

Measurement of Thermophysical Properties of Thermal Storage System - Measurement of $\text{CaCl}_2 \cdot n\text{NH}_3$ system by arbitrary heating method -

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SUMMARY

In order to measure thermophysical properties of $\text{CaCl}_2 \cdot n\text{NH}_3$ system as one of thermal storage systems, the effective thermal conductivity and the thermal diffusivity of $\text{CaCl}_2 \cdot 8\text{NH}_3$ system were measured by arbitrary heating method and compared with those of $\text{CaCl}_2 \cdot 4\text{NH}_3$ system. The values of λ and α of $\text{CaCl}_2 \cdot 8\text{NH}_3$ system in the measuring temperature range (290 K to 350 K) were $0.1 \sim 0.5 \text{ W}/(\text{m} \cdot \text{K})$ and $0.04 \sim 0.17 \times 10^{-6} \text{ m}^2/\text{s}$, respectively. It was found that the behavior of thermophysical properties of $\text{CaCl}_2 \cdot 8\text{NH}_3$ system was different from that of $\text{CaCl}_2 \cdot 4\text{NH}_3$ system.

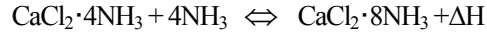
KEY WORDS: thermal storage system, thermophysical properties, ammine complex, calcium chloride, ammonia, arbitrary heating method

1. INTRODUCTION

Recently, the possibility of significant global warming resulting from emissions of greenhouse gases by fossil fuel combustion has become an important concern within the international community. In the energy sector, energy utilization technologies in many industries are expected to develop high efficiency and high performance. For thermal energy storage systems utilizing a low heat source as solar energy or hot effluent (approximately 353~373 K), the processes using the chemical reaction of anhydrous salt with NH_3 have been proposed and discussed for its practicably^{1~6)}. For example, some prototypes of energy storage unit using $\text{CaCl}_2 \cdot n\text{NH}_3$ system have been designed and measured these performances^{3~6)}.

The reaction products from anhydrous salts and ammonia are referred to as ammoniated salts or ammine complexes and the state is either solid or liquid. The reaction is similar to hydration of anhydrous salts. In this study, the chemical reaction of $\text{CaCl}_2 \cdot 4\text{NH}_3$ with 4NH_3 was chosen here for the thermal energy storage system (see the

following reversible chemical reaction: Ammoniation/Deammoniation). In this reversible reaction, ΔH (enthalpy change) is 43.8 kJ/mol-NH₃ at 0.1 MPa, 304 K¹⁾, the value of which is considerably higher than the latent heat of vaporization of liquid NH₃, 23.4 kJ/mol-NH₃ at 0.1 MPa, 240 K²⁾.



In the author's previous work¹⁰⁾, in order to measure the thermophysical properties (effective thermal conductivity and effective thermal diffusivity) of CaCl₂·nNH₃ system, the measurement unit has been developed by arbitrary heating method using Laplace transform^{7~10)} and measured effective thermal conductivity and effective thermal diffusivity of CaCl₂·4NH₃ system.

In this study, in order to develop the thermal energy storage system using CaCl₂·nNH₃ system, the thermophysical properties (effective thermal conductivity and effective thermal diffusivity) of CaCl₂·8NH₃ system were measured and compared with those of CaCl₂·4NH₃ system.

2. PRINCIPLE OF MEASUREMENT

In this study, this principle of measurement is only shown. Regarding the principle of this measurement method in detail, refer to arbitrary heating method by Iida *et al.*^{7,8,9)} and the author's previous work¹⁰⁾.

2.1. Fundamental relation of heat conduction for one dimensional cylindrical coordinate

Assuming heat flux is the direction of radius r only, where t , T and α are, respectively, time, temperature and thermal diffusivity, and $T(r,0) = \text{constant}$, that is, initial temperature distribution is uniformity.

Considering $\theta(r,t)$ as temperature difference in equation (1),

$$\theta(r,t) = T(r,t) - T(r,0) \quad (1)$$

The fundamental heat conduction equation is given by

$$\frac{\partial \theta(r,t)}{\partial t} = \alpha \left\{ \frac{\partial^2 \theta(r,t)}{\partial r^2} + \frac{1}{r} \frac{\partial \theta(r,t)}{\partial r} \right\} \quad (2)$$

Equation (2) is transformed by using Laplace transformation and substitution of $\theta(r,0) = 0$ into equation (2), and then is rewritten to the ordinary differential equation, general solution as equation (3) is given by

$$\bar{\theta} = CI_0(\sqrt{s/\alpha} \cdot r) + DK_0(\sqrt{s/\alpha} \cdot r) \quad (3)$$

where $\bar{\theta}$ and s are Laplace integration of $\{\theta(r,t)\}_{r=r}$ and Laplace parameter, and I_0 and K_0 are modified Bessel functions of the first and the second kind of zero-order, and then C and D are constants of integration, respectively.

On the other hand, heat flux $q(r,t)$ is given by Fourier's equation.

$$q(r,t) = -\lambda \frac{\partial T(r,t)}{\partial r} = -\lambda \frac{\partial \theta(r,t)}{\partial r} \quad (4)$$

where λ is thermal conductivity.

Equation (4) is transformed by Laplace transform, and then given by

$$\bar{q} = -\lambda \sqrt{\frac{s}{\alpha}} \left\{ CI_1(\sqrt{s/\alpha} \cdot r) + DK_1(\sqrt{s/\alpha} \cdot r) \right\} \quad (5)$$

2.2. Measurement system

Figure 1 shows the principle of measurement. Considering the infinite tubular sample [I] around the infinite cylindrical sample [II] in Fig. 1. In this experiment, the supplied sample is the case of cylindrical sample [II]. Hence tubular sample [I] is the case of reference sample. Assuming the heat flux is only direction of radius and the contact resistance is negligible, and the symbol \times is expressed a measuring point of temperature and the measuring point 2 is defined as the boundary surface. The temperature response $\theta(r_i, t)$ at each measuring point $i (i=0,2,R)$ is rewritten as $\theta_i(t)$, Laplace integration of each point is expressed by

$$\bar{\theta}_i = \int_0^{\infty} e^{-st} \theta_i(t) dt \quad (6)$$

In this measurement system, the temperature responses of central point in the cylindrical sample as the supplied sample and surface point of the reference sample were measured at the same time in Fig. 1.

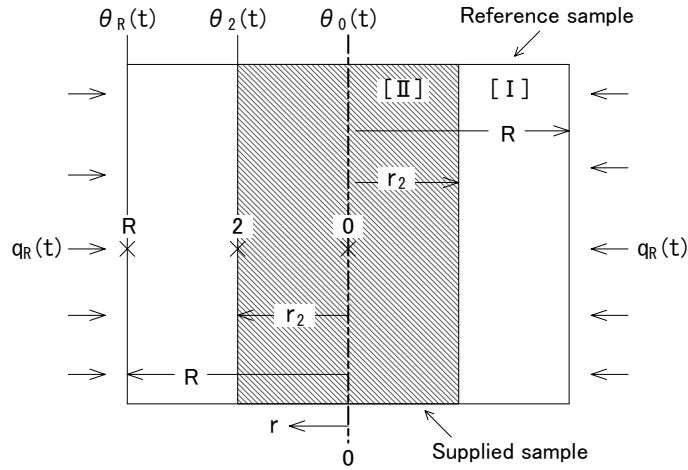


Figure 1. Principle of measurement.

Assuming α_I , λ_I and $c_{pI} \times \rho_I$ (c_p : specific heat, ρ : density) are, respectively, thermal diffusivity, thermal conductivity and heat capacity of the reference sample, and are well known. In [II], $q(0, t) = 0$. Hence $(\bar{q})_{r=0} = 0$. Thus $D_{II} = 0$ in equation (5), and substitution of $I_0(0) = 1$ into equation (5), then given by

$$\bar{\theta}_0 I_0(\sqrt{s/\alpha_{II}} \cdot r_2) - \bar{\theta}_2 = 0 \quad (7)$$

where α_{II} is thermal diffusivity of the supplied sample.

Hence, in this case, $\bar{\theta}_2 / \bar{\theta}_0$ is calculated. Thermal diffusivity α_{II} is calculated from Figure 2 immediately.

Then thermal conductivity of the supplied sample λ_{II} is given by the following equation.

$$\frac{\lambda_{II}}{\lambda_I} = \sqrt{\frac{\alpha_{II}}{\alpha_I}} \frac{1}{I_1(\sqrt{s/\alpha_{II}} \cdot r_2)} \frac{1}{\bar{\theta}_0} \{C_1 I_1(\sqrt{s/\alpha_I} \cdot r_2) - D_1 K_1(\sqrt{s/\alpha_I} \cdot r_2)\} \quad (8)$$

Then C_1 and D_1 are given by

$$C_1 = \frac{\bar{\theta}_2 K_0(\sqrt{s/\alpha_I} \cdot R) - \bar{\theta}_R K_0(\sqrt{s/\alpha_I} \cdot r_2)}{I_0(\sqrt{s/\alpha_I} \cdot r_2) K_0(\sqrt{s/\alpha_I} \cdot R) - I_0(\sqrt{s/\alpha_I} \cdot R) K_0(\sqrt{s/\alpha_I} \cdot r_2)} \quad (9)$$

$$D_1 = \frac{\bar{\theta}_2 I_0(\sqrt{s/\alpha_I} \cdot R) - \bar{\theta}_R I_0(\sqrt{s/\alpha_I} \cdot r_2)}{I_0(\sqrt{s/\alpha_I} \cdot R) K_0(\sqrt{s/\alpha_I} \cdot r_2) - I_0(\sqrt{s/\alpha_I} \cdot r_2) K_0(\sqrt{s/\alpha_I} \cdot R)} \quad (10)$$

Regarding the range of Laplace integration, its range is expressed as from t_{\max} to zero, and the relation between t_{\max} and s is expressed as the following equation by Iida et al.⁹⁾

$$8 \leq st_{\max} \leq 12$$

In this experiment, s was determined to satisfy $st_{\max} = 10$.

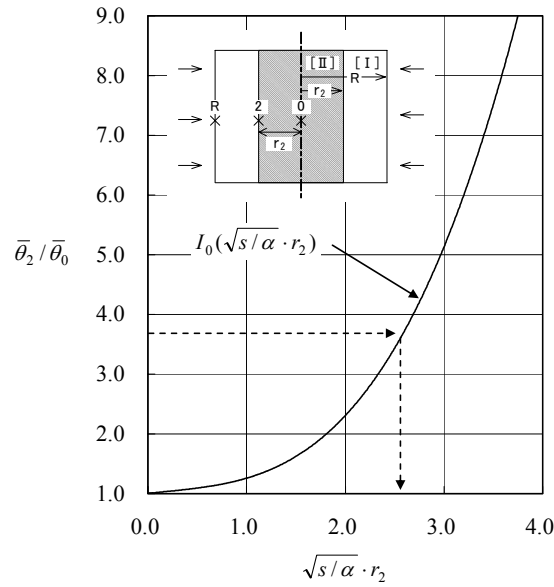


Figure 2. Determination of thermal diffusivity for temperature measurement of central point.

3. EXPERIMENTAL SECTION

3.1. Materials

CaCl_2 used in the experiment is produced by Wako Pure Chemical Industries Ltd. Japan. It is guaranteed reagent grade, and it is specified as the pure grade having minimum purity of 95.0 %. CaCl_2 is used without further purification. NH_3 gas of 99.99 % purity is provided from Seitetsu Kagaku Co. Ltd.

3.2. Experimental apparatus

Figure 3 schematically shows the experimental apparatus of the measurement system. This system consists of measurement unit (cell) as the reactor, NH₃ glass vessel, pressure regulator valve, pressure gauges, thermocouples and constant temperature water bath. The measurement cell is made of stainless steel and it is covered with water jacket, which can control the temperature in the measurement cell. The NH₃ vessel is pressure resistance glass vessel, which volume is $0.3 \times 10^{-3} \text{ m}^3$, (up to 2.0 MPa), and the volume of the liquid NH₃ is measured by a microscope with an accuracy of $\pm 0.05 \%$ of full volume ($0.5 \times 10^{-3} \text{ m}^3$).

In order to insulate the measurement unit from the surroundings, the apparatus is wrapped foamed polystyrol. The temperature in this unit is measured by using C-A type thermocouples by the digital thermometer and the temperature data as the digital signal (change of mV) transferred to the micro computer and are analyzed.

The amount of liquid NH₃ transferred to the measurement cell from the NH₃ vessel can be measured by the microscope. The temperature of the measurement cell, unit and the NH₃ vessel are controlled by using constant temperature bath having minimum accuracy within $\pm 0.1 \text{ K}$ separately.

The pressure in the vessels is measured by Bourdon gauge, which accuracy is $\pm 0.1 \%$ of full scale (up to 2.0 MPa). The pressure control in the measurement cell is carried out using the pressure regulator valve.

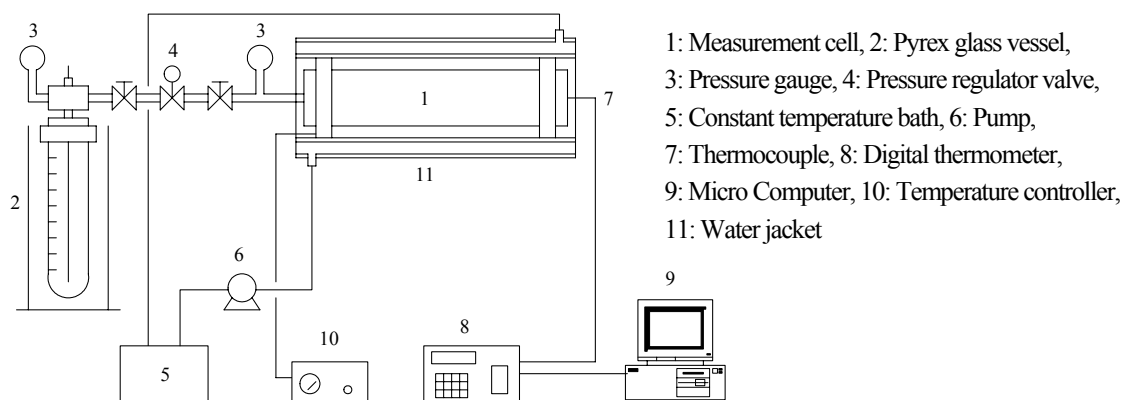


Figure 3. Schematic diagram of measurement unit.

This measurement cell consists of two major units, a stainless steel pipe (Length: 230 mm, OD: 76.3 mm, ID: 68.3 mm) and a reinforced pressure proof glass tube as the reference sample (Pyrex 7740: OD: 40.0 mm, ID: 32.0 mm), and the temperature response is measured by the stainless steel covered C-A thermocouple (ϕ 0.65 mm), which are inserted in the measurement cell. Regarding the measurement cell in detail, refer to the author's previous work¹⁰.

3.3. Experimental Procedure

3.3.1. Preparing for $\text{CaCl}_2 \cdot 8\text{NH}_3$ system (Ammoniation)

CaCl_2 of 0.218 mole (approximately 24.2 g) was crushed below size of 200 JIS mesh and was dried at 773 K approximately for 5 hours by an oven. A dried powder sample was placed in the measurement cell. It was sealed, and

worked by the vacuum pump in order to remove air and any water from this measurement cell.

The NH_3 vessel was also evacuated for 2 hours and NH_3 gas introduced from the cylinder into the NH_3 vessel, which was kept at constant temperature (273 K) by the cooling liquid. After liquid NH_3 was charged in it, its volume was measured by the microscope rapidly and recorded. Then this measurement cell was connected with the NH_3 vessel shown in Fig. 3. NH_3 gas moved to the measurement cell through the pressure regulator valve keeping constant pressure (0.5 MPa) during the reaction. The level of liquid NH_3 in the NH_3 vessel was measured by reading the scale of the NH_3 vessel using the microscope, and mole number of NH_3 absorbed to pure CaCl_2 was calculated from this volume change.

When 8 moles of NH_3 was absorbed to the pure CaCl_2 , the experiment of ammoniation is just finished.

3.3.2 Measurement of thermophysical properties

After temperature of cell is settled with the measurement temperature and the temperature of measuring points are stabilized, and start heating of the measurement cell by charging electricity to Ni-Cr wire, where heating rate and maximum heating temperature are 5 K/min. and 10 K, respectively, in order to avoid the violent reaction in the measurement cell during the measuring time. Temperature changes (change of mV) of C-A type thermocouple are measured by the digital thermo meter and input was recorded to the micro computer system, and the scan rate is every 9 seconds and the measurement time is 30 minutes.

4. RESULTS AND DISCUSSION

Figures 4 and 5 show the relation between thermophysical properties of $\text{CaCl}_2 \cdot 4\text{NH}_3$ system¹⁰ and $\text{CaCl}_2 \cdot 8\text{NH}_3$ system and temperature. λ (effective thermal conductivity) and α (effective thermal diffusivity) of $\text{CaCl}_2 \cdot 4\text{NH}_3$ system were approximately constant (0.2 W/(m·K) and $0.075 \times 10^{-6} \text{ m}^2/\text{s}$, respectively) in the measuring temperature range of 290 K to 350 K. However, λ and α of $\text{CaCl}_2 \cdot 8\text{NH}_3$ system increased with increasing temperature in the measuring temperature range (290 K to 350 K). It was found that the behavior of thermophysical properties of this system was different from that of $\text{CaCl}_2 \cdot 4\text{NH}_3$ system. The values of λ and α of $\text{CaCl}_2 \cdot 8\text{NH}_3$ system were $0.1 \sim 0.5 \text{ W}/(\text{m} \cdot \text{K})$ and $0.04 \sim 0.17 \times 10^{-6} \text{ m}^2/\text{s}$, respectively.

In order to analyze the behavior of thermophysical properties of $\text{CaCl}_2 \cdot 4\text{NH}_3$ system and $\text{CaCl}_2 \cdot 8\text{NH}_3$ system, Figures 6 and 7 show the relation between λ of $\text{CaCl}_2 \cdot 4\text{NH}_3$ system and $\text{CaCl}_2 \cdot 8\text{NH}_3$ system, pressure in the measurement cell and temperature. In Fig. 6, it was seemed that λ of $\text{CaCl}_2 \cdot 4\text{NH}_3$ system had no influence in the range of measuring temperature and measuring pressure in the measurement cell. However, in Fig. 7, λ of $\text{CaCl}_2 \cdot 8\text{NH}_3$ system increased with increasing temperature in the measuring temperature range. Regarding the reason of the difference of the behavior of both systems, it was seemed that λ of $\text{CaCl}_2 \cdot 4\text{NH}_3$ system and $\text{CaCl}_2 \cdot 8\text{NH}_3$ systems were influenced by the packed density (ρ_{bulk} : $\text{CaCl}_2 \cdot 4\text{NH}_3$ system: $0.232 \times 10^3 \text{ kg}/\text{m}^3$, $\text{CaCl}_2 \cdot 8\text{NH}_3$ system: $0.320 \times 10^3 \text{ kg}/\text{m}^3$) of those systems .

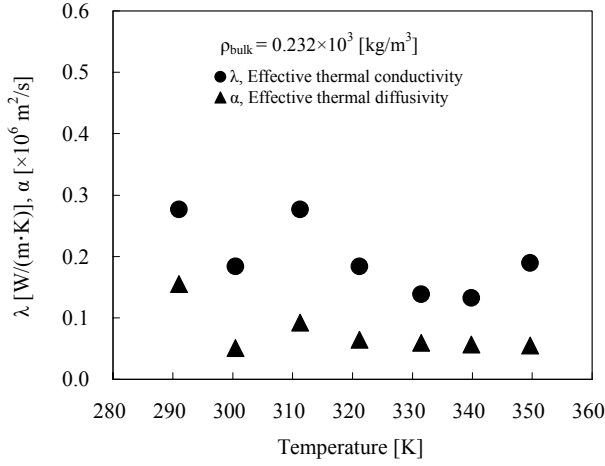


Figure 4. Relation between thermophysical properties of $\text{CaCl}_2 \cdot 4\text{NH}_3$ system and temperature¹⁰⁾.

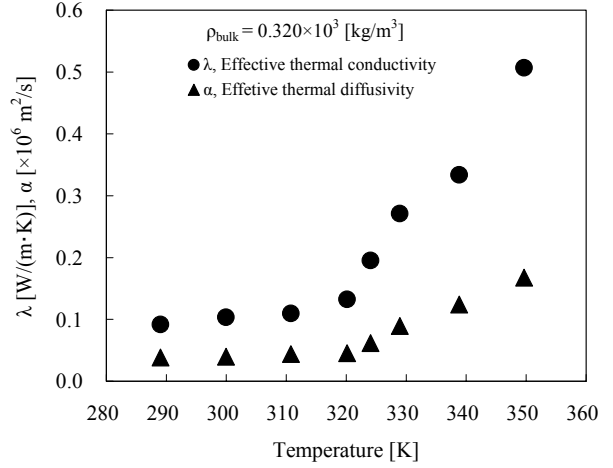


Figure 5. Relation between thermophysical properties of $\text{CaCl}_2 \cdot 8\text{NH}_3$ system and temperature.

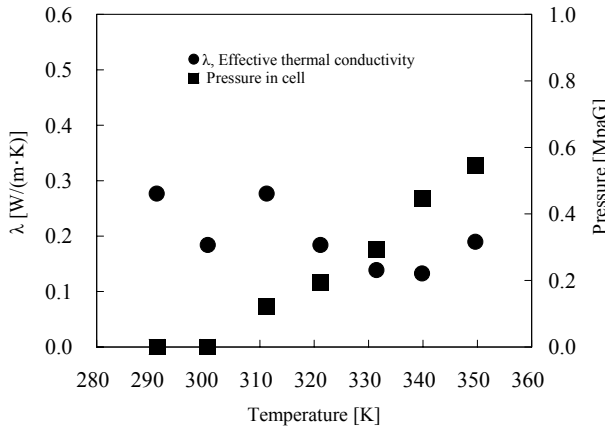


Figure 6. Relation between λ of $\text{CaCl}_2 \cdot 4\text{NH}_3$ system, pressure in the measurement cell and temperature¹⁰⁾.

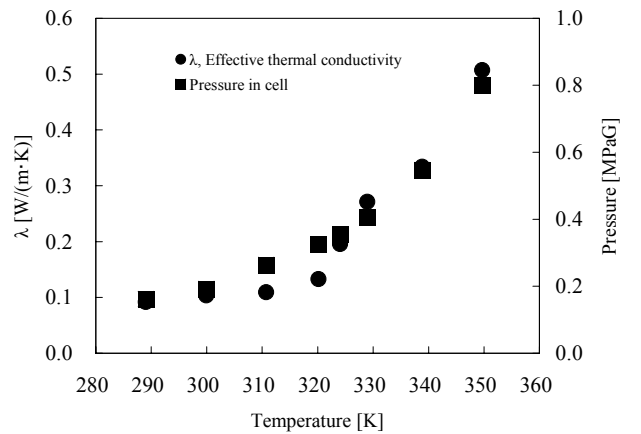


Figure 7. Relation between λ of $\text{CaCl}_2 \cdot 8\text{NH}_3$ system, pressure in the measurement cell and temperature.

In general, it is well known thermal conductivities of solids depend on many factors and are difficult to measure or predict. In particular, in porous solids, for example, the thermal conductivity is strongly dependent on the void fraction (related to the packed density in this experiment), the pore size and the fluid contained in the pore¹¹⁾.

On the other hand, a theoretical equation of thermal conductivity for porous solids has been developed as Kunii-Smith's equation (equation (11) : excluding the term of radiation)¹²⁾.

$$\lambda = \lambda_c \left(1 - \varepsilon_v + \frac{\varepsilon_v}{\phi + 2/3 \cdot \lambda_c / \lambda_d} \right) \quad (11)$$

where λ , λ_c and λ_d are effective thermal conductivity, thermal conductivity of continuous phase (NH_3 gas in this experiment) and thermal conductivity of discontinuous phase ($\text{CaCl}_2 \cdot 4\text{NH}_3$ and $\text{CaCl}_2 \cdot 8\text{NH}_3$ in this experiment), respectively, and then ε_v and ϕ are void fraction of discontinuous phase (related to the packed density in this

experiment) and ratio of fluid film thickness and particle (grain) diameter, respectively. In equation (11), it was found that the values of λ and λ_c were influenced by those of ε_v and λ_d . In this experiment, it was seemed that λ of $\text{CaCl}_2 \cdot 8\text{NH}_3$ system had the influence of λ_c , λ_d and ε_v by increasing the packed density. It is necessary to investigate the detailed effect of the void fraction and /or the packed density for the effective thermal conductivity of this system.

5. CONCLUSIONS

The thermophysical properties (effective thermal conductivity and effective thermal diffusivity) of $\text{CaCl}_2 \cdot 8\text{NH}_3$ system as a thermal energy storage system were measured by arbitrary heating method using Laplace transform and compared with those of $\text{CaCl}_2 \cdot 4\text{NH}_3$ system. As a result, the following conclusions were obtained.

λ and α of $\text{CaCl}_2 \cdot 8\text{NH}_3$ system increased with increasing temperature in the measuring temperature range. The values of λ (effective thermal conductivity) and α (effective thermal diffusivity) of $\text{CaCl}_2 \cdot 8\text{NH}_3$ system were $0.1 \sim 0.5 \text{ W}/(\text{m} \cdot \text{K})$ and $0.04 \sim 0.17 \times 10^{-6} \text{ m}^2/\text{s}$, respectively. It was found that the behavior of thermophysical properties of this system was different from that of $\text{CaCl}_2 \cdot 4\text{NH}_3$ system and seemed that the those of $\text{CaCl}_2 \cdot 8\text{NH}_3$ system had the influence of the thermal conductivity of continuous phase (NH_3 gas), the thermal conductivity of discontinuous phase ($\text{CaCl}_2 \cdot 8\text{NH}_3$) and the void fraction of discontinuous phase by the packed density.

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NOMENCLATURE

α	= thermal diffusivity and effective thermal diffusivity [m^2/s]
θ	= temperature difference [K]
$\bar{\theta}$	= Laplace integration of θ [-]: $\bar{\theta} = \int_0^{\infty} e^{-st} \theta(t) dt$
λ	= thermal conductivity and effective thermal conductivity [$\text{W}/(\text{m} \cdot \text{K})$]
ρ	= bulk density [kg/m^3]
c_p	= specific heat [$\text{kJ}/(\text{kg} \cdot \text{K})$]
C, D	= constant of integration [-]
I_0	= modified Bessel function of the first kind of zero-order [-]

K_0	= modified Bessel function of the second kind of zero-order [-]
q	= heat flux [W/m ²]
\bar{q}	= Laplace integration of q [-]
r	= radius [mm]
R	= outer diameter of sample [mm]
s	= Laplace parameter [-]
t	= time [s]
t_{\max}	= time step of measuring time [s]
T	= temperature [K]
I	= sample [I]
II	= sample [II]
i	= measuring point

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