Porous Inclusions as Hosts for Phase Change Materials in Cementitious Composites: Characterization, Thermal Performance, and Analytical Models

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ABSTRACT

This paper examines the influence of four different porous hosts (lightweight aggregates (LWA)) having different pore structure features, as hosts for phase change materials (PCM). The porosity and absorption capacity of the LWAs significantly influence the composite thermal conductivity. The incorporation of 5% of PCMs by total volume of the cementitious system reduces the composite thermal conductivity by $\geq 10\%$. The fact that the inclusions (LWAs) in these composites are by themselves heterogeneous, and contain multiple components (solid phase, PCM, water, and air) necessitate careful application of predictive models. Multi-step Mori-Tanaka mean-field homogenization methods, either based on known microstructural arrangement in the composite, or property contrast between the constituents, are applied to predict the composite thermal conductivity. A microstructural contrast factor is used to account for both the thermal conductivities and the volume fractions of the phases with the highest property contrast. Smaller contrast factors result in improved agreement of the models with the experiments, thereby aiding in the selection of suitable predictive schemes for effective properties of such multi-phase composites.

Keywords: Phase Change Materials (PCM), Microstructure, Lightweight Aggregate, Thermal Conductivity, Homogenization models

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1. INTRODUCTION

Phase change materials (PCMs) are combined sensible-and-latent thermal energy storage (TES) materials that can be used to store and release energy in the form of heat [1–4]. As the temperature increases, the endothermic phase change of PCMs from solid-to-liquid states absorbs heat, while as the temperature decreases, the exothermic liquid-to-solid transition releases heat. The incorporation of PCMs in walls and roofs has been extensively studied as a means to reduce the energy consumption in buildings [5–8]. While several approaches have been considered to incorporate PCMs in cement-based materials, the most common variants include the addition of microencapsulated PCMs directly to the concrete [9–11], or impregnation of liquid PCMs into porous inclusions that can subsequently be added as aggregates in concrete [12–17]. In the latter case, PCM in liquid state is impregnated into the pores of lightweight aggregates (LWA). This overcomes one of the main disadvantages of lightweight structures as building envelopes, i.e., their low thermal inertia. Large temperature fluctuations in such buildings can be reduced through the use of PCM incorporations, in addition to providing increased thermal insulation. This approach can also be used in applications such as bridge-decks to limit the number and/or intensity of freeze-thaw cycles experienced by concrete [18], and to reduce the rate of thermal deformation and stress development by controlling the semi-adiabatic temperature rise [19].

This paper characterizes liquid-PCM impregnated porous LWA hosts, examines the thermal performance of cementitious composites containing PCM-impregnated LWAs, and evaluates composite models to predict the thermal conductivity of such multi-component composites. Several methods to impregnate porous aggregates with PCMs have been reported [20–22]. The amount of heat stored and released by PCMs contained within the pores of LWAs depends on the pore structure of the LWA as well as the thermal properties of the PCM (i.e., enthalpy, specific heat, and phase transition temperature). Thus a fundamental characterization of PCMs and LWAs is important in properly understanding their thermal response and the efficient design of LWA-PCM composite mortars. This paper characterizes four different types of LWAs with respect to their capacity to impregnate an organic paraffin-based PCM in their material structure, and consequently influence the composite thermal properties. These porous inclusions are subsequently incorporated into cement mortars and their thermal conductivities measured using a guarded hot-plate method. Effective medium and mean-field homogenization models are used to predict the thermal conductivity of the composite mortars. Emphasis is paid to the fact that the saturated LWAs containing PCMs along with water and air are multi-phase composite materials in their own right. The impact of phase property contrast in prediction is brought out.

2. EXPERIMENTAL PROGRAM

2.1. Materials

A commercially available Type I/II ordinary portland cement (OPC) conforming to ASTM C150, a paraffin-based liquid PCM supplied by Entropy Solutions (PureTemp 24X), and four different LWAs were used. The LWAs used were pumice (PU), perlite (PE), expanded shale/clay (ESC), and expanded slate (ES). Coarse sand (CS), having a median particle size of 600 μm was used in the control mortar. The particle size distributions of all the LWAs and the CS are shown in Figure 1. The median particle size (d_{50}) of OPC was 10 μm and the median particle size for the LWAs ranged between 800 and 1200 μm . The design of cementitious mortar mixtures containing these aggregates impregnated with PCM are detailed in Section 3.

Figure 1: Particle size distributions of the LWAs and the coarse sand

2.2 LWA Pretreatment and Absorption of PCM

Since LWAs are used as PCM hosts in this study, it is important to determine their absorption capacity. Initially, LWAs were washed and sieved to remove any material finer than 150 μm (No. 100 sieve), as their contribution to total absorption is deemed negligible. The use of fine material could result in erroneous absorption values because of the increased PCM adsorption on the surfaces rather than absorption into the pores. After washing, the LWAs were placed in the oven at 100°C for 48 hours to remove any evaporable water and achieve an oven dry (OD) state. Drying beyond 48 hours resulted in negligible mass changes. The physical properties of the LWA including their relative densities in the oven dry and saturated surface dry (SSD) conditions were measured as per ASTM C128.

The absorption of PCM into the pores of the LWA was determined by soaking a known mass of LWA in the liquid PCM, PureTemp 24X, for 72 hours, after which the soaked LWA was placed in a fine mesh to

allow the excess PCM to drain. The soaking was performed at a temperature greater than the phase transition temperature of the PCM (in this case, 24°C) to keep it in the liquid state throughout. Vacuum saturation was not employed to ensure that the impregnation method can be easily replicated in practice. After a 24-hour drain period, the LWA was weighed again, and its absorption was determined. Negligible increase in absorption was observed when the soaking time was increased beyond 72 hours.

2.3 Test Methods

The porosity of the different LWAs was characterized using mercury intrusion porosimetry (MIP) carried out on oven dried samples. The mercury porosimeter is capable of exerting a maximum pressure of 414 MPa. The relationship between pore diameter and intrusion pressure was established using the Washburn equation, based on the assumption that the pores are cylindrical [23]. The contact angle and surface tension values were assumed as 117° and 0.485 N/m respectively [24].

The thermal properties (e.g. onset, peak, and phase change temperatures, enthalpy, and specific heat capacity) of the LWAs and PCM-impregnated LWAs were determined using differential scanning calorimetry (DSC) in accordance with ASTM E 1269-11. Four replicates for each specimen type were tested using aluminum pans. A temperature sweep was carried out wherein the sample was heated from -10°C to 50°C followed by cooling to -10°C in an inert nitrogen environment. A rate of temperature change (i.e., heating and cooling) of 5°C/min was used. Heat flow calibration was performed using a sapphire reference. Equation 1 was used to determine the specific heat capacity (C_p), in J/(g.K) of the LWAs prior to PCM impregnation.

$$C_p(s) = C_p(st) \cdot \frac{D_s \cdot W_{st}}{D_{st} \cdot W_s} \quad (1)$$

Here $C_p(st)$ is the specific heat capacity of the sapphire standard in J/(g.K), W_s is the mass of the specimen (mg), W_{st} is the mass of the sapphire standard (mg), D_s is the vertical displacement between the heat flow curves of the specimen holder (mW) and the specimen at a given temperature, and D_{st} is the vertical displacement between the heat flow curves of the specimen holder and sapphire standard (mW) at a given temperature.

The compressive strengths of mortars containing both the non-impregnated and PCM-impregnated LWAs were determined in accordance with ASTM C109 on 50 mm cubes at different ages.

Thermal conductivity of the mortars was determined in accordance with ASTM C 177 using a guarded hot plate apparatus (Figure 2(a)) wherein the applied power is measured in a centralized metered section. The central metered section (Figure 2(b)) is surrounded by thermally isolated guards (a small

gap separates the hot plate and guards), thus enabling 1D heat flow. Heat sinks located on the top and bottom of the apparatus dissipate the heat to ensure uniform temperatures at the outer surfaces of the specimen. Two identical (300 x 300 x 12 mm) plate specimens were used to ensure symmetrical heat flow. Cementitious specimens were tested after 28 days of hydration and allowed to dry in ambient conditions for 24 hours prior to testing. The duration of testing for each specimen was between 6-to-10 hours, as needed to establish a steady-state temperature gradient over the thickness of the specimen. Thermal conductivity (λ) was determined using Fourier's equation as:

$$\lambda = \frac{qL}{2A(T_h - T_c)} \quad (2)$$

where q is the power input to the central heater, L is the thickness of the specimen, A is the surface area of the central heater, T_h is the temperature of the hot face, and T_c is the temperature of the cold face.

Figure 2: (a) Side profile of the guarded hot plate apparatus, and (b) aerial profile of the centralized metered section for determining thermal conductivity.

3. CHARACTERIZATION OF LWAs, LWA-PCM COMPOSITES, AND DESIGN OF MORTARS

3.1. Pore Volume and PCM Absorption of LWAs

Obtaining the appropriate physical properties and pore structure characteristics of LWA that are important in PCM impregnation is critical towards material design of thermally efficient cementitious systems. Figure 3 shows the relationship between pore size and volume of mercury intruded for the different LWAs studied. Table 1 shows average specific gravities (oven dry, OD and saturated surface dry, SSD), average pore diameters, porosities, and the PCM absorption capacities after 72 hours of immersion, of the four different LWAs.

The PCM absorption capacity (Section 2.2) is an important parameter that dictates the thermal efficiency of the composite. The pumice and expanded shale/clay aggregates show higher PCM

absorption capacities than perlite and expanded slate. Since the soaking of LWA by PCM was carried out under ambient conditions (i.e., no vacuum was applied), absorption represents the volume of easily accessible pores. Even though the porosity of expanded shale/clay LWA is about 14% higher than that of the pumice LWA, it has a PCM absorption that is about 5% less than that of pumice. This can be attributed to the average pore diameter of the pumice LWA being 30% greater than that of the expanded shale/clay. Larger pore sizes at comparable porosities ensure larger absorption as shown in Table 1. For the perlite LWA, the porosity is the lowest but the absorption capacity is comparable to that of expanded slate LWA because of the much larger pore sizes which allow the PCM to penetrate most of the available pore spaces.

Figure 3: Pore diameter-pore volume relationships for the four different LWA types.

Table 1: Physical properties of lightweight aggregates

LWA	S.G. (OD)	S.G. (SSD)	Avg. Pore Diameter (μm)	Porosity	PCM Absorption, % by vol.
Pumice (PU)	1.45	1.75	516	0.39	21.1
Perlite (PE)	1.72	1.81	580	0.15	11.2
Exp. Shale/Clay (ESC)	1.07	1.33	361	0.53	15.7
Exp. Slate (ES)	1.77	1.99	247	0.30	10.6

3.2 Design of Mortar Mixtures

Ten mixtures (nine mortars, and one paste) were proportioned with a volumetric water-to-cement ratio, $(w/c)_v = 1.58$ (mass-based $w/c = 0.50$). Table 2 shows the mixture proportions and the corresponding nomenclature. For instance, the number 0 after the abbreviation for the aggregate type (see Table 1)

indicates that the LWA is a non-impregnated one where as the number 5 indicates that 5% of the overall mortar contains PCM which is impregnated into the LWAs. The mortar samples were proportioned for a constant paste volume of 50%. For the LWA mortars, 5% PCM by overall volume of the mortar was incorporated by adjusting the amount of LWA impregnated by the PCM. Since the porosities and PCM absorption capacities of LWAs were different (Table 1), combinations of LWAs impregnated with PCM and those without PCM, but saturated with water, were used to attain the overall PCM fraction of 5% by volume of the mortar.

To illustrate the mixture design process of LWA mortars containing PCM, first consider the case of pumice LWA. It has a porosity of 39% and an absorption capacity of 21% (Table 1). In other words, 21% of the total volume of LWAs will contain the PCM. If all the LWAs (which is 50% by volume of the mortar) were to be saturated with PCM, then the volume fraction of PCM in the mortar would be 21% of 50%, or 10.5%. Since the intention is to use only 5% by volume of PCM in the mortar, PCM-soaked pumice LWAs would need to be used along with non-PCM impregnated LWAs in this mortar. Thus, almost half of the total LWA to be used in this mortar will be non-impregnated ones as shown in Table 2. Alternatively, when perlite LWA with an absorption of 11.2% was considered, almost all of the LWA needed to be impregnated to achieve the desired PCM volume fraction of 5% (the volume fraction of PCM in the mortar is 11.2% of 50%, which is 5.6%). Table 2 shows the volume fractions of PCM-impregnated and non-impregnated LWAs used for different mortar mixtures.

Table 2: Mixture proportions (volumetric) used in this study

Mixture	OPC Paste (% by volume)	LWA (% by vol.)		Coarse Sand (% by vol.)
		PCM Impregnated	Non PCM – Impregnated	
OPC Paste	100	-	-	-
Plain Mortar	50	-	-	50
Mortar with LWAs (PU0, PE0, ES0, ESC0)	50	-	50	-
Mortar with PCM-impregnated LWAs				
PU5	50	23.7	26.3	-
PE5	50	44.6	5.4	-
ESC5	50	47.2	2.8	-
ES5	50	31.8	18.2	-

3.3 Thermal Properties of LWAs and LWA-PCM Mortars

3.3.1 Enthalpy of phase change (ΔH_f^0)

DSC was used to determine the specific heat capacity of the pristine LWAs as described earlier. The specific heat capacities of all the LWAs were determined at a temperature of 27.5°C (beyond the PCM phase transition). The measured specific heat capacity, shown in Table 3, ranges between 0.62-to-0.91 J/g-K, and are very similar to those reported for these materials [25–28].

Figure 4 shows the endothermic heat flow peak for the four different LWAs impregnated with PCM (up to their absorption capacity, Table 1), after 72 hours of absorption. The endothermic peak represents the heat being absorbed by the PCM (latent energy storage), as a result of phase transition. The melting point or endothermic peak occurs at 24°C for all the LWA-PCM combinations, i.e., at the intrinsic PCM phase change temperature. The difference in heat flow curves between different LWA-PCM combinations is a result of the differences in the PCM absorption capacity of the LWA (Table 1). Unsurprisingly, the degree of PCM absorption, which in turn depends on the pore structure of the LWA, influences the thermal energy storage. The total area under the heat flow curve in the temperature range between the onset and completion of phase transition, which corresponds to the enthalpy of phase change of the composite, is shown for all the LWA-PCM combinations in Table 4. The theoretical enthalpy was calculated from the amount of PCM (by mass) absorbed in the different LWA types and the enthalpy of phase change of the PCM, which in this case was 184 J/g. The calculated and measured enthalpies for all the combinations are similar, though the measured enthalpies are slightly higher. This is likely due to the presence of small amounts of PCM that adhere to the surface of the LWAs even after the draining process. The results presented are the average of three DSC runs for a given sample. The uncertainty in the measured data is on the order of 4%-to-15%.

Table 3: Specific heat capacity of the LWAs

LWA	Specific Heat Capacity (J/g-K)
Pumice	0.91
Perlite	0.62
Exp. Shale/Clay	0.68
Exp. Slate	0.88

Figure 4: DSC curves of LWAs impregnated with PCM, after 72 hours of absorption.

Table 4: Enthalpy comparison of the LWA-impregnated PCMs

LWA+PCM	Measured Enthalpy (J/g)	Calculated Enthalpy (J/g)
Pumice	31.66	30.42
Perlite	14.45	11.78
Exp. Shale/Clay	34.26	28.70
Exp. Slate	12.24	11.40

3.3.2 Thermal conductivity of LWA mortars

The thermal conductivity of all the mortars evaluated here are shown in Figure 5. The accessible pores in the LWA that contribute to its absorption capacity (Table 1) are filled with water or water and PCM. The thermal conductivity is the highest for the conventional OPC mortar because of the higher thermal conductivity of the dense quartz particles [29,30]. The reduction in thermal conductivity when regular sand is replaced by LWA (irrespective of the LWA type) is easily noted. PCM impregnated LWA mortars generally show thermal conductivities that are about 10%-to-20% lower than the regular LWA (water-saturated) mortars, at a total PCM content of 5% by volume in the mortars. This reduction in thermal conductivity can be attributed to the lower thermal conductivity of the PCM (0.15 W/m-K) as compared to that of water (0.6 W/m-K). In addition, the absorption capacity of the LWA also influences the thermal conductivity since the pores that are not accessible to water and/or PCM are filled with air that has a much lower thermal conductivity than any of the other constituents. Densification of the interface layer in LWA mortars [31] influences heat transfer and could result in diminishing some of the effects of

porosity-induced thermal conductivity reduction. The porosity and surface characteristics of LWAs are thus also important. The thermal conductivity data show that, in addition to the latent heat capacity of PCMs that help reduce energy consumption when used in building envelopes, the enhanced insulation provided by LWA concrete containing PCMs is also beneficial in energy efficient construction.

Figure 5: Thermal conductivity determined after 28 days of hydration for the paste and mortars. The first data is for OPC paste, and the rest are for mortars where the paste volume fraction is 0.50.

3.4 Compressive Strength of PCM-impregnated LWA Mortars

Previous studies suggest that the PCMs have the propensity to leak out of their LWA host, and interfere with cement hydration and mechanical property development of concrete [12,32]. The compressive strength of the different LWA mortars without and with 5% (of the total mortar volume) of PCMs impregnated in the LWAs, at different times, are shown in Figures 6(a) and (b) respectively. A comparison of these figures reveal that the compressive strengths remain rather invariant of both the LWA type and PCM incorporation in the LWAs. These results establish that LWAs can be used as effective hosts for PCM without adversely influencing the strength development. It also shows that the pre-treatment and PCM impregnation methodology described earlier can be adopted effectively without any leakage of PCM from the LWAs into the matrix. In previous studies, when there was potential for such leakage, a thin coating of cement paste on the LWAs was found to resolve it [33,34].

Figure 6: Compressive strengths as a function of time for: (a) plain LWA mortars, and (b) LWA mortars containing 5% PCM by total mortar volume, impregnated in the pores of the LWAs. The standard deviation in compressive strengths ranged between 2 and 3 MPa at early ages and 1 and 2 MPa at later ages.

4.0 PREDICTIVE MODELS FOR THERMAL CONDUCTIVITY OF LWA-PCM COMPOSITE MORTARS

As noted earlier, LWA-containing cementitious materials, are random multi-phase media consisting of the solid phase, and the distributed pore phases that can contain a combination of air, water and/or PCM. Thus, in contrast to general multi-phase media which consists of one continuous matrix and multiple inclusion types, LWA mortars consist of an inclusion phase which by itself has two or three components, as shown in Figure 7. Accurately predicting the engineering behavior of such multi-component materials is a challenging task. For two-component mixtures (matrix and one type of inclusion) with an ordered microstructure, exact models exist. When the microstructure is random, bounds on effective properties are usually adopted [35,36]. Effective medium approximations (EMA) [37] and generalized EMAs [37–39] have been proposed and validated. When geometry information is available along with the volume fractions, narrower bounds can be attained. For example, mean field homogenization models use the aspect ratio and orientation of the inclusion phase to provide accurate property descriptors [40,41].

In this paper, a simple analytical model and a simplified mean field homogenization model are used to estimate the thermal conductivity of LWA-PCM mortars. Accurate prediction of thermal properties helps develop mixture proportions for composite mortars, including the amount and type of LWA and PCM needed for desired thermal performance. However, it needs to be noted that these models cannot take into account clustering, percolation, and size effects, which can be accomplished only using detailed numerical modeling schemes.

Homogenization is executed for a two-component mixture (cement paste and LWA). Since LWA contains the solid phase, and pores containing water, air, or PCM, its effective thermal property is homogenized separately. Accurate determinations of the volume fractions of the appropriate components, the intrinsic thermal conductivity of solid phase in LWAs (considering that the thermal conductivities of water, air, and PCM are known), and the effective thermal conductivity of the LWA (i.e., including air, water, PCM) are needed for property prediction. It needs to be emphasized that the effective property of the LWA is not for an individual LWA particle, but a representative one for the entire quantity of LWAs present in the mortar. Realistically, some LWAs in the mortar contain water and air, while others contain PCM and air. The “idealized” LWA particle combines both these types as shown in Figure 7.

Figure 7: Idealized LWA for effective property determination. Some LWAs have PCM while some others have water to ensure desired PCM levels in the mortars. An “idealized” LWA is also shown, that is representative of the LWA phase.

4.1 Volume Fractions of component phases

Since all the mortars were proportioned to contain 5% of PCM by total volume, and the mortars contain 50% by volume of LWA, the volume of PCM as a fraction of total LWA volume (of all the LWAs in the mortar) is 10%. The remaining pore volume of the LWAs is filled with water and air. The amount of water filled pores is determined by subtracting the PCM volume from the LWA absorption capacity, and the remaining fraction of porosity is considered as air voids. The volume fraction of water filled pores in the LWA mortars without PCM is the same as its absorption capacity. Table 5 presents the individual phase volume fractions in the different LWAs.

Table 1: Fractions of solid, water, PCM, and air in the LWAs in the PCM-impregnated mortars. The water comes from the saturated, non-PCM impregnated LWAs added to ensure that the total PCM volume fraction in the mortar is 5%.

LWA	Porosity	Solid fraction	Absorption capacity	PCM content	Water content	Air void content
Pumice	0.39	0.61	0.211	0.1	0.111	0.179
Perlite	0.15	0.85	0.112	0.1	0.012	0.038
Exp. Slate	0.30	0.7	0.106	0.1	0.006	0.194
Exp. Shale/Clay	0.53	0.47	0.157	0.1	0.057	0.373

4.2 Intrinsic thermal properties of the components

The thermal conductivities of water, air, and PCM (0.6, 0.15, and 0.025 W/m-K respectively) are known [42,43]. The thermal conductivity of the solid phase of the different LWAs was estimated by inverse analysis using the Mori-Tanaka approach [40,44,45].

Mori-Tanaka homogenization method has been used to determine the effective properties of cement-based materials [46–49]. It approximates the interaction between the different components by considering that each inclusion is embedded, in turn, in an infinitely extended homogeneous reference medium (matrix) that is subjected to a temperature gradient. In other words, each inclusion behaves like an isolated inclusion in the matrix experiencing the average temperature gradient in the matrix as the far-field gradient. The effective thermal conductivity based on Mori-Tanaka model is given as [45]:

$$\lambda^{(c)} = \lambda^{(m)} + v^{(i)} (\lambda^{(i)} - \lambda^{(m)}) \bar{A}_{MT}^i \quad (3)$$

Here, $\lambda^{(c)}$ is the effective composite thermal conductivity; $\lambda^{(m)}$ is the thermal conductivity of matrix; $\lambda^{(i)}$ is the thermal conductivity of inclusion, $v^{(i)}$ is the inclusion volume fraction and $\bar{A}_{MT}^i$ is the Mori-Tanaka gradient concentration tensor of the inclusion, given as [45]:

$$\bar{A}_{MT}^i = \bar{A}_d^i (v^{(m)} I + v^{(i)} \bar{A}_d^i)^{-1} \quad (4)$$

Here, $v^{(m)}$ is the matrix volume fraction, i.e., $v^{(m)} = 1 - v^{(i)}$, I denotes the identity tensor and $\bar{A}_d^i$ is the gradient concentration tensor of dilute inclusions with perfect interfaces, given as [45]:

$$\bar{A}_d^i = [I - SR^{(m)} (\lambda^{(i)} - \lambda^{(m)})]^{-1} \quad (5)$$

where $R^{(m)}$ is the resistivity tensor, given as $R^{(m)} = (\lambda^{(m)})^{-1}$ and S is the Eshelby tensor [45,50]. For multiple spherical inclusions of isotropic thermal conductivity embedded in a uniform matrix, Equation 3 reduces to a scalar expression as [40,51]:

$$\lambda^c = \frac{v^m \lambda^m + \sum_{i=1}^N v^i \lambda^i \frac{3\lambda^m}{2\lambda^m + \lambda^i}}{v^m + \sum_{i=1}^N v^i \frac{3\lambda^m}{2\lambda^m + \lambda^i}} \quad (6)$$

The experimentally measured thermal conductivities of the plain LWA mortars (without PCM) were used in a two-step inverse analysis procedure to obtain the thermal conductivity of solid phase in different LWAs (See Figure 8). In the first step, the measured thermal conductivity of the different LWA mortars and the known thermal conductivity of the cement paste (see Figure 5) are used to back-calculate the thermal conductivity of the different LWAs. The second step calculates the thermal conductivity of solid phase of the LWA from the homogenized thermal conductivity of LWA obtained from Step-I and the known thermal conductivities of air and water. The solid phase thermal conductivities of pumice, perlite, expanded slate, and expanded shale/clay were obtained as 0.80, 0.59, 0.82 and 1.1 W/m-K respectively, reflecting the differences in the mineralogy of these LWAs.

Figure 8: Inverse analysis procedure for the determination of thermal conductivity of the solid phase of LWAs.

4.2.1 Predicting effective thermal conductivity of PCM-impregnated LWA mortars

Amongst the different EMAs available, Maxwell-Garnett model is used here since it has been used in the past to predict the thermal conductivity of multi-component particulate composite materials [52,53]. Other more involved predictive approaches such as Felske and Hamilton-Crosser models were also used but they were found to be similar to Maxwell-Garnett model in their predictive capability, and thus not elaborated here. The homogenized thermal conductivity λ^c can be obtained from the thermal conductivities of the matrix (λ^m) and the inclusion (λ^i) phases as:

$$\frac{\lambda^c - \lambda^m}{\lambda^c + 2\lambda^m} = \sum_{i=1}^N v^i \left[\frac{\lambda^i - \lambda^m}{\lambda^i + 2\lambda^m} \right] \quad (7)$$

In this equation, v^i the volume fraction of inclusion i and N is the number of inclusion phases.

The simplified mean-field homogenization scheme applies the Mori-Tanaka method [40,44,45]. Two different approaches are implemented. First, a two-step homogenization process, both involving the Mori-Tanaka scheme, is implemented as shown in Figure 9. In the first step, the water-filled voids, PCM-filled voids and the air voids are homogenized with the solid LWA matrix to obtain the homogenized thermal conductivity of LWA. The second step homogenizes the effective LWA (determined in Step-I) with that of the hardened cement paste matrix to determine the effective thermal conductivity of the PCM-impregnated LWA mortar.

Figure 9: Two-step Mori-Tanaka homogenization scheme for determination of thermal conductivity of PCM-impregnated LWA mortars.

The homogenization method described above relies on knowledge of the microstructural arrangements in the composite, i.e., the LWAs are dispersed in the matrix. When the microstructural arrangement is

not known, a sequential homogenization process needs to be employed. This approach homogenizes a two-component medium at any given step, and uses the homogenized results in the following step. The order of homogenization relies less on the microstructural arrangement, and is dictated by the property contrast between the components. Figure 10 depicts the stages in the four-stage homogenization approach, also involving the Mori-Tanaka method. The four-stage homogenization procedure includes the following steps: (i) the first stage of homogenization considers the solid phase of LWAs as the matrix and the water filled pores as inclusions; (ii) the homogenized thermal conductivity obtained from step-I is then input as the matrix for the second stage with the PCM filled pores as inclusions, (iii) in the third step, the resultant of the second stage serves as the matrix to which the air voids are added as inclusions to obtain the effective thermal conductivity of LWA inclusions; and (iv) the last step homogenizes the LWAs into the matrix of hardened cement paste to obtain the effective thermal conductivity of PCM-impregnated LWA mortars. This approach minimizes the effects of thermal conductivity contrast of different phases on the predicted effective property.

Figure 10: Four-step Mori-Tanaka homogenization scheme for thermal conductivity determination of mortars with PCM-impregnated LWAs.

The effective thermal conductivities of the PCM-impregnated LWA mortars predicted using the Maxwell-Garnett and Mori-Tanaka schemes are shown in Figure 11. It is immediately evident that the two-step Mori-Tanaka approach best predicts mortar thermal conductivity. The differences between the

measured and predicted results range from 7% to 13%, with the largest difference for the system that has the highest amount of air voids (expanded shale/clay; Table 5) and the least difference when the volume of air voids is the least (perlite). The thermal conductivity contrast between air voids and other components is the largest (one-to-two orders of magnitude), and hence higher volume fractions of air voids result in increased divergence of the predictions from experimental results. Presence of phases with high property contrasts limits accurate prediction of effective properties as reported in [54–56].

Figure 11: Experimental and predicted thermal conductivity values of PCM-impregnated LWA mortars.

Figure 12: Normalized change in thermal conductivity as a function of the microstructural contrast factor

To quantify the influence of the microstructural components and contrasts in their thermal conductivities on the predicted effective property, a microstructural contrast factor (ζ) is defined as:

$$\zeta = \left(\frac{\lambda_s}{v_s} - \frac{\lambda_{air}}{v_{air}} \right) \quad (8)$$

λ_s is the thermal conductivity of solid phase of the LWA, λ_{air} is the thermal conductivity of air, v_s is the volume fraction of solid phase in LWAs and v_{air} is the volume fraction of air voids in LWAs. This factor accounts for both the thermal conductivities as well as the volume fractions of the phases with the highest property contrast. Figure 12 shows the relationship between the contrast factor and the normalized change in thermal conductivity ($\kappa_{norm} = \Delta\lambda/\lambda_{exp}$), where $\Delta\lambda$ is the absolute difference between the measured and predicted thermal conductivities and λ_{exp} is the measured thermal conductivity. In this figure, κ_{norm} is represented as the average for all the four different aggregates considered. A smaller value of κ_{norm} indicates better predictive efficiency of the model. It is shown that an increase in ζ results in a lower prediction accuracy, thereby quantifying the influence of volume fractions and properties of the contrasting components on the modeling results.

5. SUMMARY AND CONCLUSIONS

The influence of LWA characteristics on PCM impregnation efficiencies, and the resulting thermal properties of the mortars are reported. Four different LWAs of different mineralogy and pore structure features were used. The LWA mortars containing 5% of PCM (by volume) showed thermal conductivities that are lower by 10% or more as compared to those of the plain LWA mortars, which can be attributed to the lower thermal conductivity of PCM as compared to that of water. This enables the utilization of PCM-incorporated LWAs in building insulation applications, along with the added advantage of PCMs in reducing the magnitude of thermal cycles. When used as a structural component, which is facilitated by the adequate structural strength, the insulation thickness can be reduced through this approach, resulting in economy.

A simple effective medium theory, and a mean-field homogenization model were used to predict the thermal conductivity of LWA-PCM mortars. An inverse analysis procedure was established to determine the thermal conductivities of the solid phase of the different LWAs. It was shown that the application of Mori-Tanaka mean-field homogenization method that considered the known microstructural arrangement of the composite (i.e., a heterogeneous inclusion in a homogeneous matrix) resulted in a better predictive capability than the use of sequential homogenization based on thermal conductivity

contrast of the different components in the composite. This finding provides guidelines on analytical modeling of effective properties of hierarchical composite materials. Moreover, such models can be employed to ensure efficient selection of PCM types (based on their thermal properties) and LWA types (based on their porosity and absorption capacity) for desired thermal performance. These models are expected to help engineers better evaluate the thermal performance of building envelopes (structural or non-structural) as a function of their constitution, leading to more accurate thermal assessment and better prediction of building energy efficiency. The understanding that the relative volume fractions of phases with the largest property contrasts (in this case, the solid phase of LWA and air), and the magnitude of these property contrasts impact the accuracy of analytical predictive schemes led to the formulation of a microstructural contrast factor. This factor was well correlated to the difference in the experimental and predicted thermal conductivities. Numerical modeling schemes are required for more efficient prediction when the contrast factors are large.

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