The enthalpy-temperature curve of new PCM Ca(NO$_3$)$_2$.4H$_2$O and Co(NO$_3$)$_2$.6H$_2$O for low-temperature latent TES

Alfriska O Silalahi$^1$, I M Sutjahja$^1$, D Kurnia$^1$ and S Wonorahardjo$^2$

$^1$Dept. of Physics, Faculty of Mathematics and Natural Sciences, Institut Teknologi Bandung
$^2$Building Technology Research Division, School of Architecture, Planning and Policy Development, Institut Teknologi Bandung

*E-mail : inge@fi.itb.ac.id, T. +62-22-2500834

Abstract. Enthalpy is one of the most important thermophysical parameters of phase-change materials (PCM). This parameter is particularly essential to predict the performance of PCM as latent heat energy storage for certain application since it determines the thermal energy storing capability around its phase change temperature. In this paper, the thermophysical parameters (solid and liquid specific heats and specific heat of fusion) and enthalpy-temperature curve of inorganic PCM of Ca(NO$_3$)$_2$.4H$_2$O and Co(NO$_3$)$_2$.6H$_2$O have been studied by analyzing the temperature vs time data during liquid-solid phase transition (solidification process) based on T-history method. The analysis of the data has been performed following the original method proposed by Zhang et al. and its modification by Hong et al. In addition, the method proposed by Marín et al. have been used to obtain the temperature-dependent enthalpy. We found that the two materials have different phase change behaviors. The obtained thermophysical parameters are then compared with the data from references.

Keywords: Phase Change Material (PCM), Ca(NO$_3$)$_2$.4H$_2$O, Co(NO$_3$)$_2$.6H$_2$O, T-history method, enthalpy–temperature curve.

1. Introduction

Energy conservation and environmental impact were concerned with energy issues today. Some data show a significant portion of energy was consumed by buildings in developing countries (www.enerdata.net, 2016) [1]. For example, Indonesia consumed about 42% for buildings of the total energy in 2001 and will also rise by around 7% per year, with electricity demand alone projected to nearly triple between 2010 and 2030 [2].

Phase change material (PCM) as the latent thermal energy storage (TES) offer many advantages compared to conventional sensible TES that only store the sensible heat. This is due to the fact that PCM show superior storage density at temperatures around its phase transition without significant change in its temperature [3-4]. Among many potential PCM for low-temperature applications such as temperature regulator in buildings, inorganic PCM from salt hydrate of Ca(NO$_3$)$_2$.4H$_2$O and Co(NO$_3$)$_2$.6H$_2$O are suitable.
From material safety data sheet (MSDS), the melting temperatures of these two kinds of hydrate compounds are around $T_m \sim 42^\circ C$ for Ca(NO$_3$)$_2$·4H$_2$O [5] and $T_m \sim 56^\circ C$ for Co(NO$_3$)$_2$·6H$_2$O [6], with rather large enthalpy for Ca(NO$_3$)$_2$·4H$_2$O (see the data in table 1). To obtain full information about the heat storage capability these two materials, the information about the thermophysical parameters that consist of liquid and solid specific heats ($c_{pl}$ and $c_{ps}$) and specific heat of fusion ($\Delta h$) are really needed.

| PCM                  | $T_m$ (°C) | $\Delta h$ (kJ/kg) | Reference |
|----------------------|------------|--------------------|-----------|
| Ca(NO$_3$)$_2$·4H$_2$O| 42         | 132                | [7]       |
|                      | 43–47      | 106–140            | [8]       |
| Co(NO$_3$)$_2$·6H$_2$O| 56         | -                  | [6]       |

One of the simple and reliable methods to obtain the thermophysical parameters ($c_{pl}$, $c_{ps}$ and $\Delta h$) of any PCM is the T-history method, proposed firstly by Zhang [9]. According to the original data analysis method proposed by Zhang [9] and its modification form by Hong [10], these parameters can be obtained from the analysis the T-history curve during solidification process according to the formula

$$
c_{pl} = \left( \frac{m_{t,w} \cdot c_{p,t} + m_w \cdot c_{p,w}}{m_p} \right) \cdot \frac{A_1}{A_1'} - \frac{m_{t,p} \cdot c_{p,t}}{m_p} \tag{1}
$$

$$
c_{ps} = \left( \frac{m_{t,w} \cdot c_{p,t} + m_w \cdot c_{p,w}}{m_p} \right) \cdot \frac{A_2}{A_2'} - \frac{m_{t,p} \cdot c_{p,t}}{m_p} \tag{2}
$$

$$
\Delta h = \left( \frac{m_{t,w} \cdot c_{p,t} + m_w \cdot c_{p,w}}{m_p} \right) \cdot \frac{A_2}{A_2'} \cdot (T_m - T_i) - \left( \frac{m_{t,p} \cdot c_{p,t} + c_{p,l} + c_{p,s}}{2} \right) \cdot (T_m - T_i) \tag{3}
$$

We note that in those above equations, $m_p$ ($m_w$) and $m_{t,p}$ ($m_{t,w}$) are the masses of PCM (water) and the mass of tube used for PCM (water); $c_{p,w}$ is the specific heat of water; $c_{p,t}$ is the specific heat of tube material. The symbols $T_m$ and $T_i$ denote the transition (melting) temperature and inflection temperature in the temperature derivative curve of PCM. In another side, set values of $\{A_1, A_2, A_3\}$ and $\{A_1', A_2', A_3'\}$ correspond to the area calculation below the curve of PCM’s and water’s temperature towards air environment, each of them for the phase regions of sensible liquid, liquid-solid phase change, and sensible solid of PCM.

In another side, the enthalpy-temperature curve as proposed by Marin et al. [11] can be obtained based on the same T-history data. In this case, the energy balance of the PCM from the beginning of the experiment involves the release of liquid sensible heat, latent heat during the phase change process, and solid sensible heat is
\[ m_p \cdot \Delta h(T_j) + m_i \cdot c_{p,i} \cdot (T_j - T_{j+1}) = \alpha \cdot A_j \cdot A_j \]  
(4)

with \( \Delta h(T_j) \) is the specific enthalpy change of the PCM in the interval \( \Delta T_j \) with \( T_j \) is the average temperature in that interval and \( A_j = \int_{t_j}^{t_{j+\Delta j}} (T - T_a) dt \) is the corresponding area for PCM. The similar equation for water as a reference is

\[ (m_i \cdot c_{p,i} + m_w \cdot c_{p,w})(T'_j - T'_{j+1}) = \alpha \cdot A'_j \cdot A'_j \]  
(5)

We note that in equation (4) \( \Delta h(T_j) \) is the enthalpy change of PCM in each interval \( \Delta T_j \),

\[ \Delta h(T_j) = \left( \frac{m_i \cdot c_{p,i} + m_w \cdot c_{p,w}}{m_p} \right) \cdot \frac{A_j}{A'_j} \cdot \Delta T'_j + m_p \cdot c_{p,j} \cdot \Delta T_j \]  
(6)

and finally, the temperature-dependent enthalpy of PCM can be obtained as

\[ h(T) = \sum_{i=1}^{N} \Delta h(T_j) + h_0 \]  
(7)

with \( h_0 \) is a constant value of enthalpy, chosen by a criterion that enthalpy at the lowest temperature of measurement is equal to zero. This method has been successfully applied to describe the enthalpy-temperature curve of several inorganic and organic PCM [11-14].

2. Methods
To characterize Ca(NO\(_3\))\(_2\)\( \cdot \)4H\(_2\)O and Co(NO\(_3\))\(_2\)\( \cdot \)6H\(_2\)O by the T-history method, about 20 gr reference sample (water) and 20 gr co_oil sample are each placed in 150 mm long glass test tube with 14 mm internal diameter and 1mm wall thickness. These tube dimensions were selected to ensure that the temperature distribution of the sample can be assumed uniform and the lumped capacitance method can be applied [15]. We note that this condition is fulfilled when the Biot number (\( Bi = hR/2\kappa \) with \( h \) is the natural convective heat-transfer coefficient of air outside the tube, \( R \) the radius of the tube and \( \kappa \) the thermal conductivity of material) is less than 0.1. Each tube is equipped with the temperature sensors (T-type thermocouple with a diameter about 1mm with an accuracy of 0.2%+1°C) that integrated to the multi-channel temperature meter from Applent (AT4508A from Applent Instruments Inc.)

Prior to the measurement, water and liquid PCM contained in the tube were heated to a high temperature \( (T_0) \) above the melting point and stabilized for a few minutes to ensure the temperature homogeneity in the whole part of the sample. The tubes are then subsequently exposed to a cooler environment \( (T_a) \) provided by cooling bath (sizes: 100×50×45cm) to cool and solidify. During that process, the temperature of the water and compounds hydrates were recorded and plotted against time until the PCM solidified.
3. Results and Discussion

The typical T-history graphs of Ca(NO$_3$)$_2$·4H$_2$O and Co(NO$_3$)$_2$·6H$_2$O materials are shown in figure 1(a) and (b). From these figures, one can see the difference in the profile of temperature drop between the two samples. In particular, Ca(NO$_3$)$_2$·4H$_2$O show rather gradual phase change while Co(NO$_3$)$_2$·6H$_2$O show rather sharp phase change with almost the same supercooling degree of about $\Delta T_s = 13^\circ\text{C}$. However, the melting temperature of each material are different, namely $T_m = 40^\circ\text{C}$ for Ca(NO$_3$)$_2$·4H$_2$O and $T_m = 50^\circ\text{C}$ for Co(NO$_3$)$_2$·6H$_2$O.

![Figure 1](image)

**Figure 1.** Typical T-history curves of (a) Ca(NO$_3$)$_2$·4H$_2$O and (b) Co(NO$_3$)$_2$·6H$_2$O with water as reference material. The temperature derivative curves of each PCM sample are also shown for further analysis of the data. In these two graphs, $T_p$, $T_w$ and $T_a$ are denoted the PCM’s temperature, water’s temperature, and air environment’s temperature.

In these two graphs, $T_0$, $T_m$ and $T_s$ each denotes the initial temperature, transition (melting) temperature and supercooling temperature of PCM, while $T_i$ and $T_f$ denote the inflection temperature and final temperature of PCM from temperature derivative curve. They are needed to determine the phase regions of PCM during solidification process, namely sensible liquid ($T_0 - T_s$), liquid-solid phase change ($T_s - T_m - T_i$), and sensible solid ($T_i - T_f$) as designated in figure 1. For analysis the data following the method proposed by Zhang (Z)/Hong (H), one might apply equations (1)−(3) and the results of the analysis are tabulated in table 2 together with the enthalpy jump values obtained from data analysis following the method proposed by Marín (M). From this table one can see that for these two hydrate compounds $c_{p,s}$ is generally larger than $c_{p,i}$. The heat of fusion, however, is smaller than the values from reference.

For temperature-dependent enthalpy, the T-history data are further analyzed following equations (6) and (7) from Marín, and the results are shown in figures 2(a) and 2(b) for the two samples.
Figure 2. The enthalpy-temperature curves of (a) Ca(NO$_3$)$_2$·4H$_2$O (b) Co(NO$_3$)$_2$·6H$_2$O. For each material, we show two curves that related to the best results from two independent measurements. $T_i$ and $T_k$ are related to the inflection point and kink position in the temperature derivative curve (see figure 1) to estimate the enthalpy jump values, $\Delta h$.

Table 2. Melting temperature ($T_m$) and thermophysical parameters ($c_{p,l}$, $c_{p,s}$ and $\Delta h$) of Ca(NO$_3$)$_2$·4H$_2$O and Co(NO$_3$)$_2$·6H$_2$O from analysis T-history data based on methods proposed by Zhang(Z)/Hong (H) and Marin (M) with average and standard deviation values ($\Delta$) for each parameter.

| Sample          | No. of meas. | $T_m$     | $c_{p,l}$  | $c_{p,s}$  | $\Delta h$ |
|-----------------|--------------|-----------|-------------|-------------|------------|
|                 |              |           | [kJ/kg.K]   | [kJ/kg.K]   | [kJ/kg]    | [kJ/kg]    |
| Ca(NO$_3$)$_2$·4H$_2$O | 1            | 38.7      | 2.03        | 1.11        | 99         | 127        |
|                 | 2            | 38.0      | 2.14        | 1.34        | 111        | 131        |
|                 | 3            | 38.3      | 2.38        | 1.95        | 89         | 151        |
| Average±Δ       |              | 38.3±0.35 | 2.18 ± 0.18 | 1.47 ± 0.43 | 100 ± 11   | 136 ± 13   |
| Co(NO$_3$)$_2$·6H$_2$O | 1            | 45.6      | 4.28        | 2.22        | 54         | 117        |
|                 | 2            | 46.2      | 3.23        | 2.18        | 87         | 131        |
|                 | 3            | 48.9      | 2.85        | 2.27        | 88         | 146        |
| average±Δ       |              | 46.9±1.76 | 3.45 ± 0.74 | 2.22 ± 0.05 | 76 ± 19    | 131 ± 15   |

From this figure, one can see that the solid-liquid phase change occurs in a rather constant temperature for Ca(NO$_3$)$_2$·4H$_2$O, while for Co(NO$_3$)$_2$·6H$_2$O the solid-liquid phase change occurs with a temperature change. Further analysis of the data has revealed the enthalpy jump ($\Delta h$), which is obtained as the difference in enthalpy values at $T_i$ and $T_k$. We note that $T_i$ and $T_k$ signify the temperatures at the beginning and end of phase change process, and they are determined from inflection point and kink position in the temperature derivative curve (figure 1). The resulted $\Delta h$ values of the two materials are listed in the last column of table 1. We note, however, that although the two materials have almost the same $\Delta h$ values, in the same
temperature range the total enthalpy value of Co(NO\textsubscript{3})\textsubscript{2}\cdot 6H\textsubscript{2}O is higher than those of Ca(NO\textsubscript{3})\textsubscript{2}\cdot 6H\textsubscript{2}O. Furthermore, \(\Delta h\) of Ca(NO\textsubscript{3})\textsubscript{2}\cdot 4H\textsubscript{2}O resemble those from reference.

4. Conclusion
We have described the T-history data of two new inorganic PCMs, namely Ca(NO\textsubscript{3})\textsubscript{2}\cdot 4H\textsubscript{2}O \((T_m \sim 40^\circ C)\) and Co(NO\textsubscript{3})\textsubscript{2}\cdot 6H\textsubscript{2}O \((T_m \sim 50^\circ C)\) based on the temperature vs temperature during solidification process with water as the reference material. The phase transition behavior of Ca(NO\textsubscript{3})\textsubscript{2}\cdot 4H\textsubscript{2}O is gradual, while Co(NO\textsubscript{3})\textsubscript{2}\cdot 6H\textsubscript{2}O show rather sharp phase change. The two material show almost the same supercooling degree about 13\(^\circ\)C. Analysis of the data based on the method proposed by Zhang and its modification by Hong have revealed the values of liquid and solid specific heats, with the average values are about \(c_{p,l} = 2.18\ \text{kJ/kg.K}\) and \(c_{p,s} = 1.47\ \text{kJ/kg.K}\) for Ca(NO\textsubscript{3})\textsubscript{2}\cdot 4H\textsubscript{2}O and \(c_{p,l} = 3.45\ \text{kJ/kg.K}\) and \(c_{p,s} = 2.22\ \text{kJ/kg.K}\) for Co(NO\textsubscript{3})\textsubscript{2}\cdot 6H\textsubscript{2}O. Further analysis of the T-history data by means of a method proposed by Marin have resulted in the temperature-dependent enthalpy, with enthalpy jump around \(\Delta h = 136\ \text{kJ/kg for Ca(NO\textsubscript{3})\textsubscript{2}\cdot 4H\textsubscript{2}O and \Delta h = 131\ \text{kJ/kg for Co(NO\textsubscript{3})\textsubscript{2}\cdot 6H\textsubscript{2}O. The overall results show that these two compound hydrates are potential candidates of inorganic PCM for low-temperature applications.

Acknowledgement
The results in this research are funded by Desentralisasi DIKTI 2016 research program under contract number: 5830/I1.C01/PL/2016.

References
[1] Enerdata 2015 World Energy Trends No.34 (www.enerdata.net)
[2] Asian Development Bank (ADB) papers on Indonesia 2015 Summary of Indonesia's Energy Sector Assesment No. 9
[3] Advances in Thermal Energy Storage Systems, Methods and Applications 2015 Edited by Luisa F. Cabeza, (Woodhead Publishing Copyright Elsevier Ltd.)
[4] Fleischer A S 2015 Thermal Energy Storage Using Phase Change Materials Fundamentals and Applications (Springer)
[5] MSDS Science Lab.com (http://www.sciencelab.com/msds.php?msdsId=9927479)
[6] MSDS Science Lab.com (http://www.sciencelab.com/msds.php?msdsId=9923525)
[7] Sharma S D and Sagara K 2005 Latent heat storage materials and systems: a review International Journal of Green Energy 2 1–56
[8] Angell C A, Tucker J C 1974 Heat capacities and fusion entropies of the tetrahydrates of calcium nitrate, cadmium nitrate, and magnesium acetate, concordance of calorimetric and relaxational ideal glass transition temperatures The journal of physical chemistry 78 278–81
[9] Zhang Y, Yi J, Yi J 1999 A simple method, the t-history method, of determining the heat of fusion, specific heat and thermal conductivity of phase-change materials Meas. Sci. Technol. 10 201–5
[10] Hong H, Kim S K, Kim YS 2004 Accuracy improvement of T-history method for measuring heat of fusion of various materials Int. Journal of Refrigeration 27 360–6
[11] Marin J M, Zalba B, Cabeza L F and Mehling H 2003 Determination of enthalpy–temperature curves of phase change materials with the temperature-history method: improvement to temperature dependent properties Meas. Science and Technology, vol. 14 184–9
[12] Sandnes B and Rekstad J 2006 Supercooling salt hydrates: stored enthalpy as a function of temperature Solar Energy 80 616–25
[13] D'Avignon K and Kummert M 2015 Assessment of t-history method variants to obtain enthalpy-
temperature curves for phase change materials with significant subcooling Journal of Thermal
Science and Engineering Applications 7 041015(1-9)

[14] Silalahi A O, Sutjahja I M, Kurnia D, and Wonorahardjo S Temperature-dependent specific enthalpy of
pcm with supercooling derived from t-history data analysis (submitted to Archives of
Thermodynamics)

[15] Bergman T L, Lavine A S, Incropera F P and Dewitt D P 2011 Fundamentals of Heat and Mass
Transfer 7th edn(New York: Wiley)