 17 | −8.0 | 16.3 | 0.833 | 630 | 2044 | 3.24 |

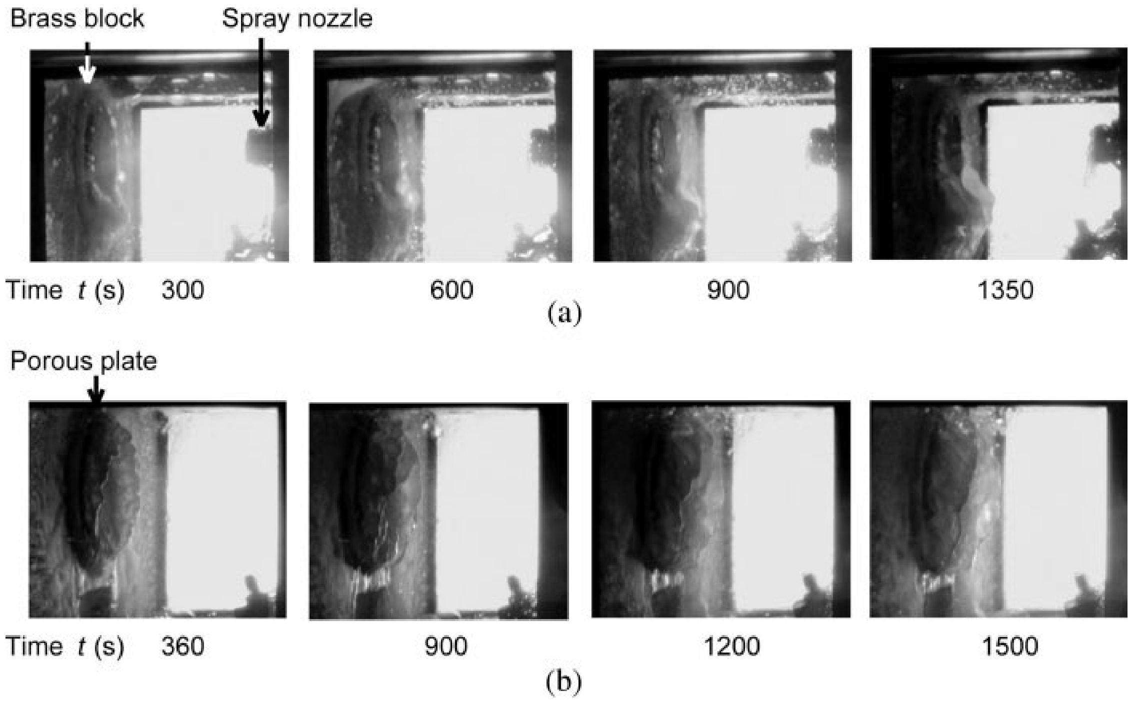

**Figure 3. Sequential videographs of the formation of HFC-32 hydrate by water spraying onto the circular surface (49-mm dia.) of a cooled brass block, (a), or the porous plate exuding cooled decane, (b). $T_w = 6.5°C$ ($\Delta T_{sub,w} = 1.8$ K), $\dot{V}_w = 0.833$ cm$^3$/s.**

Time $t$ denotes the elapsed time after the inception of hydrate formation. (a) Run 2, $P = 0.403$ MPa, $T_c = 0.5°C$ ($\Delta T_{sub,c} = 7.8$ K). (b) Run 8, $P = 0.399$ MPa, $T_{hc} = 0.5°C$ ($\Delta T_{sub,c} = 7.8$ K).

the formation of icicle-like hydrate lumps covering the nozzle surface. In fact, every experimental run performed in the previous study[5] was terminated by the occurrence of instability of the water spray due to such hydrate formation on the nozzle, which was followed by complete plugging of the nozzle. This was also the case in Runs 1–4 (listed in Table 1) performed in this study using the same brass block and the full-cone spray nozzle. In Runs 5–17 (Table 2) in which the decane-exuding assembly was used, however, we noted that the mist formation was substantially reduced. This fact may be ascribable to a difference in mechanical interaction with impinging water droplets between the solid wall and the liquid surface. It is reasonable to assume that water droplets brought into contact with the surface of a decane film flowing down the porous plate surface were apt to be captured there, instead of bouncing back into the gas phase. In fact, none of the 13 experimental runs using the decane-exuding assembly encountered any sign of nozzle plugging due to the hydrate formation. We stopped each run in this group when the decane circulation failed as the result of the descent of the decane layer in the decane/water separator (see Figure 2), which was in turn caused by the depletion of liquid water in the system due to the hydrate formation.

### *Quantitative representation of experimental results*

The primary data from each hydrate-forming experimental run were obtained in the form of the evolution of $V_g$, the cumulative volume (NTP) of HFC-32 supplied to the spray chamber after the instant of the first appearance of hydrate crystals, with time $t$ having passed after that instant. As Mori and Komae[8] recently demonstrated, the deviation of $V_g$ from the amount of HFC-32 uptake into the hydrate that has been formed under a constant pressure, $p = 0.4$ MPa, is estimated to be only about 0.5%. Thus, we can safely use $V_g$ as an index of the total amount of formed hydrate (or the total amount of HFC-32 stored in the hydrate) at each instant during the hydrate-forming process. Accordingly, $\dot{V}_g$ ($=dV_g/dt$) may be viewed as an index of the instantaneous rate of hydrate formation.

All of the $V_g$ vs. $t$ data obtained from the 17 runs listed in Tables 1 and 2 are plotted in the three graphs compiled in Figure 4. In graph (a), the data obtained with the solid brass block in this study are compared with the corresponding data obtained in the previous study by Matsuda et al.[5] Despite a slightly lower system pressure and a smaller degree of $\Delta T_{sub,c}$ in this study compared with those in the previous study, the $V_g(t)$ values obtained in this study appreciably surpass the corresponding values obtained in the previous study except for an early regime (at $t$ less than about 500 s) in each hydrate-forming process. This fact simply indicates the superiority of the full-cone spray nozzle used in this study to the flat-fan spray nozzle used in the previous study[5] for the purpose of hydrate formation on a cooled solid surface.

Graphs (b) and (c) in Figure 4 exclusively exhibit the $V_g$ vs. $t$ data obtained with the decane exuding assembly. Here,

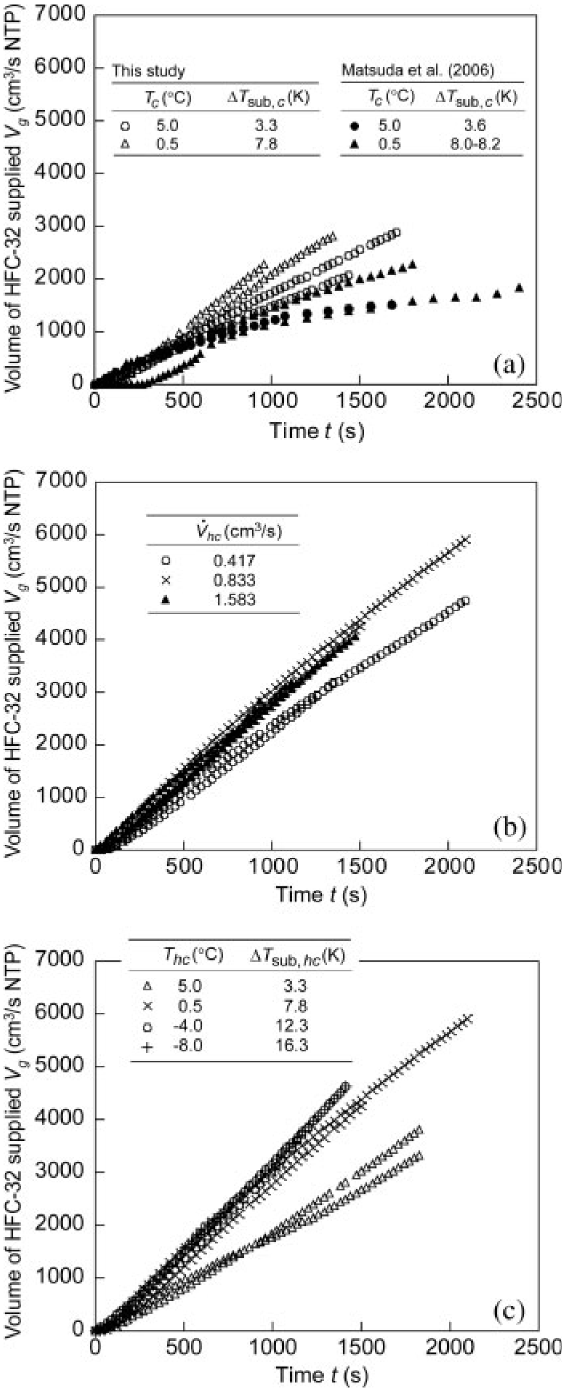

**Figure 4. Time evolution of $V_g$, the cumulative volume (NTP) of HFC-32 supplied to the spray chamber after the first appearance of hydrate crystals, in experimental runs using the solid brass block, (a), or the porous plate exuding decane, (b) and (c). $p = 0.400 \pm 0.003$ MPa, $T_w = 6.5°C$ ($\Delta T_{sub,w} = 1.8$ K), $\dot{V}_w = 0.833$ cm³/s.**

(a) Comparison of the data obtained with the full-cone spray nozzle (this study) and those obtained with the flat-fan spray nozzle (Matsuda et al.[5]). The latter data were obtained at slightly higher pressures ($p = 0.409-0.418$ MPa) and larger degrees of water subcooling ($\Delta T_{sub,w} = 2.0-2.2$ K). (b) Dependence on decane flow rate $\dot{V}_{hc}$. $T_{hc} = 0.5°C$ ($\Delta T_{sub,hc} = 7.8$ K). (c) Dependence on decane temperature $T_{hc}$. $\dot{V}_{hc} = 0.833$ cm³/s.

we find that, in every experimental run, $V_g$ increased almost linearly with $t$, i.e., $\dot{V}_g$ was held nearly constant throughout the hydrate-forming period. This fact indicates that there was no such deposition of hydrate crystals on the porous plate surface as to increasingly hinder the heat discharge to decane flowing down the surface. We also note, by comparing the $V_g$ vs. $t$ data plotted in graphs (b) and (c) to those plotted in graph (a), that the $\dot{V}_g$ values available with decane cooled to a prescribed temperature ($T_{hc}$ = 5.0 or 0.5 °C) are substantially higher than those available with the solid brass block cooled by an aqueous coolant controlled at the same temperature level ($T_c$ = 5.0 or 0.5°C).

Graph (b) demonstrates that $V_g(t)$ moderately increased as the decane flow rate $\dot{V}_{hc}$ was doubled from 0.417 to 0.833 cm³/s, but it no longer increased with the further increase in the flow rate from 0.833 to 1.583 cm³/s. It seems that the decane flow rate of about 0.8 cm³/s or, if averaged over the porous plate surface, about 0.04 cm³/(cm² s) is sufficient for removing the heat released by the hydrate formation on the surface and, at the same time, for sweeping the formed hydrate away from the surface. Presumably, a further increase in $\dot{V}_{hc}$ merely results in excessive thickening of the falling decane film, which little affects the hydrate-to-decane heat transfer.

Graph (c) shows how $V_g(t)$ varied with the temperature $T_{hc}$ or the subcooling $\Delta T_{sub,hc}$ of decane exuding from the porous plate. As expected, $V_g(t)$ increased with an increase in $\Delta T_{sub,hc}$. However, the increment in $V_g(t)$ due to each 4−4.5 K increment in $\Delta T_{sub,hc}$ tended to be reduced with an increase in $\Delta T_{sub,hc}$. The increment almost vanished at $\Delta T_{sub,hc}$ exceeding 12 K.

For characterizing the hydrate formation behavior observed in each experimental run in a quantitative but simple form, we specify the following quantities: (i) the period $\tau$ through which hydrate formation was maintained with steady water spraying and, in the case of using the decane-exuding assembly, steady decane circulation; (ii) the total volume (at NTP) of HFC-32 supplied to the spray chamber during the above period, which is given as $V_{gt} \equiv V_g$ at $t = \tau$; and (iii) $\dot{V}_{g,av}$, the average rate of HFC-32 supply to the spray chamber, defined as $\dot{V}_{g,av} \equiv V_{gt}/\tau$. These three quantities are compiled in Tables 1 and 2, and the values of $\dot{V}_{g,av}$ relevant to all of the 17 runs are plotted in the two graphs in Figure 5. Graph (a) shows the dependency of $\dot{V}_{g,av}$ on $\dot{V}_{hc}$, the flow rate of decane, while its subcooling $\Delta T_{sub,hc}$ was prescribed at the same level (7.8 K). In contrast, graph (b) shows the dependency of $\dot{V}_{g,av}$ on $\Delta T_{sub,hc}$, while the decane flow rate was fixed (0.833 cm³/s), or on $\Delta T_{sub,c}$ for the runs using the solid brass block. For comparison, the $\dot{V}_{g,av}$ values relevant to the four $V_g(t)$ data sets that were obtained in our previous study[5] and reproduced in graph (a) in Figure 4 are also plotted there. In either graph in Figure 5, we intend to compare the $\dot{V}_{g,av}$ values relevant to the experimental runs using the decane-exuding assembly to $\dot{V}_{g,max}$ given by Eq. 4 (or its half or one-third). Here, we note that the ratio of $\dot{V}_{g,av}$ to $\dot{V}_{g,max}$ tends to decrease from over 1/2 to 1/3 with an increase in $\dot{V}_{hc}$ or $\Delta T_{sub,hc}$. That is, the efficiency of the use of the sensible cool energy simultaneously supplied by both water and decane decreases with an increasing rate of its supply. Nevertheless, the values of $\dot{V}_{g,av}$-to-$\dot{V}_{g,max}$ ratio mentioned above are still higher than those available with the conven-

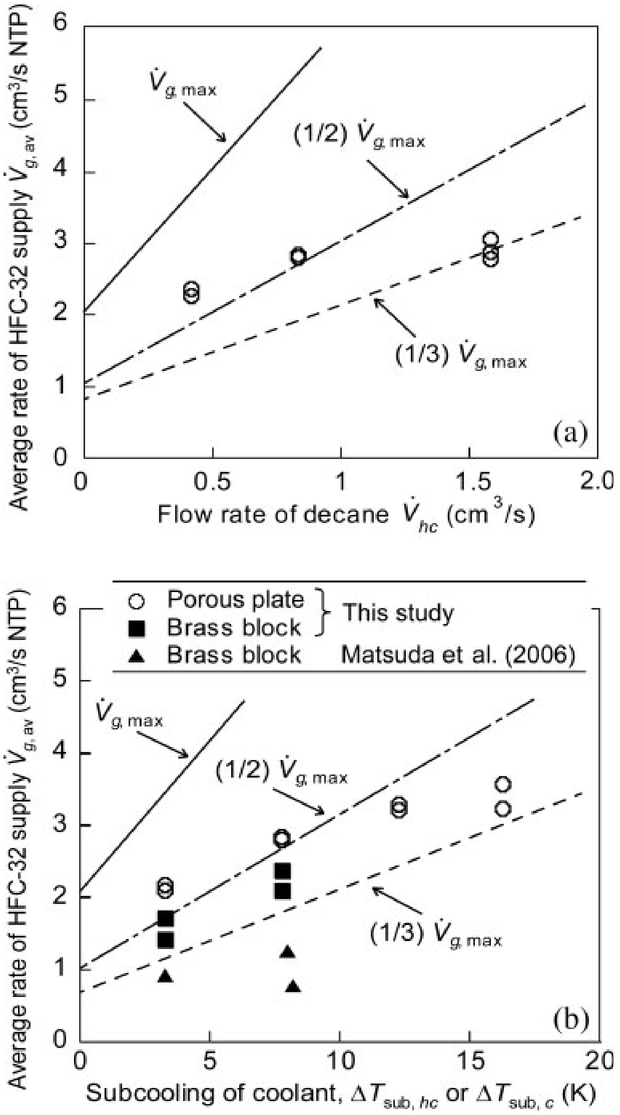

**Figure 5. Dependences of the average rate of HFC-32 supply to the spray chamber, $\dot{V}_{g,av}$, on the decane flow rate $\dot{V}_{hc}$, (a), and the decane subcooling $\Delta T_{sub,hc}$ or the subcooling of the ethylene glycol solution used for cooling the brass block, $\Delta T_{sub,c}$, (b). $p$ = 0.400 ± 0.003 MPa, $T_w$ = 6.5°C ($\Delta T_{sub,w}$ = 1.8 K), $\dot{V}_w$ = 0.833 cm$^3$/s.**

The experimental $\dot{V}_{g,av}$ data are compared with $\dot{V}_{g,max}$, the rate of HFC-32 supply that would be available when the rate of heat release by the hydrate formation balances with $\dot{Q}_{max}$, the capacity of heat discharge by water and decane circulation, or with a half or a third of $\dot{V}_{g,max}$. Note that $\dot{V}_{g,max}$ at $\dot{V}_{hc} = 0$ or $\Delta T_{sub,hc} = 0$ represents the capacity of heat discharge exclusively by water circulation. (a) $T$hc = 0.5 °C ($\Delta T$sub,hc = 7.8 K). (b) $\dot{V}_{hc}$ = 0.833 cm3/s (in the experiments using the porous plate). The data of Matsuda et al.[5] were obtained at slightly higher pressures ($p$ = 0.409−0.418 MPa) and larger degrees of water subcooling ($\Delta T$sub,w = 2.0−2.2 K).

tional water-spray technique. (Note that, as we already pointed out,[1,5] the $\dot{V}_{g,av}$ values obtained in the previous studies[9,10] of hydrate formation from methane by water spraying under pressures from 3.7 to 8.1 MPa fall in the range from one-fourth to one-third of the corresponding values of $\dot{V}_{g,max}$, the ideal rate of HFC-32 supply, which is given by substituting $\dot{Q}_{w,max}$ for $\dot{Q}_{max}$ in Eq. 5.) The higher efficiency in cool energy utilization in the present hydrate-forming system is presumably ascribable to the direct contact of water and decane, taking the form of fine water droplets partially submerged in the decane film, and to the transient heat transfer from each of such numerous droplets to the surrounding decane phase while hydrate crystals are growing on some of these droplets, thereby releasing heat there. The large interfacial area between water droplets (or water/hydrate composites) and decane per unit volume of water and also the high heat transfer coefficient available with such tiny droplets should have promoted the entire heat transfer to the decane phase. The higher efficiency in cool energy utilization is favorable for reducing the work of refrigeration in operating hydrate-forming systems.

## Concluding Remarks

This study has experimentally examined a novel operational scheme for continuous hydrate formation that comprises water spraying onto a precooled hydrophobic coolant seeping out of a porous plate in the atmosphere of a hydrate-forming feed gas. Our experiments using HFC-32 and decane as the feed gas and the hydrophobic coolant have demonstrated that the above scheme enables hydrate formation in a stable and steady manner, efficiently using the cool energy carried by the two liquids. We have found no indication of the hydrate plugging of the spray nozzle or the liquid-circulation loops throughout each hydrate-forming operation. This fact indicates the potential of the above scheme for use in industrial hydrate-forming operations. Although we have used decane, a dense hydrocarbon that could not be comprised in the hydrate, merely as the coolant to which the heat released by hydrate formation could be discharged, we may substitute a *large-molecule guest substance* (LMGS), an oily liquid with molecules that should fit into $5^{12}6^8$ cages of structure-H hydrates, for decane. In this case, the LMGS is expected not only to function as the coolant but also share the role of composing a hydrate with the feed gas and water. This possibility will be experimentally examined in due course.

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## Notation

$c_p$ = specific heat capacity under constant pressure, J kg$^{-1}$
$\tilde{h}_{hg}$ = heat of hydrate dissociation, J mol$^{-1}$
$p$ = pressure inside spray chamber, Pa
$\dot{Q}$ = total rate of heat discharge ($\dot{Q}_{hc} + \dot{Q}_w$), W
$\dot{Q}_{hc}$ = rate of heat discharge by hydrophobic coolant circulation, W
$\dot{Q}_w$ = rate of heat discharge by water circulation, W
$t$ = time lapse after the inception of hydrate formation, s
$T$ = temperature, K or °C
$\tilde{v}_g$ = molar volume of hydrate-guest gas at NTP, m$^3$ mol$^{-1}$

$V_g$ = accumulated volume at NTP of guest gas supplied to spray chamber after the inception of hydrate formation, $m^3$
$V_{gt}$ = $V_g$ at $t = \tau$, $m^3$
$\dot{V}$ = volume flow rate (at NTP for gas), $m^3\ s^{-1}$

### Abbreviation

NTP = normal temperature and pressure (0°C and 0.1013 MPa)

### Greek letters

$\Delta T_{sub}$ = degree of subcooling (magnitude of temperature deviation from $T_{eq}$), K
$\rho$ = mass density, kg $m^{-3}$
$\tau$ = $t$ at the end of the hydrate-forming period in which neither water spraying nor decane circulation was disordered, s

### Subscripts

av = average over the period from $t = 0$ to $t = \tau$
$c$ = aqueous coolant (ethylene glycol solution)
eq = gas/water/hydrate three-phase equilibrium
g = hydrate-guest gas
hc = hydrophobic coolant (decane)
max = theoretical maximum
w = water

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