

# THERMOPHYSICAL CHARACTERIZATION OF PHASE CHANGE MATERIALS WITH HEAT FLUX SENSORS

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## Abstract

The objective of this research is to use PCM (hydrated salts or others) as integrated components in a passive solar wall. The proposed Composite TROMBE Wall allows daily storage of the solar energy in a building envelope and restitution in the evening, with a possible control of the air flux in a ventilated air layer.

In this particular application, the behaviour of the rectangular shaped PCM bricks is prone to variations which require a probabilistic or statistical approach to determine their properties. Moreover, the measurements obtained by the differential calorimetric analysis (DSC) are delicate and not easily exploitable because of scale effect and of nucleation involving of crystallizations on the walls of the cells samples. Hence, the suggested approach involves experimental investigations of the total behaviour of a “material wrap” filled with phase change material (PCM).

The experimental apparatus allows providing heat storage capacities and “apparent” thermal conductivities of the PCM at the solid and liquid states, and also a measurement of the latent heat of fusion.

## 1. Introduction

This work proposes preliminary results obtained with a genuine characterization method for the determination of phase change material (PCM) thermophysical properties [Tyagi 2007, Khudhair 2004]. The overall objective is to insert these materials in a passive solar component such as the “Composite Trombe wall” [Zalewski 2002]. In this evolution of the classical Trombe wall, an insulating layer allows, when necessary, to separate the massive storage device from the heated room, and thus to control the distribution of the solar energy through a ventilated air layer. The storage element embedded within the whole device is generally composed with one heavy (massive) material like concrete, strongly capacitive and conductor of heat. The objective is here to insert PCM in the concrete heat storage element to increase the storage and improve the redistribution: parallelepipedic PCM elements of about 1 kg each are used.

From liquid to solid phase, various states coexist in the PCM. As a result, the apparent thermal properties are extremely variable. Moreover, the crystallization or fusion modes vary over the cycles: a statistical evaluation of these properties is then necessary. And this determination is the corner stone of any heat transfer predictions and control of the air fluxes through the ventilated layer. [Stritih 2004]. Thus, the primary goal here is to realise the characterization of the PCM

behavior and propose a one-dimensional (1D) model for it. In a subsequent phase, the idea is to simulate a composite solar wall involving PCMs over long periods (several weeks) and to work with the implementation of an optimal control strategy control of heat in the wall.

## 2. Material characterization

Generally, PCMs are characterized by calorimetric methods, like differential scanning calorimetry (DSC), applied to very small amounts of product. This technique is derived from the differential thermal analysis (DTA). Over the years, DSC became the reference method for thermal characterization of phase change material [Jamil 2006]. This equipment provides heat fluxes by Joule effect, which corresponds to the necessary power difference to maintain at the same temperature a “cell” containing material to be characterized and a reference cell which is generally empty.

In case of the heat capacity measurement for a sample which does not undergo phase change, the energy supplied is weak and generally not very variable. On the other hand, in the case of a fusion process, there is a rapid transient which require important heat rates from the DSC. The thermal imbalance between the two cells is then very important although the quantity of product remains low.

In practical application, the material volume is much more important, up the kilograms for instance, so the melting process occurs gradually through the material. The latter is then heterogeneous and the two phases may coexist over long periods of time before a complete fusion. Moreover, heat conduction in the solid and convection in the liquid occur [Stritih 2004]. This strongly influences the global (or apparent) behaviour of the MCP.

In the case of solidification, problems are even more complex: superfusion phenomena [Ehmimed 2003] occur. In the work presented here, the investigated materials (hydrated salts) have a melting point (announced by the manufacturer) equal to 27°C [Cristopia]. A DSC analysis has been carried out on a sample of this material using a “Perkin-Elmer” calorimeter. The measurements were coherent only in the case of fusion. The latent heat absorbed by the sample during the phase change was 186.6 J/g while the melting point was 31.74°C.

Solidification process analysis was found to be impossible because of the importance of superfusion within the PCM. The material here is not a pure substance, the exact chemical composition is not known, and the phase diagram is very complex. This introduces thermal effects which are particularly difficult to control.

The phase change material (PCM) samples embedded within the walls are 210x140x25mm parallelepipedic PCM elements.

## 3. Experimental apparatus

It was found that the determination of the overall thermophysical properties of PCMs over several cycles (solidification and fusion) requires the design of a genuine experimental device. The proposed test bench for the particular bricks of material used herein provides temperature and heat flux measurements at the material borders. The thermophysical properties can be readily obtained from these experimental data. One can also calculate the amount of energy exchanged during the variation of the samples thermodynamic states when the boundary temperatures vary.

The experimental device provides the apparent thermal conductivity by imposing a steady temperature gradient between the two faces of the sample (figure 2). The sample is located between two vertical exchanger hollow aluminium plates. Thermo regulated baths, supplying the plates, allow a fine regulation of the injected water temperature with a precision of about 0,1 °C.

Heat flux sensors and thermocouples (T) (diameter 0,1 mm, sensitivity 40  $\mu\text{V/K}$ ) are embedded within the envelope of the PCM brick. The whole thing is maintained in place by use of a slightly tighten pneumatic jack. Tangential gradients flux meters (TGFM) are used [Leclercq, 1983]. Their thickness is about 0,2 mm and their sensitivity is about 4,5  $\mu\text{V/W/m}^2$  for a sensor having an active surface area of 100  $\text{cm}^2$ . **FIGURE À REFAIRE, aligner les nombres, etc...très moche. Pensez au poster...**

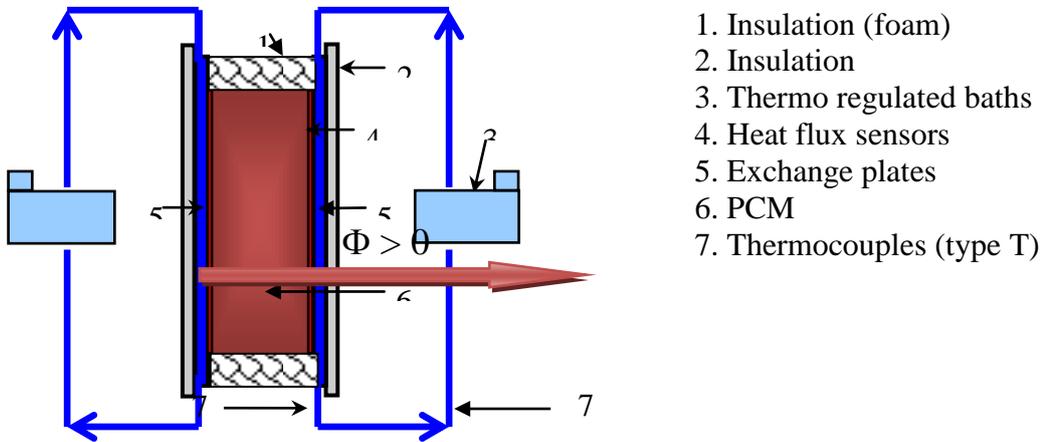


Figure 1 : *Experimental device*

The TGFM are calibrated with great care, using plane electrical resistances with size rigorously equal to those of the sensors. The calibration device [Lassue, 1993] makes it possible to calibrate these sensors within a precision range of about  $\pm 3\%$ . The temperature measurements are differential compared to a reference sensor placed in the heart of a steady state thermal sink. The various sensors are connected to a multichannel “Keithley” multimeter adapted to low level signals measurement. Experimental data are recorded with regular and adjustable time steps (10 s). The lateral side faces are insulated by 10 cm thickness polyurethane foam which reduces multidimensional heat transfer to a 1D problem.

## 4. Heat transfer measurements

Several materials were tested. The results presented herein involve a PCM so-called +27°C (it is mineral, containing potassium and calcium chlorides) which is the best suited for the proposed application. The recrystallization is announced at 24°C by the manufacturer and  $T_{\text{fusion}} = 26,9^\circ\text{C}$ , [Cristopia].

### 4. 1 Energy Storage

Initially, the material is isothermal. Then it is heated by modifying the temperature set point of the thermo regulated bath. The material will thus evolve from  $T_{\text{initial}}$  to  $T_{\text{end}}$ . Between these two permanent steady states the material stores energy. The flux meters make it possible to measure the heat fluxes exchanged at the borders of the sample. The total amount of energy stored can then be obtained from the following expression:

$$Q^* = \int_{t_{\text{initial}}}^{t_{\text{end}}} \Delta\Phi dt \quad [\text{kJ}] \quad (1)$$

Where  $\Delta\Phi$  represent the cumulated heat rate entering the sample. (figure 1). This quantity can also be expressed by:

$$Q = C_s \cdot \Delta T_s + L + C_l \cdot \Delta T_l \quad [\text{kJ/kg}] \quad (2)$$

where  $C_s$  and  $C_l$  are the average solid state and the liquid state specific heat of the material,  $\Delta T_s$  and  $\Delta T_l$  are the temperature variations for the material in solid phase and in liquid phase, and  $L$  is the latent heat of fusion.

The first results obtained pertain to the MCP 27 sample and are presented in figure 2 and figure 3. Temperatures are measured in the centre of the external and internal faces of the brick envelope to take into account a possible thermal effect produced by the envelope which contains the product. The experience consists first in imposing on the sample a superficial temperature of 15°C on each one of its faces, until obtaining a thermal steady state corresponding to an isothermal material. The heat fluxes is then zero at the initial time  $t = 0$ . It is also confirmed that the thermal losses are negligible at the isolated side faces. At a particular moment ( $t_{initial}$ ), a sharp water temperature variation is imposed in the bath. This induces a thermal evolution of the system (storage) until another state of equilibrium is obtained.

Figure 2 presents the variation of the heat storage capacity of the sample in solid phase for a temperature range that varies from 15°C to 20°C while figure 3 presents similar results for the transition from the solid to the liquid phase change 15°C to 50°C. Results for the liquid phase only were also obtained but the behaviour, despite additional natural convection heat transfer is somewhat similar to the curves presented in figure 2.

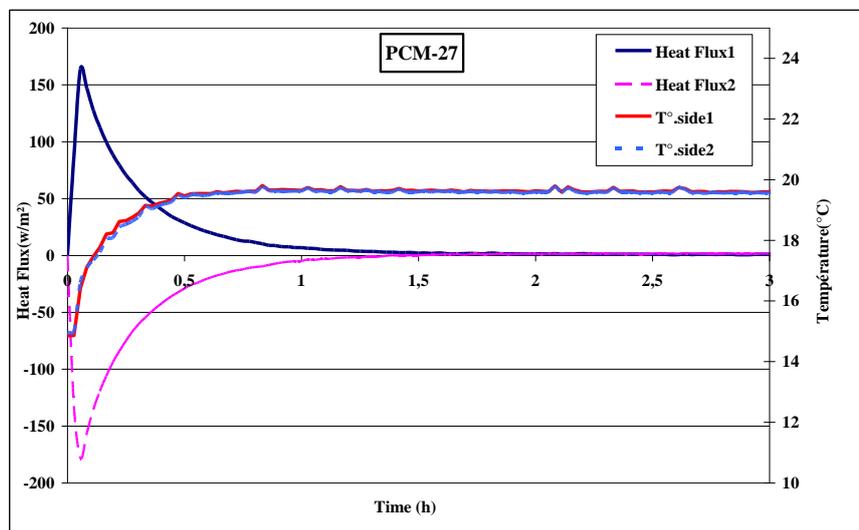


Figure 2: Heat flux and temperatures evolution of the solid phase (15°C to 20°C).

The thermal evolution from 15°C to 50°C (figure 3) allowed us to follow the complete melting process, from the solid state to the liquid state during which a great quantity of heat has been stored by the material. The selected temperatures are sufficiently far away from the zone of melting point to consider that indeed the material is strictly in one or the other state.

For the liquid and solid phases, one could notice symmetrical behaviors of flows and temperatures corresponding to the result classically obtain with a solid material without phase change. The temperatures evolve in an asymptotic way to the set point. It is also noticed that the flow evolves very quickly at the beginning of recording and then to a zero value which corresponds in a new state of balance obtained at the end of the test.

With regard to the variation between 15°C and 50°C during which there is phase change, one observes different behaviours between the temperatures measured at internal and external face of the plastic envelope, this due to the “insulating” properties (“plastic”) and to the very important latent heat absorption during the PCM fusion. A new thermal balance is reached in a little more than 3 hours. In the case of the variation from 40°C to 50°C, the material is in the liquid state. The convection generated at the time of the transitory mode is certainly the explanation for the temperature variation between the inner and external faces of the plastic envelope. This is the sole difference between the solid phase and the liquid phase (figure not shown).

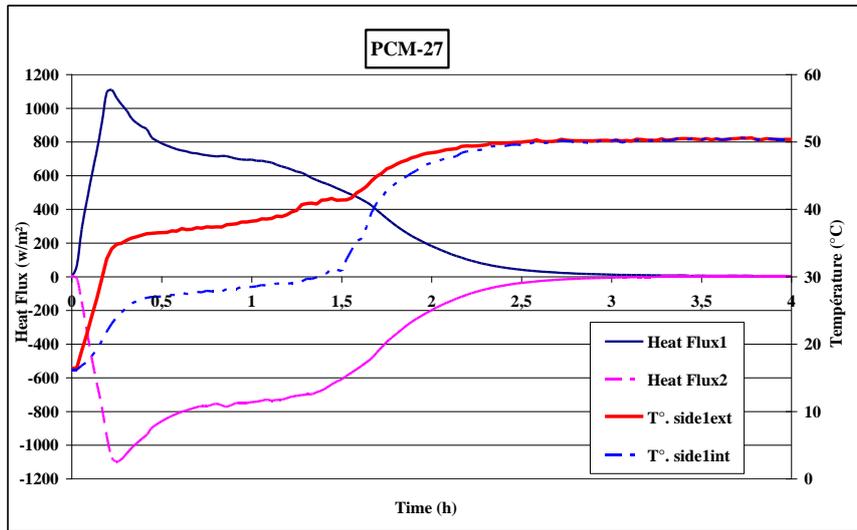


Figure 3: Heat flux and temperatures evolution from solid to liquid (15°C to 50°C).

Figure 3 shows that the heat stored is much more important than sensible heat transfer when a phase change occurs. This confirms the interest of latent heat storage.

Note on figure 4, that the thermal behavior of the sample is very particular during the fusion process. One clearly observes on this figure the different phases of the material evolution between a solid state at start and the liquid state at the end.

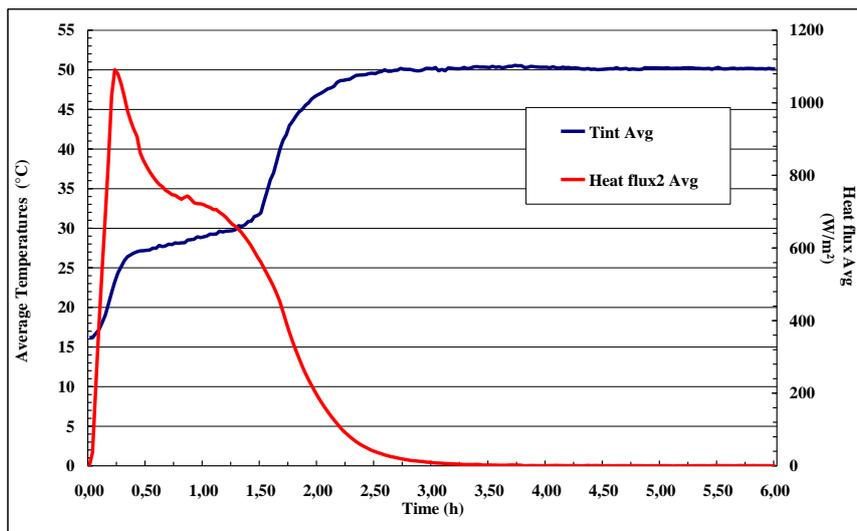


Figure 4: Average values of heat flux and temperature at the sample borders.

First, a short phase of fast increase in the temperature (the curve tends to being a straight line), which corresponds to heat storage in the solid MCP. One second phase where the temperature varies slowly near 27°C, which corresponds to latent heat storage. Finally a fast phase of rise in temperature until stabilization at the final temperature set point which is a phase of heat storage by the MCP in liquid state.

For each test, the integration of the heat flux over time determine the amount of heat stored during the process, (stationary and isothermal states ( $\Phi = 0$ )). Several tests were carried out to ensure reproducibility of the experiments. Some results are presented in table 1 (at the end of the paper).

#### 4. 1 Energy recovery

In the cooling case, where the temperature evolves from 50°C to 15°C, solidification of the material occurs. When solidification occurs, the DSC experimental method is found to be inefficient, the

superfusion phenomenon and crystallization on the walls both disturb the measurements. **Indeed, parts of the PCM which is solidified great latent heat quantities come to heat the closer PCM parts.** For our parallelepipedic sample, one observes (figure 5) these disturbances on the measured heat fluxes on the two faces of the sample. Heat fluxes are always symmetrical but have very special evolutions.

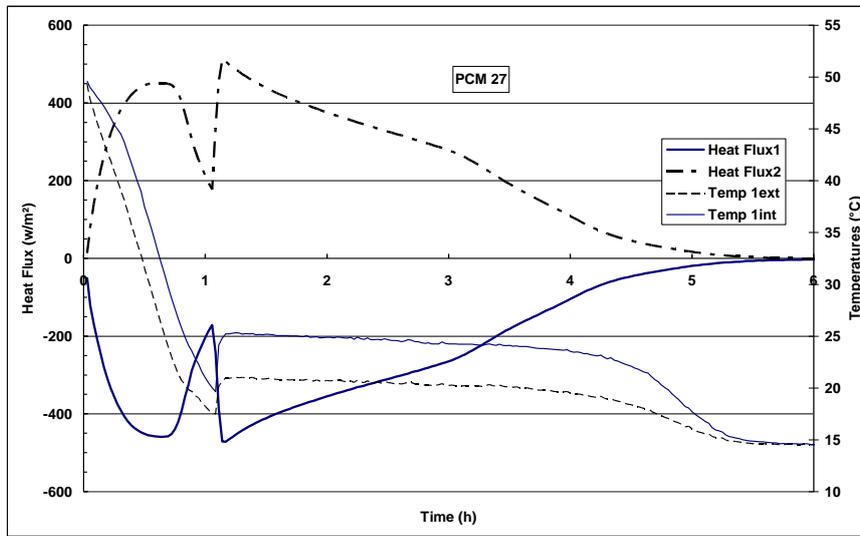


Figure 5: *Heat flux and temperatures evolutions ( $50^{\circ}\text{C} > T > 15^{\circ}\text{C}$ ).*

Initially we observe a normal evolution of measured heat flux corresponding to the cooling of the liquid phase. At the end of this phase ( $t = 45$  mn), when the temperatures of surfaces are in the vicinity of  $27^{\circ}\text{C}$ , the heat flux evolution is reversed. Then, suddenly, about 1 hour after the beginning of the test, the surface temperatures increase from  $18^{\circ}\text{C}$  to  $25^{\circ}\text{C}$  abruptly, one observes this increase of the surface temperature at the borders whereas transferred heat flux decrease. It seems that de-stored energy is reabsorbed immediately (phenomenon of superfusion). From this critical moment, the cooling of the sample continues, the material is solidified slowly and cools until it reaches the prescribed  $15^{\circ}\text{C}$ : after more than five hours, the sample reaches a equilibrium state.

Heat restitution is a very long process. At the beginning of solidification a layer of solid PCM starts to be formed on the plane surface in contact with the exchanging plate, a layer which “isolates” the liquid phase from the cooling source. Solidification continues slowly because of the low thermal conductivity of the solid PCM ( $\lambda$  is estimated at  $= 0.58$  W/m.K). The temperature of the sample surface reaches  $15^{\circ}\text{C}$  only at the end of the test. This is believed to be caused by an intrinsic a under capacity of refrigerating power of the regulated bath which cannot absorb all the heat produced during the material solidification.

This test highlights the difficulties to estimate the amount and rate of heat recovery in the material. These difficulties pertain to the existence of superfusion and also because of thermal conductivity differences between solid and liquid phases. Figure 6 shows the amount of heat stored in the material for a complete cycle.

### 4.3 Apparent thermal conductivity

In order to characterize the apparent thermal conductivity of the solid or liquid phases, the same device has been used with temperature variation on a single face only (figure 7). **The state of initial balance (isothermal) is brought back towards another state of final balance where heat flux tightens towards a non null value corresponding to a temperature gradient between the two faces of the sample.** The apparent thermal conductivities are calculated by the following expressions:

$$k_s = \frac{\Phi_{eq} \cdot e}{\Delta T_s} \quad \text{solid ;} \quad k_l = \frac{\Phi_{eq} \cdot e}{\Delta T_l} \quad \text{liquid} \quad (4)$$

where  $e$  : is the material thickness and  $\Phi_{eq}$  represents the heat flux at the end of experience.

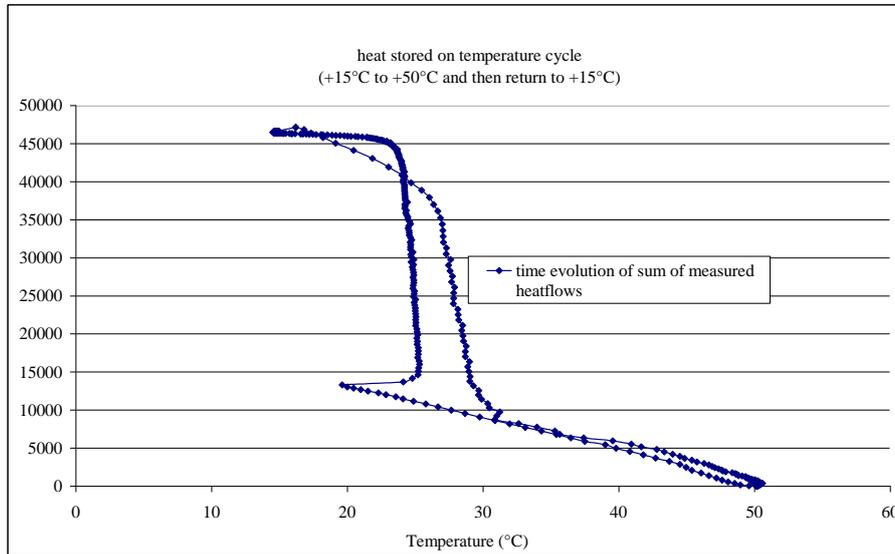


Figure 6: Heat stored during a complete cycle (15°C—50°C—15°C).

Results are presented here for the case of the solid phase only (figure 7). A similar experiment was carried out for the liquid phase (which implies convective heat transfer as well) and the apparent conductivity was also obtained with the apparatus (results not shown here).

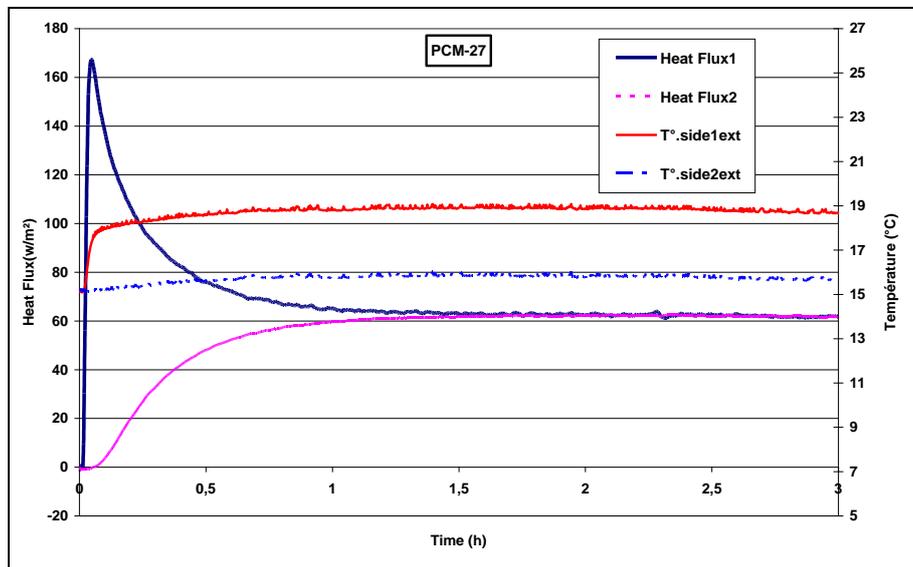


Figure 7 : Measurements with thermal variation one side of the solid sample (15°C to 20°C).

Several tests were carried out on the material to check the reproducibility of the measurements. The result were found to be satisfactory and provided an average value for the apparent thermal conductivity of 0,82 W/m°K for the liquid phase and of 0,58 W/m°K for the solid phase.

## Conclusion

In this article were presented the first results of settling an experimental method for thermal material characterization in case of phase change. The determination of the thermophysical properties could be carried out for MCP + 27 with a melting point close to normal comfort temperatures. The obtained results were very satisfactory. This method in the past was used and validated for measurement of conductivities and specific heat capacities for construction materials. In this article one shows how it can allow the study of complex material which are the PCM. In particular, heat flux measurements make it possible to highlight very specific behaviors of these products and are thus a very interesting experimental source of data which comes to complete the traditional measurement methods like calorimetric device (DSC).

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Table 1: *Thermophysical properties for PCM 27 - Sample(1,2 kg).*

		Test 1	Test 2	Average
Total stored heat (15-50°C)	J/Kg	283366	292586	287976
Heat Capacity (solid)	J/Kg°C	1752	1913	1832
Heat Capacity (liquid)	J/Kg°C	2225	2189	2207
Latent Heat	J/Kg	180016	188168	184092