

Development of a novel hydrate-based refrigeration system: A preliminary overview

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Abstract

This paper gives a preliminary overview of our attempt at developing a hydrate-based refrigeration system based on a novel conceptual design. The system forms a closed cycle, which is more or less analogous to the conventional vapor-compression refrigeration cycle. The cycle of present interest is performed by a multiphase refrigerant, which is typically a mixture of one or two hydrate-forming substances and water. The refrigerant is required to form a hydrate at a temperature as high as $\sim 30^\circ\text{C}$ or above, desirably under a modest pressure, such that the heat released by the exothermic hydrate formation can be efficiently removed by an environmental fluid such as the atmospheric air, groundwater or river water. The hydrate slurry thus formed is depressurized to dissociate at a lower temperature, typically $5\text{--}9^\circ\text{C}$, thereby absorbing heat from a space to be refrigerated. To confirm the feasibility of the above conceptual design of the hydrate-based refrigeration system, a thermodynamic analysis of the system and a simulation of its operation have been performed. Also a laboratory-scale refrigerator based on the above design was constructed and tested. The paper summarizes the results of these efforts to show the potential advantages of the hydrate-based refrigeration system over conventional ones and to give the prospects of our refrigeration-system development.

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1. Introduction

The major objective of this paper is to present a conceptual design of a refrigeration (or heat-pump) system in which a clathrate-hydrate-forming gas/liquid mixture is used as the working medium. The working medium is expected to form a clathrate hydrate (abbreviated “hydrate” hereafter) at a temperature about 30°C or even higher, desirably under a modest pressure, such that the

heat released by the hydrate formation can be efficiently removed by some environmental fluid easily available (e.g., the air, groundwater, river water, or coastal water), while the hydrate thus formed is to be dissociated under a lower pressure, thereby absorbing heat at a lower temperature, typically $5\text{--}9^\circ\text{C}$, from a space to be refrigerated. Insofar as it directly utilizes both exothermic formation and endothermic dissociation of a hydrate in the working-medium loop, the system of our interest is distinguished from the previously proposed hydrate-based cool-energy storage/utilization systems in which a clathrate hydrate is formed and stored within the lower-pressure/lower-temperature portion of the conventional vapor-compression refrigeration cycle (for example, [1–4]) or a hydrate slurry

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is used only as the secondary refrigerant (i.e., the cool-energy-conveying medium) [5,6].

Our prime incentive for investigating the above-mentioned hydrate-based refrigeration system lies in its potential for providing a higher system efficiency compared to those of conventional vapor-compression refrigeration systems. Specific reasons why we can expect such a higher efficiency with the hydrate-based refrigeration system are briefly stated below.

- (1) The heat of formation/dissociation of an ordinary hydrate per mole of the hydrate-guest gas is generally several times as large as the phase-change latent heat per mole of any fluorocarbon refrigerant used in conventional vapor-compression refrigeration systems (see Table 1).
- (2) When the guest gas and liquid water (i.e., the hydrate-host substance) are mixed and compressed together, a part of the heat generated by the gas compression is absorbed by the water having a large heat capacity, so that the compression process in the refrigeration cycle of present interest should approximate an isothermal compression process, and hence the compressor power required is greatly reduced. The intense gas/liquid mixing and hydrodynamic disturbances inevitably imposed on the guest-gas/liquid-water two-phase flow through this compression process may help the subsequent hydrate formation.

In the following sections, we describe a thermodynamic analysis and a simulation of a hypothetical hydrate-based refrigeration system, the experimental efforts to construct and test a laboratory-scale model of such a refrigeration system, the property requirements for the hydrate-guest substances for use in the system, and technical problems to be addressed in the future.

2. Thermodynamic analysis and simulation

2.1. Concept of the system and principle of its operation

Fig. 1 illustrates the conceptual design of the hydrate-based refrigeration system that we consider in this study. This system mainly consists of (i) a compressor in which a guest gas and water (or an aqueous solution of a water-soluble “second” guest substance, or water accompanied by another liquid phase of a hydrophobic “second” guest substance) are mixed and compressed, (ii) a hydrate-forming reactor in which a hydrate is formed at a temperature exceeding that in the environment of the system, thereby releasing heat to the environment, (iii) a water separator for dewatering the hydrate slurry produced in the hydrate-forming reactor, (iv) a slurry pump for conveying the hydrate slurry concentrated by the separator to a hydrate-dissociating reactor, (v) the hydrate-dissociating reactor in which the hydrate is dissociated, thereby absorbing heat from a space to be cooled, and (vi) pumps for circulating water through two water-recirculation loops to improve the fluidity of the hydrate slurry while flowing through the reactors. Each water-recirculation loop includes a water separator for adjusting the water flow rate through the main loop for the working-medium circulation. It should be noted that the slurry pump is used not to pressurize the slurry but to control the flow rate of the slurry, thereby controlling the pressure difference between the two reactors. In other words, the slurry pump plays the role of an expansion valve in a conventional vapor-compression refrigerator.

The working medium cyclically undergoes compression, hydrate formation, decompression, and hydrate dissociation, while flowing through the above-mentioned components of the system. What we can utilize in the operation of the system is either or both of the heat removal (i.e.,

Table 1
Properties of hydrates formed from different fluorocarbon refrigerants

Guest substance		C ₃ H ₈ (R290)	CH ₂ F ₂ (R32)	CH ₂ FCF ₃ (R134a)	CH ₃ CHF ₂ (R152a)
Crystal structure		II	I	II	I
Hydration number (water-to-guest molar ratio)		17.0 ± 0.1 ^a	5.75 ^b	17 ^c	5.75 ^b
Upper quadruple point (V + L _g + L _w + H equilibrium)	MPa/K	0.562/278.4 ^d	1.489/294.09 ^e	0.4144/283.13 ^f	0.4437/288.15 ^f
Heat of hydrate formation	kJ/mol-guest	129.2 ± 0.4 ^a	72 ^g	134 ^g	79 ^g
	kJ/kg-guest	2930 ± 9	1376	1310	1193
Latent heat of vaporization ^h	kJ/mol-guest	16.5	16.4	20.3	20.3
	kJ/kg-guest	374.5	315.3	198.6	307.1

^a According to Handa [7].

^b Estimated by assuming 100% occupancy of 5¹² and 5¹²6² cages.

^c Estimated by assuming 100% occupancy of 5¹²6⁴ cages.

^d According to Verma [8].

^e According to Akiya et al. [9].

^f According to Liang et al. [10].

^g Estimation based on the Clausius–Clapeyron equation.

^h Given by NIST REFPROP Version 7.0 [11].

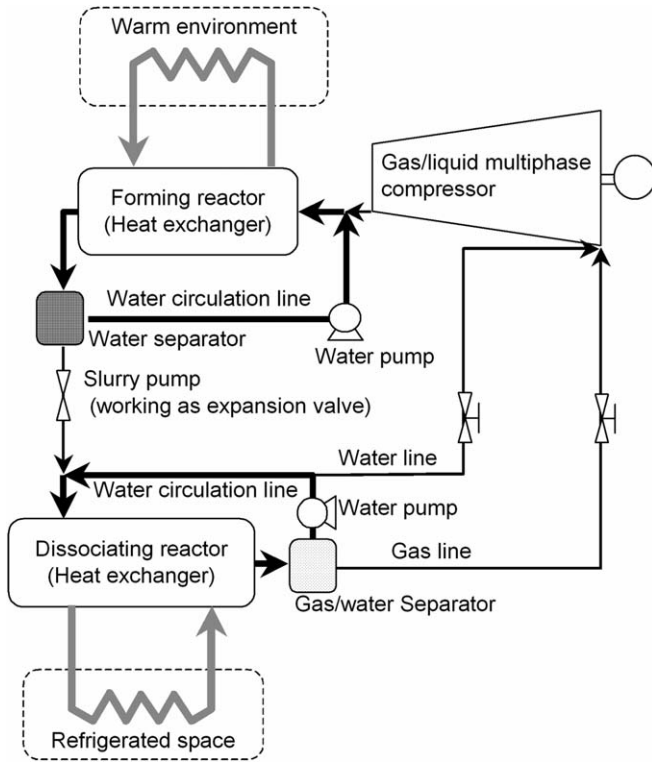


Fig. 1. Conceptual design of hydrate-based refrigeration system. The working medium of the system may be a mixture of a hydrate-guest gas and water as illustrated here. Alternatively, water may be replaced by an aqueous solution of a water-soluble “second” guest substance, or it may be accompanied by another liquid phase of a hydrophobic “second” guest substance, to provide phase-equilibrium conditions more suitable for the system.

cooling) by the hydrate-dissociating reactor and the heat release (i.e., heating) by the hydrate-forming reactor.

In the following, we show a thermodynamic simulation of the refrigeration cycle relevant to the hydrate-based system outlined above and examine the effects of some system-operational parameters on the coefficient of performance (COP) of the system.

2.2. Specification of operational parameters

2.2.1. Hydrate-forming substances

The search for guest substances (including pairs of different guest substances) suitable for the refrigeration system of present interest are now underway in our research group. The pair of HFC-32 (difluoromethane; CH_2F_2) and cyclopentane is one of the promising guest-pair candidates. Very recently, Imai et al. [12] reported their measurements of the equilibrium pressure vs. temperature (P – T) relation for the four phases – HFC-32-rich vapor (V) + cyclopentane-rich liquid (L_g) + water-rich liquid (L_w) + hydrate (H) – in the HFC-32 + cyclopentane + water three-component system. The four-phase equilibrium P – T data of Imai et al. [12] are reproduced in Fig. 2 together with the saturated vapor pressure curve for HFC-32 [11]. Because of the much lower vapor pressures of cyclopentane and water compared to

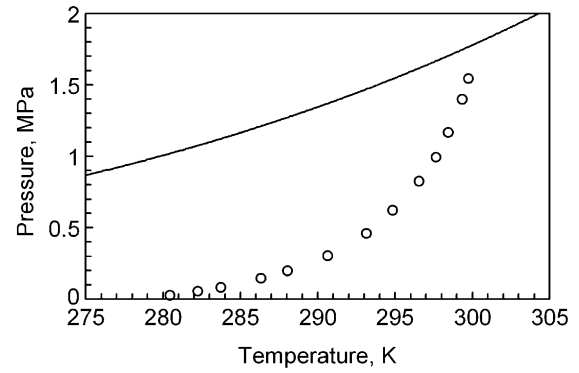


Fig. 2. Experimental data for the V + L_g + L_w + H four-phase equilibrium in the system of HFC-32 + cyclopentane + water (open circles) [12] and the saturated vapor pressure curve for HFC-32 (dashed line) [11].

that of HFC-32, the intersection of the four-phase equilibrium P – T line fitted to the data of Imai et al. [12] and the saturated-vapor pressure line for HFC-32 is considered to represent the utmost P – T condition ($P \approx 1.78$ MPa and $T \approx 27^\circ\text{C}$) that the HFC-32 + cyclopentane + water working medium can attain in each cycle. Although this temperature, $\sim 27^\circ\text{C}$, is still a few degrees short of the heat-release temperature level that we expect, we selected the HFC-32 + cyclopentane pair for use in our analysis and simulation of the refrigeration system, taking the availability of the relevant phase-equilibrium P – T data [12] into account.

2.2.2. Heat of hydrate formation and dissociation

The heat of hydrate formation available with the HFC-32 + cyclopentane guest pair is estimated to be 135 kJ per mole of HFC-32, based on the Clausius–Clapeyron equation applied to the phase-equilibrium P – T data obtained by Imai et al. [12]. The crystallographic structure and the hydration number of the HFC-32 + cyclopentane hydrate are indicated in Table 2.

2.2.3. Power of multiphase compressor

Because the changes in kinetic and potential energies of the gas (HFC-32) through its compression process are generally insignificant, the work input to an adiabatic compressor should practically be equal to the increase in enthalpy of the gas flowing through the compressor. Therefore, the power \dot{W}_g that the compressor should exert on the gas flow to increase its pressure from P_1 to P_2 may be written as follows (Fig. 3):

$$\begin{aligned} \dot{W}_g &= \frac{1}{\eta_1} \frac{1}{\eta_M} \dot{m}_g [h_g(T'_2, P_2) - h_g(T_1, P_1)] \\ &= \frac{1}{\eta_1} \frac{1}{\eta_M} \frac{1}{\eta_c} \dot{m}_g [h_g(T''_2, P_2) - h_g(T_1, P_1)], \end{aligned} \quad (1)$$

where the subscripts 1 and 2 stand for the inlet and the outlet, respectively, of the compressor, \dot{m}_g is the mass flow rate of the gas, h_g is the specific enthalpy of the gas, T' is the temperature of the gas in the actual compression process, T'' is the temperature that the gas would have in the

Table 2

Specification of operational conditions and design variables for the hypothetical refrigeration system

Hydrate crystal structure	II
Hydration number (water-to-HFC-32)	8.5
Hydration number (water-to-cyclopentane)	17
Heat of hydrate formation/dissociation	135 kJ/mol HFC-32 2.59 MJ/kg HFC-32
Flow rate of HFC-32	100 kg/h
Flow rate of water (as measured in multiphase compressor)	557 kg/h
Pressure ratio	57.2
Multiphase compressor assembly	
Adiabatic efficiency	75% ^a
Motor efficiency	94%
Inverter efficiency	96%
Efficiency for pumping liquids	85%
Hydrate-forming reactor	
Pressure and equilibrium temperature	1.67 MPa, 27.0 °C
Mean temperature of working medium	25.5 °C
Inlet and outlet temperatures of cooling water	22.5 °C, 25.0 °C
Mass fraction of hydrate in slurry at outlet of hydrate-forming reactor	0.05
in slurry pump (after dewatering)	0.6
Power of slurry pump	0.4 kW
Hydrate-dissociating reactor	
Pressure and equilibrium temperature	0.03 MPa, 7.5 °C
Mean temperature of working medium	7.5 °C
Inlet and outlet temperature of water to be cooled	14.0 °C, 9.0 °C
Water pump efficiency	85%
Heat exchanger effectiveness	75%

^a See Appendix 1.

corresponding isentropic compression process, and η_I , η_M and η_c are the inverter efficiency, the motor efficiency, and the adiabatic efficiency, respectively. In the refrigeration cycle of our interest, the pressure ratio $\gamma (=P_2/P_1)$ is rather large (≈ 57.2), and hence the temperature of the gas would be significantly increased during its compression if there were no gas-cooling effect. However, the increase in gas temperature should be subdued as the result of gas cooling by the co-flowing liquids (water and cyclopentane). Note that the turbulent multiphase mixing inside the compressor should promote the approach of the gas to thermal equilibrium with the co-flowing liquids and that the water flowing through the compressor has a much larger heat capacity than the gas. Consult Appendix 1 for some specific technologies that we can utilize to realize the multiphase compression process described above.

To enable the calculation of \dot{W}_g for the compression process with variable h and T as well as with the gas-cooling effect mentioned above, we assume the entire compression process to be a series of a large number ($n = 300$) of small increments in pressure and rewrite Eq. (1) as follows:

$$\dot{W}_g = \frac{1}{\eta_I} \frac{1}{\eta_M} \frac{1}{\eta_c} \dot{m}_g \times \sum_{i=1}^n \left[h_g(T''_{(i+1)}, P_{(i+1)}) - h_g(T_{(i)}, P_{(i)}) \right], \quad (2)$$

where the parenthesized subscript i ($= 1, 2, \dots, n$) stands for the i th pressure increment. $T_{(i)}$ in Eq. (2) is the temperature that the gas phase adiabatically compressed in the preceding

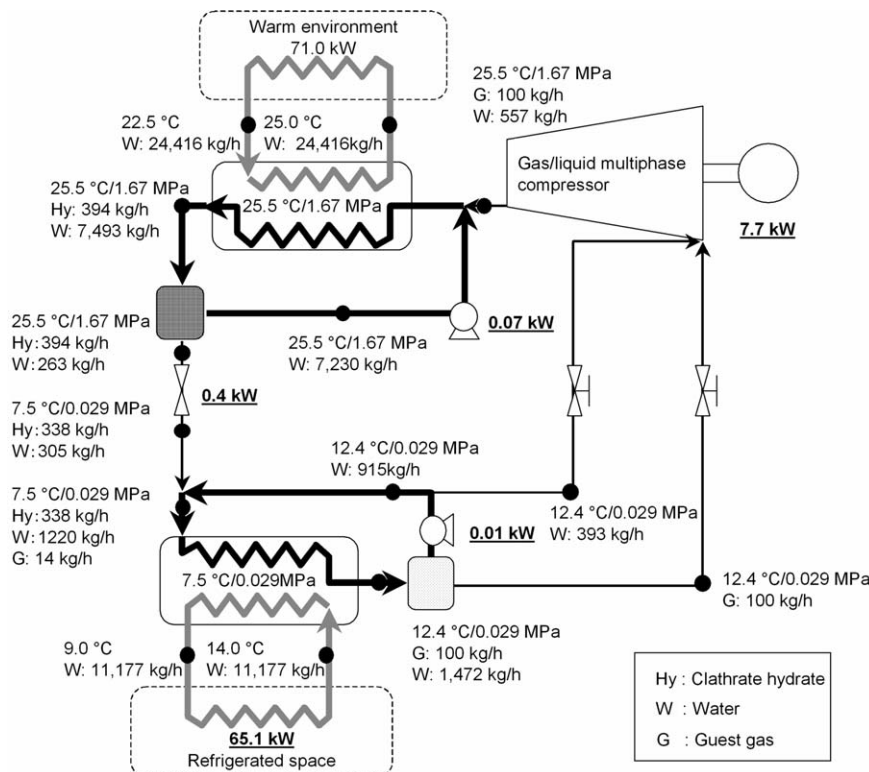


Fig. 3. Simulation of refrigeration system operated under the conditions specified in Table 2.

$(i - 1)$ th pressure increment would have if it were thermally equilibrated with the surrounding liquids (water and cyclopentane). That is, $T_{(i)}$ is determined to be the temperature that satisfies the following energy conservation equation:

$$\begin{aligned} & \dot{m}_g h_g(T_{(i-1)}, P_{(i-1)}) \\ & + \frac{1}{\eta_c} \dot{m}_g [h_g(T''_{(i)}, P_{(i)}) - h_g(T_{(i-1)}, P_{(i-1)})] \\ & + \dot{m}_w h_w(T_{(i-1)}, P_{(i-1)}) + \dot{m}_{gl} h_{gl}(T_{(i-1)}, P_{(i-1)}) \\ & = \dot{m}_g h_g(T_{(i)}, P_{(i)}) + \dot{m}_w h_w(T_{(i)}, P_{(i)}) \\ & + \dot{m}_{gl} h_{gl}(T_{(i)}, P_{(i)}), \end{aligned} \quad (3)$$

where \dot{m}_w and \dot{m}_{gl} are the mass flow rates of water and the guest liquid (cyclopentane), respectively, and h_w and h_{gl} are the specific enthalpies of water and the guest liquid, respectively. Because the vapor pressures of water and cyclopentane are sufficiently low in the temperature range relevant to the present compression process, we neglect the cooling effect due to the evaporation of water and cyclopentane into the gas phase.

In addition to the work of gas compression, the compressor simultaneously exerts work on the water and cyclopentane co-flowing with the gas. Consequently, the total power of the compressor, \dot{W}_t , is given by summing the three powers each relevant to the work of compression of one of the three fluids (HFC-32, water and cyclopentane):

$$\dot{W}_t = \dot{W}_g + \dot{W}_w + \dot{W}_{gl}, \quad (4)$$

where \dot{W}_w and \dot{W}_{gl} are the powers for pressurizing water and the guest liquid, respectively, from the inlet pressure P_1 to the outlet pressure P_2 . Assuming that both liquids are incompressible and that the changes in the potential and kinetic energies of these liquids are negligible, the sum of \dot{W}_w and \dot{W}_{gl} is calculated as

$$\dot{W}_w + \dot{W}_{gl} = \frac{1}{\eta_p} \left(\frac{\dot{m}_w}{\rho_w} + \frac{\dot{m}_{gl}}{\rho_{gl}} \right) (P_2 - P_1), \quad (5)$$

where ρ_w and ρ_{gl} are the densities of water and the guest liquid (cyclopentane), respectively and η_p is the efficiency of the multiphase compressor for pumping the liquids.

The flow rates of HFC-32, cyclopentane and water are operational parameters that we can specify rather arbitrarily. For simplicity, we adjust the flow rates of HFC-32, cyclopentane and water to be proportional to the stoichiometric HFC-32:cyclopentane:water ratio for the HFC-32 + cyclopentane hydrate – 2:1:17 (molar basis). We specify the mass flow rate of HFC-32, \dot{m}_g , to be 100 kg/h and the hydrate mass fraction in the slurry flowing through the slurry pump to be 0.6. Accordingly, the mass flow rates of cyclopentane and water, \dot{m}_{gl} and \dot{m}_w , are determined to be 67 kg/h and 557 kg/h, respectively. The specific heat capacities of cyclopentane and water are evaluated to be 1.818 kJ/(kg K) and 4.174 kJ/(kg K), respectively, according to the reference data for the STP condition (25 °C and 101.3 kPa) [11,13]. It turns out, based on the

flow rate ratio and the property evaluations specified above, that the heat-capacity flow rate of cyclopentane is no more than about 5.5% of that of water. Thus, every term of $\dot{m}_{gl} h_{gl}$ in Eq. (3) is neglected in calculating \dot{W}_g in the present simulation.

The thermal properties (entropy, enthalpy, and mass density) of HFC-32 and water in the compression process were evaluated using NIST REFPROP Version 7.0 [11].

2.2.4. Power of pumps

The powers of the liquid pumps in the water-recirculation loops each attached to the hydrate-forming or hydrate-dissociating reactor are calculated analogously to the calculations of \dot{W}_w and \dot{W}_{gl} by Eq. (5).

The mass flow rate of the hydrate slurry issuing from the water separator is given by $\dot{m}_g + \dot{m}_{gl} + \dot{m}_w$, which is deduced to be 724 kg/h. The density of the hydrate slurry is presumed to be ~ 1000 – 1100 kg/m³. Considering such slurry flow conditions, we envision using a “progressing cavity” pump with a rotor/stator mechanism (such as a NEMO[®] pump model NE manufactured by Heishin, Ltd., Kobe, Japan; 0.12–1.40 m³/h volume flow rate) as the slurry pump for conveying the hydrate slurry to the hydrate-dissociating reactor. The power of this pump is assumed to be 0.4 kW, according to pump supplier’s catalogue data. As noted in Section 2.1, this power is used not to pressurize the slurry against the hydraulic friction generated by the slurry flow, but to control its flow rate under the excessively high pressure driving force, $P_2 - P_1$, exerted on the slurry filling the pipe between the separator and the hydrate-dissociating reactor. The hydraulic aspect of this slurry flow is briefly discussed in Appendix 2.

2.2.5. Heat capacity of hydrate

Because of the lack of any experimental data for the specific heat capacity of HFC-32 + cyclopentane hydrate, we estimate it by simply extrapolating the data for tetrahydrofuran hydrate obtained in a lower temperature range (85–270 K) [14] to the higher temperature range of present interest (278–300 K).

2.2.6. Other parameters

Many operational parameters other than those mentioned above are specified for use in the present simulation. These miscellaneous parameters are summarized in Table 2.

The pressure in the hydrate-forming reactor is assumed to be adjusted to 1.67 MPa such that the corresponding four-phase equilibrium temperature is 27.0 °C. The heat generated by hydrate formation in the reactor is to be removed by groundwater supplied to a heat exchanger integrated with the reactor. The temperatures of the groundwater at the inlet and outlet of the heat exchanger are assumed to be 22.5 °C and 25.0 °C, respectively. The working medium (HFC-32 + cyclopentane + water mixture) flows into the reactor at a temperature of 25.5 °C, which is 1.5 K below the phase-equilibrium temperature corresponding to the pressure inside the reactor, and flows out

at the same temperature, 25.5 °C, but in the form of a hydrate slurry. The pressure in the hydrate-dissociating reactor is assumed to be set at 0.03 MPa to control the corresponding phase-equilibrium temperature at 7.5 °C. It is assumed that a small proportion of the hydrate in the working medium has been dissociated before flowing into the hydrate-dissociating reactor, and hence the medium is already cooled to the equilibrium temperature, 7.5 °C, at the inlet of the reactor. The temperatures of the secondary refrigerant (water) at the inlet and outlet of the heat exchanger integrated with the hydrate-dissociating reactor are assumed to be 14.0 °C and 9.0 °C, respectively, to be suitable for air-conditioning use of the refrigerant.

2.3. Results and discussion

2.3.1. Results of simulation

The results of the simulation outlined above are summarized in Fig. 3 in terms of the power inputs required for the operation of the system and the cool-energy output. The power inputs are evaluated to be 7.7 kW by the multiphase compressor, 0.4 kW by the slurry pump, and 0.1 kW by the two liquid pumps. The COP defined as the ratio of the cool-energy output (65.1 kW) to the sum of the power inputs is determined to be 8.0. The COP thus evaluated in the present simulation is considerably higher than those of the current commercial refrigeration systems for air conditioning. This is the major advantage of the hydrate-based refrigeration system over the conventional systems. The drawback of the former system may be its cooler-side temperature level (9.0 °C in the secondary refrigerant issuing out of the system) being slightly higher than that available with the conventional systems. It may be possible, however, to reduce, or even eliminate, this drawback by selecting some guest-substance pair other than the HFC-32 + cyclopentane pair assumed in our present simulation.

2.3.2. Improvement of efficiency through hydrate-slurry dewatering

The effect of dewatering of the hydrate slurry flowing into the dissociating reactor on the overall COP is indicated in Fig. 4. This figure indicates that the dewatering has a significant effect on the COP. In order to secure a COP value above 8, the slurry flowing through the slurry pump must be concentrated to increase its hydrate content to 60% (mass basis) or higher.

2.3.3. Effect of pressure ratio

The COP is also dependent on the pressure ratio γ ($=P_2/P_1$). Fig. 5 demonstrates the COP vs. γ relation for a fixed level of P_1 ($=0.029$ MPa) and that for a fixed level of P_2 ($=1.214$ MPa). An increase in γ by 16 from 42 ($=1.214$ MPa/0.029 MPa) under constant P_1 ($=0.029$ MPa) should yield an approximately 7.0% decrease in the COP, while an increase in γ by 16 from 42 under constant P_2 ($=1.214$ MPa) should yield an approximately 7.6% decrease in the COP.

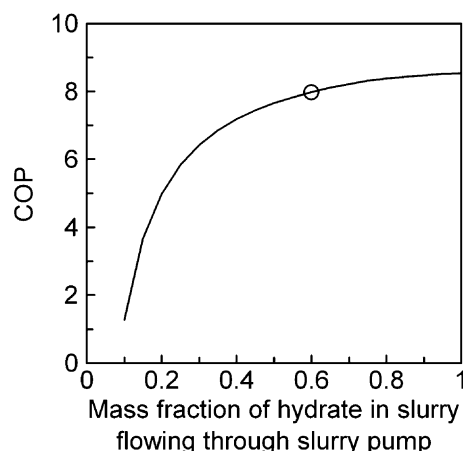


Fig. 4. Dependency of COP on the hydrate concentration in the hydrate slurry flowing into the hydrate-dissociating reactor.

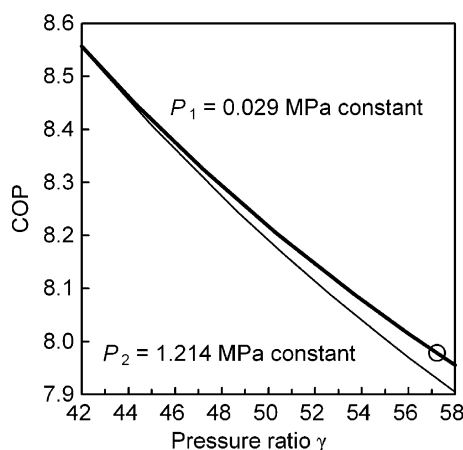


Fig. 5. Dependency of COP on the pressure ratio γ ($=P_2/P_1$). Either the compressor-inlet pressure P_1 or the outlet pressure P_2 is assumed to be held constant.

3. Laboratory-scale hydrate-based refrigeration system – its construction and test operations

3.1. System construction

To confirm the technical feasibility of the refrigeration system described above, a laboratory-scale hydrate-based refrigeration system has been constructed and used for test operations. Fig. 6 shows a schematic illustration of the system. It should be noted that this system is not a precise miniature of the hypothetical refrigeration system illustrated in Figs. 2 and 3 but a simplified experimental system for the hydrate-based refrigeration cycle that we contrived. For example, no water-recirculation loop is attached to the hydrate-dissociating reactor in this system. A conventional gas compressor and a plunger pump accompanied by a gas/water separator are substituted for the multiphase compressor. What we expected with this experimental system was to have actual experience in hydrate-based refrigeration operations and to examine if the system steadily works

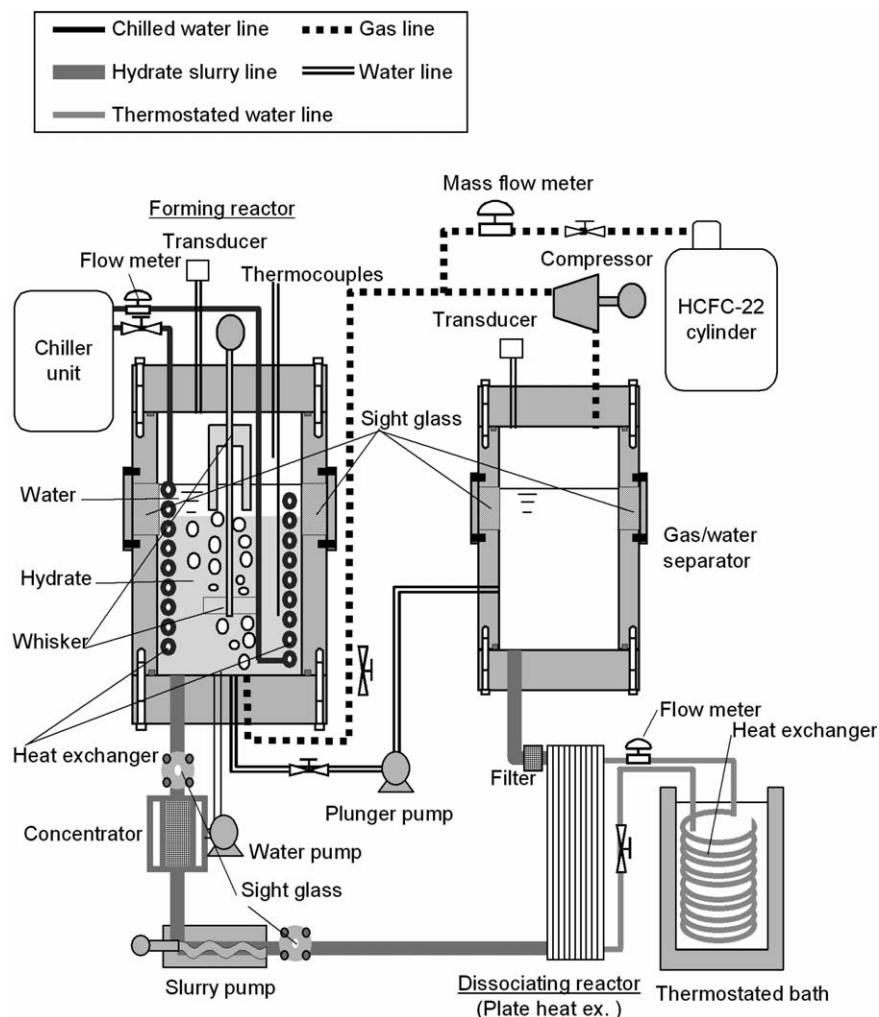


Fig. 6. Schematic of laboratory-scale hydrate-based refrigeration system.

without being hindered by, for example, hydrate plugging in some components of the system. Quantitative evaluation of the refrigeration performance is not within the scope of the tests with this system.

The hydrate-forming reactor is a cylindrical stainless-steel vessel 5 L in inside volume, which is equipped with a pair of sight glasses and a stirrer for maintaining sufficient mixing of the multiphase contents of the vessel. To simulate the heat discharge to the groundwater, cooling water is circulated through a coil-type heat exchanger installed inside the reactor and through an external chiller unit (Refrigerated Circulator model CA-1111, Tokyo Rikakikai Co., Ltd., Tokyo, Japan) with a 960-W cooling capacity. Resistance thermometers are used to measure the cooling-water temperatures at the inlet and outlet of the reactor. In order to separate excess water from the hydrate slurry formed in the reactor, a double-tube-type dewatering device with a built-in sintered metal filter of 120- μm pore size is installed next to the reactor. The water separated there is pumped back to the reactor. A slurry pump (NEMO[®] pump model 2NL-PU, Heishin, Ltd., Kobe, Japan; 5.1–58.4 L/h volume flow rate) is employed

for transporting the dewatered hydrate slurry to the hydrate-dissociating reactor. Two pairs of sight glasses are installed on the line connecting the two reactors for visual observation of the flowing slurry. A copper-brazed stainless-steel plate-type heat exchanger (model CB14, Alfa Laval Co., Ltd., Tokyo, Japan) is used as the hydrate-dissociating reactor. To simulate the cooling load, cooling water is circulated through the heat exchanger. As in the hydrate-forming reactor, resistance thermometers are installed to measure the cooling-water temperatures at the inlet and outlet of the heat exchanger. On the line back from the hydrate-dissociating reactor to the hydrate-forming reactor, a gas/liquid separator is installed. A sintered metal filter (120- μm pore size) is set between the hydrate-dissociating reactor and the gas/liquid separator to prevent possibly remaining hydrate crystals from being transported to the gas/liquid separator. The gas/liquid separator is a 5-L cylindrical stainless-steel vessel equipped with a pair of sight glasses. The water having flowed out of the separator is pressurized by a plunger pump (model SMC301-15V, Fuji Pump Co., Ltd., Mie, Japan) at a volume flow rate of ~ 0.5 L/min. The gas separated from the

water is compressed by a diaphragm compressor (model N2400, KNF Neuberger GmbH, Munzingen, France; 25 L/min volume flow rate). The water and the gas are then returned to the hydrate-forming reactor.

3.2. Procedure of operations

The hydrate-forming guest substance we used was not the HFC-32 + cyclopentane pair but a conventional refrigerant, HCFC-22 (chlorodifluoromethane, CHClF_2), which is known to form a structure-II hydrate at relatively low pressures. The working-medium loop including the two reactors, the slurry pump and the gas/liquid separator was charged with 4-L of water, and the remaining space of the loop was filled with gaseous HCFC-22. The temperature in the hydrate-forming reactor was set at 5 °C, and the pressure was set at 0.4 MPa by supplying HCFC-22 through a pressure-regulating valve from a high-pressure cylinder. After visually confirming the hydrate formation in the reactor, the slurry pump was turned on. At the same time, the two water pumps and the gas compressor were also turned on to start the circulation of the working medium. The pressures in the two reactors, the temperatures in the hydrate-forming reactor and the gas/liquid separator, and also the water temperatures at the inlet and outlet of each heat exchanger were measured and simultaneously recorded by a data logger (model NR-1000, Keyence Corp., Osaka, Japan) throughout each experimental operation.

3.3. Results of test operations

It was confirmed that the system could be operated almost steadily, maintaining continuous formation and dissociation of the hydrate. Fig. 7 shows typical snapshot pictures of the hydrate slurry observed at two locations – near the outlet of the hydrate-forming reactor (picture (a)) and at the exit of the slurry pump (picture (b)). At the latter

location, we observed considerable gas bubbling due to the hydrate dissociation. At times, the issuing of hydrate crystals from the hydrate-forming reactor was interrupted presumably due to the agglomeration of the hydrate crystals in the reactor. Nevertheless, any sign of blockage on the piping due to hydrate plugging was not detected throughout the test operations of the system.

Fig. 8 shows the chronological variations in \dot{Q}_{in} , the heat inflow into the hydrate-dissociating reactor, and \dot{Q}_{out} , the heat outflow from the hydrate-forming reactor. These heat flow data were deduced from the instantaneous cooling-water temperatures at the inlet and the outlet of the heat exchanger integrated with each reactor. These data indicate that the system was operated continuously over two hours. At present, we are engaged in optimization of the various components of the system and in detailed analyses of the system characteristics.

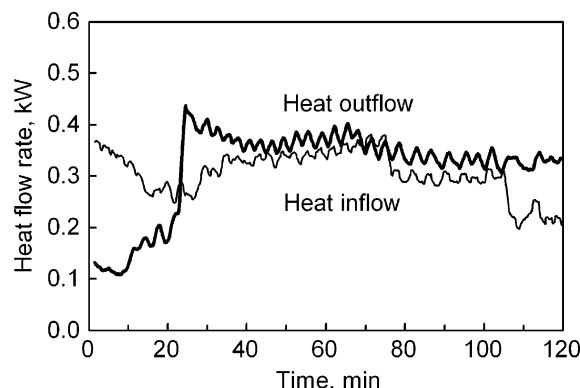


Fig. 8. Comparison between the heat inflow into the hydrate-dissociating reactor (i.e., the cool-energy output of the refrigeration system) and the heat outflow from the hydrate-forming reactor during one of the test operations. The time on the abscissa is the lapse after the slurry pump was turned on.

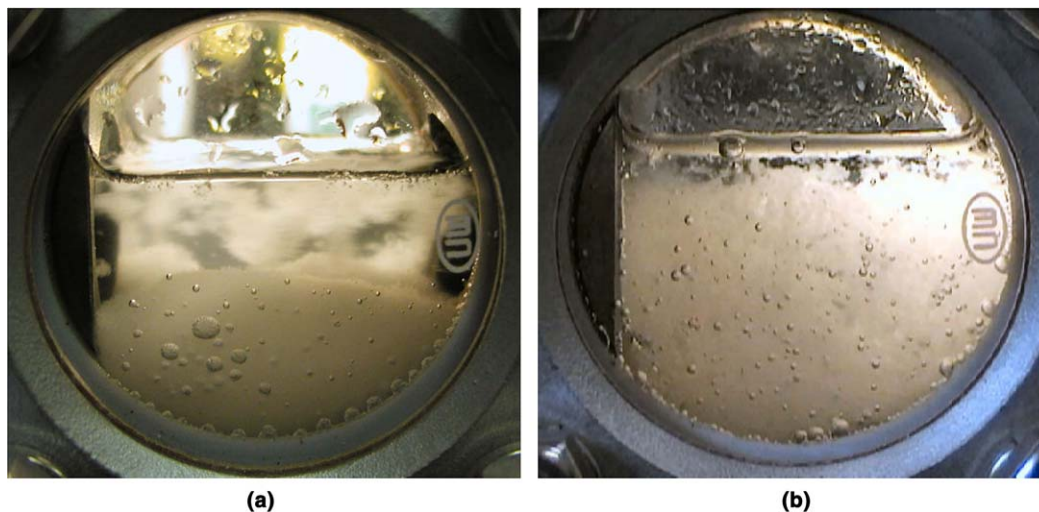


Fig. 7. Pictures of hydrate slurry observed (a) at a site close to the exit of the hydrate-forming reactor and (b) at another site near the exit of the slurry pump.

4. Requirements for hydrate-forming working media

The practical utility of the hydrate-based refrigeration system is crucially dependent on the selection of suitable hydrate-guest substances. Because the phase-equilibrium temperature (i.e., the critical temperature for the thermodynamic stability of the relevant hydrate) must substantially vary in response to a modest change in the system pressure in order to enable the system to work as a heat pump, the hydrate-guest substance, or one of the hydrate-guest substances for simultaneous use, must be in the gaseous state throughout the P – T region over which the system is to be operated. In addition to this basic requirement, we should note some specific requirements (or conditions) for the hydrate-guest substances to be combined with water to compose the working media for the refrigeration system. Such requirements are itemized below.

4.1. High maximum hydrate-formation temperature

As long as the hydrate-guest substance or one of the hydrate-guest substances in simultaneous use is in the gaseous state, the possible maximum of the hydrate-formation temperature is T_{Q2} , the temperature at the upper quadruple point for the $V + L_g + L_w + H$ four-phase equilibrium, where the L_g phase may be the condensate of the V -phase-forming guest gas (e.g., HFC-32) or a mixture of such a condensate and a less-volatile second guest substance (e.g., cyclopentane). In order to utilize an environmental fluid (the air, groundwater, river water or coastal water) as the heat reservoir to which the heat released by the hydrate formation is discharged, T_{Q2} is required to exceed the temperature of the fluid by several degrees. For possible use of the system in Japan (or other areas in the Temperate Zone or the subtropics) in the summer season, T_{Q2} should hopefully be as high as 37 °C. If a cooling tower is used to pre-cool the cooling water to be supplied to the hydrate-forming reactor up to a level close to the wet-bulb temperature of the atmosphere, the desired level of T_{Q2} may be reduced to ~32 °C. This temperature is still higher than the T_{Q2} value available with the HFC-32 + cyclopentane guest-substance pair conceived in Section 2. We are currently in search of other “guest-gas + guest-liquid” pairs possibly giving higher T_{Q2} values than the HFC-32 + cyclopentane pair. A few candidate pairs are on our waiting list for phase-equilibrium measurements, based on which we will be able to estimate the T_{Q2} values relevant to these pairs and to evaluate their suitability for the refrigeration system of the present interest.

4.2. Small temperature dependency of equilibrium pressure

As exemplified in the results of the simulation (Section 2.3.1), the major proportion of the total power input for the operation of the refrigeration system is due to the gas compression in the multiphase compressor. Obviously, the smaller the value of the pressure ratio γ , the lower is

the compression power \dot{W}_g . The adiabatic compression efficiency η_c decreases with an increase in γ . To ensure a sufficient temperature difference between the two reactors under the condition of a minimum value of γ , a small temperature dependency of the equilibrium pressure is required for the hydrate-forming guests for use in the refrigeration systems.

4.3. Large heat of hydrate formation/dissociation per mole of guest gas

Most of the compressor power is expended on compression of the guest gas. In the simulation given in Section 2, the power required for the HFC-32 gas compression, \dot{W}_g , occupies about 94% of the total compressor power ($\dot{W}_g + \dot{W}_w + \dot{W}_{gl}$). Thus, a hydrate, which has a larger heat of formation/dissociation per mole of the guest gas, is favorable for the refrigeration system to yield a larger cool-energy output per unit of compressor power. In other words, a hydrate with a larger hydration number is favorable. Unfortunately, such a hydrate should generally show a stronger temperature dependency of the equilibrium pressure, which is unfavorable as discussed in Section 4.2. (Note that, according to the Clausius–Clapeyron equation, the heat of hydrate-formation/dissociation per mole of the guest gas is proportional to dP/dT along the phase-equilibrium line.) The above antinomy leads to a consequence which may be compatible with our conventional thermodynamics-based notion about heat pumps: for a given power input, the requirement for increasing the cool-energy output conflicts with the requirement for increasing the temperature difference over which the energy is to be pumped up. A good compromise between these opposing requirements is expected in searching for the candidate hydrate-guest substances for the refrigeration system.

4.4. Safety and environmental concerns

In addition to the requirements for thermodynamic properties of hydrate-forming systems discussed above, we should be careful of the safety and environmental concerns in searching for the guest substances. To ensure sufficient acceptability of hydrate-based refrigeration systems as alternatives to conventional refrigeration systems, the guest substances for use in the former systems are required to be nontoxic, nonflammable or only slightly flammable, non-explosive, noncorrosive, environment-friendly, and inexpensive. Extensive research on guest substances (including pairs and mixtures of pure compounds) possibly meeting the above requirements is needed. Some effort has already been devoted to this task [12], and further studies on this line are now underway in our group.

5. Concluding remarks

This study is the first attempt to develop a novel refrigeration system which utilizes a hydrate-forming substance

(or substances) mixed with water as the working medium. We have performed thermodynamic analysis and simulation of a steady operation of a refrigeration system for the case where HFC-32 and cyclopentane are simultaneously used as the hydrate-guest substances, thereby forming an HFC-32 + cyclopentane + water multiphase mixture as the working medium. The simulation reveals that, if the hydrate-formation temperature (the temperature at which heat is discharged out of the system) and the hydrate-dissociating temperature (the temperature at which cool energy is supplied from the system) are adjusted to 25.5 °C and 7.5 °C, respectively, the COP of the system should be as high as 8.0. This fact indicates that the hydrate-based refrigeration system can surpass conventional refrigeration systems in thermodynamic efficiency.

In addition to such thermodynamic examinations, we constructed a laboratory-scale refrigeration system and performed experimental operations using HCFC-22 as the hydrate-guest substance. These operations demonstrated that the above system could function steadily with no sign of internal blocking by the formed hydrate.

The performance of the hydrate-based refrigeration can certainly be improved further by selecting more suitable hydrate-guest substances, improving the hardware design (i.e., the design of the hydrate-forming/hydrate-dissociating reactors, the multiphase compressor, etc.), and optimizing the system-operation conditions (such as those relevant to the slurry-concentration control).

Appendix 1. Technologies available for multiphase compression

Multiphase compressors, such as the one that we expect to use in compressing the HFC-32 gas, together with the two liquids, water and cyclopentane, are not yet widely used in various industries. Nevertheless, the technology of multiphase compression has already been well developed such that some types of gas + water compressors are now commercially available. For example, Innogy plc (Swindon, Wiltshire, UK) has developed a reciprocating quasi-isothermal compressor in which the air is cooled by a water spray [15]. The pressure ratio available with this prototype compressor is reported to be 25. Water-injected oil-free screw compressors are available from several manufacturers; for example, GP-series compressors manufactured by the Ishikawajima-Harima Heavy Industries Co. [16] are included in this category. These compressors originally designed for compressing air together with water may be applicable, possibly with minor modifications, for compressing HFC-32 together with water and cyclopentane. It should be noted, however, that none of these compressors produce a pressure ratio as high as $\gamma \approx 57.2$. At present, the most practical way to obtain a pressure ratio as high as 50 or above seems to be multiplying the compression process such that a few multiphase compressors are connected in series.

No experimental data are available on the adiabatic efficiency η_c of such multiphase compressors as those mentioned above. Nevertheless, η_c of the Innogy prototype compressor was predicted to be 78–90% using CFD simulations [15]. Based on these values, we conservatively estimated η_c to be 75% in the simulation described in Section 2 of this paper.

Appendix 2. The mechanics of hydrate-slurry flow

The hydrate slurry concentrated at the water separator, such that its hydrate content increased to 60% (mass basis), is conveyed to the hydrate-dissociating reactor (see Section 2.3.2). The hydraulic (or rheological) aspect of this slurry flow is briefly discussed here in order to validate our mechanistic understanding of the slurry conveying described in Section 2.2.4. We assume that the water separator and the hydrate-dissociating reactor are connected by a 32A steel pipe (inside diameter, $D = 39.4$ mm) and a progressing-cavity-type slurry pump. The mass flow rate of the slurry is 724 kg/h. Because the mass density of the hydrate is close to that of liquid water, we can safely assume that the volume fraction of the hydrate in the slurry, ϕ , is 0.6 and that the volume flow rate of the slurry is 724 L/h. Accordingly, the average axial velocity of the slurry, \bar{U} , turns out to be 0.165 m/s.

Recently, Darbouret et al. [6] reported their experimental study of the flow of TBAB-hydrate slurries through a circular pipe. They showed that the flow of the hydrate slurries in the laminar regime follows the Bingham model and presented the experimental data on the yield stress τ_0 and the apparent viscosity μ_0 . They also showed that the μ_0 vs. ϕ relations for the hydrate slurries are well represented by the suspension model developed by Graham et al. [17], which is written as follows:

$$\mu_0 = \mu_w(1 - s\phi)^{-2.5}, \quad (\text{A1})$$

where μ_w is the viscosity of the suspending liquid (i.e., water in the present case) and

$$s = 1 + 0.35 \left[1 - \left(1 - \frac{\phi}{0.7404} \right)^2 \right]^{1/2}. \quad (\text{A2})$$

The studies of Darbouret et al. [6] and Graham et al. [17] provide a good basis for our consideration of the hydrate slurry flow.

The friction factor for a Bingham slurry may be expressed in the following form [6]:

$$\lambda \equiv \frac{\Delta P}{(D/L)(\rho \bar{U}^2/2)} = \frac{64}{Re} \left(1 + \frac{Bm}{6} \right), \quad (\text{A3})$$

where L is the axial length of the pipe through which the slurry flows, ΔP is the pressure drop that the slurry experiences during its flow over the distance L , \bar{U} is the average axial velocity of the slurry, Re is the Reynolds number defined as $\rho \bar{U} D / \mu_0$, and Bm is the Bingham number defined as $\tau_0 D / \mu_0 \bar{U}$. Eq. (A3) is then rearranged as

$$\frac{\Delta P}{L} = \frac{16}{D} \left[2\mu_0 \left(\frac{\bar{U}}{D} \right) + \frac{1}{3} \tau_0 \right]. \quad (\text{A4})$$

Thus, we can calculate the pressure drop per unit axial length of the hydrate-slurry conveying pipe by substituting the relevant values of D ($=39.4$ mm), \bar{U} ($=0.165$ m/s), τ_0 and μ_0 into Eq. (A4). We estimate τ_0 at $\phi = 0.6$ to be 6.79 Pa, by extrapolating the τ_0 vs. ϕ plot in Fig. 8 in the paper of Darbouret et al. [6]. μ_0 is deduced to be 0.0849 Pa s from Eqs. (A1) and (A2). Consequently, we can estimate that $\Delta P/L = 1.21$ kPa/m. Because the axial length of the slurry conveying 32A pipe connecting the separator and the hydrate-dissociating reactor is possibly less than 0.5 m, the pressure drop due to the friction inside the pipe must be negligibly small compared to the pressure difference between the two reactors, $P_2 - P_1 = 1.64$ MPa. This consequence supports our idea of using a progressing-cavity-type slurry pump for the purpose of controlling the slurry flow rate, instead of pressurizing the slurry to make it flow against the hydraulic friction.

References

- [1] J.J. Tomlinson, Clathrates – A storage alternative to ice for residential cooling, in: Proceedings of the 1983 EPRI Workshop on Hot and Cold Thermal Energy Storage Technology, Palo Alto, CA, USA, January 19, 1983, Paper No. 36.
- [2] M.P. Ternes, Characterization of refrigerant-12 gas hydrate formation for heat pump cool storage applications, ASME Publication 84-AES-12, 1984.
- [3] W.J. Scaetzle, M.A. Gadalla, M. Najafi, Experimental results of cooling cycles with clathrate energy storage, in: Proceedings of the 22nd Intersociety Energy Conversion Engineering Conference, Philadelphia, PA, USA, August 10–14, 1987, pp. 1317–1323.
- [4] T. Akiya, M. Owa, M. Nakaiwa, T. Tanii, K. Nakazawa, Y. Ando, Novel cool storage system using HCFC-141b gas clathrate, in: Proceedings of the 26th Intersociety Energy Conversion Engineering Conference, vol. 6, Boston, MA, USA, August 4–9, 1991, pp. 115–119.
- [5] I. Tanasawa, S. Takao, Clathrate hydrate slurry of tetra-*n*-butylammonium bromide as a cold-storage material, in: Proceedings of the Fourth International Conference on Gas Hydrates, Yokohama, Japan, May 19–23, 2002, pp. 963–967.
- [6] M. Darbouret, M. Cournil, J.-M. Herri, Rheological study of TBAB hydrate slurries as secondary two-phase refrigerants, *Int. J. Refrig.* 28 (2005) 663–671.
- [7] Y.P. Handa, Compositions, enthalpies of dissociation, and heat capacities in the range 85 to 270 K for clathrate hydrates of methane, ethane, and propane, and enthalpy of dissociation of isobutene hydrate, as determined by a heat-flow calorimeter, *J. Chem. Thermodyn.* 18 (1986) 915–921.
- [8] V.K. Verma, Gas hydrates from liquid hydrocarbon–water systems, Ph.D. Thesis, University of Michigan, Ann Arbor, MI, University Microfilms No. 75-10, 1974.
- [9] T. Akiya, T. Shimazaki, M. Oowa, M. Matsuo, Y. Yoshida, Formation conditions of clathrate between HFC alternative refrigerants and water, *Int. J. Thermophys.* 20 (1999) 1753–1763.
- [10] D. Liang, K. Guo, R. Wang, S. Fan, Hydrate equilibrium data of 1,1,1,2-tetrafluoroethane (HFC-134a), 1,1-dichloro-1-fluoroethane (HCFC-141b) and 1,1-difluoroethane (HFC-152a), *Fluid Phase Equilib.* 187–188 (2001) 61–70.
- [11] E.W. Lemmon, M.O. McLinden, M.L. Huber, NIST Reference Fluid Thermodynamic and Transport Properties Database (REFPROP), Ver. 7.0, US Department of Commerce, 2002.
- [12] S. Imai, K. Okutani, R. Ohmura, Y.H. Mori, Phase equilibrium for clathrate hydrates formed with difluoromethane + either cyclopentane or tetra-*n*-butyl ammonium bromide, *J. Chem. Eng. Data* 50 (2005) 1783–1796.
- [13] JSME Data Book: Thermophysical Properties of Fluids, Japan Society of Mechanical Engineers, Tokyo, Japan, 1983.
- [14] Y.P. Handa, R. Hawkins, J. Murray, Calibration and testing of a Tian–Calvet heat-flow calorimeter: Enthalpies of fusion and heat capacities for ice and tetrahydrofuran hydrate in the range 85 to 270 K, *J. Chem. Thermodyn.* 16 (1984) 623–632.
- [15] H. Abdallah, M. Coney, P. Stephenson, Application of liquid sprays to achieve isothermal compression, part 2, in: Proceedings of the 17th Annual Meeting of the Institute of Liquid Atomisation and Spray Systems (2001 ILASS-Europe), Zurich, Switzerland, September 2–6, 2001.
- [16] N. Suzuki, K. Hasegawa, H. Tabata, I. Okumura, Development of oil free screw compressor GP series, *Ishikawajima-Harima Eng. Rev.* 42 (2002) 56–59 (in Japanese).
- [17] A.L. Graham, R.D. Steele, R.B. Bird, Particle clusters in concentrated suspensions. 3. Prediction of suspension viscosity, *Ind. Eng. Chem. Fundam.* 23 (1984) 420–425.