Green cementitious composites made with PCM-Recycled Brick Aggregates: Thermal Energy Storage characterization and modelling

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Abstract. This work reports the results of an extensive experimental campaign aimed at investigating the Thermal Energy Storage (TES) behavior of PCM Recycled Brick Aggregate (RBA) mortars. Test specimens for TES measurements were produced following a new spherical-shaped technique, patented as "DKK test" by the Institute of Construction and Building Materials of TU-Darmstadt. DKK was used for TES characterizing the various test samples made of plain cement paste plus porous RBAs, these latter filled with paraffinic PCM waxes. Dynamic DSC tests and conductivity measurements were also done for thermally investigating both components and composites. Moreover, the study proposes a novel numerical approach for determining the energy storage capacity of the investigated systems, setting the experimental benchmarks which were used for validation purposes. Particularly, the experimental results have been finally employed for calibrating an enthalpy-based model, at both macro- and meso-scale level, to evaluate the temperature-based thermal parameters like specific heat, conductivity, or more in a general sense, the energy storage capacity of these systems under transient heat conduction conditions. The results show very promising possibilities for using RBAs as carriers in green concrete applications.

Keywords: Recycled Brick Aggregates, Paraffin-based PCMs, Thermal Energy Storage, Enthalpy-based method, Meso-scale Simulations.

1 Introduction

The energy demand for heating and cooling the global building represents a huge share of the total energy consumption around the world (ca. 40%) [1]. It accounts for almost half its energy consumption in Europe [2]. To attenuate this number, improving the thermal efficiency of construction and building elements became one of the most important issue for energy savings of new and existing buildings [3].

Innovative solutions in this regard could include the potential of materials to store and release large amounts of thermal energy, which would be used to stabilize the inner thermal comfort of either residential or non-residential buildings. This can be achieved through an optimal use of Phase Change Materials (PCMs), which can help to minimize the additional need of primary energy for heating/cooling [4, 5]. Numerous studies on PCMs and in several fields of applications have been reported in literature. The experimental-based research on these deals with addressing the thermo-hydro-chemo-mechanical properties of cementitious materials with PCMs [6, 7, 8], where the investigated PCMs are characterized by melting temperatures that vary between 19°C - 26°C. This range corresponds to a standard temperature window for comfortable living [9].

On the other hand, available numerical and/or theoretical approaches, available in scientific literature for modelling Thermal Energy Storage (TES) and heat accumulation/liberation of PCM-based applications, arose from the solution the so-called Stefan problem [10]. Several authors, under simplified assumptions (i.e., 1D heat conduction), proposed analytical solutions for solving this problem [11]. More complex models are needed for further evaluation of the classical Stefan problem: e.g., by introducing "mushy" zones for non-isothermal PC conditions, 2D and 3D evaluations, etc. [12].

The solution methods of the Stefan problem and/or its extended formulations, can generally be subdivided into three different categories [13]: (i) Fixed grid method; (ii) Deformed grid method; and (iii) Hybrid methods. Most classical examples are those based on a further development of the fixed grid method, where the grid of spatial nodes, used for discretizing the problem, remains fixed during time, and the phase change is traced through auxiliary formulations and/or state functions. Particularly, the Enthalpy-based Approach (EA) [14], which mainly boils down into two alternative solutions (the Apparent Calorific Capacity Method (ACCM) [15] and (ii) the Heat Source Method (HSM) [16]), is the common way to solve the set of equations of the fixed grid method.

In this context, the present study investigates the TES of mortars made of RBAs containing PCMs. The results of an extensive experimental research are firstly presented for showing the TES performance of the various composites. Test data of a wide series of thermal tests [17] (in terms of DSC measurements, thermal conductivity and DKK tests [18]), carried out on PCM, aggregates, plain mortars and PCM-RBA mortars are shortly summarized. Then, a numerical procedure for simulating the effects of paraffin waxes on the thermal energy responses of these mortars produced with different amounts of PCM-RBAs is outlined.

2 Experimental campaign

An experimental program was performed to characterize the TES response of PCM-RBA mortar mixtures and their components.

2.1 Components and composites

Paraffin waxes [19], characterized by a high crystallinity and possess an excellent heat store capacity during the phase changes, were used as PCM (**Fig. 1**a). They have a melting temperature of 25 °C, a storage capacity of 230 kJ/kg approx., a latent heat capacity of almost 200 kJ/kg, a thermal conductivity of 0.20 W/m×K and densities of 880 kg/m³ in liquid and 770 kg/m³ solid states, respectively.

(a) (b) (c)

Fig. 1. (a) PCMs, (b) SB- and (c) PB- RBAs with grain groups 0.5-1mm, 1-2 mm and 2-4 mm.

Six mixtures were thus prepared following an advanced technique, proposed and patented by the *Institut für Werkstoffe im Bauwesen* of TU-Darmstadt [20], and having a w/c ratio of 0.5 and various amounts of PCM-RBA volume fractions (**Table 1**). All mixtures were prepared according to EN 196-1 [21]. Recycled bricks (labelled "SB", **Fig. 1**b) and High porosity Poroton® fired-clay blocks (labelled "PB", **Fig. 1**c) have been considered [22]. These materials, processed in the form of medium/coarse aggregates, were used as containers for storing predefined volume of PCM.

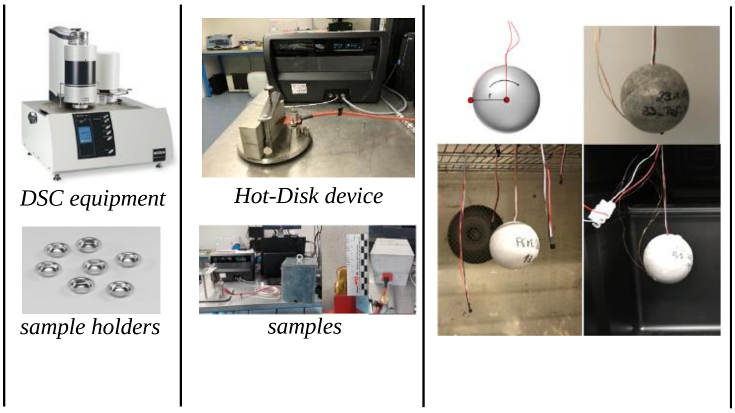
Table 1. The investigated PCM-RBA mortars.

Labels	REF-SB	SB-65	SB-80	REF-PB	PB-65	PB-80
Cement [kg/m³]	701.5	694.2	692.9	700.2	691.7	691.7
Water [kg/m³]	350.8	347.1	346.5	350.1	345.9	345.9
PCM-RBA [kg/m³]	655.2	719.3	734.0	664.0	728.9	743.9
Air cont. [V.-%]	2.3	2.9	3.0	2.4	3.1	3.1
w/c ratio [-]	0.50					

The complete description (materials, methods, results and discussion) of the experimental campaign is available in Mankel et al. [22].

2.2 DSC, Conductivity and DKK tests

Differential Scanning Calorimetry (DSC) tests, as shown in **Fig. 2**a, were done for each component of the investigated PCM-RBA mortar mixtures: i.e., surrounding cement paste, SB-, PB-RBAs and PCMs. Three samples per each component were analyzed under either heating or cooling, within the temperature range of 10 °C to 40 °C. A heating/cooling rate of 10 K×min^{-1} was employed for pastes and RBAs while the test procedure, conducted in accordance with the IEA DSC 4229 PCM Standard [23], was followed to determine the final heating/cooling rate for the considered PCMs which it was 0.25 K×min^{-1} on the final results.



(a) (b) (c)

Fig. 2. (a) DSC tests (heat storage capacities of components), (b) Hot-disk (conductivity of the composites) and (c) DKK tests (TES of the composites).

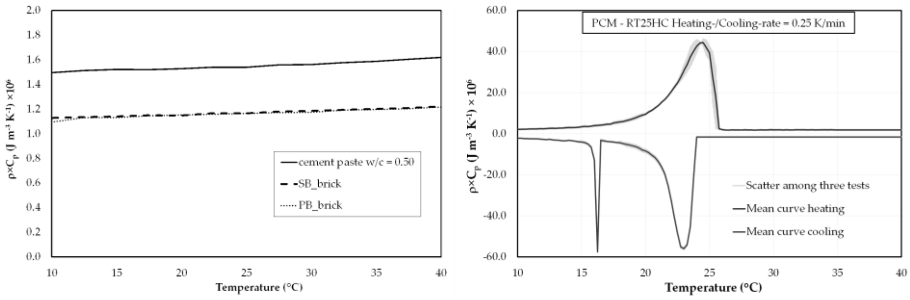
The thermal conductivity of PCM-RBA mortar mixtures was then determined using the Hot-Disk transient plane source method (**Fig. 2**b). For this purpose, three samples of 150 mm × 150 mm × 80 mm cuboids were casted and investigated. Steady-state conditions with a temperature of 20 °C were considered.

Finally, novel spherical-shaped specimens (**Fig. 2**c) were used to monitor the time-dependent TES of the PCM-RBA mortars. This non-conventional testing technique (adopted and patented under the name of *Dynamische Kugel Kalorimetrie*, DKK [18]) was followed by the authors for the thermal-energy identification of the composites. Three spherical samples were produced per each mortar. Heating tests were done by using an isothermal conditioned oven with a fixed temperature of ca. 49°, as well as cooling one were done with a climatic chamber fixing the temperature at ca. 9°C.

3 Experimental results

3.1 DSC measurements: aggregates, paste and PCMs

DSC tests were done for each component used in the PCM-RBA mixtures. The heat storage capacity has been shown in terms of bulk density times the specific heat capacity. Three samples per each component were analyzed and the mean value presented. Particularly, both heating and cooling responses for cement pastes and for both SB- and PB-RBAs, have been shown in **Fig. 3**a. These tests were done within the temperature range of 10°C - 40°C and using a heating/cooling rate of 10 K×min^{-1}.



(**a**) (**b**)

Fig. 3. DSC measurements of (a) cement paste, SB and PB RBAs and (b) Paraffin RT25HC.

The DSC results of the used paraffin wax (namely, RT25HC) are shown in **Fig. 3**b. The adopted heating/cooling rate was 0.25 K×min^{-1}, fulfilling the IEA DSC 4229 procedure [23] for PCMs. DSC curves of the considered PCM, in **Fig. 3**b, deal with a pronounced latent peak in the region close to the temperature where the phase change occurs (i.e., T_m = 24.5 °C for heating and T_m = 22.95 °C for cooling).

3.2 Thermal conductivity of PCM-RBA mortars

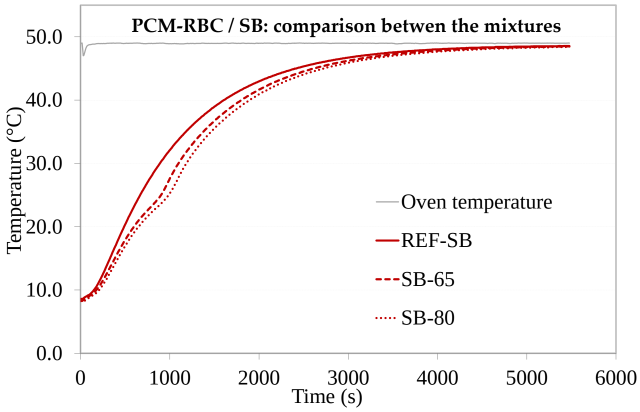
Thermal conductivities of the PCM-RBA mixtures were determined using the Hot-Disk transient plane source method. In **Table 2**, it can be observed that all mixtures have comparable λ, ranging between 0.696 W/mK (min.) and 0.846 W/mK (max. value).

Table 2. Thermal conductivity of SB-RBA and PB-RBA mixtures.

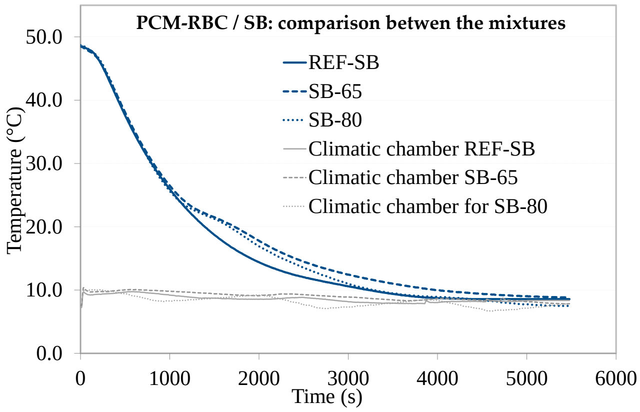
Parameter	**REF-SB**	**SB-65**	**SB-80**
λ (W/m K) (mean value)	0.846	0.768	0.768
Parameter	**REF-PB**	**PB-65**	**PB-80**
λ (W/m K) (mean value)	0.712	0.696	0.725

3.3 “DKK” test data

DKK tests were used to evaluate the time-dependent temperature evolution of the spherical-shaped PCM-RBA mortar specimens. For each considered mixture, three spherical samples were tested.



(**a**)



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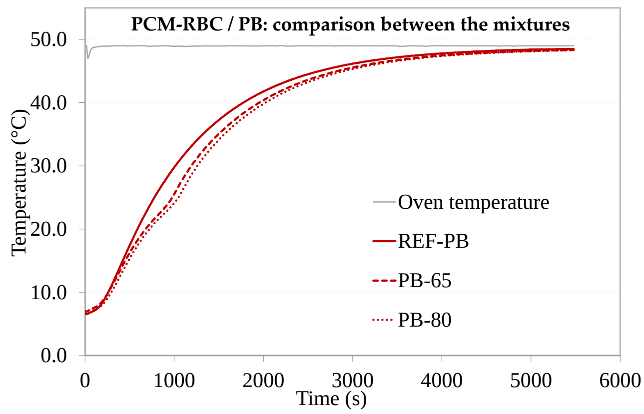

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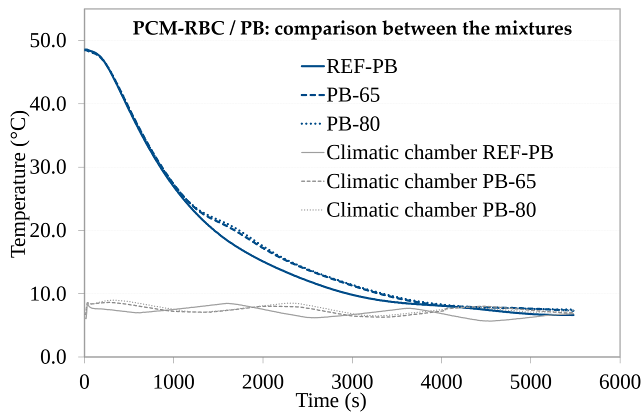


(**d**)

Fig. 4. Temperature evolutions of the DKK tests: (a) heating and (b) cooling of PCM-RBA mortars with SB bricks, (c) heating and (d) cooling of PCM-RBA mortars with PB bricks.

The results plotted in **Fig. 4** show the average results (from three spherical specimens) of the temperature evolution vs. time. Both heating and cooling results are plotted. It can be seen that, for the mortar mixtures casted with either SB or PB bricks, a delay of the temperature development takes place when PCM-RBAs, with PCM filling degrees of 65 V.-% and 80 V.-%, are taken into consideration. The presence of PCM actually shifts the temperature curve into the right/down direction under heating response (**Fig. 4** a and c) and up/left for cooling (**Fig. 4** b and d).

4 Numerical model and results

4.1 Theoretical assumption and enthalpy-based model

The most classical equation for describing a heat conduction problem with phase change phenomena can be stated by following the so-called enthalpy-based approach

$$\frac{\partial H}{\partial t} = \nabla.\left(\lambda \nabla T\right) + \dot{q}_v \qquad \forall \mathbf{x} \in \Omega \tag{1}$$

where H is the enthalpy of the system, t the time, λ the thermal conductivity of the material, which depends on the temperature T and position vector $\mathbf{x}$ (of the considered body Ω), $\dot{q}_v$ is the possible heat source term, while $\nabla.$ and ∇ are the divergence and gradient tensorial operators.

Applying the chain rule to $\frac{\partial H}{\partial t} = \frac{\partial H}{\partial T}\frac{\partial T}{\partial t}$ and by introducing the concept of the Apparent Calorific Capacity Method (ACCM), the following temperature-dependent (apparent or effective) heat capacity expression can be written

$$\frac{\partial H}{\partial T} = \rho C_{eff}\left(T\right). \tag{2}$$

Thus, Eq. (1) modifies into the following heat transfer equation

$$\rho C_{eff}\left(T\right)\frac{dT}{dt} = \nabla.\left(\lambda \nabla T\right) + \dot{q}_v \qquad \forall \mathbf{x} \in \Omega . \tag{3}$$

Finally, the description of the phase change problem is completed by introducing the Initial (IC) and Boundary Conditions (BCs) as for classical thermal problems.

A meso-scale based homogenization technique was then employed for evaluating the effective specific heat capacity C_{eff} of the PCM-RBA mortars. It is based on adopting the volume percentages of each individual component as weighting parameter. More precisely, the model smears out the specific heat capacity of the RBA, cement paste and the apparent specific heat capacity of the PCM, through adopting the volume fraction of each component as the weighting factor.

The specific heat capacities of each component were experimentally determined with DSC measurements and are those summarized in Section 3.

The evaluation of the specific heat capacities was determined in two consecutive steps. At aggregate level, the following expression is employed

$$C_{eff,PCM-RBA}(T) = \chi_{RBA} \times C_{RBA}(T) + \chi_{PCM} \times C_{app,PCM}(T) \tag{4}$$

where the PCM-RBAs were considered as lumped components of RBAs ($C_{RBA}(T)$) plus PCM ($C_{app,PCM}(T)$) and weighting their volume fractions χ_{RBA} and χ_{PCM}, the volume fraction of the recycled bricks and the filled PCMs, respectively.

At composite level (i.e., PCM-RBA mortar), the homogenized overall system of the effective specific heat capacity, C_{eff}, can be determined as

$$C_{eff}(T) = \psi_{paste} \times C_{paste}(T) + \psi_{PCM-RBA} \times C_{eff,PCM-RBA}(T) \qquad (5)$$

by weighting the heat capacities $C_{eff,PCM\text{-}RBA}(T)$ and $C_{paste}(T)$ of the individual material components by their volume fractions ψ.

The exact volume fraction ratio between PCM-RBAs and cement paste, of the investigated mixtures, were investigated by performing *µ3D-XCT-scans* of the spherical specimens as shown in **Fig. 5**.

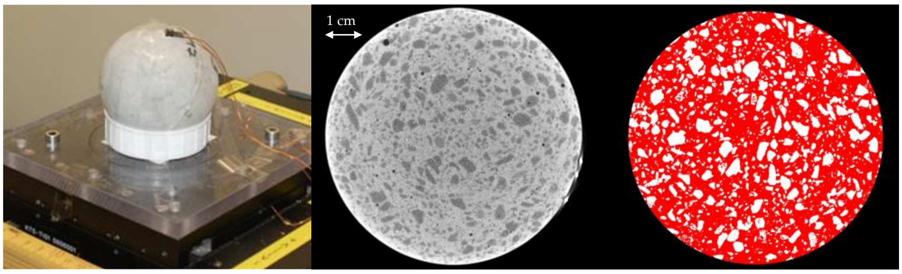


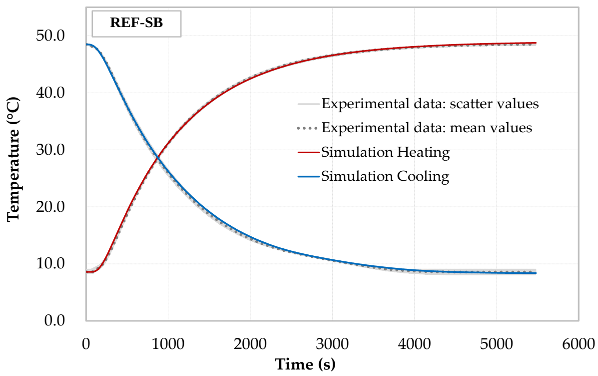
Fig. 5. µ3D-XCT-scans setup and images of the spherical specimens.

4.2 Simulations and comparisons

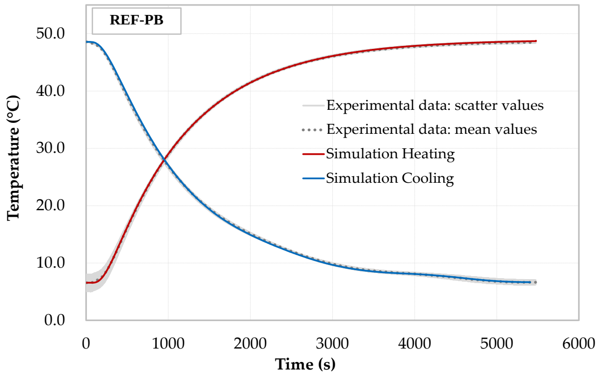
By implementing the ACCM procedure and customizing it under spherical assumptions, the temperature evolutions of the DKK specimens were simulated and compared with the corresponding experimental data.

The spherical samples made of RBA mortars (with and without PCMs) were simulated with the proposed heat flow ACCM model. The input values were obtained from the conducted experimental measurements, as well as from the $C_{eff}(T)$ described in the previous Section 4.1. The thermal conductivities were assumed as temperature-independent and measured through Hot-Disk tests, as outlined in Section 3.

For the numerical simulations, the number of Finite Difference space discretization was chosen as 100, guarantying good approximation results, while the number of time steps selected were 1000, in all simulations.



(a)



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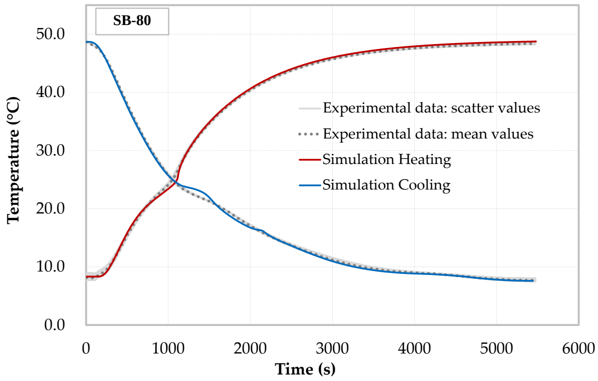
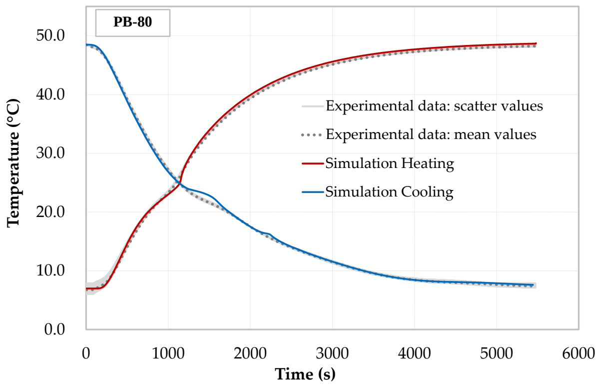


(c)



(d)

Fig. 6. Experimental "DKK" tests vs. numerical results: (a-c) SB and (b-d) PB mixtures.

In **Fig. 6**, the 4 graphs show the temperature evolutions for the control mixtures (**Fig. 6** a and b), and for that one having the maxim PCM contents: i.e., SB-80 (**Fig. 6** c), and PB-80 (**Fig. 6** d). It can be observed that the modeling approach was able to simulate the experimental temperature evolutions very accurately.

5 Conclusions

In this work, an experimental program is reported for investigating the Thermal Energy Storage (TES) capacity of cementitious mortars made of Recycled Brick Aggregates (RBAs), and used as carriers for allocate PCMs. Six mixtures were examined, all having a w/c ratio of 0.5 and various amounts of PCM-RBA fractions. Two different types of RBAs were employed, namely standard recycled bricks and high porosity Poroton® fired-clay blocks. Numerical simulations, which included a macroscopic enthalpy-based model, formulated for spherical coordinates and symmetry for predicting the thermal energy storage in the tested specimens, were also done. The experimental results were employed as benchmark for calibrate and validate the numerical procedure. Input parameters were based on mesoscale observations for taking into account the composite composition of the materials under study.

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