Hydrate Formation Using Water Spraying in a Hydrophobic Gas: a Preliminary Study

Kazuya Fukumoto, Jun-ichiro Tobe, Ryo Ohmura, and Yasuhiko H. Mori
Dept. of Mechanical Engineering, Keio University, Yokohama 223-8522, Japan

There is increasing interest in the possibility of storing and transporting natural gas in the form of clathrate hydrates, crystalline solid compounds formed by hydrogen-bonded water molecules configured into cages, each holding at most one molecule of a natural-gas-forming species such as methane, ethane, or propane. Such natural-gas hydrates can be formed and stored at much more moderate thermodynamic conditions (for example, at a temperature of ~5°C and a pressure of ~5 MPa) compared to conventional gas-storing media—liquefied natural gas for long-distance gas shipping and compressed natural gas for various small-scale uses, including natural-gas vehicles. The gas storage capacity of natural-gas hydrates is estimated to be about 160 volumes of gas at STP, which is 25–30% of that of liquefied natural gas at a temperature of −160°C and is comparable to that of compressed natural gas under pressure of ~15 MPa. Thus, the use of natural-gas hydrates as a gas-storing medium has potential merits of economy and safety.

One of the major technical barriers to realization of natural-gas hydrates storage systems is the necessity of developing a practical means of rapid hydrate formation. Because of the low solubility of hydrocarbons in water, hydrates can generally form only at the gas–water interfaces in any gas–water contact operation. Thus, some means of greatly increasing the gas–water interfacial area is desirable. Rogers et al. (1996) was probably the first demonstration of the applicability of a water-spraying technique to rapid hydrate formation. They sprayed water downward from an ultrasonic atomizer into a vertically-oriented, cylindrical, presumably steel-made cell, which was charged with ethane gas and cooled from the outside. No visual observation of the hydrate-formation process was done.

We appreciate the potential of the water spraying technique conceived by Rogers et al. (1996) for rapid hydrate formation for natural-gas storage. Nevertheless, we note that the technique still leaves room for improvement. Because hydrate formation is an exothermic reaction, the rate of hydrate formation in a water-spraying system will be controlled by the heat transfer from the system to the surroundings whenever the system is in an almost steady state. Thus, it is necessary to integrate an effective heat-removal device with the water-spray system to enable it to form hydrate continuously. In the present study, we examined our idea of spraying water against a copper block exposed to a hydrate-forming gas, while the block was steadily chilled at its backside. This spray/cooling assembly was expected to enable the simultaneous hydrate formation at, and the heat removal from, the surface of the copper block. Emphasis was placed on visual observations to understand the nature of hydrate-formation with this spray/cooling assembly.

Experimental Apparatus and Procedure

To allow detailed observations of hydrate formation in a glass-made spray chamber, we substituted HFC-32 (CH_2F_2) for natural gas, considering its capability of forming structure I hydrate at relatively low pressures (Akiya et al., 1997). Figure 1 illustrates the structure of the spray chamber we constructed. The chamber was made of a borosilicate glass cylinder, 87.2 mm ID, with flange-type stainless-steel lids. One of the lids had a large, concentric opening, through which a cylindrical copper block was inserted in such a way that its top surface, 50 mm in diameter, slightly protruded into the chamber. A spray nozzle was inserted, through the other lid, into the chamber along its axis to face the copper block. The backside of the copper block was continuously cooled by an impinging jet of an aqueous ethylene-glycol solution, which was circulated through a PID-controlled cooler/pump unit and the container covering the backside of the copper block. The spray chamber, a water reservoir from which distilled water pressed by pressure-regulated nitrogen gas was to be supplied to the nozzle, and a thermostated water bath in which the water reservoir was immersed were placed in a closed booth in which temperature-controlled air was circulated. The spray chamber was placed vertically (with the nozzle facing upward) or horizontally.

Each experimental run was commenced by: (1) charging the spray chamber with HFC-32 gas; (2) adjusting the temperatures in the water reservoir, the copper block, and the spray chamber, respectively, at prescribed levels; (3) adjusting

---

Correspondence concerning this article should be addressed to Y. H. Mori.

Current address of K. Fukumoto: Canon Inc., Ami-cho, Inashiki-gun, Ibaraki 300-1155, Japan.

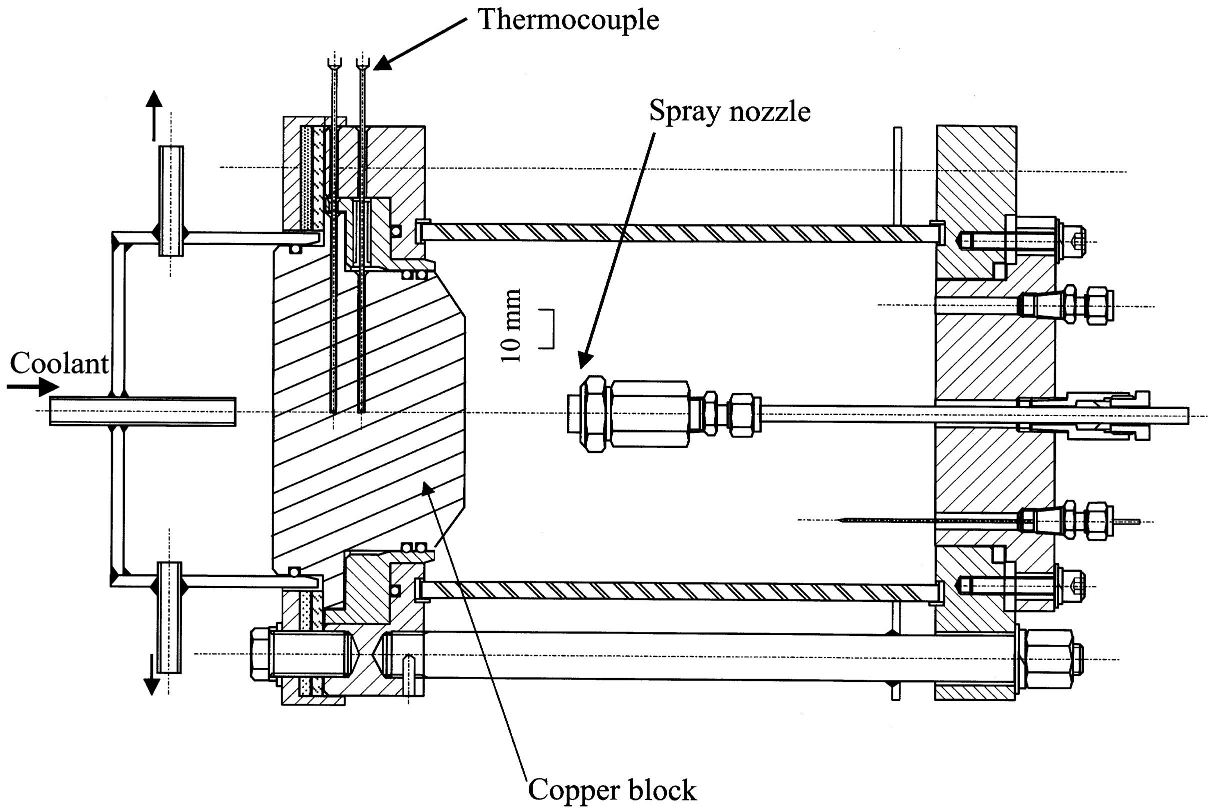


Figure 1. Spray chamber: cutting plane including the chamber axis.

the gas pressures in the spray chamber and the water reservoir; and then (4) opening the stop valve on the water line connecting the water reservoir and the spray nozzle, thereby allowing the nozzle to burst out spraying against the copper block. It was confirmed that the spatial variation in temperature in the copper block was no more than negligible. The HFC gas port on the spray chamber was closed during each run, resulting in a variation in pressure in the chamber with time. The pressure in the chamber was continuously measured by a digital pressure gauge (Valcom VPMC-D-A-1000kPa-1). Simultaneously, the hydrate formation behavior in the spray chamber was recorded by a digital video camera (Sony DCR-TRV900).

Two different nozzles were used alternatively. They were a hollow-cone spray nozzle (Model TX-SS-1) and a flat spray nozzle (Model TP-150017) both manufactured by Spraying

Table 1. Performance Data for Two Spray Nozzles Used in the Experiments

Nozzle	Spray Geometry (Opening Angle)	Flow Rate [cm^3/s]	Mean Droplet Dia. [μm]* Arithmetic	Mean Droplet Dia. [μm]* Sauter	Droplet Vel. [m/s]*
TX-SS-1	Hollow Cone (35°)	1.0	84	181	4.9
TP-150017	Flat fan (15°)	0.83	71	125	15.1

*Measured by a phase Doppler particle analyzer at a location of 50 mm away from the tip of the nozzle which was placed horizontally, while water pressurized at 200 kPa in excess of the ambient pressure was being sprayed through the nozzle.

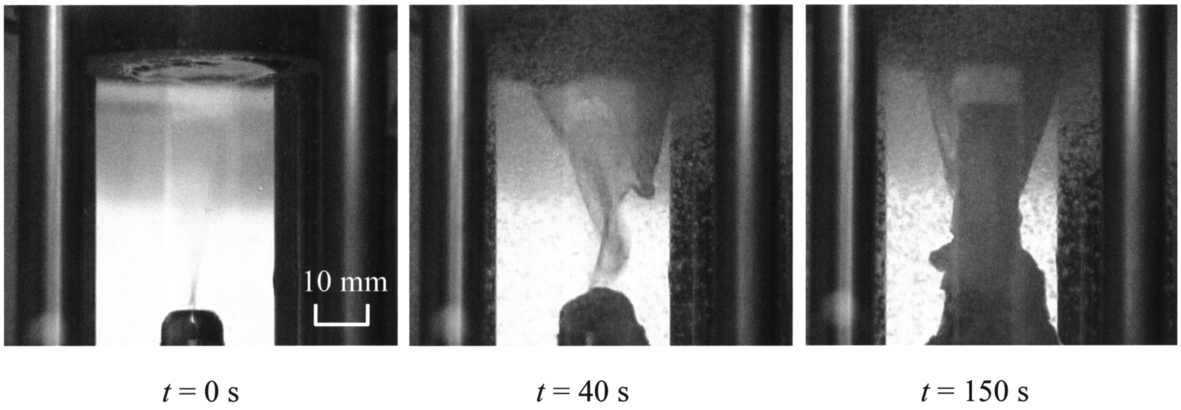


Figure 2. Hydrate formation with a hollow-cone spray nozzle placed vertically.

$T_{gas} = -2°C$, $T_{wall} = -7.5°C$, $T_{liq} = 0.5°C$, $T_{tri,i} = 10.4°C$, $p_{gas,i} = 500$ kPa, $p_{liq} = 700$ kPa, $l = 45$ mm.

Systems Co., Japan. The performance data for these nozzles are summarized in Table 1.

Results and Discussion

Irrespective of the pressure–temperature conditions in the spray chamber and the type of nozzle used, the inception of hydrate formation was erratic in the absence of any *treatment* of the copper-block surface. The treatment found to be effective in inducing immediate hydrate nucleation at the copper-block surface was to cover the surface with a thin layer of supercooled water or ice (when the copper-block temperature was below 0°C), or to place a small amount of hydrate particles on the surface, in advance of water spraying. Once hydrate formation began on the copper-block surface, we did not observe any residual effect of the advance surface treatment on the behavior of successive hydrate formation.

Typical sequences of hydrate formation are demonstrated in Figures 2, 3 and 5. Indicated below each picture is the time lapse t since the first picture in the same sequence was taken immediately after the inception of water spraying. The operational conditions set in each sequence are specified in the corresponding figure caption in terms of the temperature T_{gas} and initial pressure $p_{gas,\ i}$ of the gas in the spray chamber, the copper-block temperature T_{wall}, the temperature T_{liq} and pressure p_{liq} of water fed to the spray nozzle, the hy-

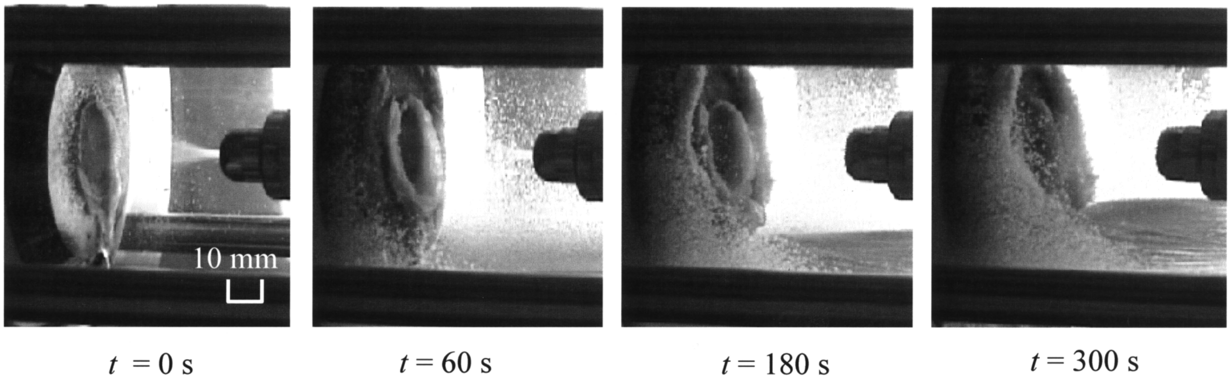


Figure 3. Hydrate formation with a hollow-cone spray nozzle placed horizontally (Run 17-2).

$T_{gas} = 2°C$; $T_{wall} = 0°C$, $T_{liq} = 0.5°C$; $T_{tri,i} = 12.1°C$, $p_{gas,i} = 600$ kPa, $p_{liq} = 800$ kPa, $l = 40$ mm.

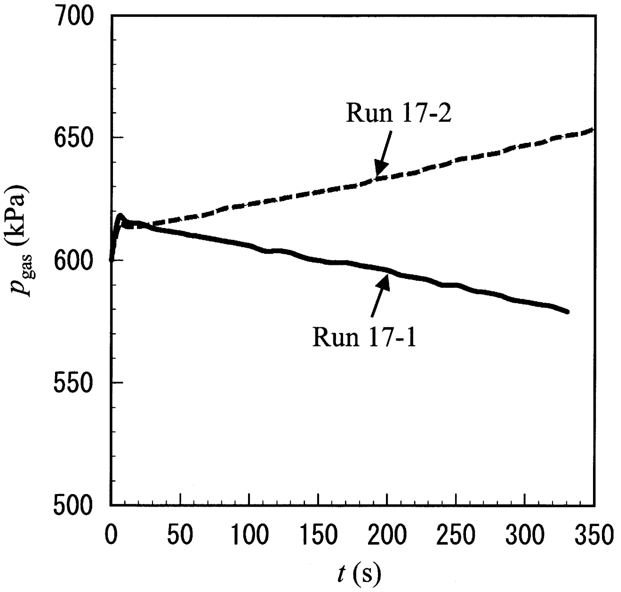


Figure 4. Changes in p_{gas}, gas pressure in the spray chamber, caused by water spraying in two different runs operated under the same conditions indicated in the caption for Figure 3.

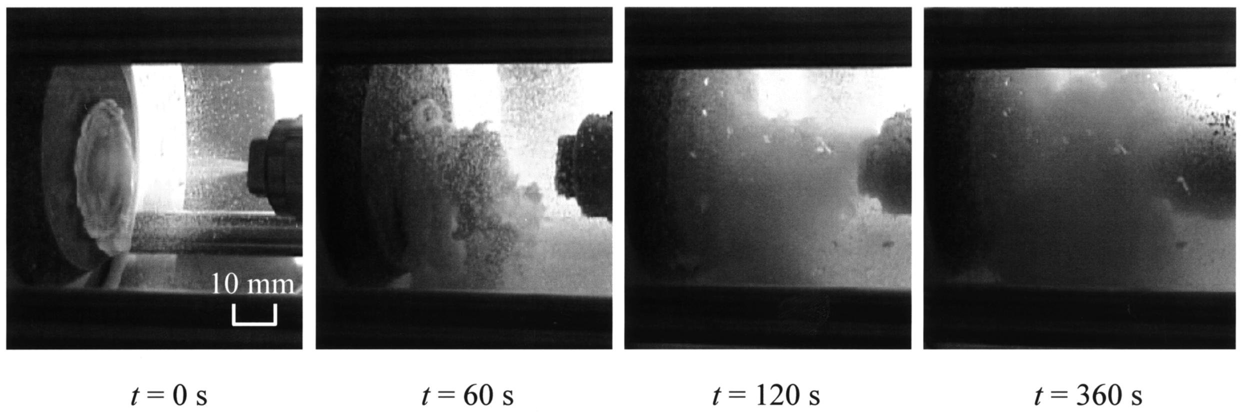
Hydrate formed in Run 17-2 as shown in Figure 3; in contrast, hydrate did not nucleate in Run 17-1.

drate/gas/liquid equilibrium temperature $T_{\text{tri},\ i}$ corresponding to the pressure $p_{\text{gas},\ i}$, and the distance between the nozzle tip and the copper-block surface l. The flow rate of water through the spray nozzle when $p_{\text{liq}} - p_{\text{gas}} =$ 200 kPa is known from Table 1, where p_{gas} is the instantaneous gas pressure in the spray chamber. It is reasonable to assume that the flow rate changes nearly in proportion to the pressure difference, $p_{\text{liq}} - p_{\text{gas}}$.

Figure 2 shows the sequence of hydrate formation when water was sprayed upward from the hollow-cone spray nozzle against the copper block facing downward. Despite our expectation that water droplets which impinged upon the copper-block surface would immediately be turned into hydrate particles and blown away from the surface, we observed that a wet (sherbet-like) hydrate deposit grew into the form of a veil or a skirt, which was then broken due to gravity and fell onto the nozzle. Such growth and breaking/falling of a hydrate skirt were repeated, often resulting in the blocking of the nozzle.

Figure 3 shows another sequence observed with the same hollow-cone spray nozzle, which was placed horizontally this time to face the vertically oriented copper-block surface. Here, we found an immediate formation of a mushy hydrate ring, which was deposited on the copper-block surface so as to prevent the spray from subsequent contact with the surface. The sprayed water impinged upon the hydrate ring, flowed outward to the periphery of the copper block, and then flowed down to the bottom of the chamber, carrying some amount of the mushy hydrate. The hydrate ring hardly grew after $t \approx 100$ s, while a hydrate *somma* continued to grow at the periphery of the copper-block surface. The liquid water having poured from the copper-block surface formed a puddle at the bottom of the chamber, which was covered by an apparently thin hydrate film.

Figure 4 compares the changes in gas pressure in the spray chamber p_{gas}, recorded in two separate runs under the same operational conditions indicated in Figure 3's caption. Hydrate formed only in Run 17-2, the run exemplified in Figure 3. No hydrate formation was noted in the other Run 17-1. Strange as it may appear, p_{gas} decreased with time only when hydrate did not form inside the chamber. The decrease in p_{gas} in Run 17-1 indicates that the rate of gas absorption into water was so high, as to compensate well the gas-compression effect of successive water injection into the closed chamber. The increase in p_{gas} in Run 17-2 is ascribable to a rather low rate of hydrate formation on the copper-block surface and also to the formation of a hydrate film over the water puddle at the bottom of the chamber, which must have prevented successive gas absorption into the puddle. (We should note



$t = 0$ s $t = 60$ s $t = 120$ s $t = 360$ s

Figure 5. Hydrate formation with a flat spray nozzle placed horizontally (Run 13-1).

$T_{\text{gas}} = 2.5$°C, $T_{\text{wall}} = 0$°C, $T_{\text{liq}} = 0.5$°C, $T_{\text{tri},i} = 12.1$°C, $p_{\text{gas},\ i} = 600$ kPa, $p_{\text{liq}} = 800$ kPa, $l = 40$ mm.

that gas-in-water solubility in the presence of the hydrate is substantially lower than that in the metastable state in the absence of any hydrate at temperatures lower than T_{tri}, the hydrate/gas/liquid equilibrium temperature, by several degrees or more (Zatsepina and Buffett, 1997).)

Figure 5 shows the sequence obtained with a flat spray nozzle when other operational conditions were almost the same as those set in the two runs, Runs 17-1 and 17-2, illustrated in Figures 3 and 4. Water injected from the flat spray nozzle impinged upon the central area of the copper-block surface and radially flowed in the form of a thin film, resulting in the formation of a hydrate ring which dammed up the radial film flow of water. The ring axially grew into the form of a hollow cylinder, while mushy hydrate, presumably formed on the copper-block surface, was continually splashed back along the inner wall of the cylinder. As it grew to 20–30 mm axially, the cylinder broke due to gravity, resulting in a major proportion of it falling to the bottom of the chamber. Such growth and breaking of the hydrate cylinder were cyclically repeated up to $t \approx 5$ min, when hydrate clods (that is, the remnants of hydrate cylinders broken so far) had been piled on the bottom of the chamber high enough to support the hydrate cylinder currently growing on the copper-block surface. Thereafter, the hydrate cylinder no longer broke, but continued to grow to envelop the nozzle. It is reasonable to assume, however, that the cyclic growth and breaking/falling of the hydrate cylinder would steadily continue, if the spray chamber had either a sufficiently deep space for storing hydrate clods beneath the copper block or some mechanism to successively remove the hydrate clods away from the copper block.

Figure 6 illustrates the changes in p_{gas} in Run 13-1 exemplified in Figure 5 and another run operated just the same as in Run 13-1. Hydrate formed in both runs. In each run, we noted a steep decrease in p_{gas}, which demonstrates a much higher rate of hydrate formation throughout this run than in Run 17-2, shown in Figures 3 and 4.

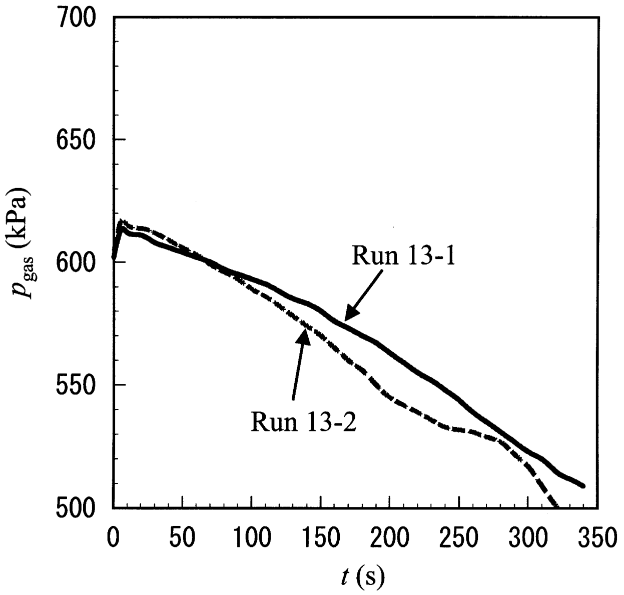


Figure 6. Changes in p_{gas} caused by water spraying in two different runs operated under the same conditions indicated in the caption for Figure 5.

Hydrate formed in both runs.

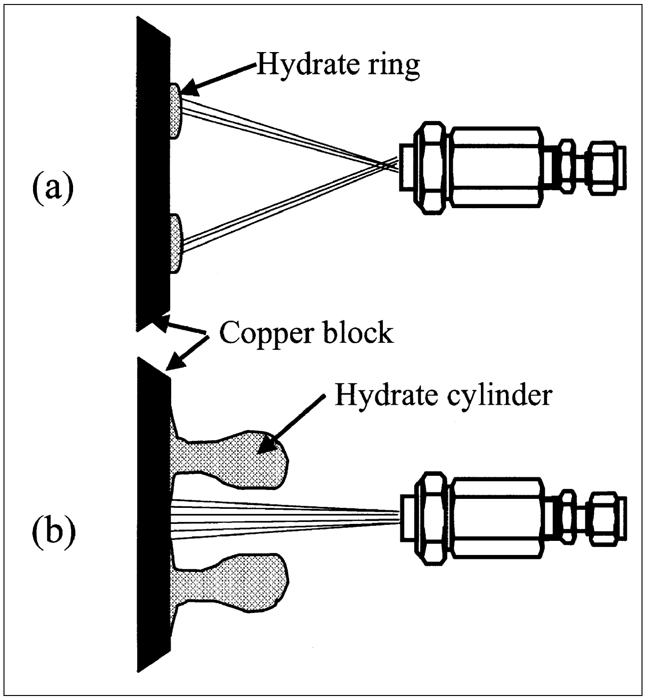


Figure 7. Hydrate formation with: (a) hollow-cone spray nozzle, (b), flat spray nozzle.

In (a), a ring-shaped hydrate deposit prevents sprayed water from directly contacting the copper-block surface. In (b), a hydrate cylinder grew in such a way that it does not interrupt the water–copper contact.

The revealed superiority of the flat spray nozzle over the hollow-cone spray nozzle seems to be ascribable mostly to the two features of the former: the smaller spray angle and the higher velocity of water droplets impinging upon the copper-block surface (see Table 1). Due to these features, a strong radial film flow of water is developed on the surface, which prevents hydrate deposition over the area of water impingement upon the surface, thereby maintaining direct water–copper contact, which is indispensable for effective removal of the heat of hydrate formation from the chamber. This interpretation is shown in Figure 7. (The smaller droplet size available with the flat spray nozzle (Table 1) might have some secondary effect, which has not been revealed in the present experiments.)

The present study may be concluded by stating that the impinging water spray device can be an effective tool for continuous hydrate production, depending on the selection of spray nozzles and on the geometric and thermal design of the spray chambers.

Acknowledgment

This study was subsidized by Grants-in-Aid for Scientific Research from the Japan Society for the Promotion of Science (grant Nos.

10450088 and 3580) and by a Keio University Special Research Grant for the Development of Graduate Schools.

Literature Cited

Akiya, T., T. Shimazaki, M. Oowa, M. Nakaiwa, T. Nakane, T. Hakuta, M. Matsuo, and Y. Toshida, "Phase Equilibria of Some Alternative Refrigerants Hydrates and Their Mixtures Using For Cool Storage Materials," *Proc. 32nd Intersoc. Energy Convers. Eng. Conf.*, Honolulu, HI, *AIChE*, New York, Vol. 3, 1652 (1997).

Rogers, R., G. Y. Yevi, and M. Swalm, "Hydrates for Storage of Natural Gas," *Proc. 2nd Int. Conf. on Natural Gas Hydrates*, Toulouse, France, 423 (1996).

Zatsepina, O. Ye., and B. A. Buffett, "Phase Equilibrium of Gas Hydrate: Implications for the Formation of Hydrate in the Deep Sea Floor, *Geophys. Res. Lett.*, **24**, 1567 (1997).

Manuscript received July 17, 2000 and revision received November 16, 2000 .