A STUDY ON THERMAL CHARACTERISTICS OF THERMAL STORAGE TANK USING PHASE CHANGE MATERIAL INSTALLED IN AN AIR DISTRIBUTION SYSTEM

Motoi YAMAHA*1, Kyoko SHUKU*2 and Shinya MISAKI*3

Thermal characteristics of a thermal storage tank containing phase change material (PCM) and installed in an air distribution system were investigated. PCM in the form of a mixture of trimethylolethane and urea with a melting temperature of 13 °C was used in flat rectangular containers. Experiments were conducted in order to examine temperature responses in a charging (freezing) process and a discharging (melting) process. Due to sub-cooling, the charging temperature was found to necessarily be below 5 °C. For the discharging process, temperature difference between the inlet and outlet was maintained at 2 – 4 °C. On the basis of the experimental results, a proposed simulation model based on the enthalpy method was used to successfully simulate the sub-cooling phenomena.

Keywords: thermal storage, phase change material, cooling, air distribution system, simulation model

1 Introduction

Phase change material (PCM), which utilizes the latent heat absorbed during phase change for energy storage, has been studied in various fields. Studies began after the oil crisis, especially in the field of solar energy. Schröder et al.1) described the characteristics of PCM needed for thermal storage, and conducted experiments on sodium sulfate for use in solar collectors.

Many different PCMs are commercially available, including salt hydrates, eutectic mixtures, and organics. Ozawa et al.2) screened materials for thermal storage, from the viewpoint of energy density and material cost in a high-temperature application of 80 – 500 °C. They found that eutectic mixtures of hydrates or chlorides are promising, in view of price and heat of fusion. He et al.3) suggested that binary mixtures of paraffin waxes could serve as low-temperature PCMs that allow melting temperature control. They measured melting temperature and heat of fusion and concluded that these materials are attractive for cool storage. Kakiuchi et al.4) have developed a new organic hydrate material in the form of a mixture of trimethylolthane and urea. Its melting temperature can be controlled within the range of 13 °C to 30 °C by means of changing the proportion of urea.

Enhancement of heat transfer is important for the utilization of PCM in a system. Inaba et al.5) studied the thermal characteristics of a fluidized-bed storage tank using shape-stabilized polyethylene pellets soaked in paraffin wax. Mehlng et al.6) reported on PCM mixed with graphite for enhancing the heat conductivity of PCM.

For application of PCM to a building, a tank containing PCM capsules is typically used in heat source plants, for example, ice or water storage tanks. As a passive method of applying PCM, Ibamoto et al.7) studied gypsum boards containing polyethylene pellets soaked in paraffin wax for improving thermal conditions in a residential building. They applied two PCMs of different melting temperatures to walls in order to equalize the temperature distribution within the room. Hoko8) simulated floor heating using PCM and evaluated the optimum melting temperature of PCM for a residence.

Since the melting temperatures of PCMs are distributed over a wide range, PCMs can be installed and used in various locations, in water distribution systems, air distribution systems, and within a room. This system can take advantage of low nighttime electricity rates without replacement or retrofitting of a heat source. The total amount of peak shift could be increased if this system is installed together with an ordinary storage system in the heat source. In this study, PCM was installed in the ducts of an air distribution system in order to reduce peak load.

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in an office building. The thermal characteristics of the storage system tank and simulation model were determined. The study was conducted by way of experiments examining the thermal response of the tank and a simulation model using the enthalpy method.

2 Experimental setup

Figure 1 shows the schematic diagram of the experimental storage tank. Although PCM containers were originally set horizontally in a raised floor, our laboratory lacked sufficient space, and therefore we set the experimental tank vertically.

Table 1 shows the thermal properties of PCM used in this study. The PCM used was organic hydrate in the form of a mixture of trimethylolmethane and urea, and its melting temperature was designed to be 13 °C. The PCM was encapsulated in a flat rectangular container, as shown in Figure 2, along with certain inorganic nucleating agents. The experimental tank was an air duct containing 16 PCM containers stacked vertically. The tank was insulated by 25 mm-thick glass wool and covered with foam rubber for additional insulation. The thermal resistance of this insulation was 1.25 m²-K/W (ignoring the convective heat transfer coefficient). The difference between stored heat and discharged heat was calculated from the temperature difference between the inlet and outlet and the velocity at the outlet, and was as high as 15 percent. The reason for the difference is considered to be inaccuracy of the velocity measurements, which were conducted using only a single sensor. The temperature difference between the inside and outside of the experimental duct was not large, since outlet air from the experimental duct diffused around the room. Consequently, heat loss from the experimental duct was actually small.

The quantities measured were temperature, humidity, and air velocity. Thermo-couples were set on the surfaces of the PCM containers, and on the air inlets, air outlets and voids in the ducts. Figure 3 shows the locations of measuring points. Temperatures of the surfaces of containers and spaces between containers were measured for the second (II) and fourth (IV) columns of containers. Temperatures inside containers were measured using thermo-couples placed in the center of the second column (II) of containers. Six sensors were installed in the inlet and outlet in such a way that each sensor covered the same area. The humidity sensors were set in the upper rows and center of the inlet and outlet sections. The air velocity was measured at the upper part of the outlet using a hot wire anemometer. These quantities were acquired by a data logger and saved on computer.

Experiments were started from the charging or freezing cycle and continued to the discharging or melting cycle. Prior to charging, the

<table>
<thead>
<tr>
<th>Table 1 Thermal properties of PCM – 13</th>
</tr>
</thead>
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<tr>
<td>Items</td>
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<tr>
<td>Melting temperature [°C]</td>
</tr>
<tr>
<td>Heat of fusion [kJ/kg]</td>
</tr>
<tr>
<td>Thermal conductivity [W/(m·K)]</td>
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<tr>
<td></td>
</tr>
<tr>
<td>Specific heat [kJ/(kg·K)]</td>
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<td></td>
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<tr>
<td></td>
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<tr>
<td>Density [kg/m³]</td>
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Figure 1 Schematic diagram of experimental setup

Figure 2 The detail of PCM container

Figure 3 Location of measuring points
Table 2 Experimental conditions

<table>
<thead>
<tr>
<th>Exp. No.</th>
<th>Mode</th>
<th>Input Temp. (average) [°C]</th>
<th>Initial Temp. of PCM [°C]</th>
<th>Air velocity (average) [m/s]</th>
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<tr>
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<td>21.1, 23.4</td>
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<tr>
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<td>22.3, 21.0</td>
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</table>

Figure 4 Experimental results for charging cycle for different input temperatures (C922, C722, and CAA22)

Air temperature was controlled to 25 °C or 15 °C. Table 2 shows the experimental conditions.

3 Results

Figure 4 shows the result of different inlet temperatures employed for examining the temperature required to freeze PCM. These internal PCM temperatures are those for the lower container. Due to subcooling, the PCM did not freeze if the input temperature was higher than 7 °C. For experiment CA22, in which the inlet temperature was set to 5 °C, the temperature inside the PCM fell and then rose again to around 10 °C, terminating the subcooling phenomenon. Therefore, inlet temperature should be less than 5 °C in order to freeze the PCM in this case.

Figures 5 and 6 show the temperature responses during a charging cycle for different input temperatures under identical air velocity conditions. The temperature inside the PCM containers dropped once below melting temperature and rose again due to the subcooling phenomenon. The internal temperatures of the PCM were measured at a single point in each horizontal row, and therefore temperature distribution along the flow direction was not known. Surface temperatures on the PCM containers in columns II and IV exhibited different responses. The surface temperature of containers the near inlet (No. 33) rose again, whereas surface temperatures of containers the near outlet (No. 55) remained constant.

For the lower inlet temperature experiment (Figure 6), the start and end of subcooling occurred earlier, and subcooling terminated at a higher temperature than in the case of CA22. The temperature difference between the inlet and outlet in CB22 was larger than CA22. Although, as shown in Figure 5, the surface temperature responses of column II and IV showed no remarkable difference, the temperature of column II started to rise earlier than did the temperature of column IV.

Figure 7 shows a comparison of various air velocities for identical input temperature conditions. For higher air velocity, the outlet temperature dropped rapidly and the subcooling phenomenon terminated earlier.

Figure 8 shows the discharge temperature response for different inlet temperatures. The results for DA22 (Figure 8 above) show that a 2 - 4 °C temperature difference existed between the inlet and outlet. The temperature difference was large at the beginning of the experiment, then became smaller and disappeared with the termination of PCM temperature rise, indicating phase change. For a lower inlet temperature (DA12; Figure 8 below), no large temperature fluctuation in the PCM was observed. The internal temperature had been maintained below melting temperature, because the inlet temperature for DA12 was relatively cold.

Figure 9 shows the temperature response during a discharging cycle for various air velocities. Lower air velocity resulted in a large temperature difference between the inlet and outlet. The period until phase change ended was shorter for higher air velocities.
molecular water. Therefore, phase change occurs within a defined temperature range because solubility depends on temperature and concentration. The temperature range of phase change should be considered.

We employed the enthalpy method, which treats the heat of fusion as a heat capacity that varies with temperature. By using this method, the governing equations became simple because the same equations can be used for both liquid phase and solid phase. Furthermore, various types of PCMs can be simulated by assuming the appropriate function.

The governing equations were treated as being one dimensional along the airflow direction. Four containers were arranged in row. From the surface temperatures shown in Figures 5 and 6, containers were observed to freeze from the inlet side to the outlet side. Although heat capacity due to phase change with respect to the thickness direction could not be ignored, we considered that the temperature distribution with respect to flow direction was dominant. If a container is thick, the distribution in the thickness direction should also be considered. However, PCMs should be designed to be thin, considering the characteristics of heat transfer for PCM. The equations used in the simulation are shown below.

The PCM temperature was calculated as follows:

$$\frac{\partial}{\partial t} \left( \rho \theta C_f (\theta) \right) = \frac{\partial}{\partial x} \left( \lambda_f \frac{\partial \theta}{\partial x} \right) + \frac{S}{\rho C_f}$$

(1)

where $\rho C_f(\theta)$ is an equivalent specific heat indicating latent heat and is a function of temperature. $S$ is heat flux through the capsule wall, as calculated by

$$S = K (\theta_a - \theta_p)$$

(2)

where $K$ is the overall heat transfer coefficient calculated by

$$K = \frac{1}{h + 1/\lambda_c}$$

(3)

Since a convectional heat transfer correlation suitable for a container surface with projections could not be found, this value was determined experimentally. Assuming that the containers can be considered to be flat surface, heat transfer was calculated by multiplying an experimental constant $b$ and an empirically determined equation.

$$N_u = b \cdot 0.037 Re^{0.8} Pr^{0.5}$$

(4)

The constant $b$ was determined by comparing the amount of heat calculated from the temperature difference between the inlet and outlet using the correlation from our experiments, the value of $b$ was 2.58.

The air temperature was calculated using a heat conduction equation and allowing for airflow, as follows:

$$\frac{\partial \theta_a}{\partial t} = \frac{\lambda_a}{\rho C_a} \frac{\partial^2 \theta_a}{\partial x^2} - u \frac{\partial \theta_a}{\partial x} - \frac{S}{\rho C_a d \theta_a}$$

(5)

4.2 Thermal properties of PCM

In our simulation method, as thermal properties such as heat capacity, density, and conductivity change with temperature, the shapes of these correlations should be determined. For heat capacity, DSC (Differential Scanning Calorimeter) is an useful method for determining this correlation. However, the sample for DSC measurement is too small, around several mg, to enable a sample having the same composition found in the containers to be used. Instead, the shape of the correlation was determined by experiments using the apparatus shown in Figure 10. The apparatus and procedure were based upon the standard for electrical floor heating. The apparatus consisted of a
container placed between heat flow sensors that measured 310mm × 310mm × 0.7mm (thickness). The sensitivity constants of heat flow sensors were 0.0729 and 0.0707mV/(W · m²), as measured by a data logger having a sensitivity of 1 μV.

The apparatus was placed in an experimental room made of insulated panels in which temperature could be controlled so as to cause phase change. In accordance with the self-standard for electrical floor heating, the apparatus was exposed to temperature fluctuation consisting of heating (7 hours), a constant high temperature (3 hours), cooling (7 hours), and a constant low temperature (7 hours). During heating and cooling, the rate of temperature change should be maintained at 5°C/h.

Because the room temperature control was conducted by a PID controller using a cooling coil and a electric re-heater in the air handling unit, controlling the rate of temperature change exactly as specified in the standard was impossible. The temperature of room was controlled to fluctuate between 0 and 30°C as same schedule as defined in the standard. On the basis of the assumption that all heat supplied to the PCM passed through the two heat flow sensors, the heat flux for each scan interval was acquired. For the measured temperature range, the product of heat flux at every 0.5°C and scan interval was calculated. The sum of values of this product at various temperatures was considered to contain some information about heat capacity, which can be called equivalent specific heat. Figure 11 describes the correlation between this equivalent specific heat and temperature of PCM. This correlation was used as $C_p^*(\theta)$, because this is the only information about PCM that we could determine. If measuring the property is difficult, then an appropriate equation, such as an error function, might substitute for the correlation.

Other thermal properties were estimated on the assumption that the change in value between solid and liquid is linear, as shown in Figure 11. Although the validity of this assumption was not confirmed, we used these values, because the range of change and influence on thermal response are not significant compared to latent heat.

### 4.3 Sub-cooling

The temperature variation after breaking sub-cooling was modeled using the relaxation process of a first-order reaction. If $A$ is assumed to be the state of a system, in a relaxation process $A$ is generally formulated as follows.

$$A = A_\infty(1 - e^{-t/T})$$

where $A_\infty$ is a state attained upon termination of relaxation, and $T$ is the time constant of the system. In our calculations, we focused on temperature. The equation was transformed into the following so as to obtain temperature.

$$\theta = \theta_0 + (\theta_\infty - \theta_0)(1 - e^{-t/T})$$

where $\theta_0, \theta_\infty,$ and $a$ were determined from experimental results. $a$ was the parameter that determined the speed of relaxation, and was 7.6 for this PCM.

Figure 12 shows the simulation model. The freezing process can be divided into four parts: sensible cooling, breaking sub-cooling, phase changing, and sensible cooling after freezing. The melted PCM was cooled by sensible heat before freezing began. If sub-cooling occurred, PCM was cooled below melting point. Once the temperature of PCM became lower than the degree of sub-cooling, the state of sub-cooling was broken and the temperature rose to around melting point. Then the temperature remained at the melting point because phase change occurred. For the melting process, the phase change appeared first, and then sensible heating followed. This process seemed to be simpler, as super-heating hardly occurred. The measured equivalent specific heat was used within the temperature range between 5°C and 20°C. Specific heat of liquid phase was used for a lower temperature, and specific heat of solid phase was used for a higher temperature.

### 4.4 Calculation results

Calculations were conducted by solving the equations by the explicit finite difference method. Flow direction was divided into ten sections, and the time interval was 0.01 second. Boundary conditions for PCM were insulated. Figure 13 shows calculation results for the charging process. Interpolated inlet temperature was used. For internal PCM temperature, the simulation results agree with the experiment until relaxation ends. The period of constant temperature during phase change was shorter than that determined experimentally, indicating that the heat of fusion is underestimated by the calculation. Outlet temperature is also underestimated slightly. For practical purposes, the simulation and experiment are in close agreement.

Figure 14 shows the calculation results for the discharging process.
charging process was divided into four parts, and the discharging process was divided into two parts. The calculation results were shown to be in close agreement for practical use. Correctly estimating the latent heat of the PCM and the convection heat transfer of the apparatus were found to be important factors influencing the accuracy of the simulation.

Nomenclature

\( \alpha \): coefficient of relaxation, \( b \): coefficient for heat transfer, \( C \): specific heat \([kJ/(kg \cdot K)]\), \( d_z \): thickness \([m]\), \( k \): overall heat transfer coefficient \([W/(m^2 \cdot K)]\), \( Q \): heat per mass during relaxation \([J]\), \( t \): time \([s]\), \( u \): air velocity \([m/s]\), \( x \): length \([m]\), \( \theta \): temperature \(^{\circ}C\), \( \rho \): density \([kg/m^3]\), \( N_u \): Nusselt number \([-]\), \( Re \): Reynolds number \([-]\), \( Pr \): Prandtl number \([-]\).

Subscripts

\( a \): property for air, \( c \): property for a container, \( p \): property for PCM, \( r \): property for relaxation termination, \( s \): property for sub-cooling termination, \( t \): property for equivalent value

Acknowledgements

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References

3) B. He, M. Gustafsson, and F. Setterwall. Tetradecane and hexadecane binary mixtures as phase change materials (PCMs) for cool storage in district cooling systems. Energy, 24, 1999.
1 はじめに

物質の相変化に伴う熱を利用する蓄熱耐熱材は、石油ショック以降、主に太陽エネルギー利用の分野で、温熱の蓄熱を目的として研究が行われた。利用に便利できるのはその耐熱性が開発されており、近況の電力ショックに対応するために、空調における希熱への対応を考えることができる。

蓄熱耐熱材の建築への応用としては、水・水蒸気熱のように熱源1次供給の屋根だけでなく、建具を含めてパッシブに利用する方法が研究されている。本研究においては、電力のピーク時、既存設備への対応、ピーク時荷量の増加を目的として、蓄熱材をダクト内に設置した蓄熱システムについて基礎的な熱特性とシミュレーションモデルを検討した。

2 実験とその結果

実験はFigure 1に示す実験装置をもちいた。ダクト内にFigure 2に示すPCMsを封入したコンテナを16個並べ、温度と速度を調整した空気を送り込む。蓄熱材にはトリメチロールエタンと尿素を主成分とし目標融点13℃として開発されたものをもとめた。

実験は蓄熱実験と放熱実験を続けて行った。測定点をFigure 3に示す。蓄熱実験ではまず、実験装置を25℃に加熱し、その蓄熱材を融解させる。温度が一定になったところで、所定の温度、風速、風向に調整された空気を送り込む。蓄熱実験は9時間行った。放熱実験結果を示すと、ダクト内を空気温度をバイパスするように調整して空調機を予熱し、その後、15℃、25℃に調整された空気を送り込み放熱実験を開始し6時間連続した。実験条件リストはTable 2に示す。

Figure 4に蓄熱に必要な温度を調べ、入熱を変化させた実験結果を示す。過冷却のため入熱温度が7℃以下ではPCMが凍結しておらず、蓄熱材には5℃以下の入熱温度が必要と判断した。Figure 5.6に示した入熱温度の異なる蓄熱実験では、出口温度は実験開始とともに下降し、出口温度差はDB22の方が大きくなっている。蓄熱材内部の温度は、過冷却現象のためいったん融点以下に下がり再び上昇している。過冷却現象はDB22入熱の方が早く起きている。蓄熱材内部温度は空気の流れ方向に1点しか測定していないが、コンテナの熱流束を観察すると、入口温度と出口温度の間に差が見られる。Figure 7に示す温度変化が実験風速の違いを示す。風速が変わることによって出口温度の下降、過冷却現象が早く起きていることがわかる。

Figure 8には入熱温度の異なる放熱実験結果を示す。DA22では、入熱温度差は2.4℃程度であり、実験初期には温度差が大きく時間がたって小さくなる。蓄熱材の温度が上昇する融解後は温度差が小さくなっている。DA22では、蓄熱材温度に激変がなく、入熱温度が低いので相変化が起きていないことがわかる。したがって、この程度の温度下では潜熱分を放熱させることことができると考えられる。

3 シミュレーションモデル

相変化を伴う熱交換問題は、移動境界問題とも呼ばれ、これらの解法として、Muray, Landisらによる固定境界法と、適当な選択変換により境界を固定する境界固定法などが提案されている。我々の対象としたシステムで、蓄熱材の出口温度が約4℃、様々な蓄熱材の特性を扱う必要がある。そこで、蓄熱材の周熱と熱容量の関係で表すエネルギー方程式を採用した。

蓄熱材は流れ方向に4枚並べており、Figure 5.6の表面温度応答から、入口側から蓄熱が起きていると考えられるので、方程式は空気の流れ方向に1次元とした。蓄熱材の温度は式(1)で表し、ここでCp(θ)は温度の関数として表される見掛けの比熱である。コンテナ壁からの蓄熱は式(2)で表され、熱流束Kは、式(3)で求められる。ここでコンテナの表面熱伝達率は、コンテナの凹凸のある表面に適用できる式が無かったため、平板に沿う乱流熱流を表す実験式に実験から補正係数を求めて計算した。出口空気温度から求めた熱流束から5=2.85とした。

シミュレーションのためには温度の関数であるCp(θ)を求める必要がある。相変化に伴う熱流はDSC示差熱流実験で測定できるが、原料がmgオーダーとなるため実験にいちじるしくPCMsでは同じ組成の資料を挙げることが困難である。そこで、電気温房自験基準で規定された熱流板による測定を行った。Figure 10に示すように蓄熱材の入った容器を熱流計でまして、温度の変動できる部材を組立、凝固・融解の間の熱流を測定する。測定時間間隔毎の熱流量を蓄熱材温度0.5℃間隔にて積算し、Figure 11に示すように関係を温度と熱流量をもとに示した。熱流量以外の物性値については、固相との値と液相での値をFigure 11下図に示すように、等温線を繋ぐだけで変化させた。

過冷却現象は化学反応における緩和過程を表す式をもって表現している。緩和過程の状態変化は式(6)で表され、今回の計算では温度の上昇、式(7)のように定量的に過冷却現象の温度を表現する式(7)におけるαは緩和過程の速度を決定するパラメーターで今回実験から求め7.6としている。

計算の過程はFigure 12に示すように分割した。蓄熱過程では、過冷却解除までの過冷却、過冷却解除中の緩和過程、緩和過程終了後の相変化、相変化後の過冷却と4つの部分に分割する。放熱過程では、相変化部分と融解後の過冷却加熱という2つの部分に分割した。

Figure 13に蓄熱過程での計算結果を示す。入口温度には実験データを内挿してよりも。蓄熱開始から蓄熱過程終了まで、計算と実測は良い一致を示している。相変化中の温度一定時間は計算の方短くており、出口温度も示していない。Figure 14に放熱過程の結果を示すが、出口温度が実験後半期で高くなっているが、これは蓄熱量の測定法。コンテナの表面熱伝達率推定法の誤差が影響していると思われ、計算方法自体は妥当なものであると考える。

4 結論

空調ダクト内に変化温度13℃の蓄熱材を封入したコンテナを設置した温度応答実験では、過冷却のため5℃以下の入熱温度でないと凝固しなかった。入熱温度が低いほど、風速が速いほど温度下降と過冷却現象の解消がある。放熱過程では、入熱温度差が2～4℃なくなることが確認された。

この蓄熱材の性能を予測するためのシミュレーションモデルを、熱流として温度変化の関数で表わすエネルギー方程式を適用し作成した。過冷却現象は、冷却時には蓄熱冷却、解消時は温度変化に化学変化の緩和過程を適用して、温度を求める。コンテナ表面での対流熱伝達率は、平面内乱流熱伝達の実験値から補正をかけた値とした。計算に必要な蓄熱材の物性値を実験値から計測した。

実験結果と比較の際は、実用的に十分な精度を得ることができたが、蓄熱材の物性値や対流熱伝達率の値は計算精度に与える影響が大きいのでこれらを適切に推定することが重要である。

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