

A novel technique for the experimental thermophysical characterization of phase change materials

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Abstract

The final objective of this work is to use phase change materials (PCMs) as integrated components in passive solar heat recovery systems. The suggested approach involves experimental investigations and characterization of the global behavior of a parallelepipedic “material wrap” filled with the PCM. The experimental apparatus permits simultaneous measurements of heat fluxes and temperatures. It also allows imposing and measuring temperatures variations with respect to selected time scales between the two predominant faces of the sample. The instantaneous heat flux measurements allow the determination of the “apparent” or overall heat storage capacities and thermal conductivities of the PCM – in the solid and liquid states – and that of the latent heat of fusion. Results were found to be very satisfactory.

Nomenclature

T	Temperature	°C
ΔT	Temperature difference	°C
$\Delta \Phi$	Heat flux difference between the two faces of the sample	W/m ²
Q	Total stored energy	J.kg ⁻¹
C	Specific heat	J.kg ⁻¹ .°C ⁻¹

L	Latent heat of fusion	J.kg^{-1}
e	Thickness	m
k	Thermal conductivity	$\text{W.m}^{-1}.\text{°C}^{-1}$
M	Mass	kg
t	Time	h

Subscripts

l	Liquid state
s	Solid state
$fusion$	Melting point
$initial$	Initial
$final$	Final
int	Internal face of the envelope
ext	External face of the envelope
$samp$	Sample (brick) which includes the PCM and its envelope
pcm	Only the phase change material
end	At the end, in steady state

1. Introduction

1.1. The interest

For many years, scientists and engineers work on the development of recovery systems allowing the storage and the use of solar energy in order to reduce the consumption of non-renewable energies and the emission of pollutants and greenhouse gases in the atmosphere.

The use of phase change materials (PCMs) seems to be particularly interesting because these are able, through melting and solidifying at specific temperatures, to store and release large amounts of energy [1] in relatively reduced volumes. PCMs are substances involving high heats of fusion which is the main reason why such materials have received great interest for many applications such as energy storage and thermal protection systems as well as in active and passive cooling processes. These possibilities and their actual limitations are well presented in the works of Tyagi and Buddhi [2] and Khudair and Farid [3]. Some of these materials also have for other principal interest to present phase change within temperature ranges closed to those of human thermal comfort in buildings [5]. Different inorganic as well as organic substances, recently well reviewed by Zalba et al. [6], have already been employed for the creation of PCMs: hydrated salts, inorganic eutectics, various non-eutectic mixtures of inorganic substances, fatty acids, organic eutectics, and paraffin waxes [3,6].

For the interested reader, excellent global reviews that pertain to phase change materials and their various applications were proposed by Tyagi and Buddhi [2], Farid et al. [4], Sharma et al. [7], Zhang et al. [8], Regin et al. [9], Mondal [10], Sethi and Sharma [11], and especially the recent one by Verma et al. [12].

1.2. The difficulties

However, despite theoretical excellent performances, PCMs are often very difficult to implement with effectiveness, due to very complex behaviors. One difficulty resides in the accurate knowledge of the relevant thermophysical properties of the materials, the appropriate methods to be used for adequate characterization, and the behavior in time of the abovementioned properties, that is their stability over numerous cycles.

Another difficulty is due to the scaling effect that is the behavior of the material encapsulated in large containers may have properties that differ significantly from those of the same material in microcapsules, for instance.

1.3. The contribution

This work presents the first results obtained at LGCgE in the context of the development of an original experimental characterization method for the determination of phase change material thermophysical properties in nearly operating conditions.

2. The global project

2.1. The composite Trombe wall

The final objective is to insert these materials in a passive solar heat recovery component. The case of the “composite Trombe wall” [13,14] is probably the system which will be retained. This “variation” of the classical Trombe wall allows daily storage of solar energy in the buildings envelope and restitution later in the evening with a possible control of air flux through a ventilated air layer (Fig. 1).

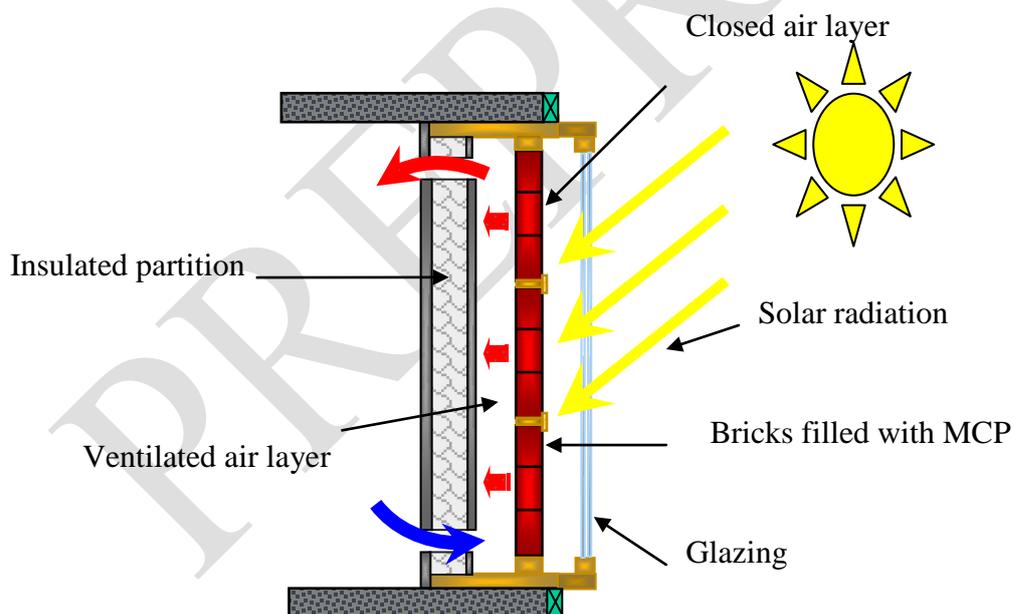


Fig. 1: Composite Solar Wall with MCP

The advantage of this type of passive solar wall is an insulating partition which allows, when necessary, to separate the massive storage wall from the heated room and thus to control the

use of the solar energy collected and stored via one ventilated air layer. This concept ensures a complete insulation of the building envelope in the event of overcast conditions and at night.

Contrary to a window by which the solar contributions are instantaneous, the “Composite TROMBE wall” allows the management of solar contributions via a storage element located in the core of the device. This storage element is generally composed of one heavy (massive) material such as concrete, strongly capacitive, and good if not excellent conductor of heat.

The objective here is twofold: reduce the size of the device in terms of occupied volume and mass, and provide heat at constant temperature suitable for human comfort. Smaller units allow more flexibility when it comes to install the device in actual buildings whereas small weight also has an effect on flexibility while reducing the stress for high resistance structures. At a later stage, the objective is to produce standard units to be installed in residential and commercial buildings.

2.2. The PCM brick

To replace the traditional sensible heat storage element by PCMs, a commercially available hydrated salt-based PCM, engineered by CRISTOPIA [6,25] and contained in polyolefin bricks, is employed. The value provided by the manufacturer for the fusion point of the solid phase is $T_f = 26,9^{\circ}\text{C}$ while the recrystallization or solidification point is $T_s = 23,5^{\circ}\text{C}$. The phase change material (hereafter called PCM 27) is conditioned in rectangular-shaped bricks with the following dimensions: 210mm x 140mm x 25mm. These parallelepiped elements are about 1 kg each. To obtain a one-dimensional overall heat transfer, in the experimental device, the lateral faces or edges are insulated with 10 cm thick polyurethane foam.

Nevertheless, this particular geometry enables two-dimensional and three-dimensional effects as shown in Fig. 2 and 3.

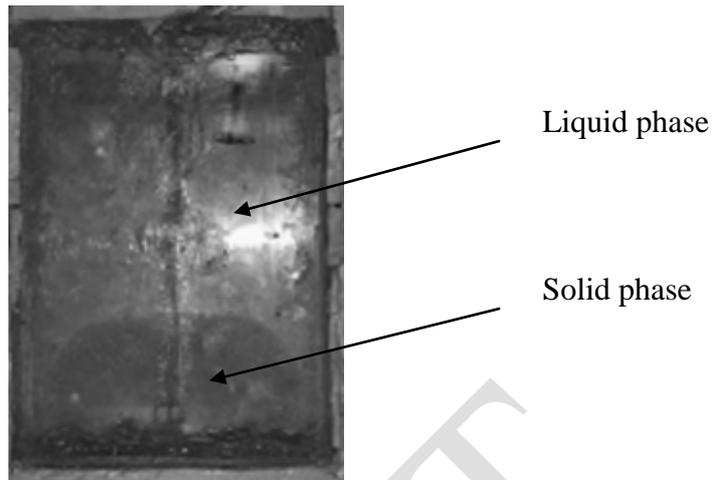


Fig. 2: Melting process, visualization of two-dimensional and three-dimensional effects.



Fig. 3: Solidification process, visualization of heterogeneous crystallization.

3. Materials characterization

3.1. A DSC approach

Generally, phase change materials are characterized by calorimetric methods like “DSC” (Differential Scanning Calorimetry) or “DTA” (Differential Thermal Analysis) [17,18,19], which use very small quantities of product. The DSC involves several advantages. The time required for a complete analysis is short and the preparation of the samples is easy. The device permits the analysis of many solid and liquid products [6]. Nevertheless, it also involves several disadvantages [20,21]. In particular, the low mass of samples used in a DSC (some mg) cannot be representative of the thermal behavior of a larger quantity (scale effect) (see Fig. 2 and Fig. 3). The wall-attachment effects can also distort the measurements.

The DSC technique is derived from the (Differential Thermal Analysis: DTA) which became the reference method for thermal characterization of phase change materials [22]. This equipment provides a heat flux (dq/dt) by Joule effect which corresponds to the necessary power to maintain a “cell” containing the sample to be characterized and a reference cell, which is generally empty, in thermal equilibrium.

$$\frac{dq}{dt} = \left(\frac{dq}{dt} \right)_{sample} - \left(\frac{dq}{dt} \right)_{référence} \quad (1)$$

In case of the heat capacity measurement for a sample which does not change of phase, the energy supplied is weak and generally not very variable. On the other hand, in the case of a fusion process, there is a transient and very fast thermal changes which requires important heat quantities over a very short period of time. Imbalance between the two cells is then very important, even if the amounts of product are small.

In practice, during actual utilization of the material, the material volume is much more important so the melting process occurs gradually in the material. The latter is then heterogeneous and several phases coexist for a long period. There are heat conduction in the solid and convection heat transfer in the liquid [23] which have great influence on the global (or apparent) behavior of the PCM.

Nevertheless, a DSC analysis has first been carried out on a material sample using a “Perkin-Elmer” calorimeter. The results obtained were consistent only in the case of fusion. Even there, some problems exist (for instance, the extrapolated end temperature is systematically too high, erroneous information is obtained when the DSC runs at a high heating/cooling rates, etc [24]).

The peak observed on Fig. 4 represents the fusion (endothermic) process of the material. The gray area is proportional to the latent heat absorbed by the sample during the phase change here 186.6 J/g. The melting point is determined as the intersection point between the prolongation of the base line and the line tangential to the peak given by the experimental device, here a temperature of $T_f=31.74^\circ\text{C}$. The procedure is usual and yet this result is relatively far away from the value provided by the product manufacturer (26.9°C).

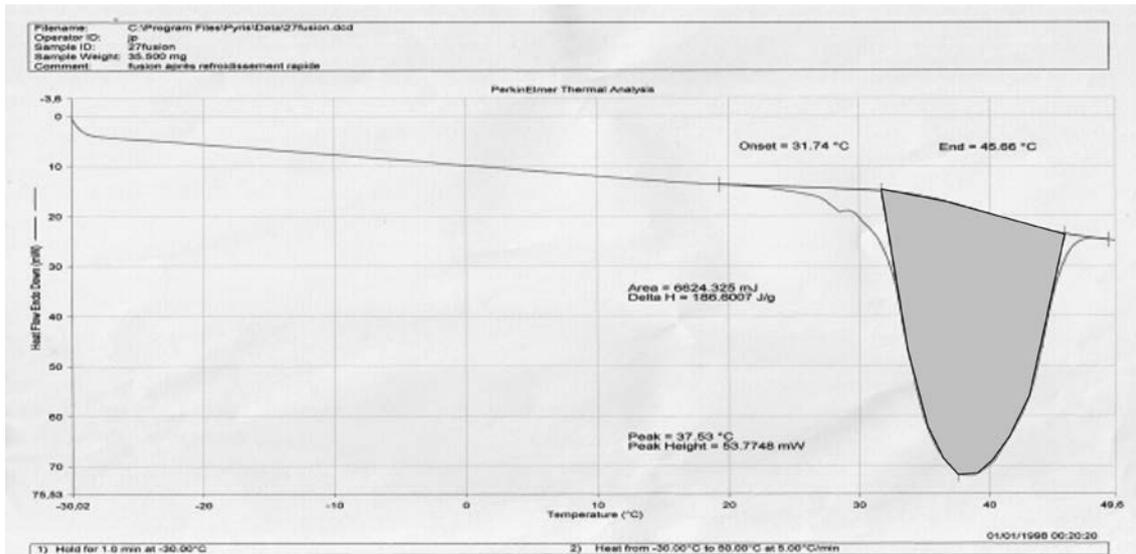


Fig. 4: Differential Scanning Calorimetry- DSC Method application (5°C/mn)

In the case of cooling, problems are more complex. With several samples of the investigated material (PCM 27), the analysis of the solidification process has been impossible because of the random importance of supercooling [15] for each sample and from one cycle to the next. The material is not a pure substance, the exact chemical composition is not known, and the phase diagram is very complex what induces thermal effects particularly difficult to control. Solidification never exactly occurred at the same temperature from one cycle to the next (recall that it should be at about 23,5°C).

3.2. A probabilistic approach

The optimal thickness for a brick-shaped PCM depends upon the real (measured) heat capacity of the element that embeds it. For concrete, the optimal thickness is about 15 cm for good energetic performances and transfer delay (3 or 4 hours) [14]. For PCMS, the optimal thickness is not as easy to obtain, Fig.3 indicates that from the liquid to the solid phase, various states and crystals coexist near the phase change temperature as the liquid cools down. This results in extremely variable apparent thermal properties of the material. Moreover, according to the past or history of the material (the number of cycles), the crystallization or fusion modes vary from one cycle to the next. This is why a probabilistic or statistical evaluation [15] of the thermophysical properties is necessary. The accurate knowledge of these properties is

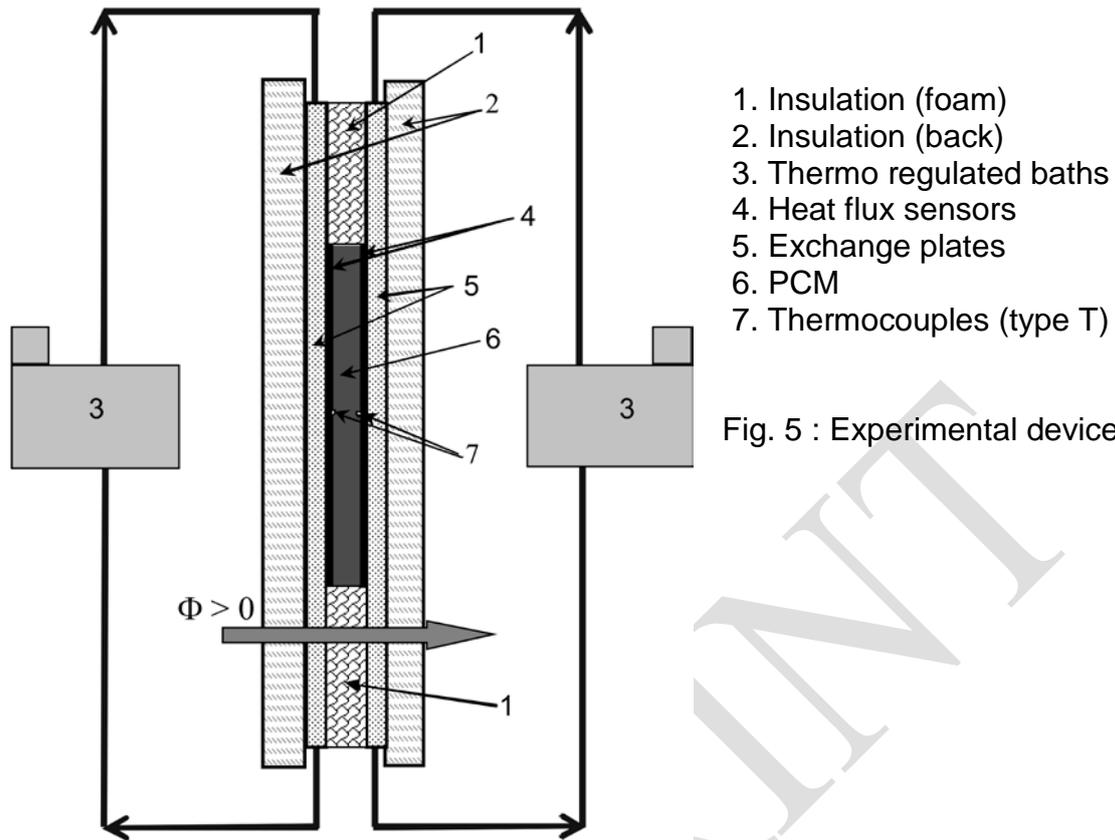
fundamental to correctly characterize the heat transfer in the wall and to have a sufficient control of it for optimum dimensioning and long term operation [16].

Here, only the “apparent” behavior, in transfer and storage according to the principal direction of energy transfer (from outdoor to indoor), will be considered thereafter, in the form of a one-dimensional model.

4. Experimental device

The search for the overall thermophysical properties of PCMs called for the design, construction, and calibration of an original experimental device. Because of the sample's geometry, the apparatus should permit the measurements of temperatures and heat fluxes at the material predominant faces (that is in the direction of heat transfer). Then, the thermophysical properties of the sample should be derived from these experimental data for temperatures and fluxes. Moreover, with the apparatus, one should also be able to determine the heat exchanged during a variation of the material thermodynamic state between two temperature levels.

Fig. 5 illustrates the principles of the experimental device that was designed and built at LGCgE. Imposing a permanent temperature gradient between the two faces of the sample, the experimental device allows determining the apparent thermal conductivity of the PCM bricks. The sample is installed vertically between two exchanger aluminium plates. Thermo regulated baths allow a fast and fine regulation of the injected water temperature with a precision of about $\pm 0,01^{\circ}\text{C}$ (JULABO model F34 HE).



Squeezed between the exchanging plates and the sample, on each of the two faces, heat flux sensors and thermocouples (T-type) (diameter 0,1 mm, sensibility $\sim 100 \mu\text{V}\cdot\text{W}^{-1}\cdot\text{m}^2$) inserted in the brick envelope are installed. The whole apparatus is maintained in place using a pneumatic jack slightly tighten. The fluxmeters used here are special “tangential gradients heat flux meters” designed, built, calibrated, and used over a period of nearly 20 years at LGCgE [26]. Their thickness is about 0,2 mm and their sensibility about $45 \mu\text{V}\cdot\text{W}^{-1}\cdot\text{m}^2$ for a sensor having an active surface of 100 cm^2 . Over the years, these sensors were the subject of regular developments and improvements making it possible to obtain highly reliable measurements [26].

These fluxmeters are calibrated, using plane electrical resistances with size rigorously equal to those of the sensors. The calibration device [27] makes it possible to calibrate these sensors with a precision of about $\pm 3\%$. The temperature measurements are differential compared to a reference sensor located in the heart of a thermal sink very stable in temperature. The various (different) sensors are connected to a multichannel multimeter

(Keithley n° 2700) adapted to low level signals measurements. Experimental data are taken and recorded with regular and adjustable step of times (here 10 s).

5. Measurements – Experimentations

Several materials were tested using the above described device. The results presented here are solely for the PCM 27 presented earlier (a mineral, containing potassium and calcium chlorides).

5.1. Energy Storage

Initially, the material is isothermal and then it is suddenly heated by modifying the temperature set point of the thermo regulated baths. The material thus evolves from temperature $T_{initial}$ to temperature T_{end} . Between these two permanent states, the material stores energy. The fluxmeters make it possible to measure the heat fluxes exchanged at the borders of the sample. The total stored energy can thus be estimated by the following expression:

$$Q = \int_{t_{initial}}^{t_{end}} \Delta\Phi dt \quad [\text{kJ}] \quad (2)$$

Where $\Delta\Phi$ is the cumulated heat flux entering the sample, (see Fig. 5). This quantity can also be expressed by the following expression:

$$Q = M_{samp} \cdot C_s \cdot \Delta T_s + M_{pcm} \cdot L + M_{samp} \cdot C_l \cdot \Delta T_l \quad [\text{kJ}] \quad (3)$$

where each variable defined in the nomenclature .

The first results are presented in Fig. 6 and Fig. 7. Temperatures are measured at the centre of the external and internal faces of the brick envelope to take into account the thermal effect (resistance) of the material which contains the product (a polyolefin envelope). The experience consists first in imposing, on the sample, a superficial constant temperature of 15°C on each of its faces, until a thermal steady state corresponding to an isothermal material is obtained. The heat fluxes are then zero at the initial time $t = 0$. A null flux at both faces confirms that the thermal losses are negligible at the isolated side faces. The experiment really starts at

($t_{initial}$); a sharp water temperature variation is imposed in the baths. This induces a thermal evolution of the system (storage) until another state of equilibrium is reached.

Fig. 6 presents the variation of the heat storage of the sample in solid phase for a temperature range that varies from 15°C to 20°C while Fig. 7 presents the results for the transition from solid to liquid phase when temperature changes from 15°C to 50°C. Results for the liquid phase only, have also been obtained and it is important to specify that the behavior, despite the expected additional natural convective heat transfer, is somewhat similar to the curves presented in Fig. 8, which presents the average values of heat flux and temperature at the sample boundaries.

On the left hand side of Fig.6, one can notice, especially when considering the heat flux curve, that the response time of the system is not instantaneous. As soon as the set point is changed from 15°C to 20°C, the heater starts and the heat flux increases as more and more hot water comes to heat up the plates. But, as the material inertia plays its role, there is a period of a few minutes for which the temperature on the envelope (side1ext and side2ext) remains almost constant. Then, the temperature follows the asymptotic increase while the corresponding heat flux measured is decreasing.

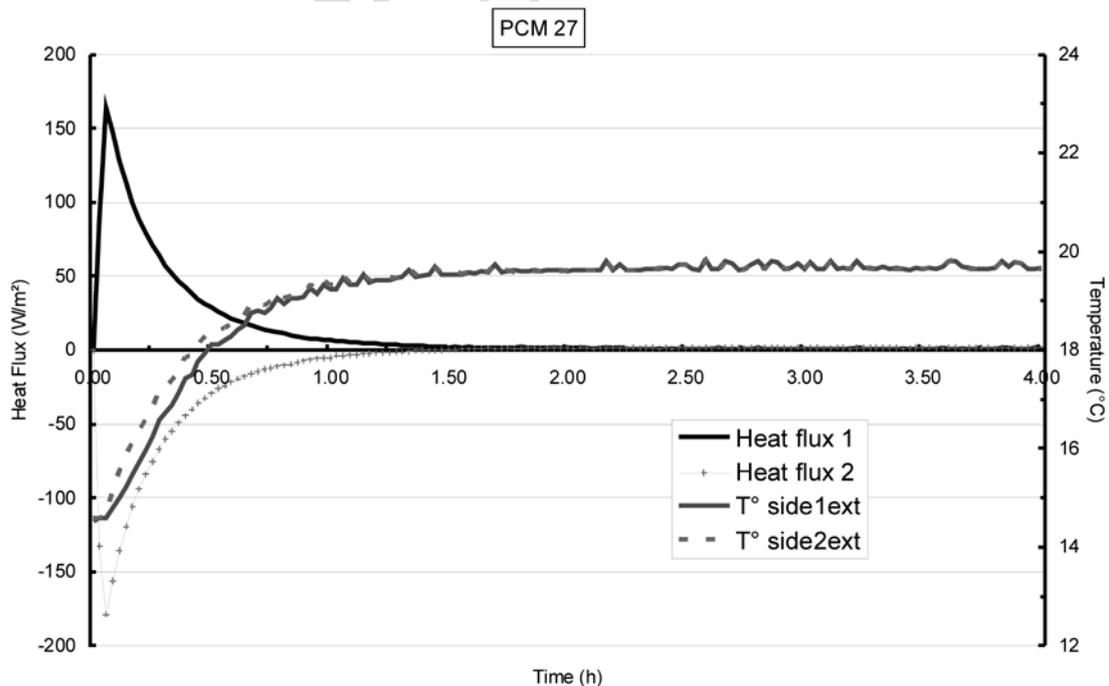


Fig. 6: Heat flux and temperatures evolution of the solid phase (15°C to 20°C).

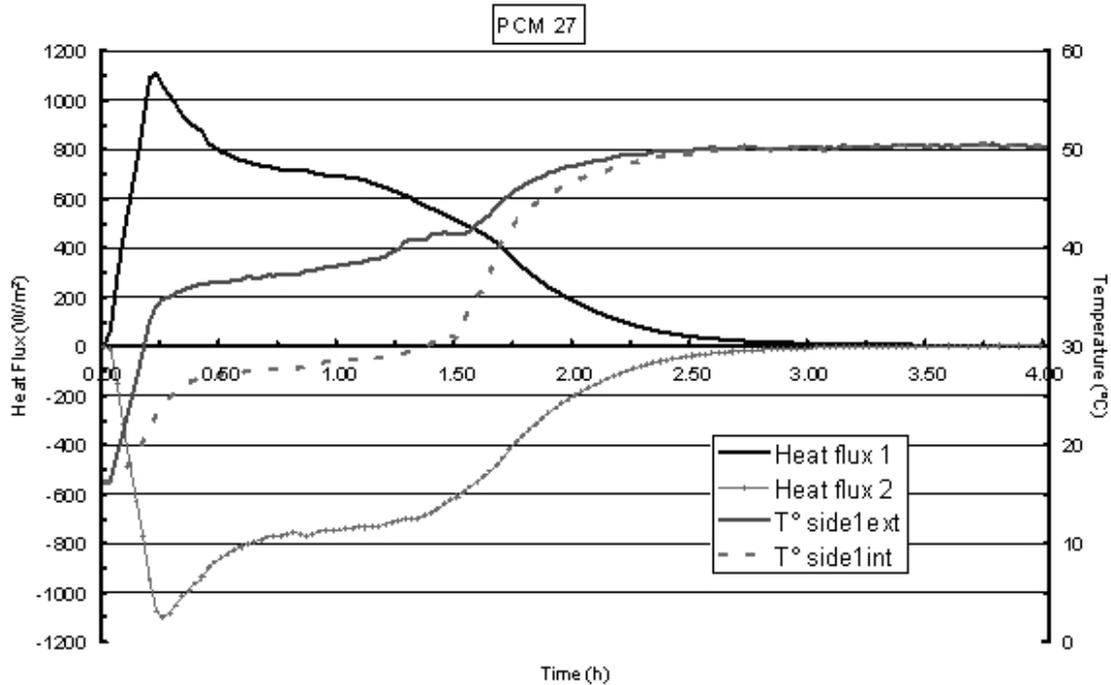


Fig. 7: Heat fluxes and temperatures evolution from solid to liquid (15°C to 50°C).

The thermal evolution from 15°C to 50°C (Fig. 7) 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 in the material. The selected initial and final temperatures are sufficiently far away from the melting point range to consider that indeed the material is strictly in one or the other state.

For the liquid and solid phases considered separately (prior to 15 minutes and after about 90 minutes), one can 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 after 90 minutes. It is also noted that the flux evolves very quickly at the beginning of the recording (sharp slopes for about 15 minutes, until melting starts) and then approaches zero which corresponds to a new state of equilibrium obtained at the end of the test.

With regard to the variation between 15°C and 50°C (Fig. 7) during which there is phase change, one observes different behaviors between the temperatures measured at the internal (side1int) and external (side1ext) faces of the “plastic” envelope. This is due to the thermal resistance of “polyolefin (thermal conductivity $k \sim 0,1 \text{ W} \cdot \text{m}^{-1} \cdot \text{°C}^{-1}$) and to the very important

latent heat absorption during the PCM fusion which produces a very important heat flux through the wall of the sample. Melting occurs, but it is shown that the polyolefin wall influences the two temperature curves. When the inner surface reaches the melting point, the outer surface is already above 35°C and as melting starts close to the inner wall of the brick, the temperature curves flatten. After about 90 minutes, most of the material is liquid and the temperature starts to increase more rapidly while the flux decreases correspondingly. 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, when the material is in the liquid state, the experimental curves obtained are similar than those for the solid state. Internal convective heat transfer makes the determination of the real heat capacity of the PCM impossible but we can obtain a realistic value for the apparent heat capacity of the sample as a whole. In fact, this apparent value is the appropriate one for future characterizations and modelling of passive solar components behaviors.

Fig. 7 shows that the heat stored is much more important than sensible heat transfer. This confirms the interest of latent heat storage.

It is seen in Fig. 8, that the thermal behavior of the sample is very particular during the fusion process. One clearly observes in this figure the different phases of the material evolution between a solid state at start and the liquid state at the end.

First, Fig.8 shows 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. A second phase of storage occurs as the temperature varies slowly from 26,5°C (line 2) to 32°C, which corresponds to the latent heat storage. The surface temperature reaches 32°C as sensible heat transfer occurs near the wall to completely melt the core of the brick which is still at 27°C at this particular moment.

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 melting point 26,5°C. From this point on, gradually, the temperature on the external faces of the sample increases slowly whereas in the middle, the material continues to melt. 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 one capacitive heat flow taking part in the heating of the liquid and solid

phases which coexist in a variable proportion and overall all of the briquette (material + envelope). At the end of this phase, in the neighborhood of 32°C, the capacitive heat overrides the latent one, the curve becomes deformed with two apparent slopes. Finally, a fast phase of temperature increase (line 3) occurs for both the liquid and envelope until stabilization at the final temperature set point which is a phase of sensible heat storage by the PCM in liquid state.

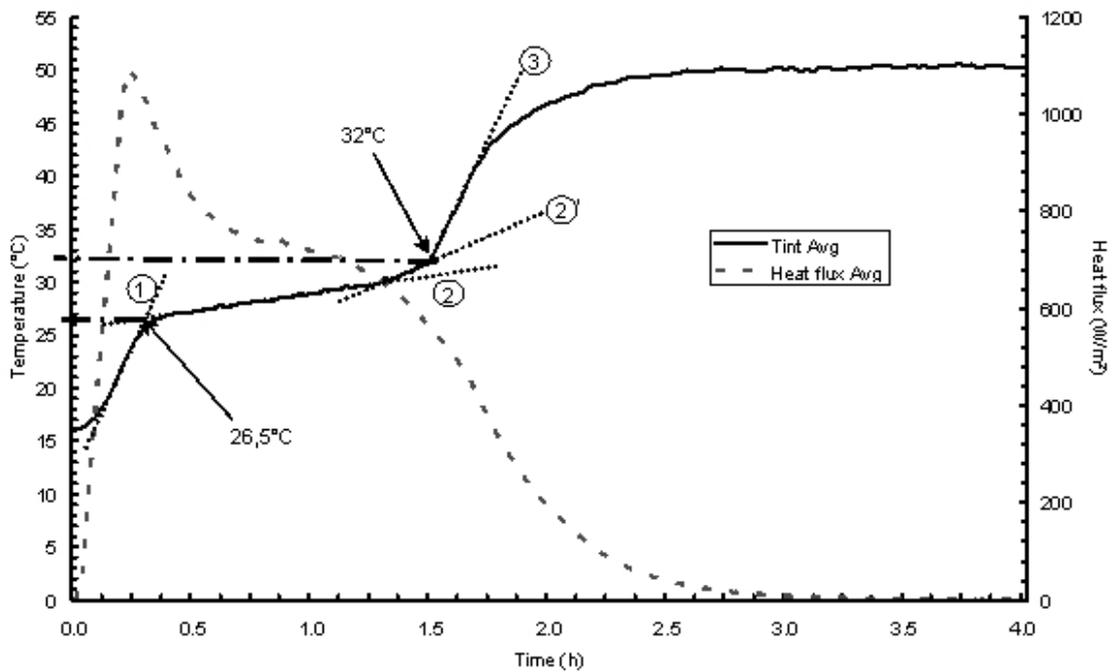


Fig. 8: Average values of heat flux and temperature at the sample boundaries

The intersection between line 1 and line 2, thus can define the beginning of the fusion of the PCM (26,5°C) and the intersection between line 2' and line 3 can defines the end of fusion (32°C) the material is entirely liquefied. If one adds up the heat accumulated between these two points, he can determine the latent heat of fusion of the PCM.

For each test, the integration of the heat flux 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 tests 1 and 2. Next, when experiments gave about the same results, this confirmed the reproducibility of the cyclic process. The error estimated for the evaluation of the latent heat is in the same order of magnitude (about 11%).

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 amount 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 was found to be slightly higher (3%). This last value is in the order of magnitude of the uncertainties on heat flux measurements and nothing better can be expected from this experimental apparatus.

<u>Tests in only one phase</u>		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
<u>Tests with fusion of the PCM</u>		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: Measurements of thermophysical properties for PCM 27

Sample (1,240 kg) – PCM (1,135 kg)

The latent heat of the PCM is obtained with the following expression (4) where $M_{s\text{amp}}$ is the total mass of the sample and $M_{p\text{cm}}$ the PCM mass.

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

The values obtained here are slightly different than 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 those into which the bricks will be used. The end of the melting phase is confirmed exactly by the DSC measurements.

5.2. Energy recovery

In the cooling case, when the temperature evolves from +50°C to +15°C, we observed the solidification of the material. We tried to use the DSC device for different cooling rates (for instance 0,1°C/mn), but no results have been obtained using this method. The DSC method is found to be completely ineffective, supercooling and crystallization on the walls are both causing disturbances on the measurements during solidification. Indeed, some parts of the liquid PCM which solidify, release great amounts of heat which, locally, melt surrounding solid parts of the PCM that just froze, and so on. For the parallelepipedic samples used herein, one observes (Fig. 9) these disturbances on the measured heat fluxes on the two faces of the sample. Heat fluxes curves are always symmetrical but with very special evolutions.

Initially, we observe a somewhat “normal” evolution of the heat fluxes corresponding to the cooling of the liquid phase. At the end of this rather stable phase ($t = 45\text{min}$), when the temperature of the surfaces is close to 27°C, the heat flux evolution is reversed. Then, suddenly, about one hour after the beginning of the test, the surface temperatures increase from +19,5°C to +25,5°C abruptly (dashed line in Fig.9). One observes this sudden increase of the surface temperatures at the borders whereas heat fluxes correspondingly decreases. It seems that the released energy of solidification is reabsorbed immediately by the material (supercooling). After this critical moment, the cooling of the sample continues normally, the material slowly solidifies and cools down to 15°C. After more than five hours, one reaches a new equilibrium state. One should keep in mind that the curves are not those of the PCM itself, but those of the external faces of the whole brick.

Heat restitution is a rather long process. Indeed, at the beginning of solidification, a layer of solid PCM is forming on the plane vertical surface in contact with the exchanging plate at a low temperature. Hence, this low conductivity solid layer, which somehow isolates the liquid PCM, forms and slows down the heat transfer to the plates. Solidification continues slowly because of this low thermal conductivity of the solid PCM (k_s estimated experimentally at $0,45 \text{ W}\cdot\text{m}^{-1}\cdot\text{°C}^{-1}$). The temperature of the sample surface is equal to 15°C only at the very end of the test. This could be a defect of refrigerating power of the regulated bath which cannot quickly absorb all the heat released during the material solidification. In these experiments, it is very difficult to separate latent and sensible heat when the PCM becomes solid. This is, in part, due to the heat transfer across the solid layer to get out of the sample.

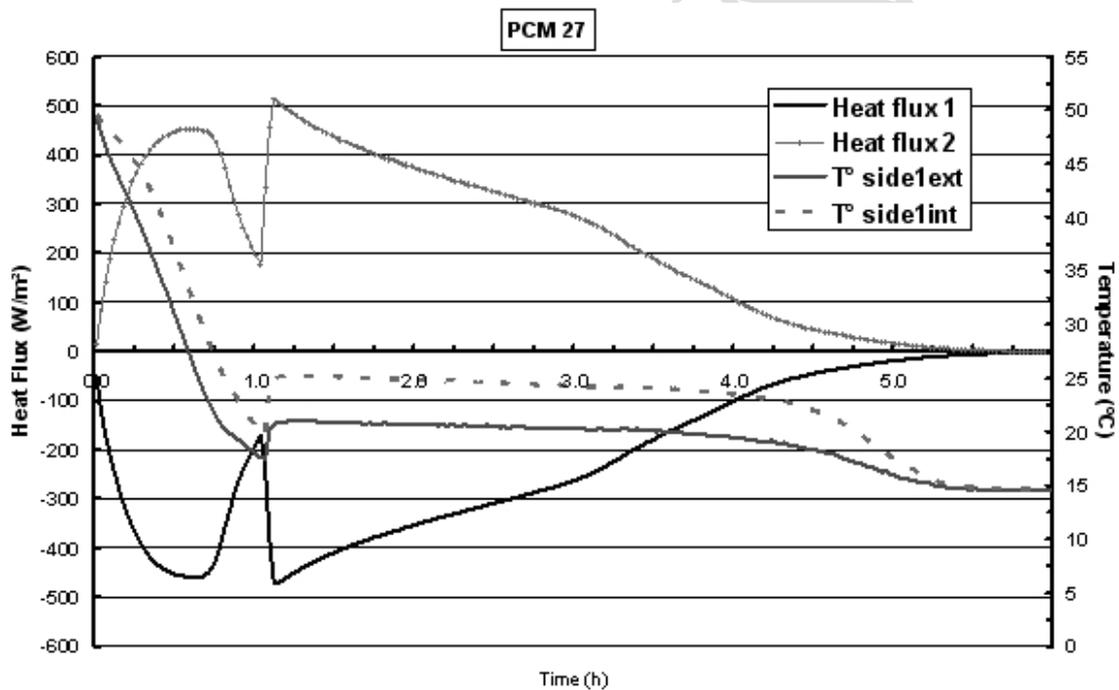


Fig. 9: Heat flux and temperatures evolutions ($50\text{°C} > T > 15\text{°C}$).

This test highlights the difficulties to estimate the amount and rate of heat recovery in the material. These difficulties pertain to the existence of supercooling and also because of thermal conductivity differences between solid and liquid phases. Fig. 10 shows the amount of heat stored in the material for a complete cycle.

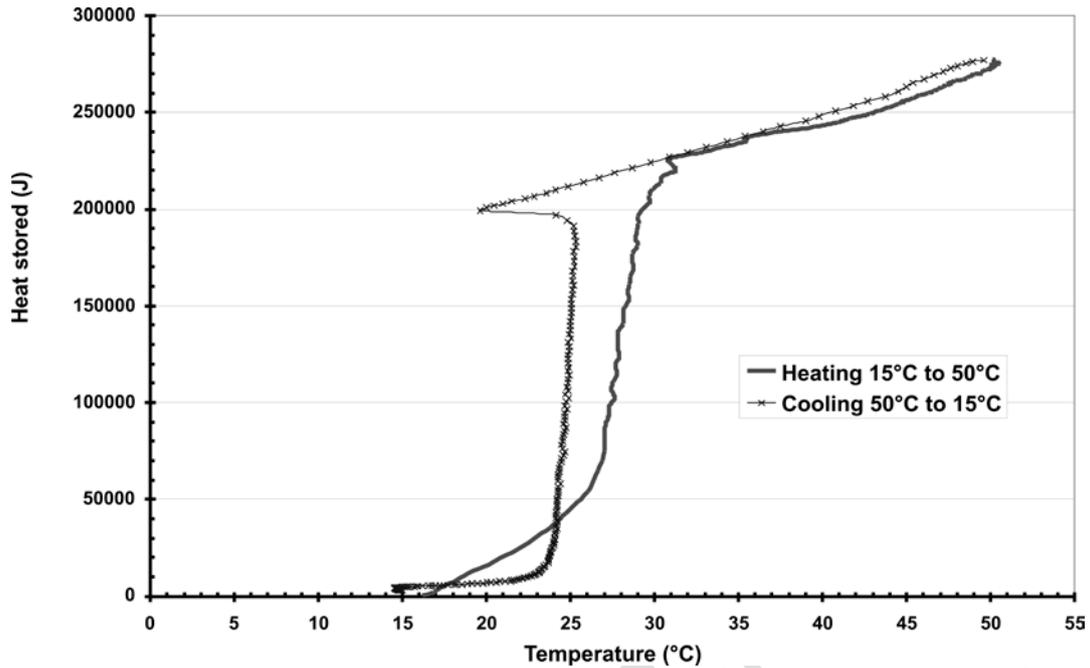


Fig.10: Heat stored on temperature cycle (15°C to +50°C and then return to +15°C)

Fig. 10 confirms that we can store a lot of heat in the PCM in a small interval of temperature variation. But we also can see that the recovery of heat is not easy with the clear presence of a subcooling peak on the cooling curve under 26,9°C. (Most cooling occurs at 24°C but the liquid phase has to drop below 20°C before solidification begins).

5.3. 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 one face only (Fig. 11 and 12). The initial state of equilibrium (isothermal) is brought towards another state of equilibrium where heat fluxes tend 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:

$$k_s = \frac{\Phi_{end} \cdot e}{\Delta T_s} \quad (5)$$

$$k_l = \frac{\Phi_{end} \cdot e}{\Delta T_l} \quad (6)$$

where the variables are defined in the nomenclature.

Three tests were carried out on the material to check the reproducibility of the measurements. The results were found to be satisfactory and gave median values of apparent thermal conductivity of $0,6 \text{ W}\cdot\text{m}^{-1}\cdot\text{C}^{-1}$ for the liquid and of $0,45 \text{ W}\cdot\text{m}^{-1}\cdot\text{C}^{-1}$ for the solid. The estimated cumulated error on conductivity measurements with the proposed method and apparatus is about 10%. This error is acceptable for our purpose but it should be mentioned that it mainly depends upon the error on temperature measurements as the temperature differences used are small. Measurements of conductivities were carried out for the different following temperature differences: (8,5 - 13,5°C); (14,5 - 19°C) and (19,5 to 24°C). The values for the conductivity, obtained for the solid state, were respectively: 0,45, 0,45 and 0,44 $\text{W}\cdot\text{m}^{-1}\cdot\text{C}^{-1}$.

The discrepancy is very small; however, one question arises. Is it the same for the apparent conductivity of the liquid state despite natural convection within the brick?

Various measurements were then carried out having in mind the potential effect of natural convection in the liquid. Conductivity measurements in the liquid state between 30 and 34°C, 34,5 and 39°C, 39,5 and 44°C, and 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 0,57, 0,58, 0,60 and 0,62 $\text{W}\cdot\text{m}^{-1}\cdot\text{C}^{-1}$. The results present a variation slightly higher than 8% among for conductivity with a light increase with respect to the temperature and an increase when the temperature variation is more important.

These results provide a better knowledge and control of the behavior of the material under the actual on-site conditions.

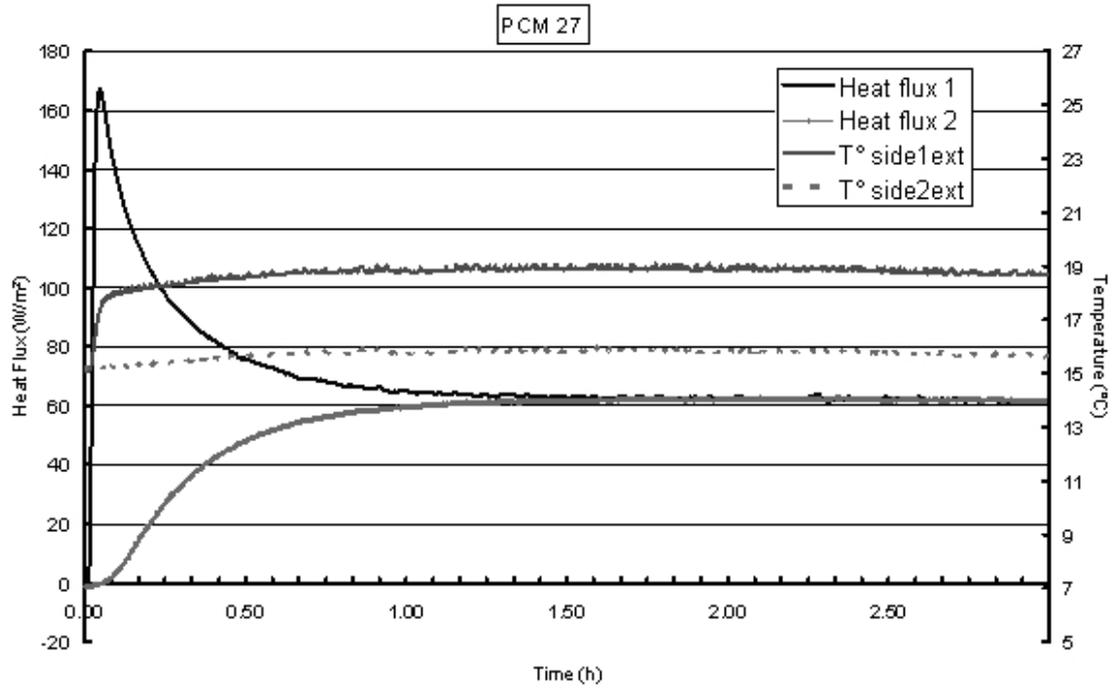


Fig. 11 : Measurements with thermal variation
on one side of the sample in solid state (15°C to 20°C).

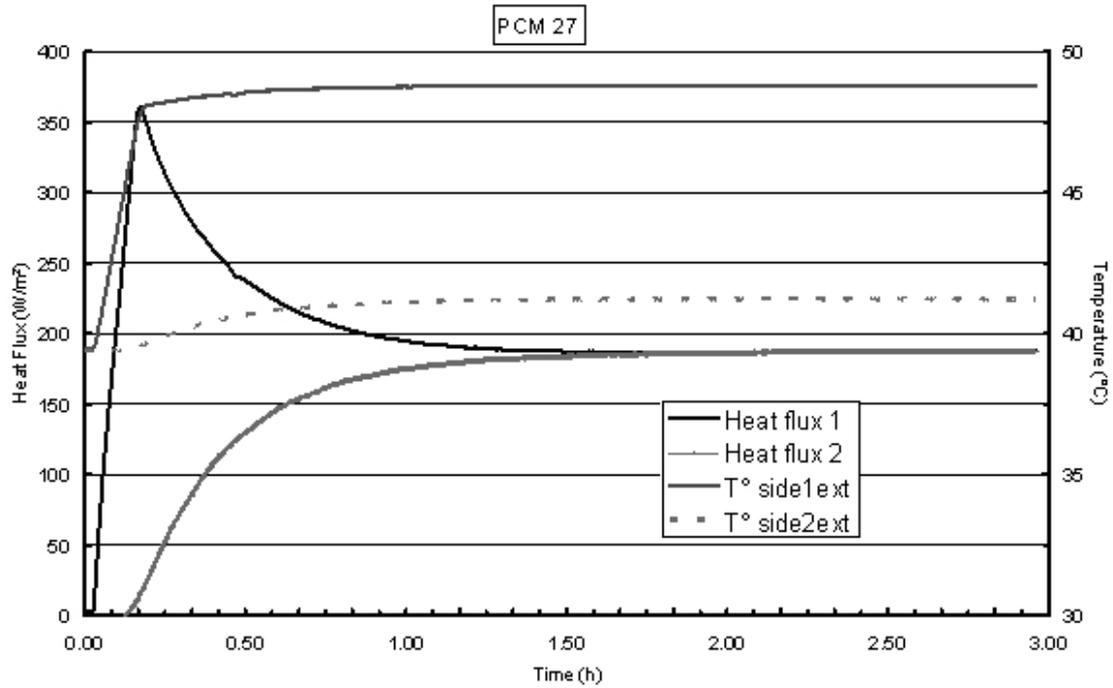


Fig. 12 : Measurements with thermal variation
on one side of the sample in liquid state (40°C to 50°C).

6. Conclusions

6.1. Summary

In this article were presented the first results obtained within the framework of a research program aimed at elaborating an original method to characterize the global or overall thermophysical properties of selected brick-shaped phase change materials in real conditions.

Although these materials rise much interest as the current energy and economic contexts are favorable, their real characterization for several practical applications remains a problem.

In the case of the materials with phase change, it is a true asset to be able to measure in real-time the heat stored or released by the storage unit, particularly when the temperature varies very slightly about the melting point whereas latent heat exchanged is very high.

The determination of the heat flux is preponderant for the knowledge of the thermodynamic state of the material and its evolution over time.

Hence, this work proposes a method for the determination of the thermophysical properties of brick-shaped phase change materials in either the liquid or the solid state as well as during the phase change of the enclosed material when both phases coexist in its “envelope” or package.

The properties measured herein are the apparent thermal conductivity and the specific heat in the solid and liquid states. The melting point and the latent heat were also experimentally determined. The experimental method is based on heat flux and temperature measurements at the boundaries of the material in the direction of the fluxes. It is done by inserting the test “brick” in contact with exchanging plates at controlled known temperatures.

The current study made it possible to highlight the influence of supercooling on the release and rate of release of heat. The interest of the developed device lies in the reliability and repeatability of the measurements, the measurement of the overall behavior of the properties of the macro-encapsulated PCM, and the low cost of the apparatus and operation fees.

Here, the determination of the thermophysical properties have be carried out for PCM 27 with a melting point close to normal comfort temperatures. The results obtained here were very satisfactory when compared to the generic properties provided by the manufacturer and show how this method can allow the study of complex-shaped materials embedding PCMs.

These flux and temperature measurements are an additional experimental data source for the material package which comes to supplement the traditional methods for the sole material like the calorimetric type (DSC) which work out with very small amounts of pure material.

6.2. Future work

In an upcoming project, the bricks of PCM will be inserted into a building wall and will be subject to much more complex thermal solicitations. The day-night cycles, and solar irradiation will replace the controlled environment and introduce sharply varying heat fluxes. These new varying sources of heat transfer will determine the successive transformations of the material. The data collected in these first experiments will hence be quite useful for the interpretation of the results. The installation of optimal energy management systems and the development of tools for numerical simulations will then allow the optimization of energy systems including PCMs.

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References

- [1] Abhat A., Low temperature latent heat thermal energy storage: Heat storage materials, *Solar Energy*, 1983, 30(4), 313-332
- [2] Tyagi V.V., Budhi D., PCM thermal storage in buildings: A state of art, *Renewable and Sustainable Energy Reviews*, 2007, 11(6), 1146-1166
- [3] Khudhair A. M. and Farid M. M., A review on energy conservation in building applications with thermal storage by latent heat using phase change materials, *Energy Conversion and Management*, 2004, 45(2), 263-275

- [4] Farid M. M., Khudhair A. M, Razack S.A.K., Al-Hallaj S., A review on phase change energy storage: materials and applications, *Energy Conversion and Management*, 2004, 45(9-10), 1597-1615
- [5] Zhu N., Ma Z., Wang S., Dynamic characteristics and energy performance of buildings using phase change materials: A review, *Energy Conversion and Management*, 2009, 50(12), 3169-3181
- [6] Zalba B., Marín JM., Cabeza LF., Mehling H., Review on thermal energy storage with phase change: materials, heat transfer analysis and applications, *Applied Thermal Engineering*, 2003, 23(3), 251-283.
- [7] Sharma A., Tyagi V.V., Chen C.R., Buddhiet D., Review on thermal energy storage with phase change materials and applications, *Renewable and Sustainable Energy Review*, 2009, 13(2), 318-345
- [8] Zhang Y., Zhou G., Lin K., Zhang Q., and Di H., Application of latent heat thermal energy storage in buildings: State-of-the-art and outlook, *Building and Environment*, 2007, 42(6), 2197-2209
- [9] Regin A. F., Solanki S.C., and Saini J.S., Heat transfer characteristics of thermal energy storage system using PCM capsules: A review, *Renewable and Sustainable Energy Reviews*, 2008, 12(9), 2438-2458
- [10] Mondal S., Phase change materials for smart textiles – An overview, *Applied Thermal Engineering*, 2008, 28(11-12), 1536-1550
- [11] Sethi V.P., Sharma S.K., Survey and evaluation of heating technologies for worldwide agricultural greenhouse applications, *Solar Energy*, 2008, 82(9), 832-859

- [12] Verma P., Varun, Singal S.K., Review of mathematical modelling on latent heat thermal energy storage systems using phase-change material, *Renewable and Sustainable Energy Reviews*, 2008, 12(4), 999-1031
- [13] Zalewski L., Lassue S., Duthoit B., Butez M., Study of solar wall - validating a simulation model, *Building and Environment*, 2002, 37, 109-121
- [14] Zalewski L., Chantant M., Lassue S., Duthoit B., Experimental thermal study of a solar wall of composite type, *Energy and Buildings*, 1997,55(1), 8-17
- [15] Ehmimed JF., Zeraouli Y., Dumas JP, Mimet A., Heat transfers model during the crystallization of a dispersed binary solution, *International Journal of Thermal Sciences*, 2003, 42(1), 33-46.
- [16] Stritih U., An experimental study of enhanced heat transfer in rectangular PCM thermal storage, *International Journal of Heat and Mass Transfer*, 2004, 47(12-13), 2841-2847
- [17] D. Banu, D. Feldman, D. Hawes, Evaluation of thermal storage as latent heat in phase change material wallboard by differential scanning calorimetry and large scale thermal testing, *Thermochimica Acta*, 1998, 317, 39-45
- [18] Rady M., Study of phase changing characteristics of granular composites using differential scanning calorimetry, *Energy Conversion and Management*, 2009, 50(5), 1210-121
- [19] Bentz DP., Turpin R., Potential applications of phase change materials in concrete technology, *Cement and Concrete Composites*, 2007, 29(7), 527-532

[20] Yinping Z; Yi J., A simple method, the -history method, of determining the heat of fusion, specific heat and thermal conductivity of phase-change materials. *Measurement Science and Technology*, 1999, 10, 201-205

[21] Cordeiro Cavalcanti F., *Caractérisation thermique de produits de l'état liquide à l'état solide*, Thèse de Doctorat., Institut National des Sciences Appliquées de Lyon, 2006.

[22] Brown Michael E., *Handbook of thermal analysis and calorimetry*, Vol.1, 2nd Ed., Elsevier, 2003.

[23] Vidalain G., Gosselin L., Lacroix M., An enhanced thermal conduction model for the prediction of convection dominated solid–liquid phase change, *International Journal of Heat and Mass Transfer*, 2009, 52 (7-8), 1753-1760

[24] He B., Martin V., Setterwall F., Phase transition temperature ranges and storage density of paraffin wax phase change materials, *Energy*, 2004, 29, 1785–1804

[25] Available from <<http://www.cristopia.com/english/products/indproducts.html>>, consulted 2010-03-15 to obtain manufacturer's parameters.

[26] Leclercq D. and They P., Apparatus for simultaneous temperature and heat flow measurement under transient conditions, *Review of Scientific Instruments*, 1983, 54, 374-380

[27] Lassue S., Guths S., Leclercq D. and Duthoit B., Natural convection by heat flux measurement and anemometry using thermoelectric effects, 3rd world conf. on experimental heat transfer, fluid mech. and thermodynamics, 1993, 831-838