Full paper no: 58

Strategy for visualisation of the activity of phase change materials by transient plane source technique

Angela Sasic Kalagasidis, Associate Professor [1]
Bijan Adl-Zarrabi, Assistant Professor [1]
Helén Jansson, Assistant Professor [1]
Billy Seng, BSc[2]

[1] Chalmers University of Technology, Gothenburg, Sweden
[2] Ecole des Mines d'Albi, Carmaux, France

KEYWORDS: *Phase change material (PCM), Passive control, Phase transition, Latent heat storage, Thermal energy storage*

SUMMARY:
Through a combination of theoretical and experimental research, this paper aims at evaluating the suitability of a transient plane heat source (TPS) method for the visualisation of the activity of phase change materials (PCMs). The TPS method provides measurements of thermal conductivity and thermal diffusivity of a material in a transient course. It has previously been tested on various building materials but not on PCMs. In this study TPS was tested in a laboratory environment on two inorganic PCMs (salt-hydrates), with melting temperatures 21 ^{o}C and 24 ^{o}C respectively. Based on the experimental trials, the technique has shown to be a valuable technique for the identification of the activity of phase change materials.

1. Introduction

From a sustainable point of view there is a need for the reduction of greenhouse gas emissions and the energy consumption in buildings. On the other hand, the constantly ongoing increase in living standard results in that both more greenhouse gases are emitted and more energy is consumed. Thus, to get this equation balanced, buildings must be more energy efficient and new types, or uses, of materials have to be taken into consideration.

Systems based on materials with thermal storage capacity could be used to reduce the use of fossil fuels used for heating and/or cooling of buildings. In principle it would be possible to use any material that undergoes phase transitions when it is heated or cooled, i.e. a more or less sudden change of the internal energy state of a material as a function of the temperature. Dependent on type of transition, e.g. solid-to-liquid or liquid-to-solid transitions, energy is either absorbed or released, respectively. If the transition involves large amounts of energy per unit mass and the transitions occur close to room temperature it is possible to use this type of materials for storing thermal energy. Such type of materials, which is commonly called phase change materials (PCMs), can be used for passive control of temperature and heat flow in in buildings

2. Thermal properties of salt hydrates

The most frequently used PCMs of today are based on organic (e.g. paraffins or fatty acids,) inorganic (e.g. salt hydrates) or eutectic (composition of two or more components) materials (Soares 2013). Salt solutions, or salt hydrates, generally have larger thermal effusivity than paraffin waxes mainly due to larger volumetric heat capacity. For that reason, salt hydrates show faster response to varying heat loads in

1

the environment and larger storage capacity per unit volume, which are preferable features for achieving efficient heat storage and release from building envelopes. Leakage from pouches, incongruent melting, large sub-cooling and corrosivity are still unresolved problems (Kosny et al. 2007, Hittle 2002), and the reasons why this type of PCM is used mainly in HVAC applications, (Hed 2009).

Even if this work is focused solely on salt hydrates, many thermal characteristics that are discussed hereafter are applicable also for other types of PCMs such as paraffin waxes.

Salt hydrates are available in a wide range of melting points of interest for building envelope applications, i.e. from +10 ^{o}C to 40 ^{o}C. Below the melting temperature, the PCM is in solid phase. Once the melting temperature is reached, typically after an increased heat load in the environment, the PCM absorb the excess heat at approximately constant temperature, i.e. the PCM starts to melt. When the whole amount of the PCM is melted, its temperature starts to increase. Similarly, when the heat load is reduced, the PCM cools down until the solidification starts. In the solidification period the stored energy is released to the environment. Examples of fully melted, partly melted and fully solidified salt hydrates in pouches are shown in Figure1.

FIG 1. Pouches with ClimSel 10, ClimSel 21 and ClimSel 28 in laboratory environment at 21 ^{o}C. (photo B. Seng). Notations ClimSel 10, ClimSel 21 and ClimSel 28 stand for salt hydrates with melting temperatures at 10 ^{o}C, 21 ^{o}C and 28 ^{o}C respectively.

Depending on the mixture, the phase change process may happen at a constant temperature or within a temperature range. While eutectic salt solutions are characterized by a single melting temperature at a given pressure, non-eutectic solutions melt over a temperature range. For binary non-eutectic solutions, one can distinguish between start and end temperature, as shown in Figure 2. Besides, an apparent specific volumetric heat capacity can be found as the first derivative of energy, for example specific enthalpy h (J/kg of PCM), over temperature change T (^{o}C)

$$c_{apparent}(T) @ \frac{dh}{dT}$$

This relation is usually highly non-linear and with a typical peak, as shown in Figure 2. For multi-component mixtures, several peaks can be detected each corresponding to the melting/solidification temperature of one of the components. The maximum apparent specific heat capacity can be several times larger than the heat capacity of a pure solid or pure liquid phase. As an example, Table 1 provides declared thermal properties of a sodium sulphate salt hydrates that were used in this investigation. Based on the data, the average apparent specific heat capacity of ClimSel 21, 10.4 kJ/kgK, can be found as a ratio between the enthalpy (156.5 kJ/kg) and the temperature range (15-30 ^{o}C) (see also Figure 2). This value is 2.5 times larger than the specific heat capacity of pure water (4.2 kJ/kgK) and 26 times larger than the specific heat capacity of dry sodium sulphate (0.4 kJ/kgK). In the same manner, the mean apparent specific heat capacity of ClimSel 24 is found to be 13.1 kJ/kg.
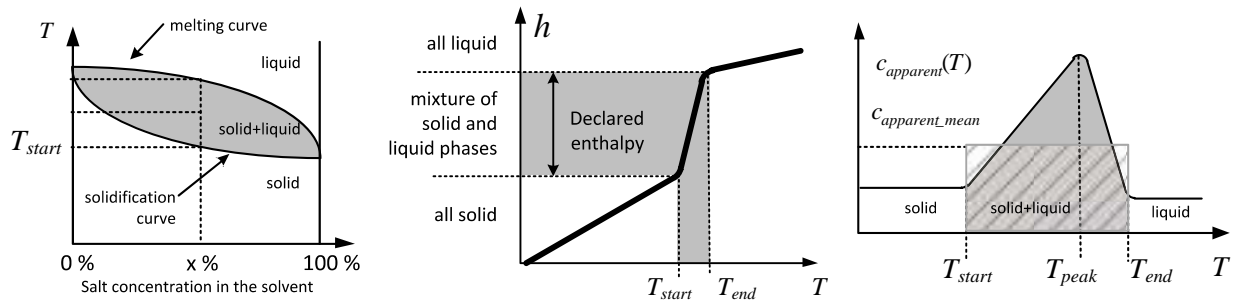
FIG 2. Left: Binary phase diagram. Middle: enthalpy change. Right: apparent specific heat capacity of PCM. All refer to a non-eutectic solution. Simplified representation.

Accurate thermal properties of PCM based materials and components are needed in numerical calculation related to energy performance of a building. The apparent specific heat capacity is a convenient thermal property for numerical modelling of PCMs (Sasic Kalagasidis 2013). Much more efforts are needed for the modelling of PCMs that melt at a constant temperature, as their apparent specific heat capacity is undefined. A multi-phase modelling is then an appropriate approach (Sasic Kalagasidis 2013).

TABLE 1. Thermal properties of ClimSel 21 from Climator Sweden AB

Name	Salt hydrate	Melting temperature [°C]	Latent heat [kJ/kg]	Density [kg/m³]	Thermal conductivity [W/mK]	Storage capacity	
						Enthalpy [kJ/kg]	Temperature range [°C]
ClimSel 21	Sodium sulphate	21	112.1	1380	0.5-0.7	156.5	15-30
ClimSel 24	Sodium sulphate	24	151.3	1380	0.5-0.7	195.7	15-30

3. TPS method applied on PCM

Transient plane heat source (TPS) method is a transient technique for simultaneously determining thermal conductivity and thermal diffusivity of materials. A plane sensor is located between two halves of a specimen and acts as a heater as well as a detector of temperature increase. The sensor is insulated between two layers of kapton (polyamide) or mica (sheet silicate minerals). The thickness of this insulation is about 25 pm. By using the measured temperature increase at the surface of the sample and the constant power applied to the heater, it is possible to solve the partial differential equation that describes the heat transfer in the specimen, using curve fitting methods (Adl-Zarrabi, 2006). Results of the analysis are thermal conductivity and thermal diffusivity of the specimen.

The TPS method (ISO 22007-2:2008) is applicable for measurements on solids, liquids, anisotropic materials, powders and amorphous structures. The selection of power and measuring time can be based on literature or experience. The measuring time can be estimated from the ratio of the probe radius to the power of two and thermal diffusivity of the specimen.

Most often measurements on PCMs are performed by Differential scanning calorimetry (DSC), as shown in Figure 3, and the T-history method (Kuznik et al. 2011) but, to the best of our knowledge, TPS has not been applied on phase change materials before. Except for that TPS is a good complement to other techniques for heat and phase transition measurements, the choice of this technique is motivated by the small size of the probe, short measuring time and high precision proved on other materials.
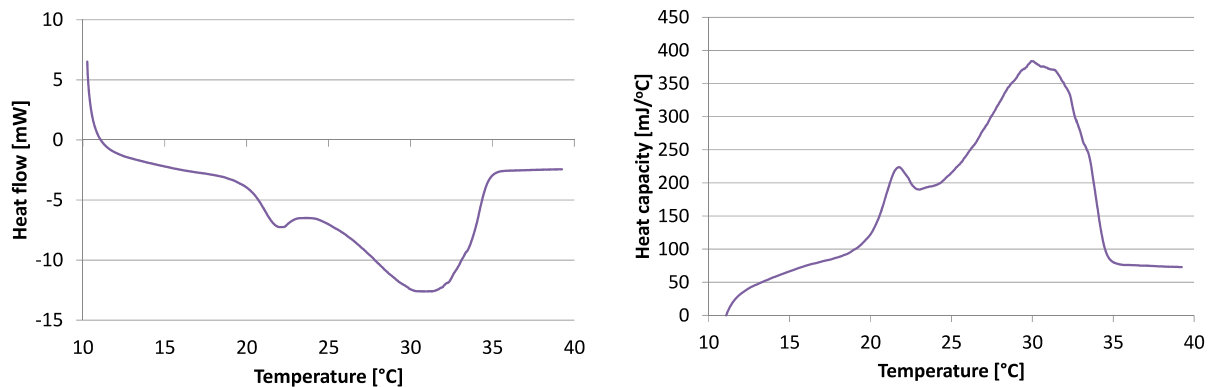
3

FIG 3. Curves showing the melting (left) and heat capacity (right) of ClimSel21 (Climator Sweden AB) obtained by Differential Scanning Calorimetry (DSC).

3.1   Direct measurements on PCM pouches

To evaluate the influence of the aluminium layer surrounding the PCM, the first attempt was to perform measurements with the probe placed directly on the pouches, both for the fully solidified and fully melted PCM. As the temperature response was almost identical in both situations, i.e. it was not possible to distinguish between the pouches with melted and solid PCM, it was concluded that the heat from the TPS-sensor was more dissipated in the aluminium layer than in the PCM. Similar issues were also described by Johansson et al. (2011) during measurements on vacuum insulation panels. Therefore, direct measurements on the PCM are suggested.

3.2   Direct measurements on PCM

In the second attempt, the sensor was thus placed in direct contact with a certain amount of PCM in a holder. The PCM was sampled from a newly opened pouch to prevent water loss since a control gravimetric analysis showed that the water loss from 2 gr of solid PCM, which was exposed to the ambient air in a Petri cup, was approximately 2 % / 4% / 6 % on a course of 1 h / 2 h / 3h. As any water loss from the PCM could lead to an alteration of the basic characteristics of the sample, the measurements were executed instantly after a sample was taken from the pouch.

A lack of standard holder for the measurements on granules of PCM was solved by using a sample holder made from a cup (120 ml) with a hole on the side through which the probe was inserted, as shown in Figure 4. The procedure was as follows: the cup was filled with the PCM up to the hole for the sensor; the sensor was inserted and an equal amount of PCM was filled over it; finally, the cup was sealed with a plastic paraffin film (Parafilm) to prevent any water loss from the specimen. The same setup was used for the measurements on melted PCM with an addition of a thermocouple, which was inserted in the cup to read the temperature of the specimen.

It was anticipated that the bulk density of the granules in the cup could vary due to irregular shape and size of the granules (see Figure 4), which would affect the results of measurements since the contact between the granules and the sensor would also vary. Therefore, the measurements were performed on differently compressed samples: without compression, i.e. with the bulk density obtained by normal filling of the cup, with small compression (slight patting), and with high compression (stronger patting).

All measurements were performed with a sensor, which is 12.8 mm in diameter and that gives the possibility to apply power of 0.1 W. The diameter of the cup was approximately four times larger than the diameter of the probe. The thickness of the PCM sample below and above the probe was about 1 cm.

FIG 4. Left: probe inserted in the cup. Middle: the cup sealed with Parafilm. Right: granules of PCM (photo B. Seng)

4. Results

4.1 Temperature response

Temperature response curves on 100 mW power supplied from the sensor are summarized in Figure 5, for melted (at 25 ^{o}C) and solid (at 20 ^{o}C) ClimSel 21. There is a clear separation between the curves obtained from the melted and solid samples. The curves obtained on the melted samples show a temperature increment of 1.2±0.1 ^{o}C after 20 s. The curves obtained on solid samples show larger temperature increment, from approximately 3.4 to 4.9 ^{o}C after the same time. The low temperature increment of melted samples can be explained by increased apparent volumetric capacity, which includes the impact of latent heat of melting. Among the solid samples, the lowest temperature increment (3.4 ^{o}C) is found on the high compressed samples, which is explained by a higher bulk density and, consequently, by a higher volumetric heat capacity of the bulk. High compressed samples are more likely to be found in the pouches from which air is evacuated, see Figure 1. Therefore, the temperature response of high compressed samples is more representative for the comparison with the results of melted samples. Note also that the response curves for all samples in the same group are closely gathered, which indicates a good repeatability and precision of the measurements.
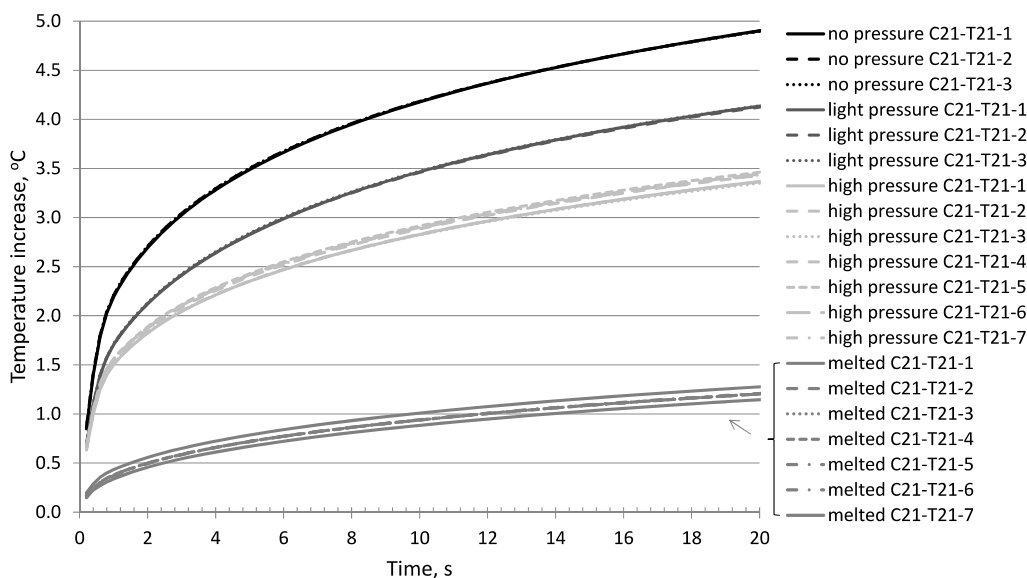

FIG 5. Temperature response curves for ClimSel 21obtained by TPS technique.

In order to verify the findings on ClimSel 21, the same measurements were done on ClimSel 24. This time, the measurements started from a melted sample (at 25 ^{o}C), after which they were repeated whenever the sample cooled down by one degree. The power supplied from the source was 200 mW. The idea was to

test the resolution of the measurements during transient phase change of the sample. The results of this attempt are summarized in Figure 6. As it can be seen, the cooling process is adequately presented with the measurements. The lowest temperature increment was found on the fully melted sample, and the highest response was recorded on the coolest samples. In this first trial of the method results for 23 ^{o}C and 24 ^{o}C were not recorded. Although the response curves are distinctly separated from each other, the difference between the fully melted and solidified[1] samples is not that large as in the previous example. One possible explanation is that the bulk density of the solidified samples was probably higher, which was achieved through a continuous process of solidification in which the air penetration in the sample was limited.
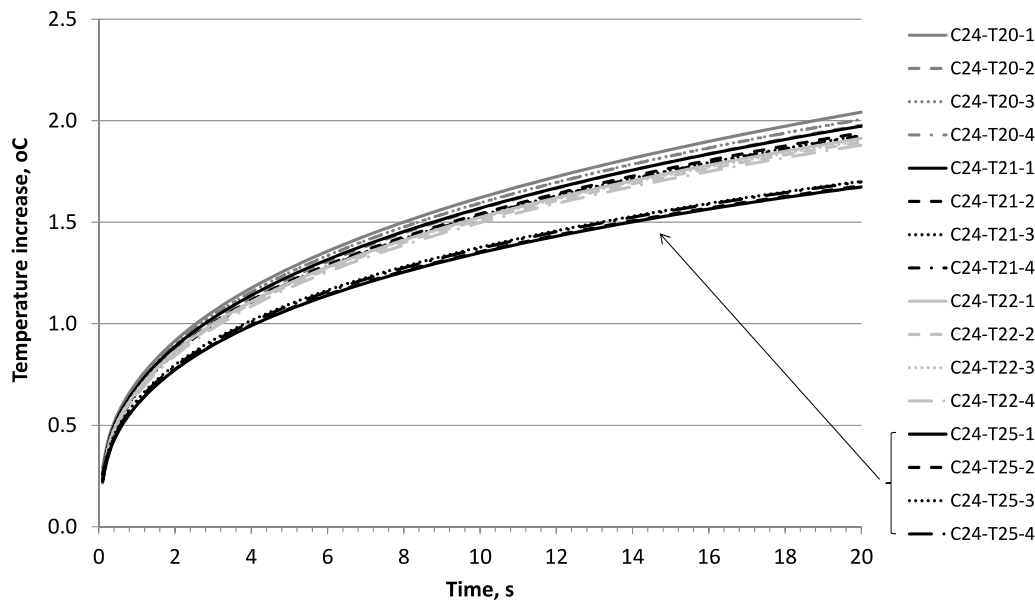

FIG 6. *Temperature response curves for ClimSel 24 obtained by TPS in the continuous cooling mode.*

4.2   Thermal properties

The TPS method was not designed for the evaluation of thermal properties of PCMs. Therefore, the results for thermal conductivity, thermal diffusivity and volumetric heat of ClimSel 21 and ClimSel 24, which were obtained by TPS and summarized in Tables 2 and 3 should be regarded as indicative. These results were determined from the temperature response curves in Figures 5 and 6 by built-in software provided together with the TPS by HotDisc (www.hotdiskinstruments.com).

The thermal conductivity of ClimSel 21 is close to the declared values in Table 1, with the lowest values found on the samples with the lowest bulk density (light compressed) samples and the highest on the melted samples. Likewise, the volumetric heat capacity increases with the bulk density of the samples while the thermal diffusivity decreases.

Similar but not exactly the same trend can be seen in the results for ClimSel 24 in Table 3. The values for thermal conductivity and volumetric heat capacity are much closer to each other and, in general, closer to the values obtained for the melted samples of ClimSel 21. As explained above, the density of these samples was less affected by air intrusion.

---

[1] It was not determined to what extent these samples were solidified

TABLE 2. Thermal properties of ClilmSel 21 determined by TPS technique. Bulk density n/a.

Sample (Number of samples)	Temperature °C	Thermal conductivity W/mK	Thermal diffusivity $\cdot10^{-6}$ m^2/s	Volumetric heat capacity kJ/(m$^3\cdot$K)
		Mean / Coefficient of variation (std. deviation/mean, %)		
Solid, light compression (3)	20	0.3370 / 0.26	1.0030 / 1.50	0.3360 / 0.25
Solid, high compression (7)	20	0.4003 / 0.68	0.4959 / 1.54	0.8077/ 1.45
Melted (7)	23-25	0.7657 / 4.32	0.3038 / 3.00	2.5295/ 11.77

TABLE 3. Thermal properties of ClilmSel 24 determined by TPS technique. Bulk density n/a.

Sample (Number of samples)	Temperature °C	Thermal conductivity W/mK	Thermal diffusivity $\cdot10^{-6}$ m^2/s	Volumetric heat capacity kJ/(m$^3\cdot$K)
		Mean / Coefficient of variation (std. deviation/mean, %)		
Solid[1] (4)	20	0.9588 / 2.01	0.3020 / 1.15	3.1768 / 5.64
Solid[1] (4)	21	1.0968 / 1.60	0.4359 / 1.12	2.5168 / 2.91
Solid[1] (4)	22	1.0812 / 1.76	0.3648 / 1.27	2.9649 / 5.64
Melted (4)	25	1.3217 / 0.53	0.4335 / 0.78	3.0497 / 5.39

For comparison, Figure 7 shows analytically obtained response curves for a material with the thermal diffusivity in the range of the values from Table 2 and 3. The analytical temperature solution is taken from Johansson et al.(2011); it represents a temperature response of a homogeneous material on heat (100 mW and 200 mW) injected from a circular plane source with radius 0.0064 m. The solution assumes maximum dispersion of heat in the material, a perfect contact between the source and the material and a perfect heat source. The theoretical temperature increment at the surface of the material, at around the circumference of the heat source is in the range 0.8-1.5 °C after 20 s, for thermal diffusivities $0.3\cdot10^{-6}$ m^2/s $-1\cdot10^{-6}$ m^2/s and for 100 mW power supplied from the source. The temperature increase is linearly proportional to the power supplied from the heat source and it's thus doubled for 200 mW (1.6-3 °C). These values can be compared to the ones in Figures 5 and 6, and Tables 2 and 3. The calculated temperature increment is in the range of the measured values by the TPS for the melted samples: 1.1-1.3 °C for ClimSel 21 and about 1.7 °C for ClimSel 24. For the solid samples with lot of air (i.e. loosely packing) between the granules, the analytical and measured response differ substantially. Nevertheless, the trend is still the same – the temperature increment is higher when the thermal diffusivity increases, as it is also shown by the measurements.
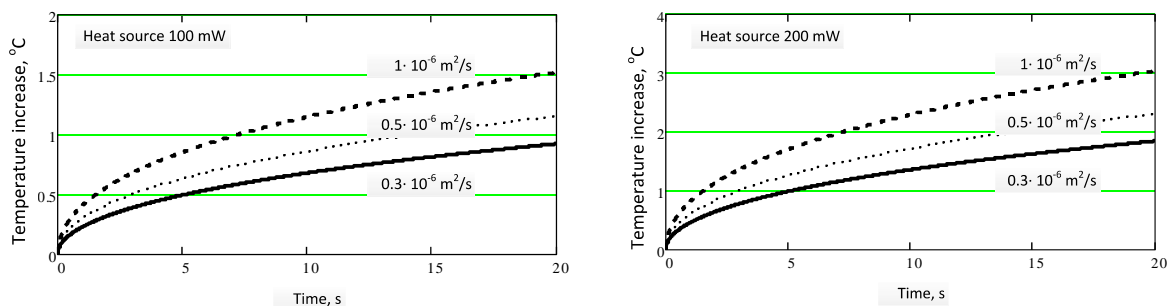

FIG 7. Theoretical temperature response curves for a material as a function of thermal diffusivity. The values for thermal diffusivity are based on the measurements, from Table 2 and Table 3.

5. Discussion

The results indicate that the TPS can detect the PCM activity with sufficient resolution. However, the results should be taken with caution due to some unresolved issues for the measuring procedure. While the

sensor was completely covered by the melted PCM, this was not the case during the measurements performed on the solid granules. The looser the packing of the grains, the less direct contact between the sensor and the grains is obtained. Ideally, a sample should be taken in a large block of compressed PCM or one should realize the measurement directly on the pouches after removing the aluminium layer. In that case, an environmental chamber at a specific atmosphere could be used to avoid any evaporation of the solvent. The original size of the grains is in millimetre range and a probe with larger radius than 6.4 mm, as used in this work, is probably more appropriate in order to account for the inhomogeneity of the sample. The issue with varying bulk densities of the solid sample could be overcome if the measurements should start from a melted sample.

6. Conclusions

The TPS technique was used in an innovative way, for the visualization of the activity of PCM (sodium sulphate hydrates) in the phase transition region. A sample holder for the TPS and the specimens was constructed and the measuring procedure was explained. The measurements with the TPS method provided temperature response curves for the fully solidified and fully melted samples with declared melting temperatures at 21 ^{o}C and 24 ^{o}C. It was found that TPS provided an exceptionally fine resolution for the temperature response curves, wherefrom it was possible to separate the samples in respect to their bulk density and the melting temperature. Based on the temperature response curves, the thermal properties of the samples were evaluated. Although these values varied in accordance with the bulk density and the melting temperatures of the samples, the absolute values were just indicative. This very first trial with using the TPS showed that the technique had potential to be used for the measurements of PCMs activation. The issues to be resolved in future are related to the bulk density of the specimen and to the size of the probe in relation to the granules of solidified PCM.

References

Adl-Zarrabi B. 2006. Using the TPS method for determining the thermal properties of concrete and wood at elevated temperature. Fire and Materials, 30:359-369.

Hed G. 2003. Use of phase change material for change of thermal inertia of buildings. In the proceeding of the 6th Expert Meeting and Workshop of Annex 17. Available on www.kth.se/abe/inst/byv/publ.

Hittle D. C. 2002. Phase Change Materials in Floor Tiles for Thermal Energy Storage. Topical Report. Award No. DE-FC26-00NT40999. Colorado State University. Fort Collins, CO 80523. Available on https://www.etde.org/etdeweb/servlets/purl/820428/820428.pdf

ISO 22007-2:2008. Plastics. Determination of thermal conductivity and thermal diffusivity. Part 2: Transient plane heat source (hot disc) method

Johansson P., Adl-Zarrabi B., Hagentoft C-E. 2011. Measurements of Thermal properties of Vacuum Insulation Panels by using Transient Plane Source Sensor. Proceedings of the 10th International Vacuum Insulation Symposium. Ottawa, Canada, pp. 18-21.

Kosny J., Yarbrough D., Miller W., Petrie T., Childs P., Syed A.M., Leuthold D. 2007. Thermal Performance of PCM-Enhanced Building Envelope Systems. *Proceedings of Thermal Performance of the Exterior Envelopes of Whole Buildings*, X International Conference.

Kuznik F., David D., Johannes K., Roux J-J. 2011. A review of phase change materials integrated in building walls. Renewable and Sustainable Energy Reviews (15) 379-391

Sasic Kalagasidis A. A multi-level modelling and evaluation of thermal performance of phase change materials in buildings. J of Build P Simulation, DOI:10.1080/19401493.2013.764547

Soares N., Costa J.,J., Caspar A.R., Santos P. 2013. Review of passive PCM latent heat thermal energy storage systems towards buildings' energy efficiency. Energy and Buildings (59), pp 82-103.