Abstract. The thermophysical parameters of inorganic phase change material (PCM) of CaCl$_2$·6H$_2$O added by 1%wt BaSO$_4$ as the nucleating agent has been studied by analyzing the temperature vs time data during liquid-solid phase transition (solidification process) based on the original T-history method and its modification form. The PCM sample and water as reference material are placed in a cylindrical tube with chosen dimensions to fulfill the criterion that the Biot number $Bi$ is less than 0.1. To extract the values of mean specific heat capacities of solid and liquid PCM and the heat of fusion related to liquid-solid phase change, hot liquid PCM in the tube with temperature above its melting point was suddenly exposed to a cool atmosphere to allow the gradual solidification process. We compared the results with reference data, both from direct measurements of Differential Scanning Calorimetry (DSC) and indirect measurement of the same method.

1. Introduction
In this era the problem of energy crisis is still been an interested issues to be solved. Thermal energy storage (TES) is an alternative technology to be considered, because it can stored the energy to be used at a later time for heating and cooling applications [1-2]. TES are used particularly in buildings as an heat exchange system to keep the thermal comfort of occupants, due to the fact that it can help the balance between energy demand and supply [3-4]. They can also reduce the electrical energy consumption and its peak demand, as well as to reduce CO$_2$ emissions that mainly contribute to the local and global warming.

Compared to brick, wood, concrete, and glass as the conventional examples of sensible TES, TES based on phase change material (PCM) is one of the feasible ways for energy conservation in the future. In this case PCM as the medium of latent TES can store relatively large heat at temperatures around its phase transition (solid-liquid), and releasing the absorbed heat back to the environment when the ambient temperature is lower than the temperature of the material. The performance of PCM is mainly determined by its thermophysical parameters that consist of liquid ($c_{p,l}$) and solid ($c_{p,s}$) specific heats and the heat fusion ($h_m$). For building application, inorganic PCM of CaCl$_2$·6H$_2$O with melting temperature around 29ºC and relatively high heat of fusion is very good candidate [5]. In this paper the thermophysical parameters of CaCl$_2$·6H$_2$O added by 0.1%wt BaSO$_4$ as
the nucleating agent are determined by means of T-history method proposed firstly by Yinping et al. [6]. The data analysis follow the method by Yinping and its modification form by Hong et al. [7]. The results are then compared with references data, both resulted from direct (DSC) measurement and indirect measurement of the same method.

Based on T-history method, during the lowering of temperature in cool air environment below the melting temperature, CaCl₂.6H₂O will experience the sensible and latent heats release, while water as reference material will just experience the sensible heat release. The energy equations that related to specific heat capacities of liquid and solid PCM as well as the heat of fusion related to liquid-solid phase change are described in the following equations (i.e. first column of table 1), while the corresponding energy equations for water as the reference material are described in the second column of the same table. In other side the phase boundaries of PCM and water that consist of period, temperature and time ranges, and area calculation for further analysis of the data are described in table 2.

### Table 1. Energy equations for PCM and water during the lowering of temperature in cool air environment.

| Energy equations for PCM | Energy equations for water (reference) |
|-------------------------|----------------------------------------|
| \((m_{p}, c_{p,l} + m_{i,p} c_{p,i}) (T_0 - T_s) = hA_1 A_i\) | \((m_{i,w}, c_{p,l} + m_{w} c_{p,w}) (T_0 - T_s) = hA_1 A'_i\) |
| \((m_{i,p} c_{p,l} + m_{w} \frac{c_{p,l} + c_{p,s}}{2} (T_m - T_i) + m_{w} h_m = hA_2 A_2\) | \((m_{i,w}, c_{p,l} + m_{w} c_{p,w}) (T_m - T_i) = hA_2 A'_2\) |
| \((m_{i,p} c_{p,l} + m_{p} c_{p,s}) (T_i - T_f) = hA_3 A_3\) | \((m_{i,w}, c_{p,l} + m_{w} c_{p,w}) (T_i - T_f) = hA_3 A'_3\) |

In those above equations, the masses of the PCM, water and tube used for PCM and water are each denoted as \(m_p\), \(m_w\), \(m_{i,p}\), \(m_{i,w}\); the liquid and solid specific heats of PCM as \(c_{p,l}\) and \(c_{p,s}\); the water and tube specific heats as \(c_{p,w}\) and \(c_{p,t}\); and the heat of fusion of PCM as \(h_m\). In addition, \(A_e\) is the convective heat-transfer area of the tube, while two set values of \(\{A_1, A'_1, A_2\}\) for PCM and \(\{A'_2, A'_3\}\) for water correspond to the area below the curve of PCM’s and water’s temperatures towards air environment, with the full expression given in the last column of table 2.

### Table 2. Period, temperature and time ranges, and area of each period used for analysis of T-history curves of PCM and water. The time-dependent temperature values of PCM and water are denoted by \(T_p\) and \(T_w\), respectively.

| Period          | Temperature Range | Range of time | Area       |
|-----------------|-------------------|---------------|------------|
| Sensible liquid | \(T_0 - T_s\)     | \(t_0 - t_1\) | \(A_1 = \int_{t_0}^{t_1} (T_p - T_s) \, dt\) |
| Phase change    | \(T_s - T_m - T_i\) | \(t_1 - t_2\) | \(A_2 = \int_{t_1}^{t_2} (T_p - T_i) \, dt\) |
| Sensible solid  | \(T_i - T_f\)    | \(t_2 - t_3\) | \(A_3 = \int_{t_2}^{t_3} (T_p - T_f) \, dt\) |
| Sensible liquid | \(T_0 - T_s\)     | \(t'_0 - t'_1\) | \(A'_3 = \int_{t'_0}^{t'_1} (T_w - T_s) \, dt\) |
| Sensible liquid | \(T_m - T_i\)     | \(t'_1 - t'_i\) | \(A'_2 = \int_{t'_1}^{t'_i} (T_w - T_i) \, dt\) |
| Sensible liquid | \(T_i - T_f\)    | \(t'_i - t'_f\) | \(A'_1 = \int_{t'_i}^{t'_f} (T_w - T_f) \, dt\) |
Finally, the thermophysical parameters of PCM consist of the liquid and solid specific heats \( c_{p,l} \) and \( c_{p,s} \) and the heat of fusion \( h_m \) derived from this method are expressed as,

\[
c_{p,l} = \frac{m_{l,u} c_{p,l} + m_u c_{p,u} A_1}{A_p} \frac{m_{l,p} c_{p,l}}{m_p}
\]

\[
c_{p,s} = \frac{m_{l,u} c_{p,l} + m_u c_{p,u} A_3}{A_3} \frac{m_{l,p} c_{p,l}}{m_p}
\]

\[
h_m = \frac{m_{l,u} c_{p,l} + m_u c_{p,u} A_2}{A_2} (T_m - T_i) - \frac{m_{l,p} c_{p,l} + c_{p,s}}{2} (T_m - T_i)
\]

2. Methods

The salt hydrate CaCl\(_2\).6H\(_2\)O as inorganic PCM and nucleator BaSO\(_4\) were purchased from Sigma Aldrich. About 20gr CaCl\(_2\).6H\(_2\)O added with 0.1%wt BaSO\(_4\) as nucleating agent and 20gr reference sample (water) were placed in the separate tube. The tube dimensions were chosen to ensure the one-dimensional heat transfer along the length of the tube as measured by the Biot number \( Bi = \frac{hR}{2k} \), with \( h \) is the natural convective heat-transfer coefficient of air outside the tube, \( R \) is the radius of the tube, and \( k \) is the thermal conductivity of PCM) is smaller than 0.1 to apply the lumped capacitance method [6]. Each tube was equipped with the temperature sensors (T-type thermocouple with diameter about 1mm) that integrated to the data logger (Applent AT4508A from Applent Instruments Inc.) and computer.

For T-history measurement, the test tube containing molten PCM was suddenly put into the cool air environment at a temperature lower than the melting temperature of PCM \( (T_m) \) so that solidification can be initiated. The temperature vs time data were then recorded automatically by data logger connected to a computer.

3. Results and Discussion

The typical T-history curves that show the graphs of temperature vs time of PCM CaCl\(_2\).6H\(_2\)O+0.1%wt BaSO\(_4\) and water as the reference is typically shown in figure1. From this figure, upon cooling in cool air CaCl\(_2\).6H\(_2\)O experience the temperature change and liquid to solid phase transition, with supercooling and solidification temperature are each denoted by \( T_s \) and \( T_m \), while the difference between them is denoted as the supercooling degree \( (\Delta T_m = T_s - T_m) \). The average and standard deviation values of \( T_s \), \( T_m \) and \( \Delta T_m \) from 5 set of data experiments are \( T_s \approx (24.58 \pm 0.77)^\circ \text{C} \), \( T_m \approx (26.34 \pm 0.44)^\circ \text{C} \) and \( \Delta T_m \approx (1.76 \pm 0.58)^\circ \text{C} \), respectively. We note that the resulted solidification temperature (heat release) is lower than the reported values [8] of melting temperature (heat absorption) based on exothermic mode of DSC measurement, which commonly occur in other kinds of material. The relatively small value of supercooling degree mark the effectiveness of BaSO\(_4\) as the nucleating agent for the crystallization process of CaCl\(_2\).6H\(_2\)O as reported before in Ref. [9].
Figure 1. The typical T-history curves of water and CaCl$_2$.6H$_2$O +0.1%wt BaSO$_4$ in cool airbath.

For further analysis of the data, we show in figure 2 the area under the curve for PCM and water for each phase boundaries along with the temperature derivative curve of PCM (figure 2(a)). We note that during the phase transition the temperature keeps constant in the latent heat release (denoted by $T_m$ in figure 1), but decreases exponentially in cooling process accompanying sensible heat alone. Thus, following the procedure introduced by Hong et al. [7], the end of phase transition process was determined from the inflection point of the first derivative of T-history curve (figure2(a)). In addition, $t_3$ that mark the transformation of overall PCM to become solid was determined from the difference in the trend of temperature derivative for low and high temperature part just after the inflection point.

Figure2. Illustration for the analysis of T-history curve of: (a) CaCl$_2$.6H$_2$O+0.1%wt BaSO$_4$ and (b) water, that show the phase boundaries for sensible liquid, liquid to solid phase change, and sensible solid phases as well as the area under the curve.

The results for specific heats of the liquid and solid PCM and the heat of fusion based on equation (1), (2) and (3) are shown in table 3.
Table 3. The values of liquid specific heat, solid specific heat and the heat of fusion of CaCl₂·6H₂O+0.1%wt BaSO₄.

| Method | Ref | No. of Iteration | cₚ,l [kJ/kg.K] | cₚ,s [kJ/kg.K] | hₘ [kJ/kg] |
|--------|-----|------------------|----------------|----------------|------------|
| TH     |     | 1                | 2.36           | 2.12           | 188        |
|        |     | 2                | 2.13           | 2.07           | 186        |
|        |     | 3                | 2.18           | 2.49           | 174        |
|        |     | 4                | 2.33           | 2.31           | 186        |
|        |     | 5                | 2.70           | 1.84           | 188        |
| TH     | [8] | -                | 2.23           | 2.17           | 184 + 6    |
| DSC    | [8] | -                | 1.9            | 1.6            | 212        |
| DSC    | [5] | -                | -              | -              | 190.8      |
| DTA    | [10]| -                | -              | -              | 190.8      |
| DSC    | [11]| -                | -              | -              | 160        |
| DSC    | [12]| -                | 2.1            | 1.4            | 140        |

We note that the resulted average values of cₚ,l, cₚ,s and hₘ are in close agreement with those obtained from the same T-history method (TH), DSC, and DTA. In particular, cₚ,l is higher than cₚ,s. The slight difference might due to additional dopant of BaSO₄ that more or less give the influence to the resulted values.

4. Conclusion

We have determined the thermophysical parameters of inorganic PCM CaCl₂·6H₂O+0.1%wt BaSO₄ as the nucleator by means of T-history method. Analysis of the data have led to the values of mean specific heat of the liquid, cₚ,l≈(2.34±0.22)kJ/kg.K; mean specific heat of the solid, cₚ,s≈(2.17±0.25)kJ/kg.K; and the heat of fusion, hₘ≈(184±6)kJ/kg. These values are close to the references data, both obtained from the same method or Differential Scanning Calorimetry (DSC) measurement. The difference might be due to the fact of additional BaSO₄ as the nucleator agent.

Acknowledgement

This research is financially supported by Kementrian Riset Teknologi dan Pendidikan Tinggi Indonesia through the Desentralisasi 2016 research program under contract number: 583p/I1.C01/PL/2016.

References

[1] Dincer I and Rosen M 2010 Energy Storage System and Applications (Ontario Canada: A John Wiley and Sons, Ltd., Publication).
[2] Harald M and Cabeza L F 2008 Heat and Cold Storage with PCM an Up to Date Introduction Into Basics and Applications (Berlin, Germany: Springer).
[3] Tyagi V V and Buddhi D 2007 PCM thermal storage in buildings: A state of art Renewable and Sustainable Energy Reviews11 1146–1166.
[4] Ostermana E, Tyagi V V, Butalaa V, Rahimb N A and Stritih U 2012 Review of PCM based cooling technologies for buildings Energy and Buildings49 37–49.
[5] Lane G A 1980 Low temperature heat storage with phase change materialsInt. J. Ambient Energy1 155–68.
[6] Yinping Z, Yi J and Yi J1999A simple method, the T–history method of determining the heat of fusion, specific heat and thermal conductivity of phase-change materialsMeas. Sci. Technol.10201–5.
[7] Hong H, Kimb S K and Kim YS 2004 Accuracy improvement of T-history method for measuring heat of fusion of various materials Int. Journal of Refrigeration 27 360–6.

[8] Hasan A, McCormack S J, Huang M J and Norton B2014 Characterization of phase change materials for thermal control of photovoltaics using Differential Scanning Calorimetry and Temperature History Method Energy Conversion and Management 81 322–329.

[9] Lane G A 1992 Phase change materials for energy storage nucleation to prevent supercooling Solar Energy Materials and Solar Cells 27 135-60

[10] Telkes M 1975 Thermal storage for solar heating and cooling, Proceedings of the Workshop on Solar Energy Storage Subsystems for the Heating and Cooling of Buildings Charlottesville (Virginia, USA)

[11] Abhat A 1983 Low temperature latent heat thermal energy storage: heat storage materials Solar Energy 30 313–32

[12] Tyagi VV and Buddhi D 2008 Thermal cycle testing of calcium chloride hexahydrate as a possible PCM for latent heat storage Sol Energy Mater Sol Cells 92(8) 891–9.