DETERMINATION OF THERMO-PHYSICAL PROPERTIES OF A SMART HEXADECANE PHASE CHANGE MATERIAL -GYPSUM COMPOSITE AS BUILDING ENERGY STORAGE SYSTEM

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Abstract

Smart gypsum composite was manufactured by adding copper tubes containing Hexadecane Phase Change Materials (HPCMs) in order to develop building materials with high thermal energy storage (TES) capacity useful for being applied in high comfort constructive systems. Firstly, an investigation by means of a differential scanning calorimeter (DSC) was carried out to obtain the latent heat and the transition temperature of HPCMs. Secondly, an additional study was conducted to gauge the improvement of energy storage performance in classical construction material (Gypsum/copper tubes) filled with paraffin developed to improve different properties of PCM and open a wide field of applications to latent heat storage systems. The objective of this research is to use PCM composite 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. Experimental investigations of the thermophysical properties of the considered composite (Gypsum/copper tubes) have shown that the material combines a high heat storage potential and an improved heat transfer at the same time. Besides, the results showed that the shape-stabilized phase change material prevents the leakage of the molten paraffin during phase transition and proved a good thermal stability.

Keywords: *Gypsum, Hexadecane Phase change material (HPCM), Thermal Energy storage (TES), Transient Guarded Hot Plate Method (TGHPM), DSC analysis.*

Introduction:

As mismatch between energy supply and demand rises increasingly, thermal storage systems designed to reduce it and to save energy in buildings have received correspondingly more and more interest [1]. Under this circumstance, thermal energy storage is the most preferable techniques to be applied in building construction in order to develop the energy efficiency [2]. In particular, latent heat energy storage with phase change material is taken as the most promising method due to its large energy storage capacity and its ability to store thermal energy at relatively constant temperatures [4–3].

Large kinds of phase change materials (organic, inorganic and eutectic) have been investigated as latent heat thermal energy storage materials. Among them, paraffin is designed as the best candidate for preparation of smart PCMs in diverse application do to its important heat storage capacity, good thermal and chemical stability, little super-cooling, and low cost [5-6]. The problem of paraffin is its low thermal conductivity and leakage, which can hinders its applications. It extends the period of charging and discharging process of the thermal energy storage and can reduce the rate of storing and releasing energy of PCM.

For over three decades, research projects investigated several techniques for enhancing the thermal storage of the PCM. The most common techniques are:

- rising the heat transfer area either by, using heat pipes [7]), application of multitubes heat exchangers [8], or utilization of finned tubes [9].
- enhancing the PCM thermal conductivity either by dispersing high conductivity particles within the PCM [10, 12, 13, 14], integrating a metallic matrix into the PCM, utilizing of bubble agitation in the PCM [11] and impregnating a porous graphite matrix with PCM [15,16].

The present work aims at developing new construction material for utilize in high-comfort constructive and to contribute to elucidating our knowledge and understanding of the effects of the PCM incorporated in building material. This material consists of copper tubes filled with HPCM which are regularly spaced and aligned in a gypsum matrix. The prepared composite shows features of high energy storage density, a high thermal conductivity of heat exchange, and an absence of molten paraffin leakage. This paper is focused on the experimental investigation of the thermal energy storage properties improvement of a new composite PCM. The melting temperature, latent and sensible specific heat of the PCM was characterized using DSC (Differential Scanning Calorimetry). The thermophysical properties of the elaborated material have been measured using Transient Guarded Hot Plate Method (TGHPM).

1. Experimental study

1.1. Studied material:

Two samples of identical dimensions (200 × 200 × 62 mm^3) have been considered.

The first is gypsum with empty copper tube. The second is gypsum composite with copper tube containing PCM (hexadecane). Hexadecane is a saturated hydrocarbon of the alkenes family, purchased from *Sigma-Aldrich* with the purity of 99%. The melting temperature of the HPCM provided by *Sigma-Aldrich* is 18°C.

The preparation of the PCM composite goes through different steps:

Firstly, copper tubes are positioned and aligned in a mold (200 × 200×e mm^3) with an equidistant distribution of 25mm between the tubes (see fig1-a-) .Therefore, a certain quantity of gypsum was mixed with a few milliliters of water, and then it was stirred continuously at high speed until a pasty mixture was obtained (figure 2). The gained mixture was injected into the mold, slightly compressed at an ambient temperature for 48 h. Finally, HPCM was melted at a temperature above the melting temperature. After that, all copper tubes were filled with the molten paraffin wax very rapidly by using a hermetic syringe.

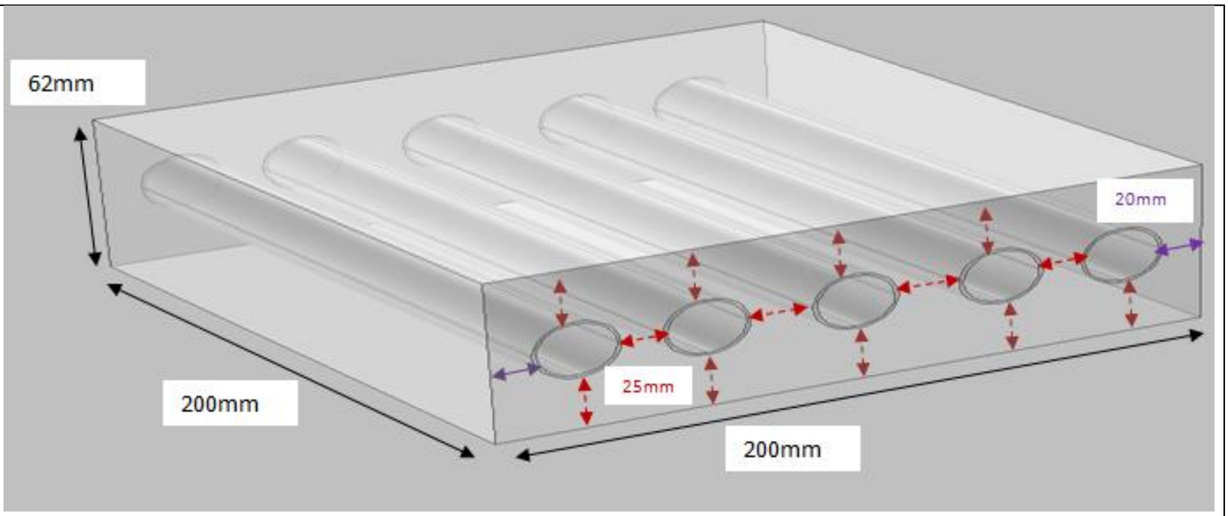

Fig1-a-: Model of Composite: gypsum /copper tubes

Fig1-b-: Composite: gypsum /copper tubes (12 mm outer diameter and 11.2mm inner diameter).

Fig. 2. Pasty mixture (gypsum + water).

1.2. Experimental set-up:

Fig. 3 illustrates an experimental facility used in the present and previous studies by Trigui et al[17]. The facility included two plate heat exchangers of aluminum between them a parallelepiped shaped composite sample (200×200×e mm^3) is sandwiched. Thermo regulated baths, supplying the plates, allow the heating and cooling needed to simulate diverse thermal conditions. The lateral sides of the studied composite are insulated by expanded polystyrene which reduces the heat transfer into the external ambient condition. Between the exchanging plates and the sample, in order to measure heat flux and temperature on each face of the sample, heat flux sensors and T-type thermocouples are placed on both sides of the sample. All sensors are connected to an USB acquisition device controlled by a Labview program adapted to measure temperature fluctuations and heat flux exchanged during melting and cooling processes. Experimental data are recorded with regular and adjustable time steps (6 s).

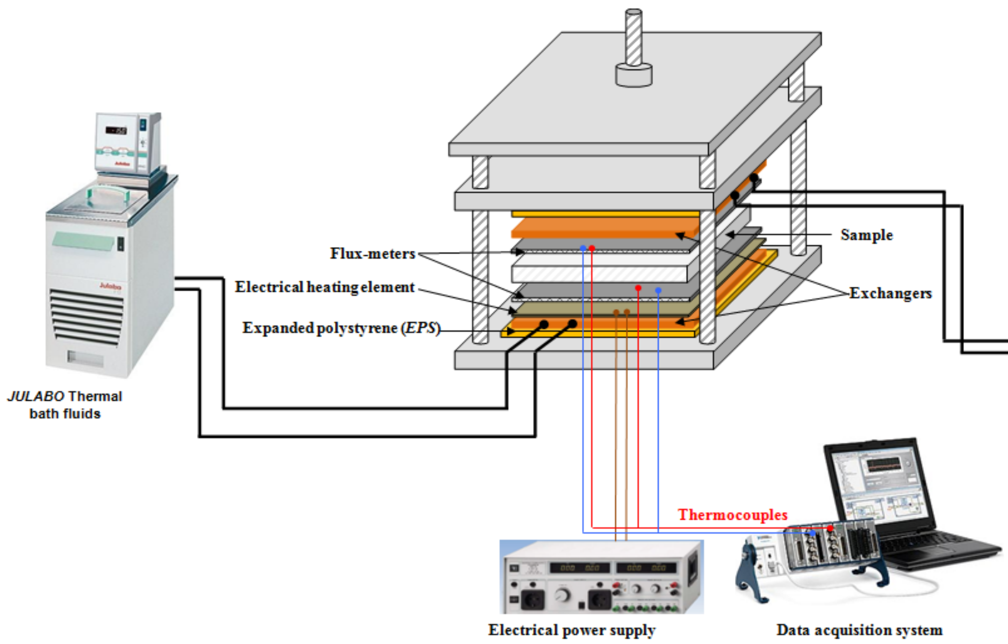

Fig 3: Transient Guarded Hot Plate Method (TGHPM)

2. Results and discussion:

2.1Determination of thermophysical properties of the composite-PCM:

This section aimed to perform out determination of various thermophysical proprieties of the specimen during the solid or liquid state of the PCM.

2.1.1. Apparent thermal conductivity:

In order to measure the solid and the liquid thermal apparent conductivity of such sample, several tests were carried out by means of Transient Guarded Hot Plate Method (TGHPM). The characterization has been realized far away from the melting temperature, in order to be sure that the PCM is at solid or liquid state. This test is done by imposing a thermal gradient between up and down sides of the composites until observing a zero heat flux (equilibrium state).

Thereby, the apparent thermal conductivity of the sample is determined via the following expression [18, 19]:

$$\lambda_{s,l} = e.\frac{\sum \varphi_{s,l}}{2.\Delta T_{s,l}} \quad (1)$$

Where e is the thickness of the specimen and $\sum \varphi_{s,l}$ is the sum of measured heat fluxes.

The evolution of heat fluxes and the measured temperatures on both sides of the sample in tow cases: when the paraffin is in solid or liquid state are illustrated in fig 5-6.

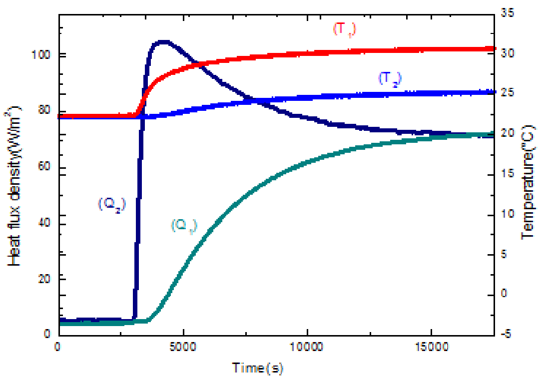

Fig 4*: Measurements with thermal variation of the liquid sample (22°C to 30°C) for gypsum /copper tubes filled*

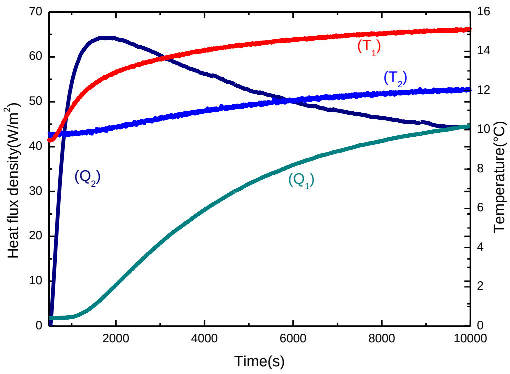

Fig 5: *Measurements with thermal variation of the solid sample (10°C to17°C) for gypsum /copper tubes filled with paraffin*

A symmetrical behavior of heat fluxes and temperatures measured on both faces of the composite sample can be observed in Figs. 4 and 5, which correspond to the results classically obtained with a solid material without phase change (fig.6).

Both figures show that the sample is isothermal at the beginning. Therefore, a thermal gradient was imposed which cause a temperature increase only in the bottom face of the composite up to second thermal equilibrium was established .

Adopting Eq. (1), the thermal conductivity of the composite-PCM could be measured employing the value of the temperature difference and the average value of the heat fluxes when a steady state is reached.

Several tests were carried out on the composite material to check the reproducibility of the measurement. The results were found to be satisfactory; they provided an average thermal conductivity of 0.73 W $m^{-1}K^{-1}$for the PCM in solid phase and an average thermal conductivity of 0.83 W $m^{-1}K^{-1}$when the PCM is in liquid phase. And their associated uncertainties when the paraffin is in solid and in liquid phases are respectively 6.2% and 6

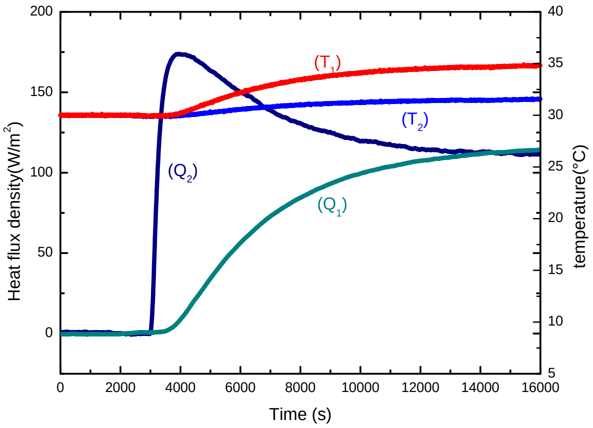

Fig 6: *Measurements with thermal variation one side of the solid sample (30°C to 35°C) for gypsum /copper tubes*

The experiences carried out with the composite (gypsum/copper tube without PCM) have yielded its thermal conductivity 0.99W m^{-1} K^{-1} in the temperature range 31°C – 35°C .The thermal conductivity is in this manner present a large difference with the composite PCM. Consequently, the incorporation of PCM in the copper tube decreases the thermal conductivity, which is a disadvantage for heat transfer. So, the subject of the following section is to study the effect on heat storage capacity.

2. 1.2.Sensible heat and apparent heat capacity:

To measure the specific heat capacity and specific heat of a material, the method used here is consisted in simultaneously measuring the heat flux $f_{1,ex}$ and $f_{2,ex}$ and the temperatures T_1 and T_2 on the two faces of the sample (T_1 and T_2 are the two thermocouples integrated in the flux sensors) . Initially, the exchangers are maintained at a constant temperature until reaching a zero heat flux density on both faces of the sample. Then, the temperature of the exchangers was augmented and maintained until thermal equilibrium. Between these two permanent steady states, the sample stores or liberates a quantity of sensible heat which establishes the variation of the internal energy of the system.

The evaluation of the specific heat capacity is given by the following equation [20]:

$$Q_{sens} = \frac{1}{\rho . e} \int_{tinit}^{tend} \Delta\phi . dt \; = C_p . (T_{end} - T_{init}) \qquad (2)$$

$\Delta\phi$ represents the cumulated heat rate entering the sample; C_p :apparent specific heat capacity composite (*kJ/kg.°C*); ρ : density of the sample; *e*: thickness of the sample.

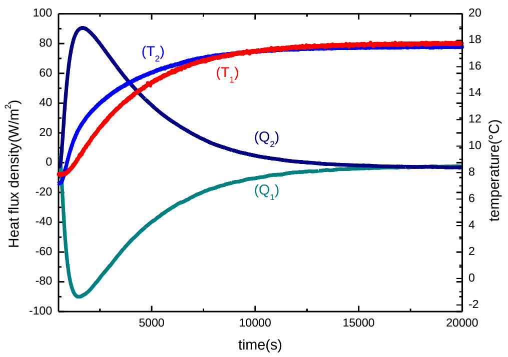

Fig7: Heat flux and temperatures evolution during the solid phase

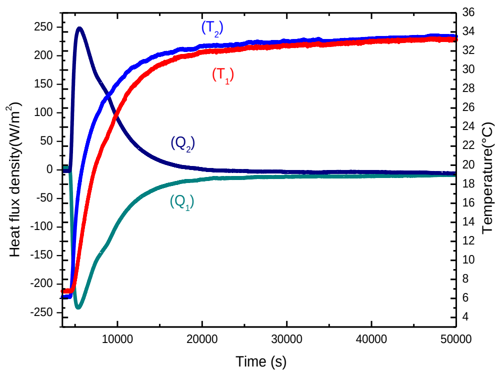

Fig8: Heat flux and temperatures evolution during the liquid phase

Figs. 8 and 7 point up an example of sensible heat storage in solid and liquid states, respectively. One clearly observe a symmetrical behavior of heat fluxes and temperatures measured on both faces of the composite sample and note that the measured temperatures on the lower (T_1) and the upper (T_2) faces of the material evolve in an asymptotic way toward the set point. In addition, we can note that the flow evolves very quickly at the begging of data collection and then fall to zero, which corresponds to the attainment of a new state balance at the end of the test. This confirms that the lateral thermal losses are negligible. The quantities of heat stored and the heat capacities of the solid and liquid states are given in Table 3. These values will be helpful for determining the apparent latent heat of the sample.

The apparent specific heat of the sample without PCM is calculated according to the temperature solicitations exposed in Fig.9.

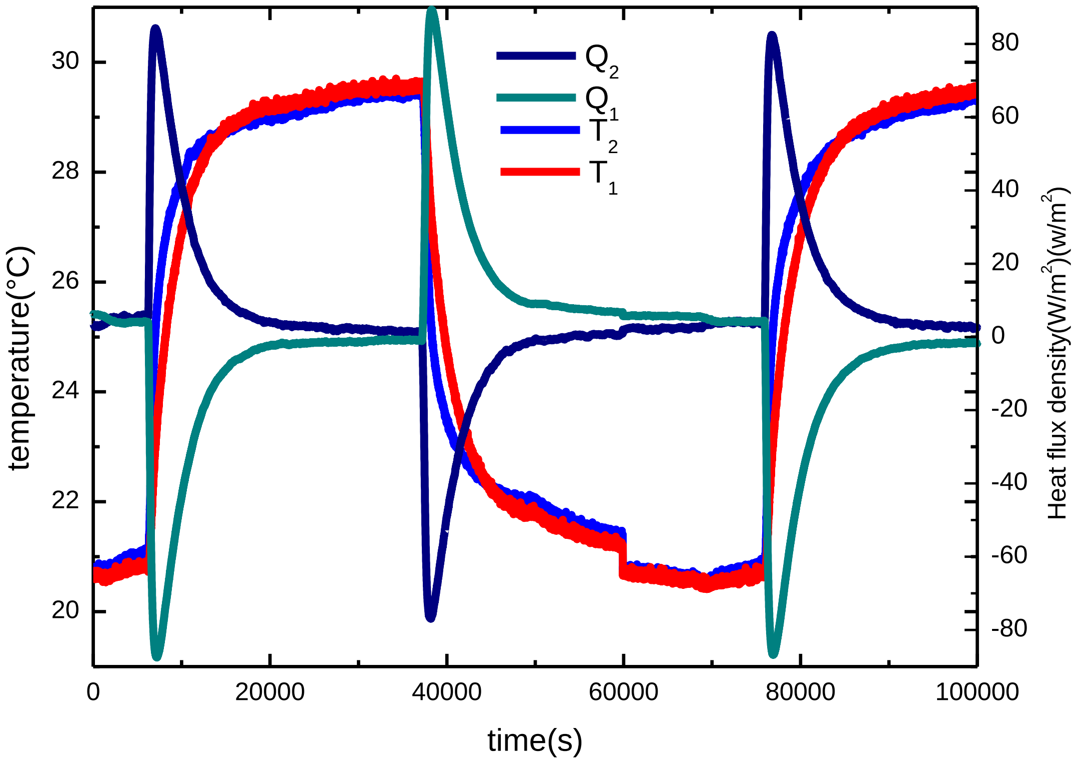

Fig9: Determination of the apparent thermal capacity: gypsum/copper tube without PCM

At the starting of the test, the sample is maintained at a constant initial temperature T_{ini} 5.8°C. The temperature is then increased to T_{end} = 10.8 °C.

It should be noted here that a stabilization time must be allowed after every temperature setting change. This period authorizes the sample to evolve towards its thermal equilibrium state. This occurs (see Fig.9) when the measured heat fluxes are becoming zero. As soon as the sample reaches its equilibrium state, the heat recovery process starts. Finally, the sample is excited until it reaches the initial temperature. It should be noted that both processes are iterated in order to show the repeatability of measurements. Thus, the average apparent specific heat capacity calculated from these six values is 880 J kg $^{-1}$ K^{-1}.

2.1.3. Latent heat

In order to determine the latent heat of solid/liquid phase change of the different samples in this work , as well as the phase change temperatures, an experimental process in which slowly progressive temperature deviation have been set on the specimen has been used.

This method consists in simultaneously measuring of heat flux and temperatures on both lateral sides of the sample.

The thermal evolution from 6°C to 33 °C (Fig. 10) allowed us to follow the complete melting process, from the solid to the liquid state, during which a large quantity of heat has been stored by the material. The selected temperatures are sufficiently far from the zone of melting point to consider that indeed the material is strictly in one or in the other state.

Regarding to the variation of the flux density between 6 °C and 33°C, where there is phase change, initially, the system is isothermal and then a new thermal balance is reached. Between these two isothermal states, the composite stores sensible and latent heat.

The total amount of energy per mass stored can then be obtained from the following expression:

$$Q = Q_{sens} + L_m = (Cp_s.\Delta T_s + Cp_l.\Delta T_l) + L_m \qquad \text{[kJ/kg]} \qquad (3)$$

Cp_s and Cp_l are the average solid state and the liquid state specific heat of the material, ΔT_s and ΔT_l are the temperature variations for the material in solid phase and in liquid phase, and L_m is the latent heat of melting. By subtraction of sensible heat to the quantity of the total heat accumulated, the latent heat L_m can be evaluated.

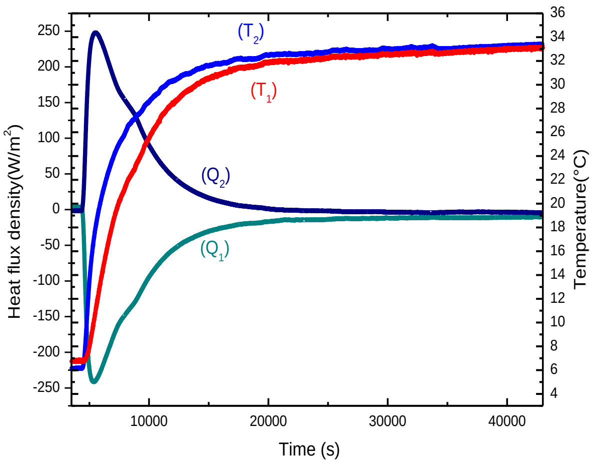

Fig10: Heat flux and temperatures evolution from solid to liquid

The composite PCM stores 14% more energy than classical sample (see table1). In order to demonstrate the import of thermal storage by latent heat, heat stored and the quantity of latent heat is presented in Table1. We note that the quantity of heat stored in the different samples in the form of latent heat is very important regarding the percentage of paraffin in the composite and the difference in temperature imposed.

Table1: Quantity of heat stored and specific heat capacity at different state for gypsum /copper tubes composites.

Samples	Q_{sens} *(kJ)*		*Cp (kJ /kg. °C)*		*Q (kJ)*	L_m *(kJ)*
	solid (7.7-17.5°C)	***liquid*** (23.5-32°C)	***solid*** (7.717.5°C)	***liquid*** (23.5-32°C)	***evolution*** (6.7-32.5°C)	
gypsum /copper tubes without HPCM	7.89	-	0.88	-	32.9	-
gypsum /copper tubes with HPCM	10.60	12.65	1.10	1.26	47.41	24.16

Conclusion

An investigation through DSC and TGHPM was used to determine the phase change temperature and latent heat of HPCM conditioned in copper tubes and the thermophysical properties of composite with or without HPCM, such as apparent thermal conductivity, apparent thermal heat capacity and latent heat.

In order to point out the importance of including HPCM in building materials, a comparative study has been realized. The results of the current study successfully showed that the investigated composite (Gypsum-copper tubes) with HPCM liquid could offer important advantages for thermal storage systems. Conditioning the paraffin inside copper tubes has two objectives: (i) to avoid leaks of the molten paraffin during phase transition, (ii) to improve the low thermal conductivity of the paraffin thus enhance the rate of storing and releasing of thermal energy.

The obtained results led to the following conclusions of the present work:

1-The test results exhibit that the condition of HPCM into the copper tubes incorporating in gypsum decreases the thermal conductivity which should be an additional advantage because the addition of HPCM do not only enhance the TES capacity, but also improve the insulating properties of the gypsum.

2-In the solid and liquid phases, the heat storage capacity improved with including HPCM.

3-The latent heat and the capacity of storing thermal energy as latent heat determined by transient guarded hot plates method (TGHPM) are a viable approach of the utilization of solar heat, a green source of energy, and the optimization of energy consumption in buildings.

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Nomenclature

e *Composite width*
t *Times*
ρ *Density of composite,* $kg.m^{-3}$
T *Temperature, °C*
C_p *Specific heat capacity,* $kJ / kg.°C$
λ *Thermal conductivity,* $W.m^{-1}.K^{-1}$
Q *Energy per mass stored,* J / g *or* kJ / kg
L *Latent heat of fusion (* kJ / kg *)*

ϕ *Density of heat flux,* W / m^2

Subscripts

$1,2$ *Lower and higher face of the composite*
$init$ *Initial thermal steady state*
end *Final thermal steady state*
$sens$ *Sensible*
s *Solid state*
l *Liquid state*
m *Melting*
c *Crystallization*