

Improving the thermal behaviour of bricks by incorporating shape-stabilized phase change materials

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Abstract. The addition of a new shape-stabilized phase change material (ssPCM) in ceramic elements having large porosity has been carried out. In that way, a novel form-stable PCM based on bricks was developed. In order to study the incorporation of the thermoregulatory material in the composites, bricks with different porosities have been manufactured. In this work the ssPCM was synthesized using polyethylene glycol (PEG) as PCM and tetraethyl orthosilicate (TEOS) as supporter precursor by sol-gel method. The initial liquid product can be further turned into solid by neutralization procedures. ssPCM in its liquid form is adsorbed inside the porous brick by capillary action and it is further stabilized by controlling its gelation time, obtaining the new form-stable PCM. The adsorption curves, the long-term stability after 100 cycles of heating and cooling processes and the improved thermal energy storage capacities for the obtained samples have been studied. Different composites containing between 15 to 110 wt% of ssPCM respect to the initial dried mass of brick have been obtained, with thermal capacities within 8.94 to 28.80 kWh/m³. The Fick's law was used to predict the adsorption curves and only one diffusion coefficient was required to predict the content of the ssPCM into the bricks, independently of their porosity. Besides, all the samples exhibited a high long-term thermal stability influenced by the additional stabilizer effect of the ceramic matrix.

1. Introduction

The current contribution of buildings in the world's energy consumption and greenhouse gas emissions and the expectations of energy demand growth for this sector in the future evidence the need to increase the energy efficiency of dwellings. Most of the energy consumption of a dwelling could be reduce by applying thermal energy storage (TES) systems, especially attending to the large surface of buildings exposed to the sun.

Between the different TES methods, latent heat energy storage system (LHTES) is the most common due to their high energy storage density with a small temperature range between storing and releasing processes. LHTES is carried out by using a convenient phase-change material (PCM), which is able to absorb and release abundant amount of heat during its phase change process [1, 2].

The integration of PCMs into construction materials such as gypsum, rigid polyurethane foam, concrete or bricks could minimize the peak temperatures throughout the day, decreasing temperature fluctuations and therefore reducing the energy consumption of heating and cooling devices [3].

Bricks are ones of the most important building materials used around the world, attending to their insulating and refractory characteristics. Nevertheless, there is a lack of studies for improving their thermal storage capacity [4]. To date, the reported improvements in thermal properties of bricks have



been carried out with additional layers of PCM, which increase the wall thickness, or by hollow bricks, filling their voids with PCM and hence suppressing the initial function of the gaps (lightness and thermal isolation) [5-7]. On the other hand, some simulations suggest that the maximum performance of PCM included in bricks is achieved when the material is located near the outdoor [8]. With these premises, the use of solid bricks containing PCMs applied in the façade of buildings is an alternative option in order to enhance their energy efficiency.

Taking into account the manufacturing process of bricks the addition of thermoregulatory materials is affected by the brick-firing process. Thus, the PCMs must be added once the brick was completely manufactured. The ways for addition are the direct incorporation or by means of microencapsulated materials. Nevertheless, the common used PCMs leakage from the brick when they are in liquid phase and the incorporation of microcapsules requires a large pore volume and size which could be deleterious for its mechanical properties. In order to solve these problems an in-situ shape-stabilized PCM (ssPCM) is proposed to be incorporated in bricks, obtaining a new form-stable composite.

Shape-stabilized PCMs and form-stable PCMs are constituted by an organic substance working as heat accumulator, and a supporting matrix which provides structural strength and prevents the leakage of the melted organic component. These compounds preserve the solid state even though the phase-change substance turns from solid to liquid [9]. Although the terms form-stable and shape-stabilized appear interchangeably in literature they are related with different compounds.

Form-stable PCMs are obtained using a solid porous material (supporting material), by immersion or vacuum impregnation in liquid PCM. On the contrary, in order to produce shape-stabilized PCMs the supporting material is melted with the PCM at high temperature and further cooled until the carrier material becomes solid.

In this work, a different kind of shape-stabilized PCM without melted supporting material is proposed. The carrier matrix based on silica is in situ synthesized within the PCM from an alkoxide precursor. Using polyethylene glycol (PEG) as PCM and tetraethyl orthosilicate (TEOS) as precursor, a liquid mixture is obtained. This liquid product can be turned into solid by sol-gel method, controlling the pH value of the medium. The initial PEG-TEOS mixture can be incorporated in building materials by vacuum impregnation or immersion in its liquid state, before being solidified. ssPCM in its liquid form is adsorbed inside the porous of the brick by capillary action and it is further stabilized by controlling its gelation time, obtaining the new form-stable PCM.

In this paper the addition of the ssPCM in ceramic materials having large porosity has been carried out by immersion technique. The adsorption curves, the improved thermal energy storage capacities and the long-term stability after 100 cycles of heating and cooling processes for the obtained samples have been analyzed. Different composites containing between 15 to 110 wt% of ssPCM respect to the initial dried mass of brick have been obtained. From the adsorption curves, the effective diffusion coefficients were estimated and used to predict the amount of ssPCM loaded to the brick and independently of the added biomass. Besides, the obtained results allow to quantify the thermal capacity of the composites and known the effect of the brick as stabilizer.

2. Materials and methods

2.1. Brick composites

In order to obtain different porosities in the bricks various percentages of biomass were inserted in the initial mixture with clay, resulting in a homogeneous paste. This paste was molded and baked at 940°C, obtaining bricks with a porosity related with the quantity of added biomass (table 1).

The ssPCM synthesized by sol-gel method is based on polyethylene glycol having a molecular weight of 1000 g/mol (PEG1000) and tetraethylorthosilicate (TEOS) who is the alkoxide precursor of the inorganic matrix. PEG1000 exhibits a melting point of 35 °C, crystallization temperature of 27 °C and a latent heat of 145 J/g. The ssPCM was incorporated in bricks with different porosities by immersion technique, before being stabilized.

During the immersion process the temperature was set at 50°C. The bricks were immersed in the PEG-TEOS mixture and removed at different times. After this process, they were smeared with a NaOH

solution to promote the gelation of the ssPCM into the porous of the bricks and further, the wet bricks were placed into an oven at 50°C for 24 hours. In order to calculate the diffusivity of the liquid in the building material, each sample was weighted before and after the ssPCM incorporation. In that way, three bricks were spent for each adsorption time.

2.2. Porosity

Three samples of 10 x 6 x 3 cm for each type of brick were weighted in order to calculate their apparent densities (ρ^*). Then, these three prismatic probes were used for determining the composite density (ρ^{comp}) by helium pycnometry (Micromeritics Accupyc 1330). The porosity (ε) was calculated using the air density (ρ^{air}) with the Eq. 1.

$$\varepsilon = \frac{\rho^{comp} - \rho^*}{\rho^{comp} - \rho^{air}} \quad (1)$$

Table 1 shows the diverse kind of obtained bricks relating the amount of added biomass with their final porosity.

Table 1. Content of biomass for each type of brick and their final porosity.

Sample	Biomass (wt%)	Porosity
A	0	0.440
B	10	0.603
C	15	0.673
D	20	0.735
E	25	0.769

2.3. Leakage test

With the aim of studying the thermal stability of the obtained form-stable PCMs a leakage test was accomplished. The study was conducted using a climatic chamber (NUVE TK120) with a 65% of relative humidity. In the climatic chamber, the samples are subjected to 100 thermal cycles, heating up (5 to 45 °C) and cooling down (45 to 5 °C) at heating and cooling rates of 0.29 and 0.28 °C/min respectively. Each temperature steady state was hold during 1 hour. Their weights were measured before and after the cycles in order to quantify the amount of leaked material.

2.4. Experimental equipment for the thermal behaviour tests

The thermal behavior of composites has been studied using a homemade equipment described and proved in previous works [10]. The experimental device is shown in figure 1a. Tests were carried out applying a thermostatic bath set-point step change from 15 to 42 °C while temperatures at different sample locations and the inlet and outlet heat fluxes were registered with time. The dimensions of the samples were of 10x6x3 cm. Six thermocouples of K-type were located across the probe thickness: two in the external sample surface (Tup), two in the middle (Tmiddle) and the other two on the aluminum cell (Tdown). The heat fluxes were measured by using gSKIN®-XI and gSKIN®-XP heat flow sensors for monitoring the inlet and outlet heat fluxes on line, figure 1b.

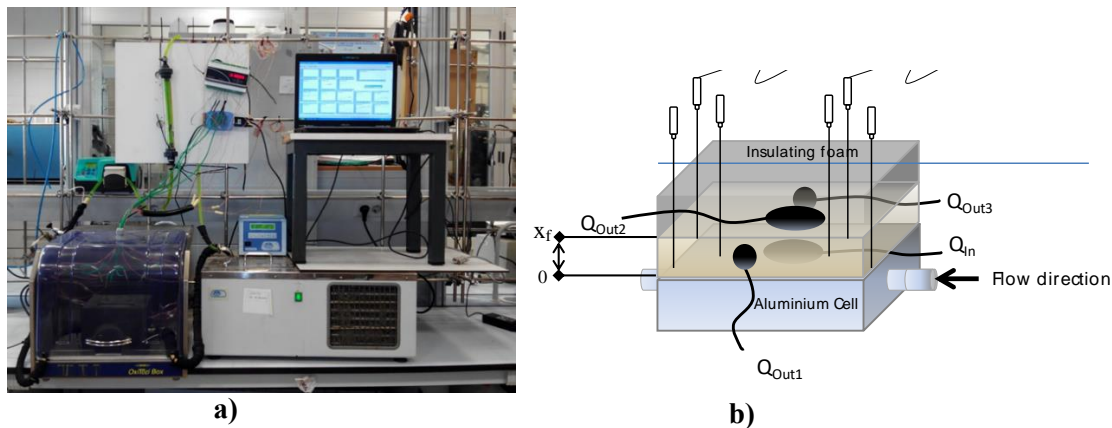


Figure 1. Experimental device for the materials thermal behaviour tests: a) photo; b) sketch of the heat flux sensor position.

3. Results and discussion

3.1. Adsorption capacity

The maximum adsorption capacity (grams of ssPCM per gram of dried brick) of each type of brick was reached after 72 hours of immersion. Figure 2 displays the maximum adsorption capacity respect to the porosity of dried brick. As expected, the higher the porosity, the higher the amount of adsorbed ssPCM by the building composite following an exponential growth. The brick without biomass in their manufacturing process presents the lowest content of PCM, 17.4 g of ssPCM per 100 g of dried brick, while the sample with the greatest porosity is able to store up to 111 g of ssPCM in the same mass of dried brick.

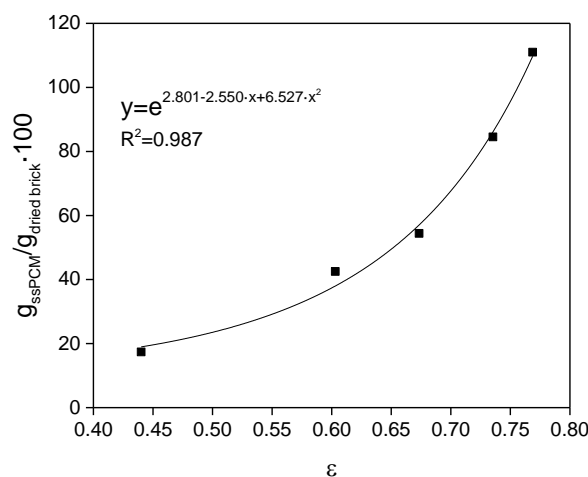


Figure 2. Maximum adsorption capacity for each porosity.

3.2. Diffusion coefficients

In order to study the diffusion process of the ssPCM inside the porous bricks, the amount of accumulated compound was measured over time. Fick's second law can be used to predict the load of the bricks by means of ssPCM diffusion as function of the time. Considering all concentrations as grams of ssPCM per 100 grams of dried brick, q_e is the equilibrium content (maximum adsorption capacity), q_t the accumulated ssPCM during a determined period of time t and q_o the initial liquid content (0 in this case),

the fraction of not accumulated ssPCM can be calculated by the next expression.

$$E = \frac{q_e - q_t}{q_e - q_o} = \frac{\text{liquid that remains to be accumulated}}{\text{total accumulation capacity}} \quad (2)$$

Taking into account some assumptions, Sherwood and Newman have found an analytical solution for the diffusion in a brick with four coated faces, allowing the propagation through the other two opposite faces (one-dimensional) and a slab thickness of $2l$ (Eq. 3).

$$E_l = \frac{8}{\pi^2} \cdot \left(e^{-D_{eff} \cdot t \cdot \left(\frac{\pi}{2 \cdot l}\right)^2} + \frac{1}{9} \cdot e^{-9 \cdot D_{eff} \cdot t \cdot \left(\frac{\pi}{2 \cdot l}\right)^2} + \frac{1}{25} \cdot e^{-25 \cdot D_{eff} \cdot t \cdot \left(\frac{\pi}{2 \cdot l}\right)^2} + \dots \right) \quad (3)$$

Where D_{eff} is the effective diffusion coefficient of the liquid ssPCM.

In the present case, this approximation is not applicable because the diffusion in a rectangular parallelepiped takes place in three dimensions through their 6 faces, with $2a$, $2b$ and $2c$ as dimensions. Hence, Eq. 4 describes the not accumulated fraction of ssPCM [11].

$$E = E_a \cdot E_b \cdot E_c \quad (4)$$

Effective diffusion coefficient (D_{eff}) appears as parameter of the Eq. 4, and it is lower than the diffusion coefficient, D_{AB} , in the absence of a porous medium. The relation between both diffusion coefficients is established by means of porosity (ε), tortuosity (τ) and constrictivity (δ) factors (Eq.5).

$$D_{eff} = \frac{\varepsilon \cdot \delta}{\tau^2} \cdot D_{AB} \quad (5)$$

From the experimental results and using Eqs. 4 and 5, it is possible to obtain only one diffusion coefficient of the liquid ssPCM into the bricks (D_{AB}) from the effective diffusion coefficients obtained for all studied composites. All the experimental data was fitted together by assuming a proportionality between D_{eff} respect to the porosity of the brick and an unique value of D_{AB} of $3.56 \cdot 10^{-8} \text{ m}^2/\text{s}$ was achieved. Table 2 presents the D_{eff} values and the coefficient of determination R^2 in order to check the accuracy between the experimental values of E and the theoretical ones.

Table 2. Effective diffusion coefficients of the ssPCM for each type of brick.

Sample	$D_{eff} (\text{m}^2/\text{s})$	R^2
A	$1.13 \cdot 10^{-8}$	0.957
B	$1.54 \cdot 10^{-8}$	0.966
C	$1.72 \cdot 10^{-8}$	0.970
D	$1.88 \cdot 10^{-8}$	0.959
E	$1.97 \cdot 10^{-8}$	0.989

All the values are in a logical range and lower than the effective diffusion coefficient for water in bricks ($9 \cdot 10^{-7} \text{ m}^2/\text{s}$). It is due to the lower molecular weight of water compared with the corresponding liquid ssPCM and also, the known and established relationship that exists between the diffusion coefficient and molecular weight. For the diffusion of a liquid into a solid, the diffusion coefficient is proportional to the square root of the inverse of the molecular weight. The calculated D_{eff} coefficients allow us to predict the adsorption of ssPCM in the bricks. As an example, figure 3 presents the experimental data and the theoretical values of the accumulated ssPCM for bricks D and E. The good agreement between the curves demonstrate the suitability of the Fick's law for fitting the experimental data.

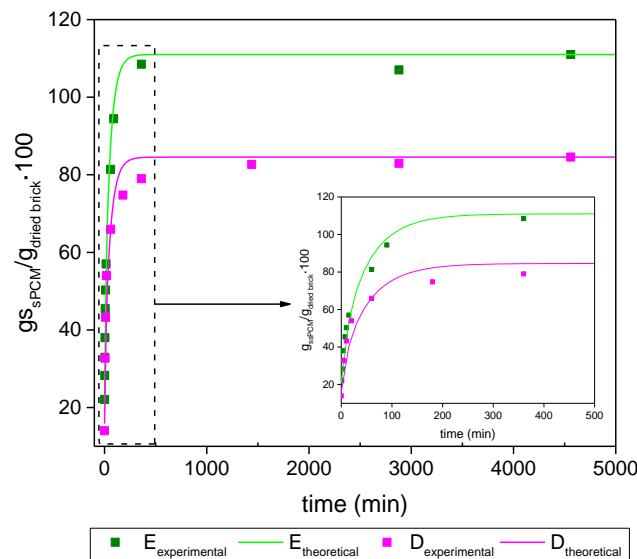


Figure 3. Theoretical prediction for the adsorption compare with the experimental results for E and D bricks.

3.3. Leakage test

The study of long-term stability determine the lifetime of the material, studying the leakage of the PCM with the time. In a previous work the stability of the neutralized ssPCM (without brick) after 100 thermal cycles was studied, checking that the compound lost the 12 wt% of their mass. Figure 4 shows the weight loss of the obtained form-stable PCMs after 100 thermal cycles. Two zones can be observed, the first one corresponds with a porosity up to 0.6 without leakage, indicating a high stabilization of the ssPCM inside the bricks. In the second one, attending to the high porosity of the bricks, the ssPCM leakage appears. This behaviour occurs because of the high porosity, in that case the adsorption starts to take place without interaction between the ssPCM and the brick. However, the sample with the largest leakage presents only a weight loss of 0.96 wt%. This value can be considered as negligible taking into account the initial PCM content (52 wt%). In this way, it can be concluded that the bricks are acting as an additional stabilizer, retaining the ssPCM inside them.

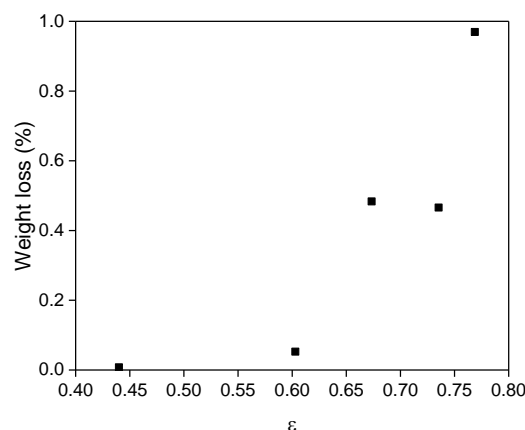


Figure 4. Leakage test. Effect of the brick porosity.

3.4. Thermal energy storage capacity

In order to confirm the increase in the TES capacity by incorporating ssPCMs into bricks, the accumulated heat was quantified by making an energy balance between the input and output heat fluxes

during the transient state in the heating process. As an example, figure 5 displays the accumulation profiles for different ssPCM content in D type bricks. It can be observed that the brick with 84 wt% of ssPCM is able to absorb energy during 8 hours. Amount of energy that corresponds with 5 additional hours of energy absorption respect to a conventional brick. Thus, it is possible to affirm that the time of comfort is sharply increased when ssPCMs are incorporated inside the ceramic materials. Besides, the wider peaks observed when ssPCMs are incorporated in the brick indicate that these materials present a large TES capacity.

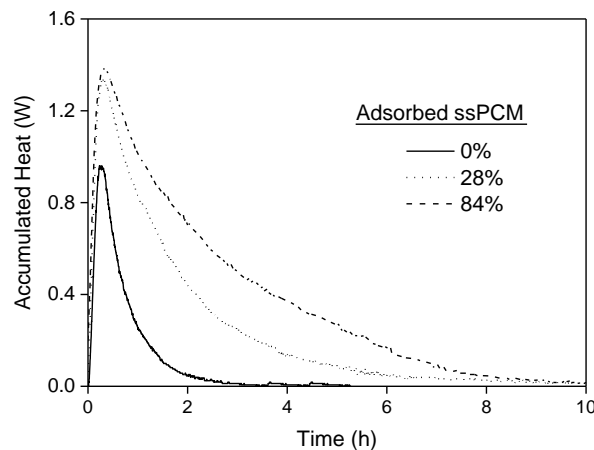


Figure 5. Accumulated heat of the bricks with different amount of ssPCM adsorbed when subjected to a thermostatic bath set-point step change from 15 to 42 °C.

With the accumulation curves it is possible to calculate the TES capacity of each obtained composite (Eq. 6).

$$TES \left(\frac{kWh}{m^3} \right) = \int_0^{t_f} (Q_{in} - Q_{out}) \cdot \frac{\rho}{3.6 \cdot 10^6} dt \quad (6)$$

Where $(Q_{in} - Q_{out})$ (J) represents the energy balance between the heat fluxes and ρ is the density of the composite (kg/m^3).

Table 3 summarizes the TES capacities for all the samples. As expected, for each type of brick the higher the ssPCM content, the higher the TES capacity. These results indicate that it is possible to produce thermoregulatory bricks having a TES capacity thirteen times higher than those of conventional ones, saturating the brick with a thermoregulatory material having a latent heat of fusion of 145 J/g. The wide temperature range available for developing form-stable PCMs opens a range of possibilities for their application as building elements in which is not possible to add the thermoregulatory material in a solid way.

Table 3. TES capacities (kWh/m^3) for the different form-stable PCMs produced.

$g_{ssPCM}/100 g_{dried\ brick}$	A	B	C	D	E
0	6.87	5.01	5.18	3.44	2.12
15	8.94	5.82	11.58	6.12	6.54
25	-	4.08	14.50	10.70	4.23
50	-	7.39	25.09	11.59	8.22
80	-	-	-	21.23	11.06
110	-	-	-	-	28.80

4. Conclusions

Different thermoregulating composites containing within 15 to 110 wt% of ssPCM respect to the initial dried mass of brick have been obtained with thermal capacities from 8.94 to 28.80 kWh/m³, respectively. The diffusion process of the ssPCM inside the porous bricks has been studied. The experimental data of amount of accumulated compound was measured over time and fitted together by assuming a proportionality between D_{eff} respect to the porosity of the brick, obtaining an unique value of D_{AB} of $3.56 \cdot 10^{-8}$ m²/s. The calculated D_{eff} coefficients allow us to predict the content of the ssPCM for all the synthesized composites independently of their porosity.

Regarding with the leakage test, bricks are acting as an additional stabilizer, retaining the ssPCM inside them. Hence, all developed thermoregulating composited exhibited a high long-term thermal stability. Finally, these results indicated that it was possible to produce thermoregulatory bricks having a TES capacity thirteen times higher than those of conventional ones. Accordingly, the time of comfort was sharply increased when ssPCMs were incorporated inside the ceramic materials.

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