

Characterization of metals and salts-based thermal energy storage materials using energy balance method

Swati Agarwala | Narayan K. Prabhu 

Department of Metallurgical and Materials Engineering, National Institute of Technology Karnataka, Surathkal, Karnataka, India

Correspondence

Narayan K. Prabhu, Department of Metallurgical and Materials Engineering, National Institute of Technology Karnataka, Surathkal, Karnataka 575025, India.
Email: prabhukn_2002@yahoo.co.in

Abstract

Thermal energy storage technologies minimize the imbalance between energy production and demand. In this context, latent heat storage materials are of great importance as they have a higher density of energy storage as compared with the sensible heat storage materials. The present study involves the characterization of energy storage materials using an energy balance cooling curve analysis method. The method estimates the convective heat transfer coefficient in the solidification range to characterize the phase change materials for applications in energy storage. The method is more beneficial than the Computer Aided Cooling Curve analysis methods as it eliminates baseline calculations and the associated fitting errors. Metals (Sn) and salts (KNO_3 and NaNO_3) were used in the present work. Phase change characteristics like the rate of cooling, liquidus and solidus temperatures, time for solidification, and enthalpy of phase change were estimated for both metals and salts. It was observed that the energy balance cooling curve analysis method worked very well for metals but not well suited for low conductivity salts. Salts could not be characterized since the thermal gradient existing within the salt sample was not considered in this method.

KEYWORDS

computer aided cooling curve analysis (CACCA) method, energy balance, energy storage, solidification, thermal analysis

1 | INTRODUCTION

The increase in the level of greenhouse gases and fuel cost have made it very important to look for new technologies, which can effectively utilize the renewable sources of energy like solar energy. The core of the problem lies in the need to store the excess solar energy, which will be otherwise wasted. This will reduce the gap between energy production and consumption. Energy storage will improve the efficiency and reliability of the energy systems and also reduce the wastage of energy. It will basically make the system more cost-effective.

To store the thermal energy, latent heat thermal energy storage system (LHTES) using phase change materials (PCM) are used as they have higher energy storage densities. When compared with sensible heat thermal energy storage systems the quantity of the material needed is much less in LHTES. PCM stores the heat of fusion during phase transformations, which occurs at a constant temperature or in small temperature interval, which corresponds to the phase change temperature of the PCM.

There are various types of PCMs being used for energy storage applications. They can basically be categorized as organics, inorganics, and metals. Organic PCMs are suitable for low-temperature applications making them unfit for energy storage in solar plants. They have low thermal conductivity causing the longer charging and discharging cycles. The varieties chosen in this study offer materials spread over a wide range of temperature and are suitable for high-temperature thermal energy storage applications, such as solar plants by virtue of their higher melting points. They can be used for temperature ranges up to 900°C. Inorganic salts and metals are chosen as they have a higher latent heat of fusion and thermal conductivity as compared to their organic counterparts.¹

To use the PCM for TES systems, a reliable and accurate data of the solidification parameters, transition temperatures, and enthalpies of these materials is a basic requirement.

Thermal analysis is a suitable technique used for the characterization of the PCMs. In this technique, the temperature dependent properties of the sample are measured. Depending on the property being measured, thermal analysis are of various types.

The method that is generally used for the characterization of PCMs to calculate the phase change enthalpy and the solidification parameters in most of the research is Differential Scanning Calorimetry (DSC). However, the utilization of this technique has reduced because of the associated flaws like the small sample size used in the technique (30-50 mg). This is a limitation only in the case of inhomogeneous materials where the property is not uniformly distributed. In this case, the results obtained from DSC reflects the properties of the given sample and does not represent the material as a whole as the sample size used is too small. Another drawback is the overestimation of the supercooling because of the small sample size. The loss of latent heat because of this overestimation is not taken into account in the DSC measurements. Therefore, the measured enthalpy is lower than the original value. The DSC results are very much affected by the heating and cooling rates used, which develops the inaccuracy in the measured data. These flaws limits the usage of DSC and bring out the need for alternate characterization technique.^{2,3}

Many researchers have used alternate calorimetric method for PCM characterization, which is T history method which overcomes the limitation of small size, unlike DSC. This method incorporates

the use of reference material. In this method, the temperature history variation over a temperature range between the reference and the PCM is analyzed and solidification parameters are calculated. This method was successfully used in many researches mainly focusing on organics (low-temperature PCMs). However, its usage in high-temperature applications was limited. The choice of the reference materials for high-temperature application was the main concern and that too with L/D ratio greater than 16 made this method inappropriate for high-temperature studies. Even corrosion at high temperature was a challenge.^{3,4}

Because of the limitations of the above techniques, a new method called computer-aided cooling curve analysis (CACCA) has gained attention. The basis of the CACCA method lies in the analysis of the cooling curve or the thermal history of the solidifying sample. It can provide information about the composition of the alloy, the phase change enthalpy, fraction solidified, the amounts and types of phases that solidify, and even dendrite coherency.⁵

This method is extensively used for melt quality control in the foundry. It can also be used to assess the solidification parameters, such as cooling rate, start and end of solidification points, solidification time, and the latent heat. For this reason, researchers have taken interest in finding out new methods to analyze the cooling curves of metals and alloys during their solidification giving rise to what is called as CACCA.⁶

The methods using CACCA as the basis differ in terms of the experimental devices used and in the careful investigation of the results.⁵

Newtonian and Fourier methods on the basis of CACCA technique have gained importance with time. Both methods could characterize PCMs only during the cooling cycle. The usage of these methods in the heating phase was limited. The Newtonian technique was on the basis of the thermal history analysis of the material using a single thermocouple at the center. It involved a linear fitting of the liquidus and solidus points. However, the thermal gradient of the sample was not considered. This limitation was taken care of in the Fourier technique by incorporating two thermocouples. Both the techniques involved the calculation of zero curve, also called as the baseline, which included the linear fitting. In these methods, the results obtained were affected by the fitting techniques used for baseline calculations, which could be the source of error in the measured values.

In the present work, quantitative characterization of the PCMs on the basis of the simple energy conservation equations that did not depend on the baseline curves has been used. This method takes into account the thermal history of the sample and the mold used in the cooling process, which is used to experimentally determine the phase change enthalpy of the used samples.⁶

The experimental setup is very similar to the Newtonian technique using only one thermocouple at the center of the sample. The difference is that this method estimates the convective heat transfer coefficient in the solidification range without any usage of baseline calculations for the characterization. The temperature variation in the sample is recorded during the cooling cycle. This temperature history will depict the cooling process of the sample over a temperature range inclusive of the phase transformations during that period. The cooling rate curve or the first derivative curve is an important aspect here. The phase change in the sample is reflected as a sudden change in the slope of the curve, which makes it a perfect tool to accurately estimate the phase transition temperatures. The decrease in slope on the first derivative curve is reflective of the cooling process of the sample whereas an increase in slope reflects the start of the phase transformation. The cooling rate approaches zero during the phase transformation period.

The thermal history, cooling rate, solidification time, phase transition temperature, liquidus and solidus points, and latent heat of the material can be determined using this method. Both

salts and metals were used in this research to assess the suitability of this method for PCM characterization.

2 | MATERIALS AND METHODS

In this work, the cooling and solidification process of the PCM samples have been analyzed. The samples used are tin (Sn) as a pure metal and potassium nitrate (KNO_3) and sodium nitrate (NaNO_3) as salts. The mass and the specific heat capacity of the samples and the mold used in the present investigation are tabulated in Table 1.

These samples of known weight were taken in a stainless-steel container of 0.055 m diameter and 0.075 m height. They were then heated in the furnace above their melting point to obtain the molten sample. The schematic representation of the simplified energy balance experimental setup is shown in Figure 1.

The experiment's photograph, which includes the heating furnace, sample container, and the data acquisition system is shown in Figure 2.

The top and bottom surfaces of the setup were thermally insulated. The cooling process of these samples was then analyzed. To record the thermal history of the cooling sample, calibrated K-type 1 mm Inconel sheath thermocouple (T1) was used at the center of the molten sample. The scanning frequency selected for the temperature data acquisition was 2 Hz. NI USB 9213 data acquisition setup was used for acquiring temperature data. The experimentally obtained cooling curves were further analyzed and processed to determine the solidification parameters of the sample. The primary information of the phase change temperature was obtained from the cooling curves whereas the phase change temperatures, solidification time, liquidus and solidus points, and the cooling rates were obtained from the cooling rate curves, which is nothing but the first derivative curve of the cooling curve.

In this method, we assume that the sample and the container start cooling at the same time and with the same cooling rate.⁶ The energy balance equation with no phase change can be written as equation (1).

$$[(mCp)_s + (mCp)_{Mo}] \frac{dT}{dt} = -hA(T_s - T_o) \quad (1)$$

$$h = \frac{[(mCp)_s + (mCp)_{Mo}] \frac{dT}{dt}}{-A(T_s - T_o)} \quad (2)$$

where m is the mass (kg), Cp is the specific heat capacity (J/kgK), dT/dt is the cooling rate ($^{\circ}\text{C/s}$), A is the area of heat exchange (m^2), T_m is the thermocouple temperature ($^{\circ}\text{C}$), and T_o is the ambient

TABLE 1 Mass and specific heat capacity values of the samples.

Properties	Sn	KNO_3	NaNO_3	Stainless-steel mold
Mass, kg	0.5	0.214	0.227	0.039
Average Specific heat capacity, kJ/kg K	0.253 ⁶	1.20 ⁷	1.11 ⁸	0.502 ⁹

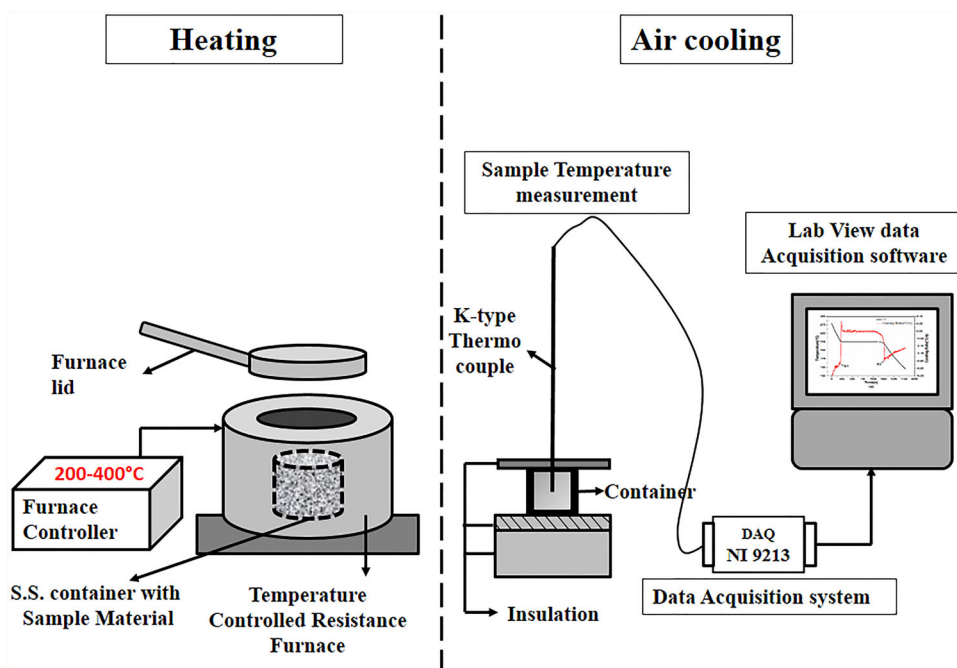


FIGURE 1 Schematic representation of the simplified energy balance experimental setup [Color figure can be viewed at wileyonlinelibrary.com]

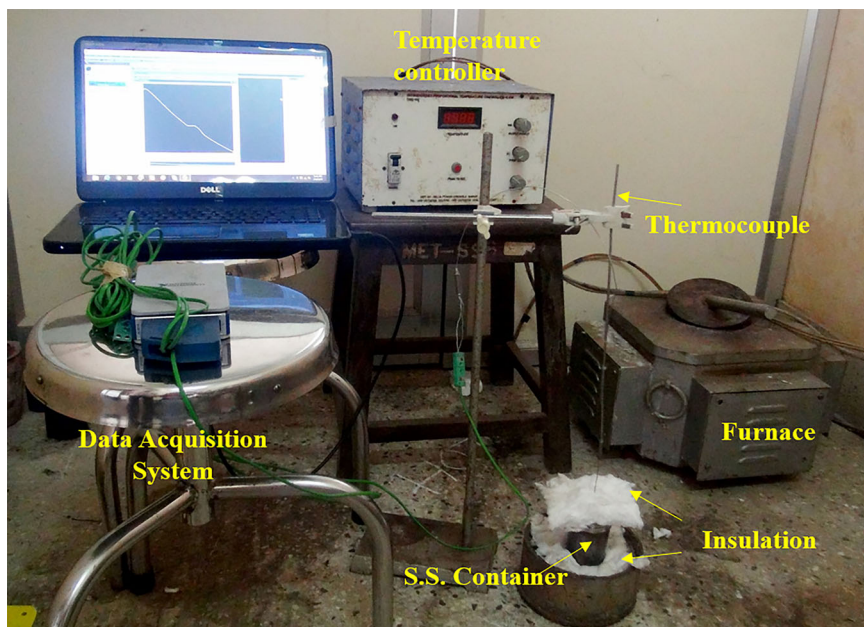


FIGURE 2 Photograph of the experimental setup [Color figure can be viewed at wileyonlinelibrary.com]

temperature ($^{\circ}\text{C}$). The subscript S refers to sample and M_o refers to the mold. Using this equation (2), the heat transfer coefficient (h) was calculated for the sample during the no phase change interval.

The mass and specific heat capacity of the sample and mold, the ambient temperature, and the experimentally obtained data, such as the cooling rate of the sample and the cooling temperature data of the sample were used in the above calculations to determine h as a function of temperature. This calculated heat transfer coefficient was fitted with the third order polynomial equation to estimate the “ h ” values during the phase transformation period. The estimated “ h ” values were then used in the energy balance equation during the phase change to calculate the phase change enthalpy released at every time step (Q_{inst}) as per equations (3,4). The latent heat of the sample (H_f) was calculated using equation (5).

$$[(mCp)_S + (mCp)_{M_o}] \frac{dT}{dt} - m_S H_f \frac{dF_s}{dt} = -hA(T_S - T_O) \quad (3)$$

$$Q_{\text{inst}} = m_S H_f \frac{dF_s}{dt} = -hA(T_S - T_O) - [(mCp)_S + (mCp)_{M_o}] \frac{dT}{dt} \quad (4)$$

$$H_f = \frac{Q_{\text{total}}}{m_S} = \frac{1}{m_S} \int_{t_l}^{t_s} Q_{\text{inst}} dt \quad (5)$$

Where, F_s is the fraction solidified, Q_{total} is the net heat released by the sample (J), and t_l and t_s refer to the liquidus and solidus points, respectively. The algorithmic structure of the CACCA program used in this work has been shown in Figure 3.

3 | RESULTS

The solidification parameters of Sn, KNO_3 , and NaNO_3 were obtained using the simplified energy conservation equation in the CACCA analysis. The path of solidification for Sn and KNO_3 samples in the stainless-steel containers were obtained. The basic information obtained from the solidification path is the phase transition temperature. The first derivative curves were superimposed on the temperature curves. These cooling curves and their first derivative curves for Sn, KNO_3 , and NaNO_3 obtained are represented in the Figures 4A, 5A, and 6A, respectively. The liquidus and solidus points were marked as E1 and E2, respectively on the first derivative curves.

The variation of heat transfer coefficient with respect to temperature, in the no phase transformation region, is represented in Figure 4B. The estimated heat transfer coefficient for the phase change region obtained after the polynomial fitting of the third order in the case of Sn is also shown in the same figure.

The variation of heat transfer coefficient with respect to temperature in the no phase change region for KNO_3 and NaNO_3 are represented in Figures 5B and 6B, respectively.

4 | DISCUSSION

As per the thermal history and the cooling rate curves of Sn shown in the Figure 4A, the phase change of the metal begins at 214.8 seconds and at 226.3°C temperature. This point is known as

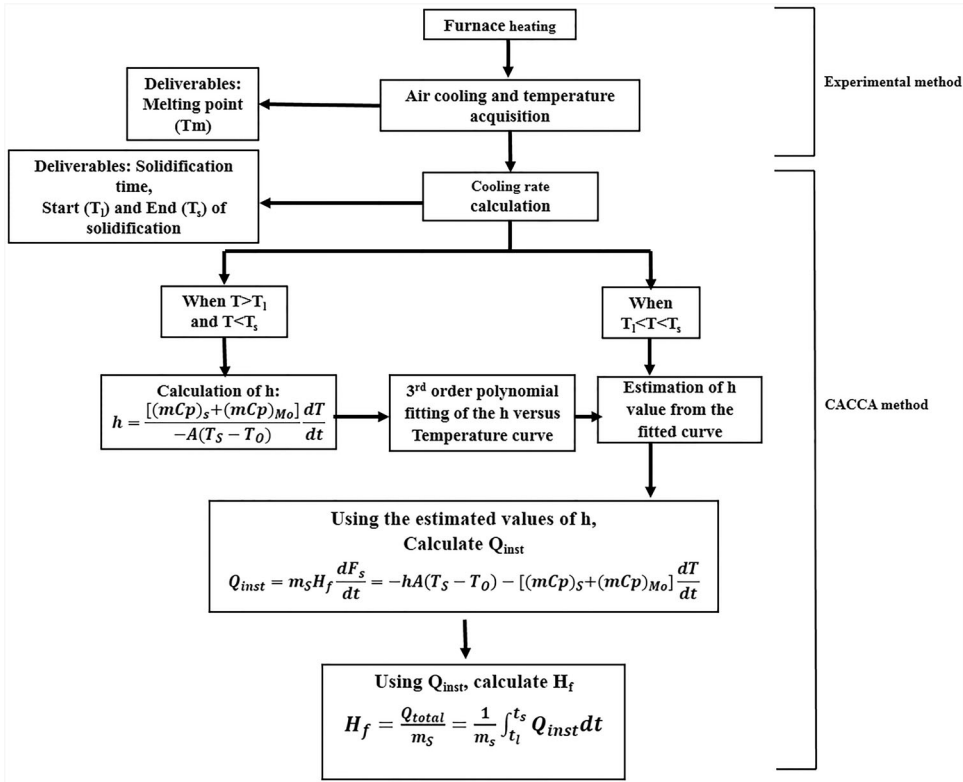


FIGURE 3 Algorithm structure of the CACCA program used in this work. CACCA, computer-aided cooling curve analysis

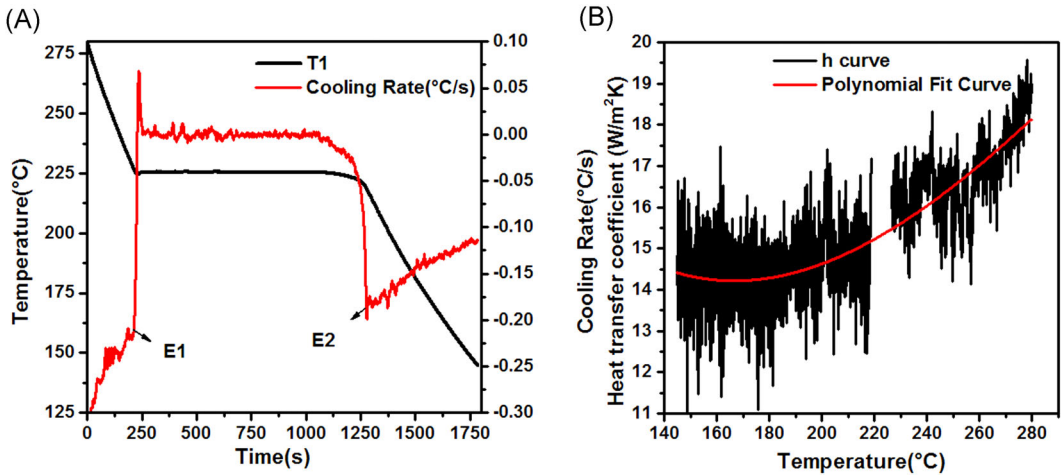


FIGURE 4 A, Cooling curve and the 1st derivative curve of Sn. B, The variation of heat transfer coefficient with respect to a temperature of Sn [Color figure can be viewed at wileyonlinelibrary.com]

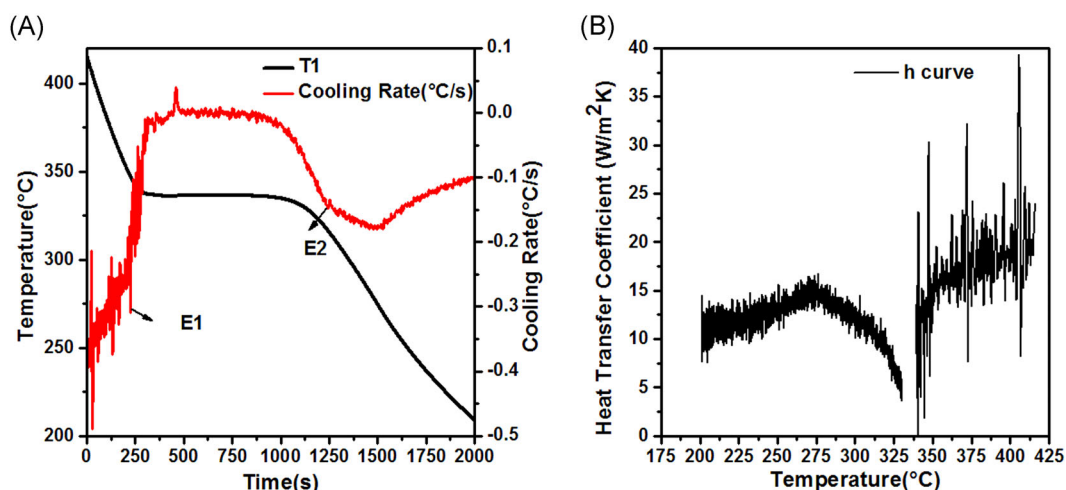


FIGURE 5 A, Cooling curve and the first derivative curve of KNO_3 . B, The variation of heat transfer coefficient with respect to the temperature of KNO_3 [Color figure can be viewed at wileyonlinelibrary.com]

the liquidus point. The end of phase change was observed at 1276.2 seconds at a temperature of 218.8°C. This point marks the end of solidification and is referred to as the solidus point. The melting point of Sn is at 225.5°C, which is the phase change temperature for Sn. The time taken for complete solidification was about 1061.4 seconds.

Similarly in the case of salts (KNO_3) as shown in Figure 5A, the phase change temperature was found to be 336°C. The liquidus point, from the cooling rate curves, was found to be 276 seconds and was recorded at a temperature of 339.5°C. The solidus point of the salt was found to be 1114 seconds and was recorded at a temperature of 330.3°C. KNO_3 took about 838 seconds for its complete solidification. The onset and the end of solidification were evident by a sudden change of slope in the cooling rate curve.

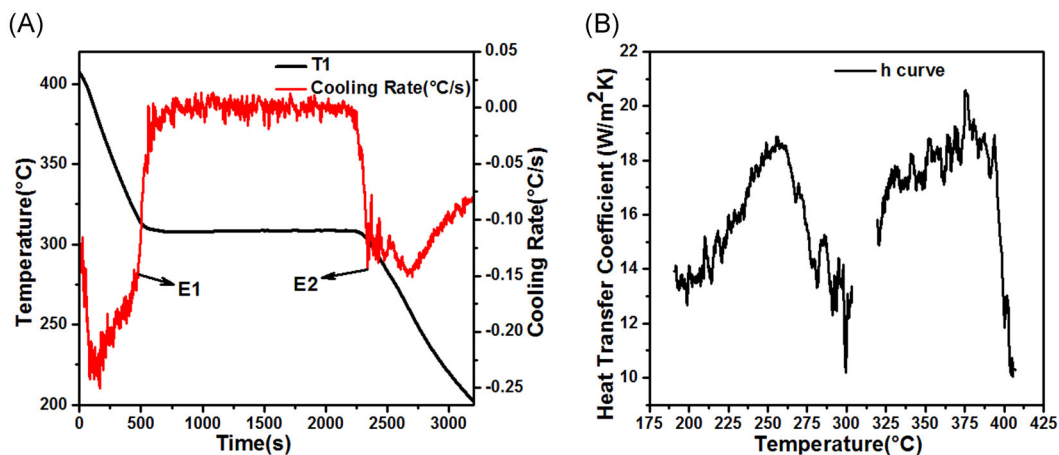


FIGURE 6 A, Cooling curve and the first derivative curve of NaNO_3 . B, The variation of heat transfer coefficient with respect to the temperature of NaNO_3 [Color figure can be viewed at wileyonlinelibrary.com]

TABLE 2 Phase change characteristics of Sn, KNO₃, and NaNO₃

Parameters	Sn	KNO ₃	NaNO ₃
Melting point	225.6°C	336°C	308.25°C
Solidification time	1061.4 s	838 s	1865 s
E ₁ : Liquidus point	226.3°C, 214.8 s	339.5°C, 276 s	316.4°C, 475.5 s
E ₂ : Solidus point	218.8°C, 1276.2 s	330.3°C, 1114 s	302.5°C, 2340.5 s

In the case of NaNO₃ as shown in Figure 6A, the phase change temperature was measured to be 308.2°C. The start and end of solidification were found to be at 475.5 seconds and 2340.5 seconds, respectively. The recorded temperatures at those points were 316.4°C and 302.5°C, respectively. The total time taken for solidification in case of NaNO₃ was about 1865s. The phase change characteristics of metal, as well as salts used in this work, are tabulated in Table 2.

The latent heat values of Sn calculated using this method was 59.7 kJ/kg, which is in agreement with the reported literature data of 60 kJ/kg.⁶ However, the estimation of *h* values during the phase change period in the case of salts (KNO₃ and NaNO₃) was found to be cumbersome. The *h* values as a function of temperature, in no phase change region (in the case of salts), did not follow the fitting trend of polynomial third order as shown in Figures 5B and 6B. Thus, the “*h*” values in the region of phase change could not be estimated correctly. The latent heat values calculated using the third order polynomial fitting was approximately 87% higher than the reported literature values in case of KNO₃, whereas for NaNO₃, the measured phase change enthalpy was 107% higher than the reported literature data.

The values of heat transfer coefficient in the phase change region could not be correctly estimated in the case of salts because of the non-fulfillment of the Biot number (*Bi*) criterion for the lumped thermal system. To ensure uniform thermal distribution within the sample the *Bi* should be less than 0.1.⁷ In the case of Sn, the *Bi* criterion was satisfied ensuring that the temperature distribution is same at all points within the sample but same was not in the case of salts. This meant that there is an existence of thermal gradient within the salt sample, which is not considered in this method. It is clearly shown that the heat transfer coefficient did not follow the same best fit before and after solidification.

Therefore, the characterization method fails in the case of salts. Hence, further experimental modifications are needed to use this technique for salts.

5 | CONCLUSIONS

The energy balance method used in this work is a simple and inexpensive technique to determine the phase change characteristics of metal-based energy storage materials. It provides a good approximation of the phase change enthalpy without any baseline calculations in the case of metals. The calculated latent heat value for Sn was found to be 59.7 kJ/kg, which was in agreement with the reported literature value of 60 kJ/kg.⁶ However, the latent heat of salts could not be estimated accurately because of the existence of a thermal gradient within the sample. The measured phase change enthalpies using energy balance method were 87% and 107% higher than the values reported in the literature for KNO₃ (89 kJ/kg)⁷ and NaNO₃ (172 kJ/kg),⁸ respectively.

ORCID

Narayan K. Prabhu  <http://orcid.org/0000-0002-8359-2587>

REFERENCES

1. Sharma A, Tyagi VV, Chen CR, Buddhi D. Review on thermal energy storage with phase change materials and applications. *Renew and Sustain Energy Rev.* 2009;13:318-345.
2. Mehling H, Cabeza LF. Heat and cold storage with PCM: an up to date introduction into basics and applications. *Heat and Mass Transfer.* 2008 ed. Berlin Heidelberg: Springer-Verlag; 2008:57-102.
3. Sudheer R, Prabhu KN. Characterization of metal-PCMs for thermal energy storage applications. *Mater Sci Forum.* 2015;830-831:505-508.
4. Yinping Z, Yi J, Yi J. A simple method, the -history method, of determining the heat of fusion, specific heat and thermal conductivity of phase-change materials. *Meas Sci Technol.* 1998;10:201-205.
5. Barlow JO, Stefanescu DM. Computer-aided cooling curve analysis revisited. *AFS Trans.* 1997;105:349-354.
6. Rivera C, Villeda A & Argaez M (2017) Cooling Curve Analysis Method using a Simplified Energy Balance. 6th Engineering, Science and Technology Conference 2017, KnE Engineering, 383-392.
7. Sudheer R, Prabhu KN. A computer aided cooling curve analysis method to study phase change materials for thermal energy storage applications. *Mater Des.* 2016;95:198-203.
8. Tooklang P, Vaivudh S, Sukchai S, Rakwichian W. Thermal distribution performance of NPCM: NaCl, NaNO₃ and KNO₃ in the thermal storage system. *Energy and Power Eng. J Clin Microbiol.* 2014;6:174-185.
9. https://www.engineersedge.com/materials/specific_heat_capacity_of_metals_13259.htm (accessed on 23/07/2018)

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