

A Comparative Study of Phase Changing Characteristics of Granular Phase Change Materials Using DSC and T-History Methods

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Abstract: In the present article, differential scanning calorimetry (DSC) and a modified T-history method have been used to study the phase changing behavior of granular composites. Further modifications and improvements of the two methods are employed to handle granular materials undergoing phase change over a temperature range. A simple procedure has been advised to obtain accurate results from the DSC measurements based on the estimation of the thermal resistance between the sample and its enclosure. The concept of enthalpy and its relationship with temperature has been employed in the T-history analysis to obtain enthalpy-temperature and apparent heat capacity curves similar to those obtained using DSC. Comparisons have been made between the results of the two methods to highlight the critical issues concerning their applications.

Keywords: Phase change, energy storage, DSC, T-history

1 Introduction

The research of advanced phase change materials (PCM) is a key element for enhancing the performance of latent heat thermal energy storage (LHTES) systems. Progress in this domain is of practical importance for many applications such as solar energy systems, air conditioning, and energy efficient buildings. In recent years, granular phase changing composites obtained by micro or macro-encapsulating the PCM (usually paraffin) in highly porous solid structures with protecting envelopes have been developed using different encapsulation techniques (Zhang et al., 2005). The encapsulation process ensures that the PCM, when in the liquid form, does not leak out of granulates. Implementation of EPCM in LHTES systems offers a number of interesting features as due to direct contact between the heat transfer fluid and

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the EPCM particles. Namely, high amount of energy stored per unit volume, high heat transfer rates due to small particle diameter, and flexibility in applications.

Characterization of the phase changing behavior of granular materials is an important issue for design and optimization of LHTES systems. Storage density and phase change temperatures are very important parameters since they decide the storage system capacity, size, and application range.

Differential scanning calorimeter (DSC) is a popular method for determining the heat of fusion and specific heat of materials. Scanning calorimeters are built with twin experimental sites, one site is for the sample under test and the other is empty or contains a reference material. The heat flow rate to the sample under analysis is measured while the temperature of the instrument is controlled to follow a desired program. In the heat flux type DSC (Herwaarden, 1999), the reference and the sample are both heated by the oven through a thermal resistance (gaseous or a solid circular disk). The temperature difference between the sample and reference pans is measured and directly converted into heat flow rates difference. Characterizing granulate PCMs using DSC requires special care to assure that the thermophysical properties of samples (1–10 mg) are those of the bulk materials used in practical systems. The main difficulty of DSC characterization of granular PCM lies in the heterogeneity and structure of the sample as it significantly affects the details of the heat transfer between the sample pan and PCM material.

Previous studies on the characterization of granular PCMs using DSC have been reported in (Nagano et al., 2004, Zhang et al., 2005). The thermal energy storage density of the composite was shown to have linear relationship with the volume fraction of PCM. The phase changing temperatures obtained from DSC curves were shown to be affected by the porous materials in a more complicated way. However, direct classical analysis of the DSC measurements has been performed and the effects of cooling and heating rates on the results have not been investigated.

The T-history method is an alternative simple and low cost technique for characterization of PCMs. In the original T-history method (Zhang and Jiang, 1999), the PCM sample and a sample with known thermal properties (distilled water) of the same initial homogeneous temperature (T_o) are suddenly subject to ambient air with a room temperature of (T_a) which can be time dependent. Their temperature history upon cooling down is recorded. Comparison of both curves, using a mathematical description of the heat transfer, allows the determination of the heat capacity of the solid and liquid phases and the latent heat of fusion (cp_s , cp_l , ΔH_f) of the PCM sample from the known specific heat (cp_w) of the reference material. However, the original T-history method has a restriction on the accuracy of thermophysical properties owing to the introduction of some invalid physical assumptions. Further improvements on the method related to set-up configuration (Zhang and Jiang,

1999) and determination of the end of latent heat period for materials solidifying without supercooling (Peck et al., 2006), as assumed in the original method, have been suggested. In the T-history studies reported above, the PCM material has a homogeneous structure and phase change occurs at a fixed temperature. Characterization of granular PCMs using the T-history method has not been studied.

The objective of the present study is to perform direct analysis and comparisons on the measurements of phase change characteristics of granular PCMs using DSC and T-history methods, highlight the critical issues related to the analysis of measurement results, and suggest suitable modifications to improve the accuracy of measurements. The results presented and discussed in the present study are obtained using RUBITHERM GR27 EPCM. The composition of the granule is 65% ceramics and 35% paraffin wax by weight with particle diameter between 1-3 mm. The interest in these materials is motivated from their recent applications in energy systems [Nagano et al., 2006, Rady et al., 2009].

2 Characterization of EPCM using DSC

A heat flux type DSC has been used to study the phase changing behavior of the granular composite. A schematic diagram of the heat flux type DSC is shown in Fig. 1. It is a twin instrument comprising sample and reference calorimeters that are essentially identical. The apparatus provide differential heat flow rate measurements between the sample and reference. The sample and reference are surrounded by a sample and reference containers and the containers are placed on the sample and reference plates. The containers and plates are contained in a uniform temperature enclosure. When the furnace is heated at a constant rate, heat flows through the disk to the sample and reference. The present DSC measurements have been carried out using TA Q100 differential scanning calorimeter (DSC) (TA Instruments, Newcastle, DE, USA), equipped with a refrigerated cooling system with cooling temperature up to -90 °C. Nitrogen is used as purge gas at a flow rate of 24 ml/min. Hermetically sealed aluminum pans are used to avoid any moisture loss during the analysis.

DSC curves characterizing melting and solidification of the composite material have been obtained using different values of heating/cooling rates (0.5 °C/min, 5 °C/min, 10 °C/min). In the experiments, EPCM samples are sealed in the aluminum sample pan, equilibrium of the sample is first achieved at 15 °C, then the sample is heated at the required heating rate (0.5, 5.0, 10 °C/min) to 40 °C, equilibrated at 40 °C, cooled to 15 °C at the required cooling rate (0.5, 5.0, 10 °C/min), equilibrated at 15 °C, and then finally heated at the required heating rate to 40 °C. A four axis robotic device automatically loads the sample and reference pan of the DSC. An empty aluminum pan is used as a reference. Data acquisition and analysis are

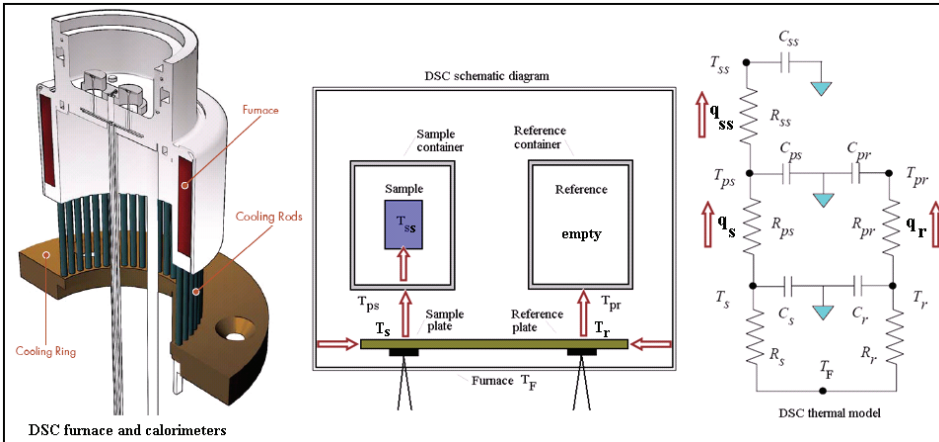


Figure 1: A schematic diagram of a heat flux type DSC and the corresponding DSC thermal model.

performed using Universal Analysis 2000 software (TA Instruments). Export files including the heat flux, temperature, time, and purge flow are exported for further analysis of measurements.

Analysis of DSC measurements is based on the variation of the heat flow signal with temperature. Figure 2 shows a typical variation of DSC heat flow signal during heating of a PCM. Five characteristic temperatures can be determined from the heat flow signal. The onset T_{on} and endset T_{end} temperatures are the temperatures where the DSC heat flow curve separates from the base line. The extrapolated starting temperature T_s and the extrapolated ending temperature T_e are the temperatures at the intersection of the base line and the tangents at the inflection points of the DSC curve on both sides of the peak temperature T_p which is the temperature at the peak of the DSC curve. As shown in Fig. 2, the integrated area between the base line and the DSC curve, QDSC in $J^\circ C/(kg s)$, has the following form:

$$Q_{DSC} = \int (q_{baseline} - q_{DSC\ curve}) \cdot dT \quad (1)$$

The heat of fusion (latent heat of phase change) $\Delta H_f = \Delta Q_{pc}$ in J/kg is obtained from Q_{DSC} as given by Eq. (2). Where β is the rate of imposed temperature increase ($\beta = dT/dt$):

$$\Delta H_f = Q_{pc} = \int (q_{baseline} - q_{DSC\ curve}) \cdot dT \cdot (dt/dT) = (Q_{DSC} \cdot dt/dT) = Q_{DSC}/\beta \quad (2)$$

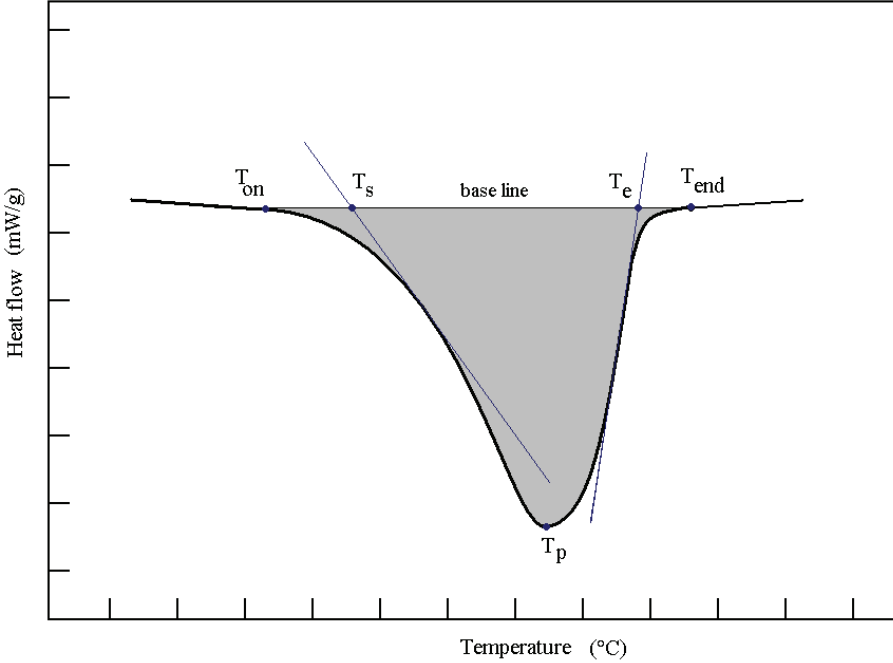


Figure 2: Typical variation of DSC heat flow signal during heating of a PCM.

The above description refers to classical direct analysis of DSC measurements. Actually, knowing the thermal resistances within the DSC is essential to accurately interpret the results from DSC. For this purpose, the calorimeter is analyzed, using systems of ordinary differential equations, as a series of different but uniform temperature objects (heat capacities) connected by appropriate thermal resistances (see Fig. 1) (Dong and Hunt, 2005, Danley, 2003). In this analog circuit T , R , and C are temperatures, thermal resistances and heat capacities. Subscripts s , r , ps , pr , ss indicate sample and reference calorimeters, sample and reference pans and sample. The heat flow rate between the sample calorimeter and pan (\dot{q}_s), the reference calorimeter and its pan (\dot{q}_r), and the sample and its pan (\dot{q}_{ss}) are given by Eq.(3). The specific heat capacity of the empty reference pan c_{pan} is given by Eq. (4).

$$\dot{q}_s = \frac{T_F - T_S}{R_s} - C_s \frac{dT_s}{dt}, \quad \dot{q}_r = \frac{T_F - T_r}{R_r} - C_r \frac{dT_r}{dt}, \quad \dot{q}_{ss} = \dot{q}_s - m_{ps} c_{pan} \frac{dT_{ps}}{dt} \quad (3)$$

$$c_{pan} = \dot{q}_r / (m_{pr} dT_{pr} / dt) \quad (4)$$

Now, the equation for \dot{q}_{ss} which is the objective of measurement is written as:

$$\dot{q}_{ss} = \dot{q}_s - \dot{q}_r \frac{m_{ps} (dT_{ps}/dt)}{m_{pr} (dT_{pr}/dt)} \quad (5)$$

The sample and reference pan temperatures may be obtained using expressions for heat exchange through the contact resistance between sample and reference pans and calorimeters.

$$T_{ps} = T_s - \dot{q}_s R_{ps}, \quad T_{pr} = T_r - \dot{q}_r R_{pr} \quad (6)$$

Application of this analysis requires specific calibration procedure for the DSC instrument. These have been performed following the DSC manufacturer recommendations using an empty DSC pan, sapphire and indium, respectively. The sample and reference calorimeter thermal resistances and heat capacities used in Eq. (3), (R_s, R_r, c_s, c_r), are found using a two-step calibration procedure. In the first step, the empty DSC is heated at constant rate and the second step is a repeat of the first except that sapphire samples without pans are placed on both the sample and reference. The plate to pan contact resistances (R_{ps}, R_{pr}) are obtained from a semi-empirical contact resistance function (Danely, 2003). Three measurements are used to obtain the required temperatures and temperature differences between sample and reference calorimeter, the temperature difference across the sample calorimeter thermal resistance and the temperature at the base of the sensor assembly. Details of this analysis and calibration can be found elsewhere (Danely, 2003, 2004).

The above calibration and analysis eliminates smearing effects induced by the thermal resistance and capacitances of the calorimeter and its pans. Referring to Fig. 1, there remains the analysis of heat flow path between the sample pan (T_{ps}) and the sample material (T_{ss}) across the heat transfer resistance R_{ss} . In fact, the output signals from the DSC are the values of sample pan temperature (T_{ps}), heat flow between the sample and its pan \dot{q}_{ss} , and time (t). This analysis depends on the thermal capacity of the sample (c_{ss}). The heat transfer resistance R_{ss} is a critical element and sample dependent. For the present analysis, it is function of the sample structure and the contact surface between the sample material and the sample pan. The heat balance equation for heat transfer between the sample pan and sample material is as follows:

$$\dot{q}_{ss} = C_{ss} (dT_{ss}/dt) = (T_{ps} - T_{ss})/R_{ss} \quad (7)$$

Due to high thermal conductivity of the sample pan metal, it is assumed that the envelope of the sample is at the sample plate temperature that is programmed to be a linear function $T_{ps} = \beta t + T_o$. Where T_o is the initial equilibrium temperature. In

the limit of very small values of cooling/heating rate $\beta \rightarrow 0$, the values of T_{ps} and T_{ss} are approximately equal ($T_{ps} = T_{ss} = T_{so}$). As due to the very small volume of sample container, the value of thermal resistance R_{ss} can be considered as purely conductive. Under the assumption of small variation of thermal conductivity with temperature, the value of R_{ss} can be considered constant for a given sample. Considering the peak temperatures (T_p) obtained at different values of cooling rates (see Fig. 3), Equation (7) can be rearranged to calculate the thermal resistance R_{ss} as given by Eq.(8). Where the subscripts 1, 2, and i refer to different values of cooling rates.

$$R_{ss} = (T_{ps} - T_{so}/\dot{q}_{ss})_1 = (T_{ps} - T_{so}/\dot{q}_{ss})_2 = (T_{ps} - T_{so}/\dot{q}_{ss})_i \quad (8)$$

For the above approach to be correct, since R_{ss} is constant, the peak points of DSC curve obtained at different values of cooling rates (different values of β) should form a straight line intersecting the $\dot{q}_{ss}=0$ line at the correct sample temperature T_{so} corresponding to the measured peak temperature. The estimation of thermal resistance between the sample material and its pan allows correcting the abscissa of DSC curve and drawing the variation of heat flow to the sample as function of actual sample temperature using the relation: $T_{ss} = T_{ps} - \dot{q}_{ss}R_{ss}$. Figure 3 demonstrates the correctness of the above approach to estimate the thermal resistance R_{ss} . It can be observed that the curve peaks obtained using different cooling rates are located on a single straight line. This is true also for the case of heating. However, the thermal resistances during melting and solidification of the sample have different values.

The variation of sample temperature with plate temperature for different values of heat flow and corrections of the DSC curve for heating and cooling are shown in Fig. 4. It can be observed that the difference between sample plate temperature and sample material temperature increases with the increase of cooling rate. The difference is marginal outside the phase change regions and becomes important during the phase change process. Corrections in terms of the DSC heat flow variation with temperature are significant. It should be noted that the amount of phase change latent heat remains the same before and after correction. However, the functional dependence of latent heat evolution on temperature is significantly modified by the instrument thermal resistance effects.

The above methodology of measurements and corrections allows separating the kinetics of phase transformation from the kinetics of the instrument. As shown in Fig. 4, the shape of the corrected DSC curve depends significantly on the heating/cooling rate. The characteristic temperatures evaluated from the DSC curve thus differ considerably. In the melting process, there is an enlarged temperature range for latent heat evolution as compared to the solidification process at the same rate of heating or cooling. This enlargement increases with the increase of heating

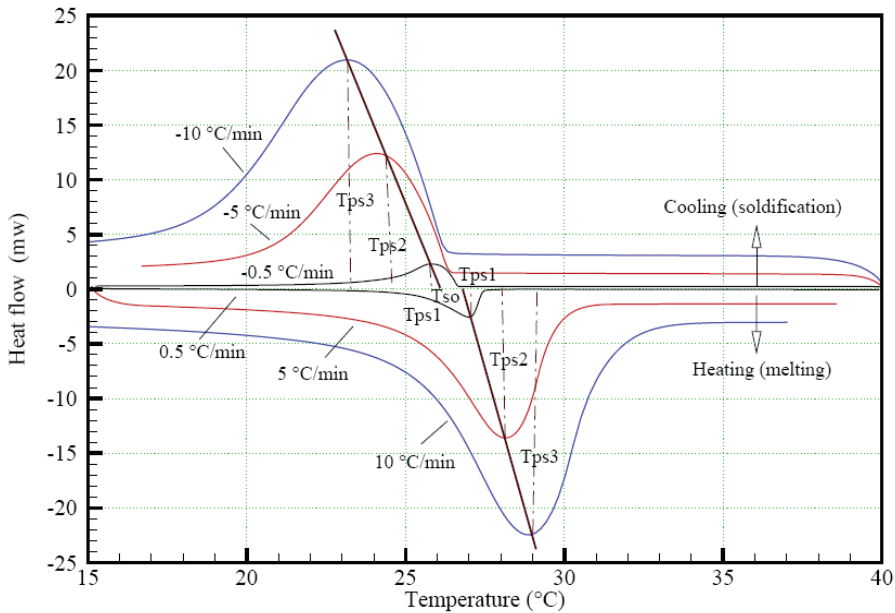


Figure 3: Estimation of the thermal resistance between the sample container and sample material.

rate.

3 Characterization of EPCM using the T-History method

The experimental system set-up built to realize the T-history measurements in the present study (see Fig. 5) consists of test glass tubes of 150 mm height and 8 mm inside diameter and glass thickness of 1 mm ; hot water bath for heating the sample and the reference to initial temperature; insulated cool down chamber for subsequent cooling of the samples ; type T thermocouples of 0.1 mm diameter to measure the temperature of the PCM, water and ambient; and an HP data acquisition equipment connected to a computer for time recording of the data into files for further treatment. The PCM sample and distilled water are contained in two identical vertical tubes. Since the Biot number ($Bi = hR/2k$, where R is the tube radius, k is the thermal conductivity of PCM and h the natural convection heat transfer coefficient of air outside tube) is less than 0.1, the temperature distribution in the sample can be regarded as uniform and the lumped capacitance method can be used for heat transfer analysis. Moreover, if the ratio of the length to diameter of the tube is larger than 10, it is justifiable to assume that the heat transfer is approximately

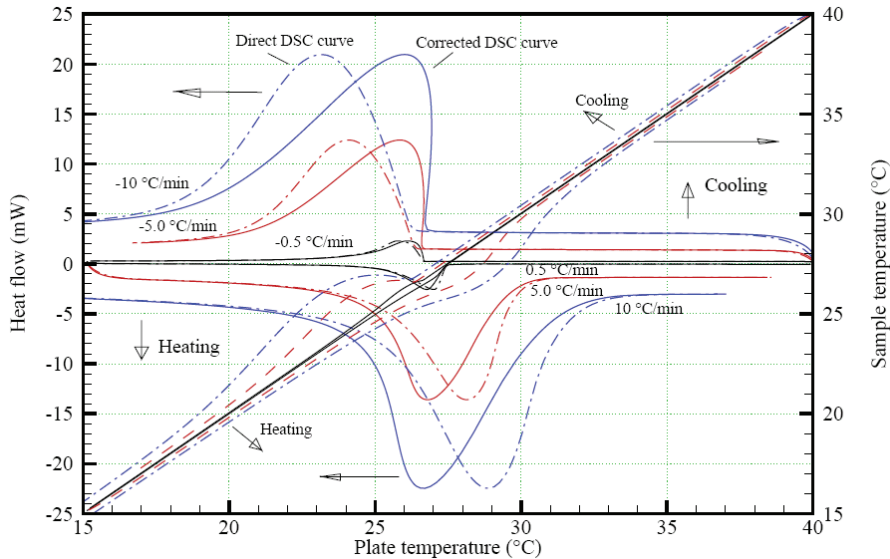


Figure 4: Variation of sample temperature with plate temperature and correction of the DSC curve.

one dimensional and neglect the axial conduction heat transfer along the sample material. Three thermocouples have been inserted at different heights in each tube to verify the vertical homogeneity of temperature.

A typical temperature history curve obtained using GR27 is shown in Fig. 6. The original analysis of the T-history method is limited by the assumption of constant temperature independent specific heats and the difficulty of determining the limits of solid and liquid phases that may reduce the accuracy of calculation. Rady et al. (2008) proposed the use of inflection points of the curve representing rate of variation of normalized temperature difference between the PCM and ambient (θ) to mark the beginning and end of phase change process and discussed the difficulties related to this determination for materials undergoing phase change over a temperature range.

It is therefore more appropriate, instead of using the concept of variation of temperature with time, to use the concept of enthalpy and its relationship with temperature (Marín et al., 2003). The method is based on considering small equal variation of temperature ΔT_i for the PCM sample and water and calculating the corresponding time intervals Δt_p and Δt_w , respectively. Energy balances of the PCM sample (in terms of PCM enthalpy) of mass m_p and water sample of mass m_w for these time

intervals are given by Eqs. (9) and (10).

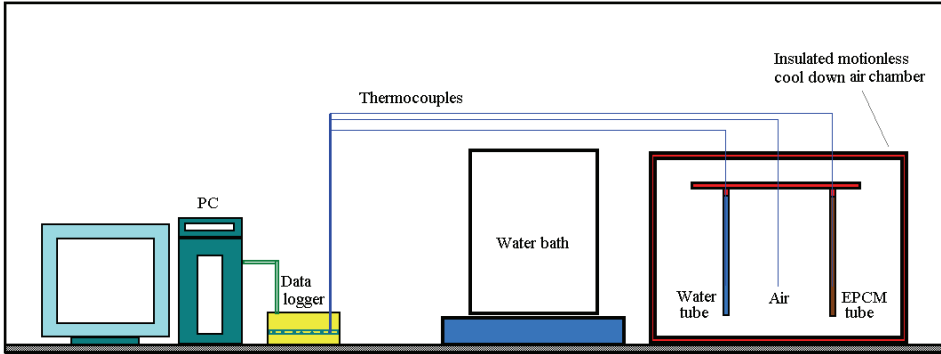


Figure 5: Experimental set-up for the T-History method.

In these equations: h is the convection heat transfer coefficient, A_t is the test tube surface area and subscripts w , t , and p refer to the water sample, tube, and PCM sample, respectively.

$$m_t c_{pt} (T_i - T_{i+1}) + m_p \Delta H_p(T_i) = h A_t \int_{t_p}^{t_p + \Delta t_p} (T - T_a) dt = h A_t A_{pi} \quad (9)$$

$$(m_t c_{pt} + m_w c_{pw}) (T_i - T_{i+1}) = h A_t \int_{t_w}^{t_w + \Delta t_w} (T - T_a) dt = h A_t A_{wi} \quad (10)$$

From which, the enthalpy change of the PCM in the interval ΔT_i is obtained as:

$$\Delta H_p(T_i) = \frac{(m_t c_{pt} + m_w c_{pw})}{m_p} \frac{A_{pi}}{A_{wi}} \Delta T_i - \frac{m_t}{m_p} c_{pt} \Delta T_i \quad (11)$$

Where, T_i is the average temperature during the time interval. A_{pi} and A_{wi} refer to the temperature-time integration values for PCM and water during the time interval. Assuming a constant value of H_{po} as reference, the enthalpy-temperature curve can be determined as the sum of the enthalpy intervals, Eq.(12). The specific heat values of the PCM at each point can be calculated as the slope of the curve at the point selected, $c_p = dH/dT$.

$$H_p(T) = H_{po} + \sum_{i=1}^N \Delta H_p(T_i) \quad (12)$$

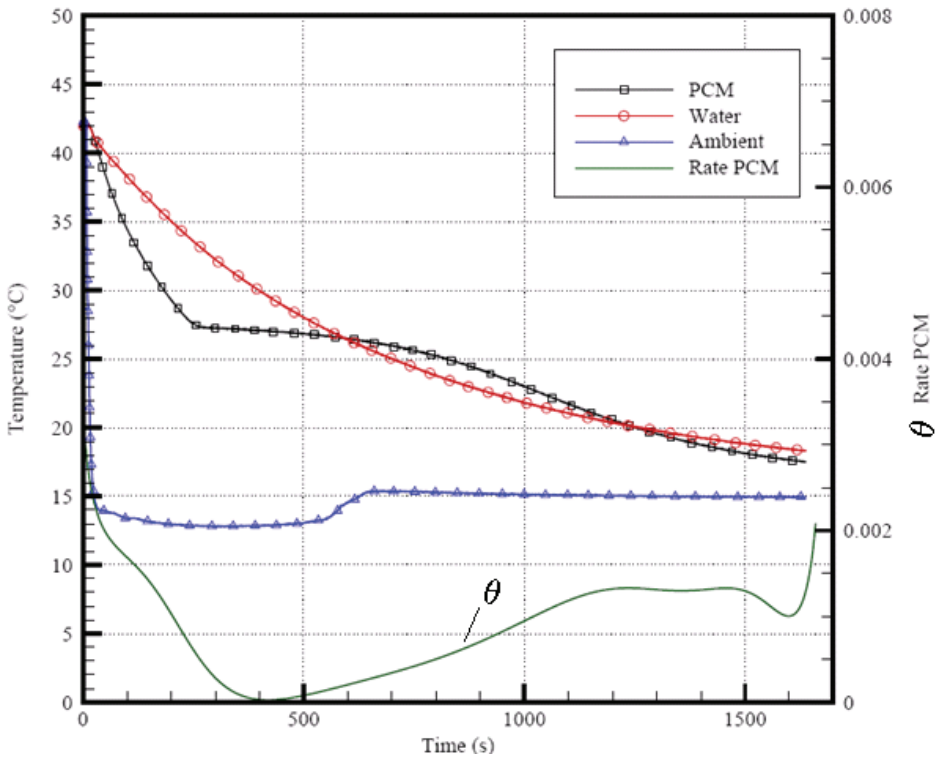


Figure 6: Temperature-history curve during cooling for GR27, sample (1-3 mm particles).

Using the enthalpy formulation in the analysis of the T-history method, the representation of the values of $\Delta H_p(T_i)$ versus time results in a curve very similar to that obtained by a DSC, see Fig. 7. The enthalpy–temperature curves are obtained using a computer program that implements the method explained above. One can notice that the resulting ΔH_p and c_{pa} curves are similar in nature to the curves obtained from DSC measurements. The beginning and end of phase change can be identified easily using the apparent heat capacity curve that is similar to the heat flux curve in DSC measurements. The separation points of the apparent heat capacity curve from the basic curve in the solid and liquid regions are easily distinguished from Fig. 7. Figure 7 clearly demonstrates the errors that might be obtained in the calculation of cp_s and cp_l using inaccurate temperature values for the beginning and end of phase change.

4 Comparisons and Discussion

The interest in the enthalpy formulation of the T-history measurements is the characterization of enthalpy function of the phase change material that can be easily implemented in the design and optimization of energy storage systems and is an important parameter for accurate numerical simulation of the storage unit performance. The enthalpy change (storage density) within the phase transition temperature range can be also obtained from the integral analysis of DSC curves (ΔH_{pc}). Taking the enthalpy $H_o = 0$ J/kg at a reference temperature (sample temperature at the beginning of the cooling/heating cycles), the enthalpy as function of temperature $H(T)$ can be obtained as :

$$H(T) = H_o + \int_{t_o}^t q_{DSC\ Curve} dt \quad (13)$$

Figure 8 shows the enthalpy –temperature curve obtained from the integral analysis of DSC curve that can be compared with Fig. 7 obtained using the modified T-history method.

Table 1 summarizes GR27 phase change characteristics obtained using DSC at low cooling rates (minimum errors and corrections of DSC measurements). It should be noted that the latent heat of solidification or melting ($\Delta H_f = \Delta Q_{pc}$) does not depend on the DSC heating/cooling rate. The equality of latent heat of melting and solidification (within 5%) demonstrates the quantitative accuracy of the present measurements. Results obtained using the T-history method are listed in Tab. 2. The value of ΔH_f obtained using the original method is close to values obtained by using DSC (Rady et al., 2008). It should be noted that, in the original T-history method (based on temperature-time analysis) the values of specific heats are assumed constant. Another point that should be mentioned concerns the values of ΔH_{pc} obtained using the enthalpy temperature analysis of the T-history method. In fact, this value is the difference in enthalpy of GR27 at $T=29$ °C and 21 °C. The difference between ΔH_{pc} and ΔH_f is due to the variation of specific heat with temperature that is not accounted for in the original T-history method. In fact, ΔH_{pc} represents the overall storage capacity of GR27 in the temperature range of 21 to 29 °C. On the other hand the value of ΔH_f obtained from either DSC analysis or original T-history method represents the latent heat of fusion.

The evolution of latent heat using DSC is shown to be sensitive to the cooling and heating rates. This can be explained by the fact that solute distribution within the phases depends on several factors including nucleation kinetics, diffusion rate of species and chemical activities. High heating or cooling rate would promote the

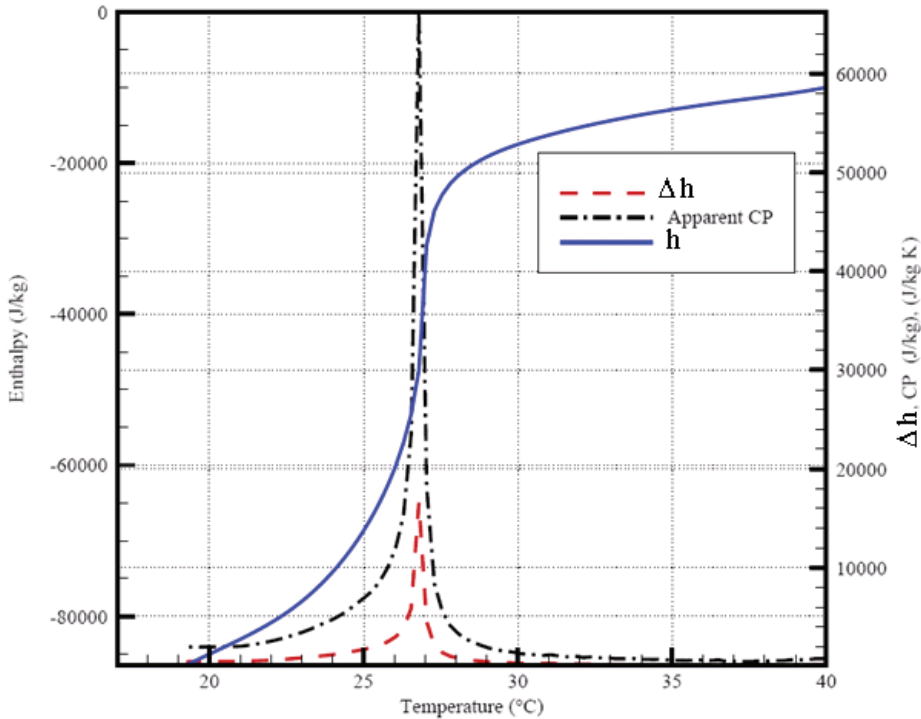


Figure 7: Enthalpy and apparent specific heat variation with temperature for GR27 sample.

development of thermal and chemical non-equilibrium effects inside the sample material during melting and solidification. DSC results at very low scanning rate are very close to the equilibrium conditions. As compared to the freezing process, an enlarged extrapolated end temperature is observed in the melting process. This can be explained as due to the lower heat conductivity and poor heat convection properties in the solid state compared to the liquid phase. Also, inside limited porous space, volume increment of melting PCM leads to pressure increment. According to Clapeyron equation, volume and pressure increments lead to elevation of melting temperature.

5 Conclusion

Differential scanning calorimetry (DSC) and a modified T-history method have been used to study the phase changing behavior of granular composites. Direct

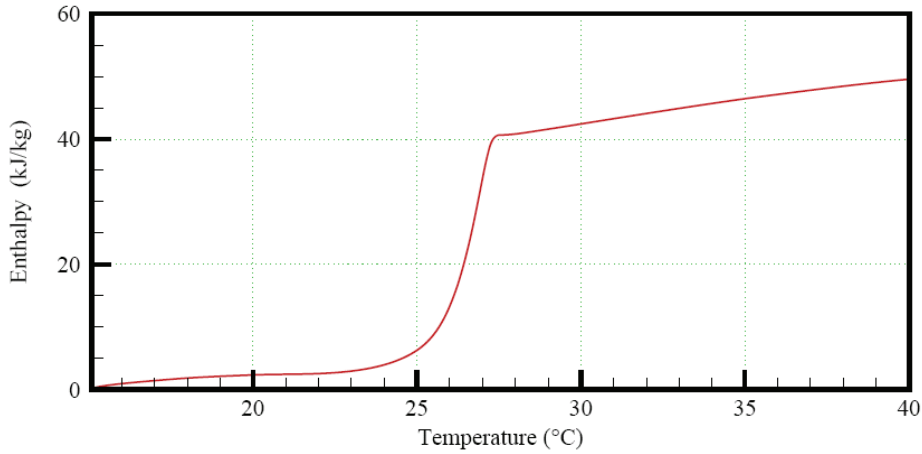


Figure 8: Enthalpy variation with temperature for GR27 at 0.5 °C/min heating rate.

Table 1: GR27 characteristics using DSC.

Rate	ΔH_f (kJ/kg)	T_{on} (°C)	T_{end} (°C)
(-0.5 °C/min)	41.17	27.50	19.16
(+0.5 °C/min)	43.16	20.55	28.33

Table 2: GR27 characteristics, T-history method.

	T_{m1} (°C)	T_{m2} (°C)	c_{ps} (J/kg.K)
Original	26.95	20.63	2225
Modified	29.00	21.00	2044
	c_{pl} (J/kg.K)	ΔH_f (kJ/kg)	ΔH_{pc} (kJ/kg)
Original	2087	49.30	
Modified	1921		64.85

utilization of the measured DSC curves could result in an inexact representation of the sample enthalpy change and incorrect results of mathematical modeling during design and optimization of LHTES systems. A simple procedure has been advised to obtain accurate results from the DSC measurements. The corrections are found to be significant at high values of heating/cooling rates. High DSC heating or cooling rates promote the development of thermal and chemical non-equilibrium effects inside the sample material and result in an increase in the temperature range for melting and solidification. The latent heat of phase change ($\Delta H_f = \Delta Q_{pc}$) is

found to be essentially independent on the DSC heating/cooling rate.

Further modifications and improvements of the T-history method are employed to handle granular materials undergoing phase change over a temperature range. The accuracy of the original T-history method is shown to be limited by the assumption of constant temperature independent specific heats and the difficulty of determining the limits of solid and liquid phases. The concept of enthalpy and its relationship with temperature has been employed in the analysis to overcome these difficulties. Enthalpy-temperature and apparent heat capacity curves similar to those obtained using DSC have been developed for the granular EPCM. These characteristic curves are useful for accurate design, modeling, and optimization of LHTES systems. Comparisons have been made between the results of the two methods to highlight the critical issues concerning their applications and interpretation of measurement results.

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