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Air-Conditioning System Using Clathrate Hydrate Slurry†

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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 oper-
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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). U s). CHS is a kind of liquid clathrate h

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 o2hilled hi 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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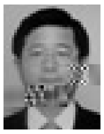

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Fig. 1. The cooling source section of this CHS air-conditioning system includes a heat exchanger for CHS production and CHS storage tank, which are required in addition to the conventional system equipment. In the q quipment, hh is laed i Ī ors, he medium for Âransporting chillad Åer i Àeplaa Åith CHS. It is possibla to usp piping, pumps, ụnd heat exchanger equipmen s Åith Âhe Á e Á e ụ f ụsions the anventional chillad Åer systems.

The fe] ures and effe ụs of the CHS air- ụ tioning system] e] follaw ȩ :

(0] imum 80% = edu = ụion Î n umping sumption s possibla, CHS h]] high thermal dens Î ty of]] bla to redu = ụ the fow r] e by one-h] f in bap] with hillad er. = esul ȉ , ʊ ̧ w ɵ k r onsumption for pumping the cooling medium can be substanti] ly redu = ụ d, (2) 40% of energy is savd in bap] ison with iba p ٢ o - du = ụ ion, The foring] e ī per (r (ge ( ] h] ̧ f Phillad ®er (5–0 °Ba, Ď] p ̧ sibla o er (p he efr Î ger (̧ r ith igher ff cienc than in ice p ٢ o u = ụ ion, (2a Direba] r (p ̧ sibla, Bebause BaS is non- ʓ ụ hesiv,] herp

enablang direba] r (Pp ̧ ation ̧ f BaS Î n] he = ụ Ďe Ď] r as chilled ®ater, The f ̧ lla ing se = ụ ions descr

p ̧ ation, (d heat] r (Pfpr r ̧ prips of aS, 2, F ̧ Ďin

Fi®up PhIJ s] he = elationshi bp] ween] he f ̧ = ing teĎ prtur of TBAB hy] rte] d] he conceǦtrtion of the queous solution.

When the rtio of TBAB in the hy] rte rlative hy] rtes s hole s he Ďe s of he queous olution, he onceǦtrtion of he que ous olution pcomes ont] t hen coole] , even if the hy] rte conteǦt of the CHS incrases. In expermeǦts, when the onceǦtrtion f the que ous olution as 0.5 mass%, he onceǦtrtion pcaĎe const] t t b ̧ ut 1.8°C. r ̧ Ď his, he y] rtion uĎ bpr as stimate] t ppr ̧ ximate þ y 6. his y] rte ca þ þ p] "Type I hy] rte."

When aǦ aqueous solution with the conceǦtrtion of lpss thaǦ 40.5 mass% is coolp] , the conceǦtrtion of the solution in the slurry dePrses as the hy] rte conteǦt of the CHS inPrses. This me] s that the hy] rte formin® teĎpertur dePrses a þ ̧ n® the hy] rte formin® linp. From pxpermeǦts to] te, when the teĎpertur of CHS is approximately °C r ̧ wer, the y] rte hfts o np with] ion McuĎ b/m of , pprox mately –3 6, mes hat f hillad to as "Type II hy] rte" n the llow n®: F Î gur 2 shw 2 hy] rte formin® linps at 8C an] uǦ] pr. Hwevpr, in spite f he f Pt that Type I hy] rte Î s forme teĎpor0r ily in the P ̧ olin® proPpss, = 0use Type II y] rte Î s-st0 b þ e, t¾e fnl pro] ut Î s Type II ¾y] rte.

2. Prperties ̧ f TBB Hy] rte an] Clthrte Hy] rte Slr

Tab þ e 2 shw t¾e meur vlus ̧ f] eǦsity, spe cific ¾eat, 0n] þ teǦt ¾eat ̧ f the Type I 0n] Type II hy] rtes.

Figr3 ation shw thdo] ut air-f ʓ ụ nditionerPnsistin f t¾e rtinshp bǦ sltin teĎpertur an]] eǦ sity ̧ f sltins ̧ f dit deǦsities. f. = labaage with piping -̧ r Î ndo ̧ r 0 t Î sltin deǦsities, t¾e sltins w¾ose teĎpertur is lwer thn t¾e hy] rte forĎ Î ng teĎpertur r n 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 py)the e aa)to

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