Phase Change Materials:
Experimental Measurements of Thermophysical Properties

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Abstract

The final objective of the research presented here is to use PCM (hydrated salts or others) as integrated components in a dynamic or active solar wall. The suggested approach involves experimental investigations of the global behavior of a particular polyolefin container filled with phase change material (PCM) starting with simultaneous measurements of heat flux and temperatures. The experimental apparatus permits to impose and measure temperatures variations with respect to selected time scales between the two faces of the sample. This allows the determination of the 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. These measurements are average values in the temperature ranges of the experimentation.

The overall objective of the project is to characterize several samples of PCMs and then propose an appropriate model to simulate their 2D behaviors, and finally to further refine the model to represent a 2D behavior by an equivalent 1D model. As a result, this would be incorporated in an overall numerical simulation for modeling the complete solar components.

Keywords: : *Experimental work, melting and solidification, phase change material, heat fluxmeters.*

1. Introduction

This work proposes experimental results obtained with a genuine characterization method for the determination of phase change material (PCM) thermophysical properties [1,2]. The overall objective is to insert these materials in a passive solar component such as the "Dynamic Trombe wall" [3,4] (Fig.1).
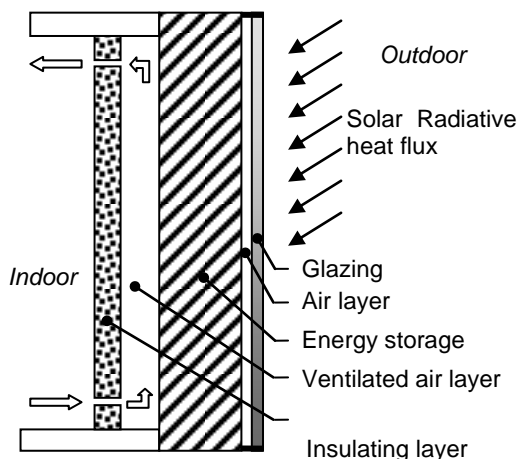

Fig. 1. Composite Trombe wall schematic

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 such as concrete, strongly capacitive, and conductor of heat. The objective is here to insert PCM in the concrete heat storage element to increase the storage capacity, reduce the size of the storage unit, and improve the heat redistribution: parallelepipedic PCM elements (or bricks) 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 cornerstone of any heat transfer predictions and control of the air fluxes through the ventilated layer. [5]. 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.

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The paper first discusses material characterization. Then, the experimental apparatus used to investigate the "bricks" of PCM is presented. Section 4 is the core of the paper as it presents the measurement of various heat transfer properties for the selected material.

Then, several general remarks will conclude this paper.

2. Calorimetric characterization

Generally, these materials are characterized by calorimetric methods like "DSC" (Differential Scanning Calorimetry) or "DTA" (differential thermal analysis) [6, 7, 8, 9], which is applied to very small quantities of product. The DSC has several advantages. The time of analysis is short and the preparation of the samples is easy. The device allows the analysis of many solid and liquid products [10] but also presents some disadvantages in this context [11,12]. In particular the low mass of sample used in a DSC (some mg) can not be representative of the thermal behavior of a larger quantity (scale effect). The wall-attachment effects can also distort the results of measurement. The DSC technique is derived from the (DTA) which became the reference method for thermal characterization of phase change material. This equipment provides heat flux dq/dt 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 the 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 requires 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 [5]. This strongly influences the global (or apparent) behaviour of the MCP.

In the case of solidification, problems are even more complex: superfusion phenomena [8] occur. In the work presented here, the investigated materials (hydrated salts) have a melting point (reported by the manufacturer) equal to 27°C [13]. 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 parallel epipedic PCM elements called "bricks" herein.

3. Experimental apparatus

In 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 (fig. 2). 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 (fig. 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.
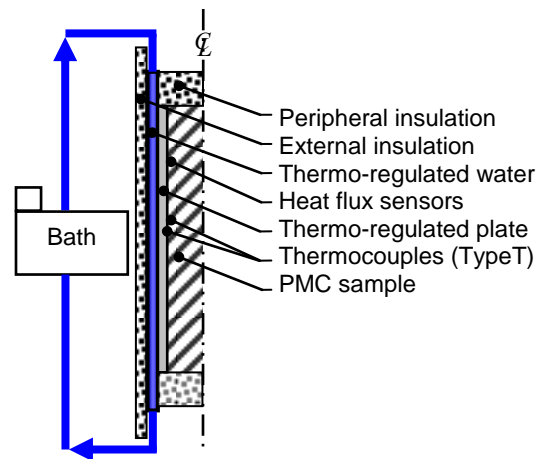

Fig. 2. Schematic of the left-hand side of the genuine experimental apparatus. The set-up is symmetrical with respect to the centerline although the bath temperature may be different to evaluate apparent thermal conductivity .

Heat flux sensors and thermocouples (T-type, diameter 0,1 mm, sensitivity 40 µV/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 [14]. Their thickness is about 0,2 mm and their sensitivity is about 4,5 µV/W/m^2 for a sensor having an active surface area of 100 cm^2

The TGFM are calibrated with great care, using plane electrical resistances with size rigorously equal to those of the sensors. The calibration device [15] makes it possible to calibrate these sensors within a precision range of about ± 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 reported at 24°C by the manufacturer and T_{fusion} = 26,9°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 on both sides. The material will thus evolve from $T_{initial}$ to T_{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:

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

Where $\Delta\Phi$ represent the cumulative heat rate entering the sample. Through the thermo-regulated plates (fig. 1). This cumulative quantity can also be expressed by:

$$Q = C_s.\Delta T_s + L + C_l.\Delta T_l \quad [kJ/kg] \tag{2}$$

where C_S and C_i are the average solid state and the liquid state specific heat of the material, ΔT_s and ΔT_{i} 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 3 and figure 4 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.
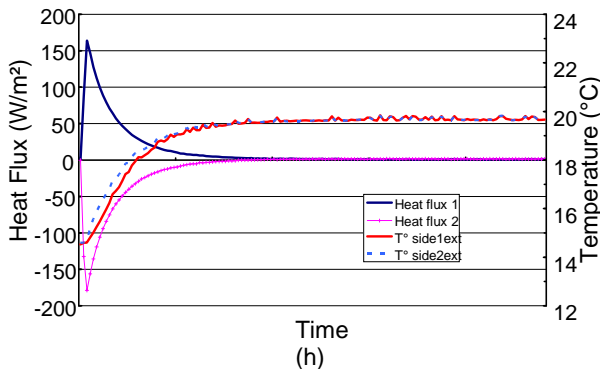

Fig. 3. Heat flux and temperatures evolution of the solid phase (15°C to 20°C).

Figure 3 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 4 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 3.
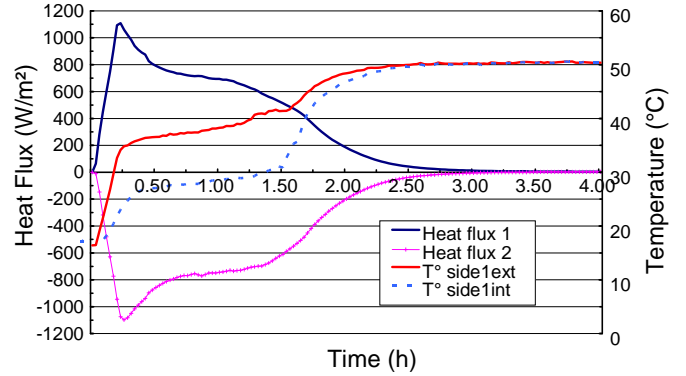

Fig. 4. Heat flux and temperatures evolution from solid to liquid (15°C to 50°C).

The thermal evolution from 15°C to 50°C (fig. 4) allowed 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 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 obtained 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 equilibrium state 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 is mainly due to the "insulating" properties ("polyolefin") 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 4 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.

One can note in figure 5, that the thermal behavior of the sample is very particular during the fusion process. Whether the temperature or heat flux curve is considered, many observations can be made between the moment the material start melting and the material becomes completely liquid.

First, a short phase of fast increase in the temperature (the curve tends to being a straight line: cf. line 1), which corresponds to heat storage in the solid PCM. The heat flux also increases (dashed line). Then melting begins in a second phase where the temperature varies slowly from about 26,5°C (line 2) to 32°C. This corresponds to the start of latent heat storage.

The change of the curve slope between the heating of solid phase and the beginning of fusion is rather clear and thus gives a good indication on where is located the characteristic started melting point. The material is thus put to melt starting from this point. Gradually, the temperature on the external faces of the sample increases slowly whereas in the middle, the material continues to melt. The temperature curve is not flat as expected from the theory as much of the newly melted liquid absorbs heat while the solid phase is still melting. The heat flow stored in this phase is for a great part latent heat which causes fusion of the material and in a much smaller proportion sensible heat stored in the liquid phase and the polyolefin envelope of the brick. At the end of this phase, in the neighborhoods of 32°C, the sensible heat absorption overrides the latent one as there is less and less solid phase: the curve shows another inflexion point. Finally a final phase of rise in temperature (line 3) is observed after all the material becomes liquid and the temperature rises until stabilization at the final temperature set point which is a phase of heat storage by the PCM in liquid state.
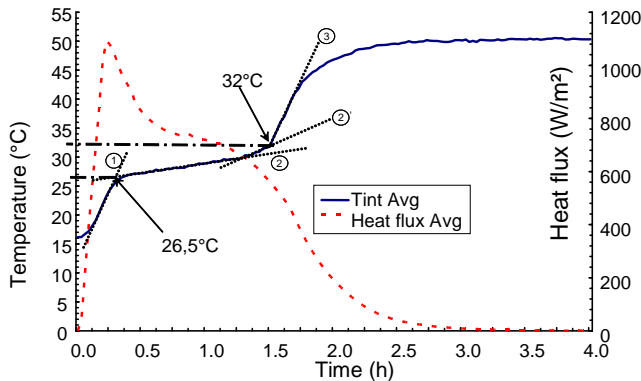

Fig.5. Average values of heat flux and temperature at the sample borders).

The intersection between line 1 and line 2, thus can define the beginning of the fusion process (26,5°C) and the intersection between line 2' and line 3 determines the end of fusion (32°C): the material is entirely liquefied. Accounting for the total heat transfer between these two points, it is possible to determine the latent heat of fusion of the particular PCM involved here.

For each test, the integration of the heat flux (dash line) over time determines the amount of heat stored during the process. Several tests were carried out to ensure reproducibility of the experiments. Some results are gathered in table 1.

The estimated measurement uncertainty, for the evaluation of the heat-storage capacity, is about 11%. This value does not take into account the possible variations due to the history of the thermal stresses imposed on material. Here for every measurement, a test "zero" has been realized before the tests 1 and 2. The error estimated for the evaluation of the latent heat is of the same order of magnitude.

To validate these results, it has been possible to compare the quantity of stored energy measured by the fluxmeters during the test (numerical integration of heat fluxes from 15°C to 50°C) and the quantity of heat stored calculated with eq. 2. The total quantity of heat stored by the brick (mass 1,240 kg) measured using the heat flux meters is 283,366 kJ (test1) while the estimated calculated value is 280,807 kJ. The difference between the two values is less than 1% For the second test, the difference is higher (3%). This last value is in the magnitude order of the uncertainies on heatflux measurements.

Tests in only one phase		First test	Second test	average
Heat Capacity (solid phase) (15-20°C)	J/Kg°C	1695	1851	1773
Heat Capacity (liquid phase) (40-50°C)	J/Kg°C	2153	2118	2135

Tests with fusion of the PCM		Test 1	Test 2	Average
Total heat stored (15-50°C)	J/Kg	283366	292586	287976
Latent Heat	J/Kg	167687	175280	171484

Table 1: Thermophysical properties for PCM 27 – Sample (1,240 kg) – PCM (1,135 kg)

The latent heat of the PCM is determinate with the following expression (4) where M_{samp} is the total mass of the sample and M_{pcm} the PCM mass.

$$L = \frac{Q^* - M_{samp}.C_s.\Delta T_s - M_{samp}.C_l.\Delta T_l}{M_{pcm}} \quad [kJ] \qquad (4)$$

The obtained values are slightly different from those provided by the DSC or the manufacturer. They are the apparent heat capacities of the sample (PCM+envelope) and latent heat of the material in conditions closed to thus in which it will be used.

4.2. Energy recovery

In the cooling case, when the temperature evolves from 50°C to 15°C, solidification of the material occurs. The DSC technique was considered for the characterization of the material. Different rates of temperature variation were investigated, but the technique failed to provide any results as superfusion and crystallization on the internal walls disturbed measurements during the phase change. Indeed parts of the PCM which is solidified release great amount of heat which in turn melts already solidified PCM parts. For the parallelepipedic sample, one observes (fig. 6) these disturbances on the measured heat fluxes on the two

faces of the sample. Heat fluxes are always symmetrical but have very special evolutions.

Initially a "normal" evolution of measured heat flux corresponding to the cooling of the liquid phase is observed. Then, when t = 45 mn (when the internal and external temperatures of surfaces are near 27°C), the heat flux evolution is reversed. This is caused by the solid phase which starts to release heat. Then, suddenly, about one hour after the beginning of the test, the internal surface temperature increases from about 18°C to 25°C abruptly, this increase of the surfaces temperatures is present at the borders whereas transferred heat flux decreases. It seems that de-stored energy is reabsorbed immediately by the material (phenomenon of superfusion). From this critical moment, the cooling of the sample continues, the material is solidified slowly and cools until 15°C. After more than five hours, one reaches a new equilibrium state.
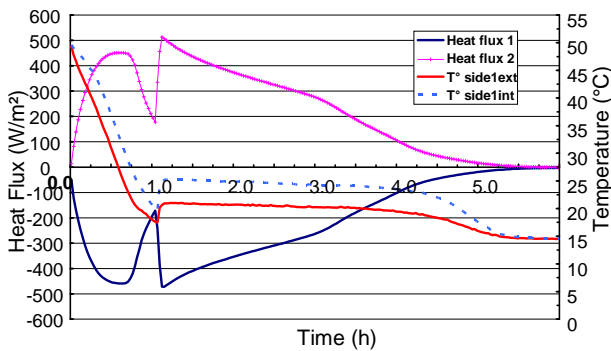

Fig. 6: Heat flux and temperatures evolutions (50°C > T > 15°C).

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. This layer somewhat isolates the liquid PCM from the cold surfaces. Solidification continues slowly because of low thermal conductivity of the solid PCM (conductivity estimated in experiments at 0,45 W/m.K). The temperature of the sample surface is equal to 15°C only at the end of the test. This can be with a defect of refrigerating power of the regulated bath which cannot quickly 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 the solid and liquid phases. Fig. 7 shows the amount of heat stored in the material for a complete cycle. For this particular sample of results, it can be observed that it was possible to obtain a liquid phase at 18°C although the manufacturer specified a fusion point à 27°C.

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 variations on a single face only (fig. 8 and 9). The state of initial balance (isothermal) is brought back towards another state of final equilibrium where heat flux tightens towards a non null value corresponding to a temperature gradient between the two faces of the sample. Apparent thermal conductivities are calculated by the following equations:

$$k_S = \frac{\Phi_{eq}.e}{\Delta T_s}\,; \qquad k_l = \frac{\Phi_{eq}.e}{\Delta T_l} \qquad (5)$$

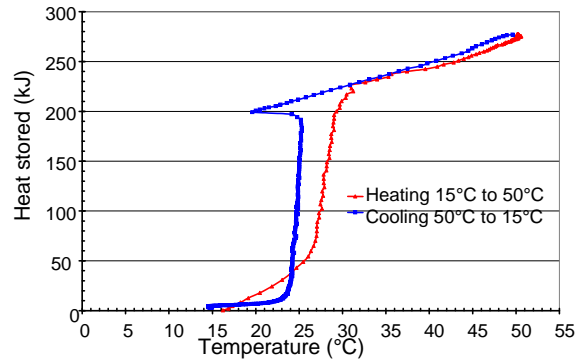where e is the material thickness and Φ is the heat flux value at the end of experience.

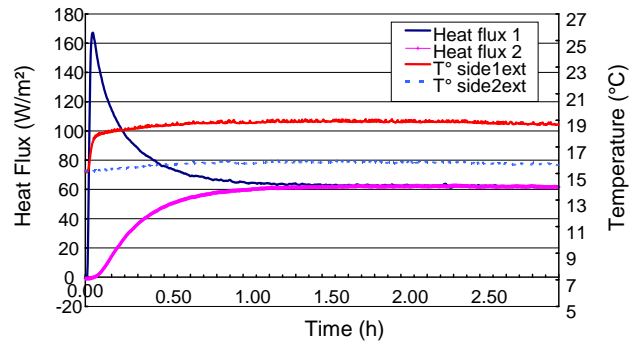Fig. 7: Heat stored on temperature cycle (15°C to +50°C and then return to +15°C)

Fig. 8 : Measurements with thermal variation on one side of the sample in solid state (15°C to 20°C).
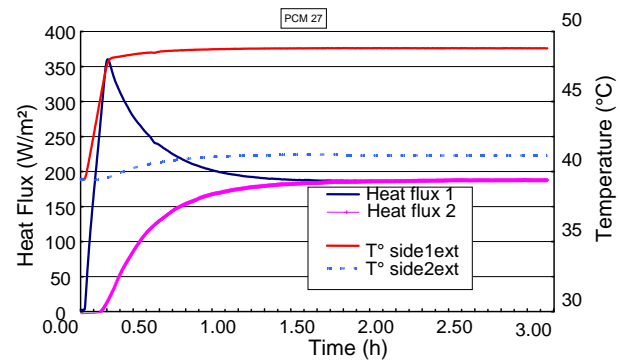

Fig. 9 : Measurement with thermal variation on one side of the sample in liquid state (40°C to 50°C).

Several tests were carried out on the material to check the reproducibility of the measurement. The results were found to be satisfactory and provided median values of apparent thermal conductivities: 0,600 W/m°C for the liquid and of 0,450 W/m°K for the solid. The estimated error on conductivity measurements is about 10%. Measurements of thermal conductivities were carried out for the different following temperatures levels: (8,5-13,5°C); (14,5-19°C) and (19,5 to 24°C). The conductivities values obtained for the solid state in theses cases (k_s) were respectively the following ones: 0,451 W/m°K, 0,450 W/m°K, and 0,441 W/m°K. The difference between these various values is within the range of the uncertainty.

However, the question arose of stating whether this technique is valid for the liquid phase because it is well known that natural convection will occur in the container (brick) Various measurements were thus made bearing this in mind.. Conductivities measurements in the liquid state between 30 and 34°C, 34,5 and 39°C, 39,5 and 44°C then finally with a more important difference in temperature (to increase the convection) between 41 and 49°C were carried out. The estimated values are respectively 0,568, 0,582, 0,596 and 0,619 $W.m^{-1}.°C^{-1}$.

The results present a global variation slightly higher than 8%. Conductivity increases with temperature and, as expected, higher conductivities are measured under steeper gradients as these drive the convective transfer which results in a higher apparent conductivity.

It is worth mentioning that global results for the whole units are required. The properties of the material alone are of mitigated interest as the bricks will form the basic elements of the recovery units.

6. Conclusion

In this article were presented the results for the thermal characterization of phase change material by use of a genuine experimental apparatus. The determination of the thermophysical properties of a specific material were obtained in a range that encompasses ambient conditions (a melting point close to normal comfort temperatures). The results obtained were very satisfactory for the upcoming use of the material tested. The proposed method was adapted from one used in the past for measurements of global thermal conductivities and specific heats of construction materials. The paper demonstrates that in can be applied to PCMs. In particular, heat flux measurements at the material outer surface 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 such as calorimetric devices (DSC). These measurements can now be used to validate a numerical method designed to simulate the same phenomena in the context of parametric studies [16]. Indeed, the final objective of the research presented here is to use PCM (hydrated salts or others) as integrated components in a dynamic or active solar wall.

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