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Air-Conditioning System Using Clathrate Hydrate Slurry†

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Abstract:

JFE Engineering has developed clathrate hydrate slurry (CHS) for use in next-generation energy-saving air-conditioning systems. Clathrate hydrate slurry is suitable for cooling applications as it possesses latent heat in the range of 5–12°C, has a cooling storage capacity 2–3 times as large as that of the conventional chilled water, and displays excellent pumpability. Because CHS is a cooling medium with high thermal density, air-conditioning systems using CHS are expected to substantially reduce cooling medium transportation costs and make an important contribution to energy savings, with attendant benefits in reducing CO_2 emissions. This paper describes the properties of CHS and the results of a trial calculation of the energy-saving effect of an office building air-conditioning system using CHS.

1. Introduction

Energy consumption for air-conditioning in general private and public sectors has increased year by year. Thus, from the viewpoints of both energy conservation and reduced CO_2 emissions, further energy-saving measures are necessary. Moreover, because heating/cooling loads are concentrated in the daytime hours, technical development to enable load leveling in electric power consumption is also desirable.

In response to these needs, regenerative air-conditioning systems using water or ice as a cooling storage medium have been widely adopted. With cooling storage using chilled water, the refrigerator can be operated at a high coefficient of performance (COP), but using a storage tank of the same capacity, the amount of cooling storage is smaller than with ice. On the other hand, with ice, power consumption is high due to the low COP of the refrigerator.

In the temperature range used in air-conditioning (approx. 5–12°C), a substantial energy-saving effect can be expected in air-conditioning systems if the cooling medium has a high thermal density (high unit cooling storage capacity) and is suitable for both cooling storage and pumping.

The cooling medium developed in this work is a fluid of a mixed solid-liquid phase type, consisting of fine particles and an aqueous solution of clathrate hydrate slurry (CHS). This new cooling storage medium is well-suited to air-conditioning, as it has a high thermal density in the temperature range of 5–12°C and excellent properties for pumping and transportation.

This paper describes the features of CHS and the results of a trial calculation for an air-conditioning system using this new cooling medium.[1–3)]

2. Features and Properties of Clathrate Hydrate Slurry

Although gaseous clathrate hydrates use gases such as flon or methane as the guest molecule, the hydrate in CHS is a kind of liquid clathrate hydrate with tetra-n-butylammonium bromide (TBAB) as the guest molecule. When an aqueous solution of TBAB which has been dissolved in water is cooled while flowing, hydrate particles of 10–100 μm in size form in the solution, producing a fluid hydrate slurry, as shown in **Photo 1**.

Tetra-n-butylammonium bromide is a registered chemical under the Law for Regulation of Examination and Manufacture, Etc. of Chemical Substances (Chemical Examination Law), and therefore does not come under the provisions of the Safety and Hygiene Law, Poison Control Law, or Fire Services Act. **Table 1** shows the results of acute toxicity test. This hydrate has excellent long-term stability and does not show changes in thermal properties after repeated use.

The concept of application of CHS to air-conditioning systems for office buildings is shown in

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Photo 1 CHS (clathrate hydrate slurry)

Table 1 Results of acute toxicity test

LD_{50} (Rat, Oral)	Male : 1 414 mg/kg Female : 1 542 mg/kg
LC_{50} (Cyprinodont, 96 hrs)	3 340 mg/*l*

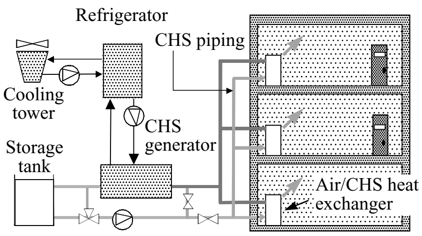

Fig. 1 Air-conditioning system using CHS

Fig. 1. The cooling source section of this CHS air-conditioning system includes a heat exchanger for CHS production and CHS storage tank, which are required in addition to the conventional system equipment. In the secondary side equipment, which is located indoors, the medium for transporting chilled water is replaced with CHS. It is possible to use piping, pumps, and heat exchanger equipments with the same specifications as in the conventional chilled water systems.

The features and effects of the CHS air-conditioning system are as follows:

(1) Maximum 80% reduction in pumping power consumption is possible.

CHS has a high thermal density of 10–17 Mcal/m^3, or 2–3 times that of chilled water, making it possible to reduce the flow rate by one-half in comparison with chilled water. As a result, power consumption for pumping the cooling medium can be substantially reduced.

(2) 40% of energy is saved in comparison with ice production.

The forming temperature of CHS is in the same range as that of chilled water (5–12°C), making it possible to operate the refrigerator with higher efficiency than in ice production.

(3) Direct transportation to indoor air-conditioners is possible.

Because CHS is non-cohesive, there is no danger of blockage in piping or indoor air-conditioners, enabling direct transportation of CHS in the same manner as chilled water.

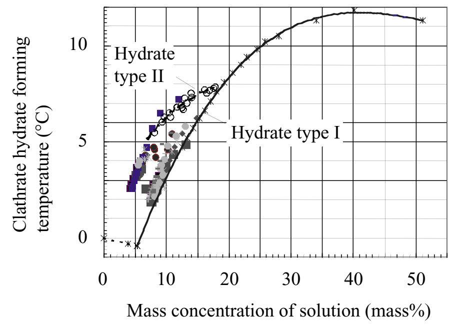

Fig. 2 Formation of TBAB hydrate

The following sections describe the forming, transportation, and heat transfer properties of CHS.

2.1 Forming Properties of TBAB Hydrate

Figure 2 shows the relationship between the forming temperature of TBAB hydrate and the concentration of the aqueous solution.

When the ratio of TBAB in the hydrate relative hydrates as a whole is the same as the concentration of the aqueous solution, the concentration of the aqueous solution becomes constant when the solution is cooled, even if the hydrate content of the CHS increases. In experiments, when the concentration of the aqueous solution was 40.5 mass%, the concentration became constant at about 11.8°C. From this, the hydration number was estimated at approximately 26. This hydrate is called “Type I hydrate.”

When an aqueous solution with the concentration of less than 40.5 mass% is cooled, the concentration of the solution in the slurry decreases as the hydrate content of the CHS increases. This means that the hydrate forming temperature decreases along the hydrate forming line. From experiments to date, when the temperature of CHS is approximately 8°C or lower, the hydrate shifts to one with a hydration number of approximately 36, referred to as “Type II hydrate” in the following: Figure 2 shows 2 hydrate forming lines at 8°C and under. However, in spite of the fact that Type I hydrate is formed temporarily in the cooling process, because Type II hydrate is stable, the final product is Type II hydrate.

2.2 Properties of TBAB Hydrate and Clathrate Hydrate Slurry

Table 2 shows the measured values of density, specific heat, and latent heat of the Type I and Type II hydrates.

Figure 3 shows the results of an investigation of the relationship between solution temperature and density of solutions of different densities.[4] With the respective solution densities, the solutions whose temperature is lower than the hydrate forming temperature are in a

Table 2 Thermophysical properties of TBAB hydrate

Thermophysical property		TBAB hydrate	
		Type I	Type II
Density	(kg/m³)	1.08×10^3	1.03×10^3
Specific heat	(kJ/kgK)	2.22	–
Latent heat	(kJ/kg)	193	205

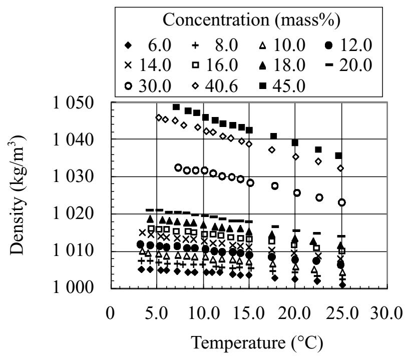

Fig. 3 Density vs. temperature of aqueous solution

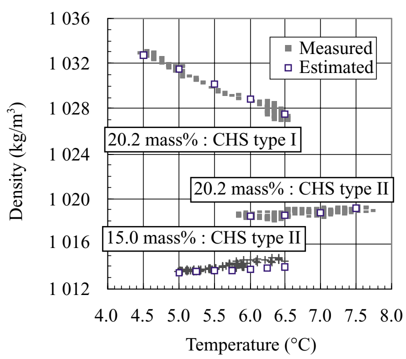

Fig. 4 Density vs. temperature of clathrate hydrate slurry

supercooled condition.

The relationship between temperature and density for CHS Type I and Type II was obtained using thermocouples and a vibrating type densitometer as shown in **Fig. 4**. The values measured with the vibrating-type densitometer show the relationship between the temperature and density for the CHS formed from 20.2 mass% and 15.0 mass% aqueous solutions.

Because the 20.2 mass% aqueous solution formed CHS Type I at approximately 8.1°C, it may be noted that the density of Type I in Fig. 4 shows measured results with a supercooling degree in the range of 1.5°C to 3.5°C.

Although CHS Type I has a high density in comparison with an aqueous solution of the same concentration, Type II shows virtually the same density as the aqueous solution.

The thermal density (specific enthalpy) and solid fraction (ratio of hydrate particles in CHS) of CHS can be obtained from the hydrate forming line and latent heat and specific heat of the hydrates and specific heat of the aqueous solution.[5] **Figure 5** shows the relationship between temperature and specific enthalpy for CHS at

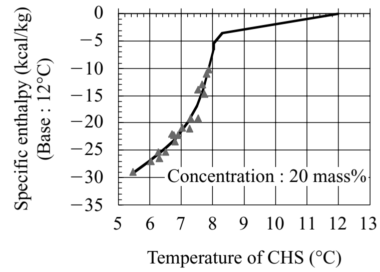

Fig. 5 Specific enthalpy of CHS vs. temperature

an aqueous solution concentration of 20 mass% (specific enthalpy is expressed assuming 12°C is 0). At approximately 7.6°C, CHS with a specific enthalpy (thermal density) twice that of chilled water is obtained (at a temperature difference of 7°C).

2.3 Transportation Properties of Clathrate Hydrate Slurry

An important feature of CHS is the fact that it can be used not only as a cooling storage medium but also as a high density cooling transportation medium. Because CHS is a fluid with the consistency of soft ice cream, the flow is stable and does not cohere and block piping or heat exchangers, valves, etc of air-conditioners.

Figure 6 shows a comparison of transportation power consumption with CHS and chilled water for the thermal density (specific enthalpy) of CHS at a fixed cooling transfer rate (115 kW), based on experimental data for transportation with 50 A piping.[6] With CHS, slurry is transported on the outward route at 5–8°C and returns as an aqueous solution at 12°C. With chilled water, the water temperature is 5°C on the outward route and 12°C on the return route. At a cooling transfer rate of 115 kW, the chilled water flow rate is equivalent to 2 m/s.

The above experiment showed that transportation power consumption can be reduced to approximately 1/5 to 1/2 that with chilled water by using CHS with a thermal density of −50 to −72 kJ/kg. It is also possible to use smaller diameter transportation piping to reduce equipment cost, or conversely, to increase the cooling transfer rate with equipment of the same specifications.

When using a mixed solid-liquid phase fluid, there was concern that the solid phase might not be distributed evenly due to a segregated flow of solid particles

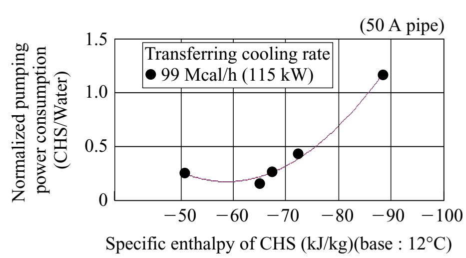

Fig. 6 Comparison of power consumption for CHS

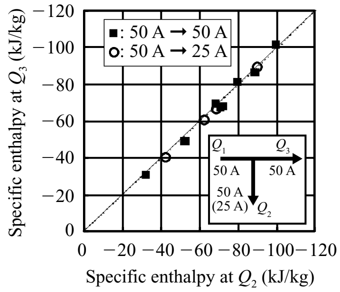

Fig. 7 Distribution characteristics of Tee pipe element

at junctions between straight tubes and branch tubes. Therefore, to investigate the possible segregated flow of hydrate particles at piping junctions, samples of CHS were taken after tee-joint (90°) horizontal junctions from a 50 A straight pipe to a 50 A or 25 A branch pipe, and their specific enthalpy was compared. The junction flow rate ratio, Q_2/Q_1 (Q_1: Flow rate on straight pipe side, Q_2: Flow rate on junction pipe side) is in the range of 0.08–0.92. The experimental results are shown in **Fig. 7**. This experiment confirmed that CHS particles are distributed uniformly, showing that CHS can be applied to piping systems which include junctions.

2.4 Heat Transfer Properties of Clathrate Hydrate Slurry

As one example of a heat exchanger, **Fig. 8** shows the relationship of heat exchange (cooling load) to the CHS flow rate in heat exchange between CHS and water with a fan coil unit (rated flow rate: 1.7×10^{-4} m^3/s, cooling capacity: 3.66 kW), which is generally used in air-conditioners.

The thermal density of the CHS used in this experiment was approximately 50–70 kJ/kg. The measured range of flow rate was 1.5×10^{-5} to 2.0×10^{-4} m^3/s. The air flow rate of the fan coil unit was constant at approximately 2.0×10^{-4} m^3/s.

When using CHS in an air heat exchanger, the cooling load increased in comparison with water in the measured range in this experiment, being about 2.3–3.5 times greater than that of water in the range of flow rate from 1.5×10^{-5} to 8.0×10^{-5} m^3/s. It was also found that the same cooling capacity as with water supply at 1.75×10^{-4} m^3/s, which is the rated flow rate of this device, can be realized with CHS at a flow rate of approximately 0.8×10^{-4} m^3/s.

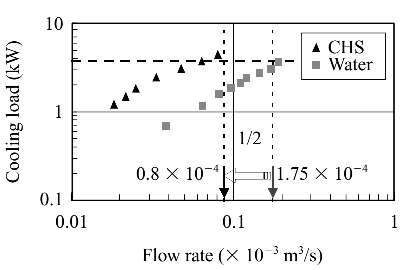

Fig. 8 Performance of heat exchange for fan coil unit

3. Example of Trial Calculation of Energy Savings

3.1 Conditions for Trial Calculation

A trial calculation of annual power consumption for cooling was made assuming application of a CHS air-conditioning system in a 15 000 m^2 scale office building. For comparison purposes, a trial calculation was also made for a non-regenerative type chilled-water air-conditioning system.

As cooling load conditions for the trial calculation, the unit cooling load was assumed to be 93 W/m^2, full cooling load equivalent time, 1 462 h, and annual cooling operating time, 7 200 h. The monthly and 24-hour load patterns follow those specified for designing urban office buildings (cooling load during both daytime and nighttime throughout the year). As power rate conditions, a base rate of ¥1 560/kW · month was assumed for commercial power. Seasonal power consumption rates (running rates) were assumed to be ¥12.02/kWh in summer and ¥10.93/kWh in other seasons. For nighttime power, a rate of ¥3.25/kWh was used.

Figure 9 shows the flow of the air-conditioning system using chilled water; **Fig. 10** shows the CHS system.

The chilled-water system was a closed one consisting of refrigerators (200 RT × 2, coefficient of performance, COP: 6.36, 7/12°C), and chilled water pumps (121 m^3/h × 50 m × 28 kW × 2 units).[7)]

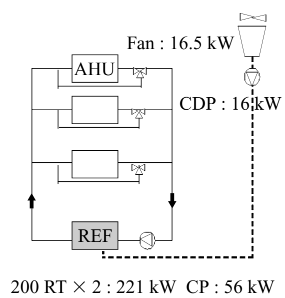

Fig. 9 Air-conditioning system using chilled water

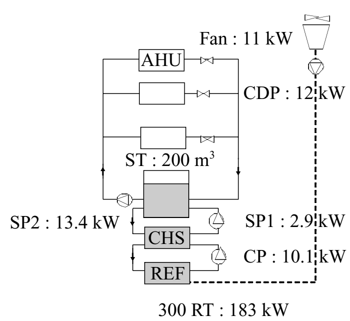

Fig. 10 Air-conditioning system using CHS

The CHS system comprised a refrigerator (300 RT × 1, COP: 5.76, 4/9°C), CHS production unit (300 RT × 1), CHS storage tank (200 m^3, heat storage capacity: 2 570 Mcal, cooling storage density: 15 Mcal/m^3), chilled water primary pump (181 m^3 × 12 m × 10 kW), CHS primary pump (90.7 m^3 × 7 m × 2.9 kW), and CHS secondary pump (121 m^3 × 24 m × 13.4 kW; variable current control).

3.2 Results of Trial Calculation

Figure 11 shows the annual power consumption for cooling with 2 systems (excluding power for air-conditioner fans). With the CHS system, power consumption was reduced by approximately 36% in comparison with the chilled-water system. The main reasons for this reduction were shortening of the on-load operating time of the low efficiency refrigerator section by CHS heat storage, and a reduction in pump power consumption by supplying high thermal density CHS directly to the secondary side air-conditioners.

Figure 12 shows the annual power costs for cooling with the two systems. In comparison with the chilled water system, contract (base) power can be reduced by 77 kW with the CHS system, and a saving of approximately 42% in running power cost can be achieved by taking advantage of low-cost nighttime power.

As described above, significant reduction can be achieved in both power consumption and power cost with the CHS air-conditioning system in comparison with the conventional chilled-water system.

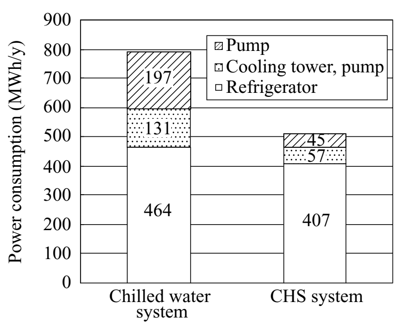

Fig. 11 Power consumption for chilled water system and CHS system

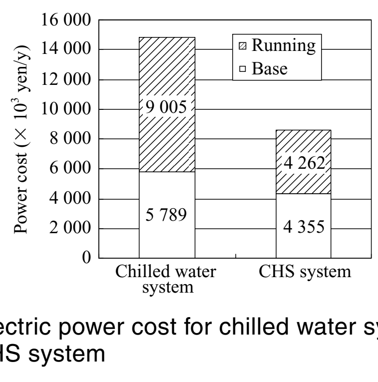

Fig. 12 Electric power cost for chilled water system and CHS system

4. Conclusion

Clathrate hydrate slurry (CHS) is a newly developed cooling medium for use in air-conditioning systems which enables storage and transportation of cooling at a high thermal density. In this study, it was found that a large reduction in pumping power consumption and other advantages can be expected with CHS in comparison with conventional chilled-water systems. As a high thermal density medium, CHS also makes it possible to reduce equipment cost by employing more compact cooling storage tanks and smaller-diameter piping, or conversely, to increase the amount of cooling transfer with existing piping.

With the development of this CHS medium, expansion to new next-generation energy-saving air-conditioning systems is considered possible, responding to increasing demand for air-conditioning in the general private and public sectors. Clathrate hydrate slurry is also expected to make important contributions to CO_2 reduction through energy saving, and to load leveling in electric power consumption.

Future plans include the development of an optimal design technology for machinery/ systems and an operation control technology for CHS, aiming at practical application of air-conditioning systems using CHS.

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