

Article

Thermal Conductivity Behavior and Modeling of Microencapsulated Phase Change Material-Modified Cement Composites

Qiling Wang ^{1,2}, Yaxin Tao ^{2,*}, Fengjun Chen ¹, Chao Tan ^{3,*}, Eddie Koenders ⁴, Xiaojian Wu ¹, Xiaoming Chen ¹ and Yong Yuan ²

¹ Shanghai Construction Co., Ltd., Shanghai 201114, China

² College of Civil Engineering, Tongji University, Shanghai 200092, China

³ Hunan Provincial Communications Planning, Survey & Design Institute Co., Ltd., Changsha 410200, China

⁴ Institute of Construction and Building Materials, Technical University of Darmstadt, Darmstadt 64287, Germany

* Correspondence: taoyaxin@tongji.edu.cn (Y.T.); tanchao@hnjtsjy.com (C.T.)

Abstract

Microencapsulated phase change material (MPCM)-modified cement composites have attracted increasing attention for energy-efficient buildings and thermal energy storage applications. Accurate prediction of thermal conductivity is essential for optimizing thermal management performance. However, quantitative understanding of the multiscale heat transfer mechanisms in MPCM-modified cement composites remains relatively limited. In this study, the thermal transport behavior of MPCM-modified cement composites was investigated through experimental characterization and multiscale theoretical modeling. A micro–macro combinatorial accumulation approach was developed based on representative volume element (RVE) construction and cumulative thermal interactions to characterize hierarchical heat transfer mechanisms within the composite system. The proposed model enables quantitative prediction of thermal conductivity for inclusions with different geometries and accumulation states. The results revealed that the proposed MMCA model successfully captured the multiscale evolution of thermal conductivity by considering cumulative RVE effects and inclusion geometrical characteristics. The effective thermal conductivity decreased from 0.802 to 0.519 W/(m·K) as the MPCM volume fraction increased from 0 to 0.217, corresponding to a reduction of approximately 35.3%. Furthermore, the accumulation of RVEs exhibited a rapid reduction followed by stabilization of thermal conductivity, revealing the scale-dependent heat transfer behavior induced by hierarchical inclusion interactions. The main contribution of this work is the establishment of a physics-based multiscale framework that quantitatively links MPCM inclusion characteristics, cumulative thermal interactions, and macroscopic thermal conductivity, providing new insights into the micro-to-macro heat transfer mechanisms of PCM-modified cement composites. This study offers theoretical support for the multiscale design and thermal performance optimization of PCM-modified energy-functional cementitious materials.

Keywords: cement composites; phase change material; thermal conductivity; model; inclusion geometry

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1. Introduction

Construction under extremely high or low temperatures presents significant challenges to infrastructure performance and durability [1–5]. Phase change materials (PCMs), owing to their large latent heat, offer substantial advantages in mitigating temperature-induced risks and reducing energy consumption during the construction and service stages [6–11]. MPCM exhibits good compatibility with cement, forming MPCM-modified cement composites, an emerging eco-friendly construction material with promising thermal regulation capability [12–15]. Several studies have investigated their mechanical and thermophysical properties [16–18]. Among these properties, thermal conductivity plays a pivotal role, as it governs the heat transfer behavior of the composite and strongly influences the overall thermal performance of related structures [19–22].

Typically, the incorporation of MPCM leads to a reduction in the thermal conductivity of cement-based composites [23–25]. This phenomenon can be attributed to two main factors. First, MPCM generally possess lower thermal conductivity than the cement matrix, resulting in decreased bulk conductivity [26–28]. Second, the addition of MPCM introduces extra micropores into the hardened matrix, where the trapped air acts as a high thermal-resistance medium, further suppressing heat transfer [29,30]. Such reduced conductivity provides enhanced thermal insulation. For instance, Wang et al. [31] applied MPCM-modified concrete to the support structures of high-temperature tunnels to mitigate geothermal hazards, while Gu et al. [32] incorporated both MPCM and foam into cementitious materials to further reduce heat transfer. However, lower thermal conductivity also weakens the heat charging-discharging efficiency of MPCM, thereby limiting their latent-heat storage capability. To overcome this drawback, several approaches have been proposed to enhance the thermal conductivity of PCM-modified cementitious composites: (i) modifying MPCM with high-conductivity fillers (e.g., graphite) [33–35]; (ii) co-dispersing MPCM and thermally conductive additives within the cement matrix [36–39]; (iii) employing advanced encapsulation techniques to minimize pore generation during mixing [40]; and (iv) applying densification treatments to the matrix, such as high-temperature curing [17] or silane-based surface ammonization [41]. It is worth noting that different engineering applications require different levels of thermal conductivity in MPCM-modified cement composites. Although numerous studies have explored techniques for adjusting thermal conductivity, only limited research has quantitatively elucidated the microstructural heat-transfer mechanisms in such composites. This gap hinders the accurate design and scenario-specific optimization of their thermal performance.

Several models have been proposed to estimate the thermal conductivity of MPCM-modified cement composites. Within the micromechanical theoretical framework, the Mori–Tanaka homogenization method has been employed to account for the contrast in phase properties when predicting the effective thermal conductivity of such composites [42–44]. The self-consistent homogenization method has also been utilized, in which MPCM inclusions are generally idealized as thin shells [45] or spherical particles [46]. Following the concept of thermal resistance and capacity (RC) networks, Shi et al. [47] used serial and parallel connection models to evaluate the thermal conductivity of form-stable basalt-fiber composite concrete with MPCM. Wang et al. [48] further integrated the RC network with a finite-difference frequency-domain model to simulate the heat-transfer behavior of cemented backfill incorporating MPCM. Jayalath et al. [49] developed a three-dimensional two-phase random composite model, demonstrating good agreement between numerical predictions and experimental measurements. By assuming one-dimensional heat transfer, Lachheb et al. [34] proposed an inverse analysis technique to determine thermal conductivity from periodic temperature experiments. In addition, several simplified empirical approaches, such as mass-fraction [7,50] or volume-fraction weighted averaging [51], as well as regression-based fitting from experimental data [52], have been

adopted for the practical estimation of thermal conductivity. Although these models provide convenient predictions, limited studies have quantitatively addressed the linkage between microscopic heat-transfer mechanisms and the macroscopic thermal performance of MPCM-modified cement composites. Consequently, a research gap remains regarding performance-oriented design that considers multi-scale features and diverse MPCM geometries, which continues to hinder the broader application of this material.

In this study, the evolution of thermal conductivity in MPCM-modified cement composites under different states was experimentally characterized. A micro-macro combinatorial accumulation (MMCA) model was developed to predict their effective thermal conductivity from multiple perspectives. The model was validated against both experimental measurements and literature data and benchmarked against several typical existing models. Moreover, the MMCA model enabled quantitative analysis of the coupling between microscopic heat-transfer mechanisms and macroscopic thermal performance, revealing the effects of specimen thickness and encapsulated geometry of paraffin particles. Overall, the developed model offers a clearer physical basis and better accounts for key influencing factors, providing useful guidance for the design and application of this energy-functional cementitious material.

The paper is structured as follows. Section 2 investigates the thermal conductivity evolution of MPCM-modified cement pastes through experiments. Section 3 presents the development and validation of the MMCA model, followed by the quantitative discussion about effects of specimen size and MPCM geometry. Conclusions are drawn in Section 5.

2. Experiments on the Thermal Conductivity of MPCM-Modified Cement Composites

2.1. Experimental Setup

2.1.1. Materials and Mixture

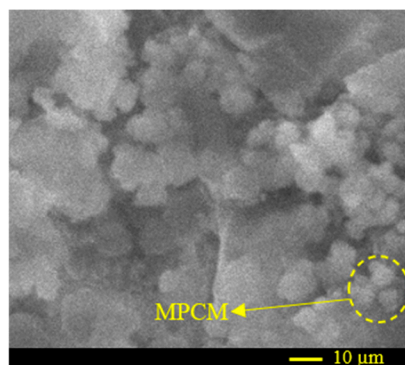
Type I Portland cement manufactured by Fushun Cement Plant (Fushun, China) was selected as the primary binder in experiments, characterized by a density of 3.11 g/cm³ and a specific surface area of 358 m²/kg. Its detailed chemical compounds are provided in Table 1. The MPCM incorporated into the cement matrix comprised a paraffin-based core (C₁₈H₃₈) encapsulated within a polymethyl methacrylate (PMMA) shell, which was manufactured by Hebei Ruosen Technology Co., Ltd. (Hebei, China). The resulting microcapsules formed a fine white powder with particle sizes ranging from 5 to 10 µm. The SEM observation of MPCM is shown in Figure 1. This MPCM was non-toxic, environmentally safe, and exhibited no chemical interaction with cement during the hydration process. The phase change occurred within the temperature range of 27.6–40.9 °C, making them suitable for thermal energy regulation in cementitious systems. A comprehensive summary of its physical characteristics is presented in Table 2.

Table 1. Major chemical compounds in cement.

Component	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃	Na ₂ O	Loss	CL-
mass proportion [%]	20.96	4.13	3.03	63.88	2.90	2.38	0.56	2.14	0.02

Table 2. Physical characteristics of MPCM.

State of PCM	Density [kg/m ³]	Thermal Conductivity [W/(m·K)]	Specific Heat [J/(g·K)]	Latent Heat [kJ/kg]
solid PCM	880	0.230	1.670	166
liquid PCM	802	0.217	1.670	166

**Figure 1.** SEM observation of MPCM.

2.1.2. Specimen Preparation

The procedure of specimen preparation was composed of mixing, curing, and drying periods, see Figure 2. The specimen dimensions (300 × 300 × 20 mm) were selected according to the requirements of the guarded hot plate thermal conductivity measurement system, ensuring stable one-dimensional heat transfer, minimizing edge effects, and improving the accuracy and reliability of the thermal conductivity measurements. In the mixing period, the uniformly mixed MPCM, cement, and water were blended thoroughly in a cement paste mixer and then incrementally placed into detachable steel molds, as illustrated in Figure 2a. After each layer was cast, the mold was gently tapped with a small wooden mallet to ensure uniform distribution and compaction of the MPCM-modified cement paste. The steel molds, with dimensions of 300×300×20 mm, were cleaned, dried, and evenly coated with oil to facilitate later demolding. In the curing period, after 24 h of curing in a curing chamber, the specimens were demolded, see Figure 2b. The top and bottom surfaces of the specimens were then polished with sandpaper to ensure flatness. Subsequently, the polished specimens were transferred to a standard curing room and immersed in water at a constant temperature of 20 °C until reaching a curing age of 90 days. After reaching the designated curing age, the specimens entered the drying period, during which they were oven-dried for 24 h to prepare for testing.

Throughout the experiment, a constant water-to-cement ratio of 0.5 was applied. Five distinct mixtures were prepared, each containing a MPCM-to-cement mass fraction of 0, 5, 10, 15, and 20%. Thus, five groups of specimens were prepared. For better analysis of thermal conductivity in the subsequent discussion, the corresponding volume fractions for the five groups were calculated based on the fundamental material parameters provided in Section 2.1.1, yielding values of 0, 6.5, 12.2, 17.2, and 21.7%, respectively.

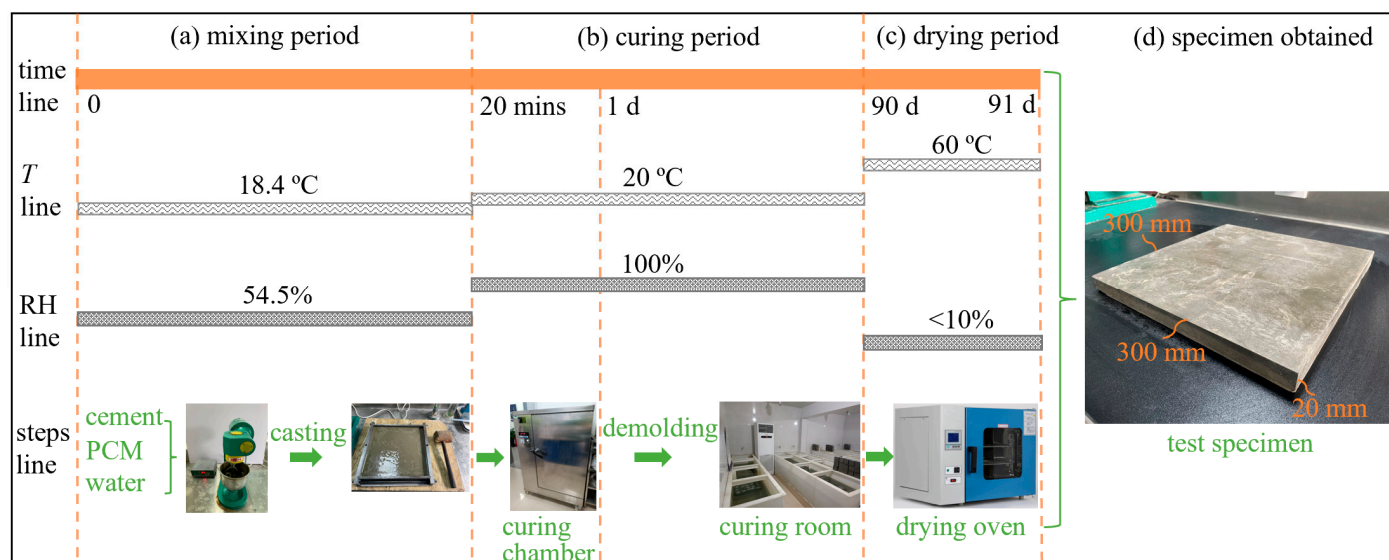


Figure 2. The preparation procedure for specimens.

2.1.3. Testing Method and Conditions

The guarded hot plate method was adopted to test the thermal conductivity of MPCM-modified cement, which is based on the principle of steady state heat conduction. The IMDRY3001-II guarded hot plate thermal conductivity measurement system was chosen, which was a combination of a computer, thermostatic bath, test box, and circulating fluid, see Figure 3. The test box was composed of the cold plate, hot plate, guard plate, temperature sensors, and specimen, where the two specimens were placed between the hot plate and cold plate. The hot plate served as the heat source, supplying thermal energy to the specimen in the test. Meanwhile, the guard plate minimized the heat loss, ensuring that heat transfer predominantly occurred in the vertical direction towards the cold plate, see Figure 3c. Furthermore, the temperature sensors can monitor the temperature evolutions precisely. This configuration facilitated accurate measurement of the thermal conductivity by controlling the heat flow path and reducing heat losses, thereby enhancing the reliability and precision of the experimental results.

To investigate the effects of the PCM phase state on thermal conductivity, three testing temperatures, i.e., 20, 35, and 50 °C, were selected. Given the phase change range of the PCM from 27.6 to 40.9 °C, the selected temperatures, 20, 35, and 50 °C, ensured that the PCM was completely in the solid, melting, and liquid states, respectively. Combined with the different volume fraction levels of MPCM in the specimen, a total of 15 testing conditions were set in the experiments, see Table 3. The thermal conductivity was measured three times under each testing condition, and the average value was calculated. If the deviation of any individual measurement from the average exceeded 5%, an additional test was conducted.

Table 3. Testing conditions in the experiments.

Testing Temperature	Mass Fraction of MPCM	Volume Fraction of MPCM	Curing Conditions
20, 35, and 50 °C	0, 5, 10, 15, and 20%	0, 6.5, 12.2, 17.2, and 21.7%	0–20 min: 18.4 °C, 54.5% RH; 20 min–90 d: 20 °C, 100% RH

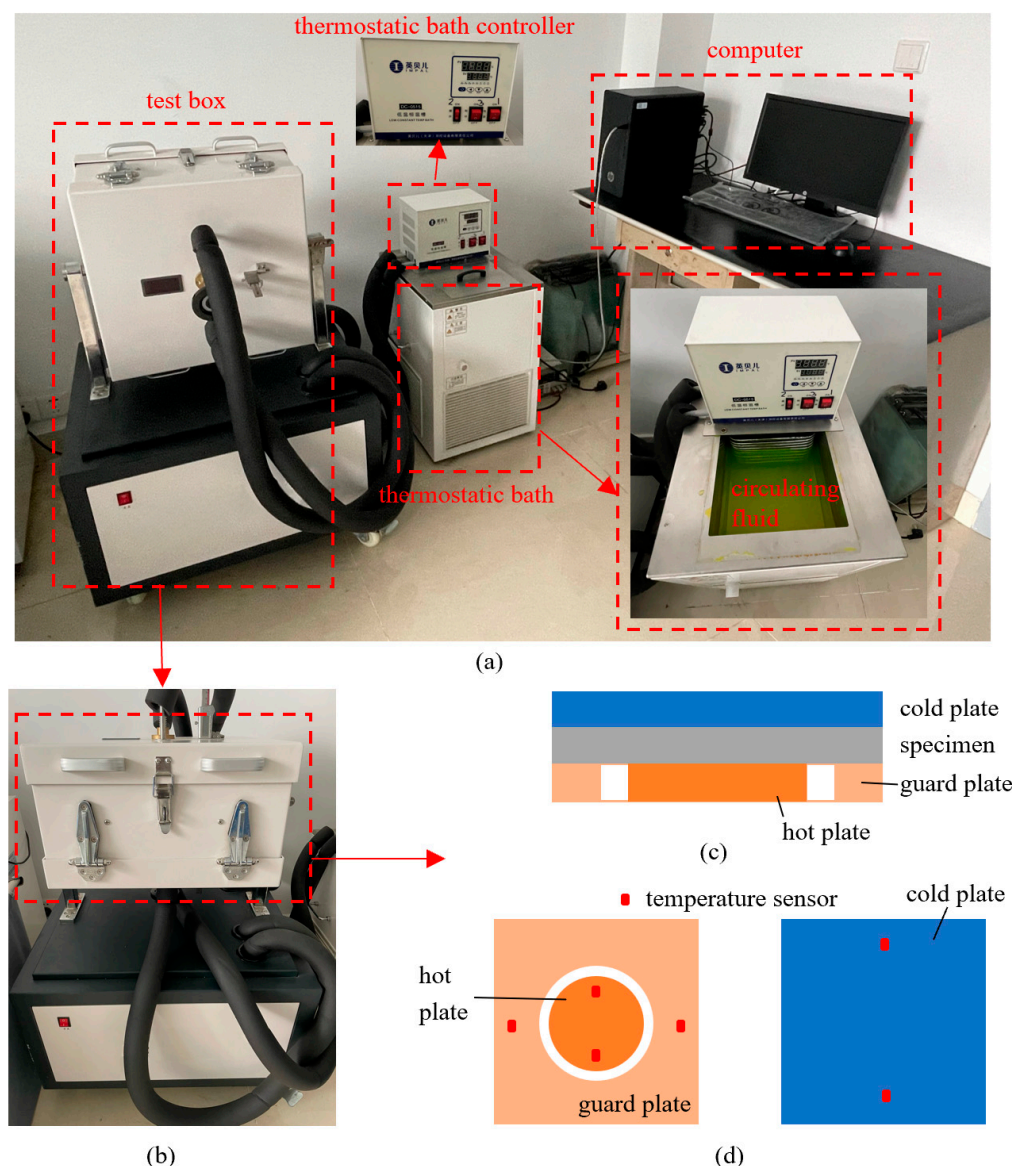


Figure 3. The IMDRY3001-II guarded hot plate thermal conductivity measurement system; (a) shows different components of the system; (b) is the appearance of test box; (c,d) display the internal configuration of the test box, including the cold plate, hot plate, guard plate, temperature sensor, and specimen.

2.2. Results Analysis

The thermal conductivity of MPCM-modified cement at five volume fraction levels (0.000, 0.065, 0.122, 0.172, and 0.217) was measured using the guarded hot plate method under three different testing temperatures (20, 35, and 50 °C). The evolutions of thermal conductivity with volume fraction of MPCM (f_{PCM}) are shown in Figure 4, and the corresponding values are summarized in Table 4.

Table 4. Thermal conductivity and nondimensionalization of thermal conductivity of MPCM-modified cement under different testing conditions.

Mass Fraction of MPCM [%]	Volume Fraction of MPCM, f_{PCM} [-]	Average Thermal Conductivity, λ [W/(m·K)]			Nonmenless of Thermal Conductivity, N_λ [-]		
		20 °C	35 °C	50 °C	20 °C	35 °C	50 °C
0	0.000	0.802	0.799	0.797	1.000	0.996	0.994

5	0.065	0.635	0.627	0.622	0.792	0.782	0.776
10	0.122	0.592	0.584	0.581	0.738	0.728	0.724
15	0.172	0.537	0.531	0.526	0.670	0.662	0.656
20	0.217	0.519	0.516	0.510	0.647	0.643	0.636

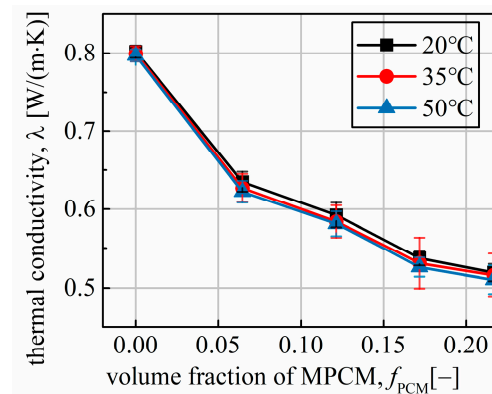


Figure 4. The evolution of thermal conductivity with volume fraction of MPCM.

At all three testing temperatures, the thermal conductivity decreased with the increasing volume fraction of MPCM in the MPCM-modified cement paste specimens, as shown in Figure 4. This behavior can be attributed to two main factors. First, the intrinsic thermal conductivity of MPCM is considerably lower than that of the cement matrix, resulting in the interruption of continuous heat-transfer pathways. Second, previous studies [53–55] have shown that the incorporation of MPCM may reduce the dispersion uniformity of the microcapsules and introduce additional air voids and porosity into the cementitious matrix, thereby increasing the thermal resistance because entrapped air exhibits an extremely low thermal conductivity. Consequently, the effective thermal conductivity decreases continuously with the increasing MPCM content. Under the 20 °C condition, when the MPCM volume fraction increased from 0 to 0.217, the thermal conductivity decreased from 0.802 to 0.519 W/(m·K), corresponding to a reduction of approximately 35.3%. At testing temperatures of 20, 35, and 50 °C, the MPCM was in the solid, melting, and liquid phases, respectively. As the testing temperature increased from 20 to 50 °C, the thermal conductivity of the pure cement paste specimen decreased slightly, from 0.802 to 0.797 W/(m·K), indicating minimal influence. However, in MPCM-modified cement paste, the temperature-induced phase transitions of the MPCM led to a more significant reduction in composite thermal conductivity, as illustrated in Figure 4 and summarized in Table 4. The test error was more pronounced under the 35 °C condition, as it was difficult to ensure the consistent melting state of the PCM in each test, see Figure 4.

Furthermore, the thermal conductivity of MPCM-modified cement was non-dimensionalized using the pure cement paste specimens at the 20 °C temperature condition as the reference, following Equation (1)

$$N_{\lambda} = \frac{\lambda}{\lambda_{0\%, 20^{\circ}\text{C}}} \quad (1)$$

The dimensionless thermal conductivity values were also presented in Table 4, and the fitting curves were also obtained, see Figure 5. The dimensionless thermal conductivity values decreased with the increase of volume fraction of MPCM, see Figure 5, and the fitting formulas of dimensionless thermal conductivity at different temperatures followed Equation (2).

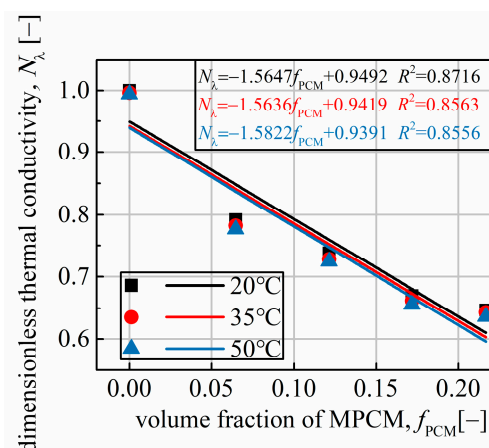


Figure 5. The evolutions of dimensionless thermal conductivity with the volume fraction of MPCM and the fitting curves.

$$N_{\lambda} = \begin{cases} -1.5647f_{\text{PCM}} + 0.9492 & R^2 = 0.8716 \quad (20^{\circ}\text{C, solid}) \\ -1.5636f_{\text{PCM}} + 0.9419 & R^2 = 0.8563 \quad (35^{\circ}\text{C, solid-liquid}) \\ -1.5822f_{\text{PCM}} + 0.9391 & R^2 = 0.8556 \quad (50^{\circ}\text{C, liquid}) \end{cases} \quad (2)$$

3. Micro-Macro Combinatorial Accumulation Model for Thermal Conductivity

3.1. Establishment of the Micro-Macro Combinatorial Accumulation Model (MMCA Model)

The macroscopic heat transfer characteristics of MPCM-modified cement paste are the cumulative result of the heat transfer behavior of microscopic representative volume elements (RVEs). By following the three steps, (1) selecting appropriate RVEs, (2) establishing the heat transfer constitutive model at the microscale, and (3) analyzing the micro-macro accumulation mechanism, it is possible to develop a micro-macro combinatorial accumulation model for the effective thermal conductivity of MPCM-modified cement and to elucidate the underlying mechanism.

3.1.1. Establishment of RVE

Since the thermal conductivity coefficient has the dimension of $\text{W}/(\text{m}\cdot\text{K})$, the dimensional analysis indicates that the thermal conductivity of MPCM-modified cement is scale-dependent. Thus, the RVE of MPCM-modified cementitious material is established based on the volume fraction of MPCM, i.e., f_{PCM} , defined in Equation (3).

$$f_{\text{PCM}} = \frac{V_{\text{PCM}}}{V_{\text{c}}}, \quad (3)$$

where V_{PCM} and V_{c} represent the volume of MPCM and cement composites, respectively. The values of f_{PCM} under different testing conditions are shown in Table 4.

The procedure for establishing the RVE is illustrated in Figure 6. First, a vertical strip element with a width of $2d$ is extracted from the side view of the test specimen, as shown in Figure 6a,b. Subsequently, a rectangular element with a width of $2d$ is selected from the vertical strip element, representing the cement composites, see Figure 6b,c. An inclusion is placed at the center of the rectangle to represent the MPCM, see Figure 6d. The ratio between the volume of MPCM and the cement in Figure 6d follows the definition of volume fraction f_{PCM} in Equation (3). For better establishment of the model and later analysis, the inclusion is idealized as a perfect sphere based on the equivalent volume method, following

$$r = \left(\frac{3V_{\text{PCM}}}{4\pi} \right)^{1/3}. \quad (4)$$

r denotes the equivalent radius of the MPCM particle.

The idealized two-dimensional RVE model is shown in Figure 6e. The ratio between the equivalent radius r and d is proportional to the volume fraction f_{PCM} , following

$$\frac{\pi r^2}{4d^2} \propto f_{\text{PCM}}^{\frac{2}{3}}. \quad (5)$$

To account for the geometric effects of inclusion, a shape factor function $f(C)$ is imported. These geometric effects diminish with the increased number of RVEs. Based on this formulation and Equation (5), the relation between r and d is proposed to be defined as Equation (6).

$$\frac{r}{d} = \frac{2}{\sqrt{\pi}} f_{\text{PCM}}^{\frac{1}{3}} \cdot f(C) \quad (0 < r \leq d), \quad (6)$$

where the shape factor function $f(C)$ followed

$$f(C) = (C)^{1/(\beta-m)}. \quad (7)$$

m denotes the number of RVEs traversed by the heat flux. β is the model coefficient. The shape compactness C of the inclusion is given by

$$C = \frac{36\pi V_{\text{PCM}}^2}{S_{\text{PCM}}^3}, \quad (8)$$

where S_{PCM} denotes the surface area of inclusion. C ranges from 0 to 1. If the inclusion is a perfect sphere, C is equal to 1.

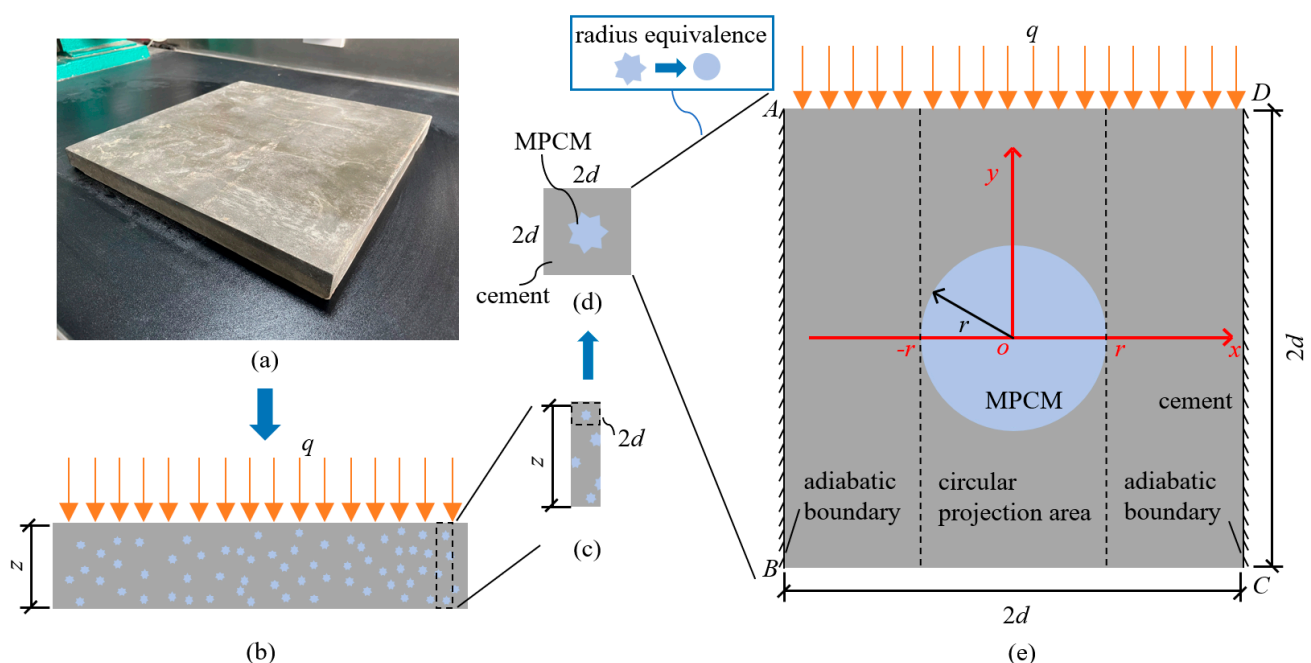


Figure 6. The procedure for establishing the RVE; (a) shows the test specimen; (b) shows the side view of test specimen; (c) is a vertical strip element with a width of $2d$; (d) displays the cement with the MPCM particle; (e) displays the two-dimensional RVE.

To facilitate the development of the constitutive model for RVE, a Cartesian coordinate system is established at the center of the element. The projection of the circular

boundary onto the x-axis is defined as the circular projection area, see Figure 6d. To construct a physically reasonable model, the following assumptions are made:

- A uniformly distributed heat flux enters the RVE perpendicularly through boundary AD .
- The probability of heat flux entering the RVE is uniform along boundary AD .
- The heat flux tends to flow vertically downward within the RVE following the principle of minimum thermal potential.
- All constituent materials are considered homogeneous and isotropic.
- No local thermal accumulation occurs within the RVE.
- Boundaries AB and CD are assumed to be adiabatic.
- The volume change of RVE with temperature is neglected.
- The interfacial thermal resistance between the MPCM and the cement matrix is neglected.

3.1.2. Heat Transfer and Constitutive Model of RVEs

The microscopic heat transfer mechanisms of three typical RVEs are briefly analyzed, as shown in Figure 7. Figure 7a represents a homogeneous medium. Figure 7b shows a homogeneous medium with an adiabatic circular void at the center, and Figure 7c depicts a homogeneous medium containing a central circular region composed of another homogeneous material.

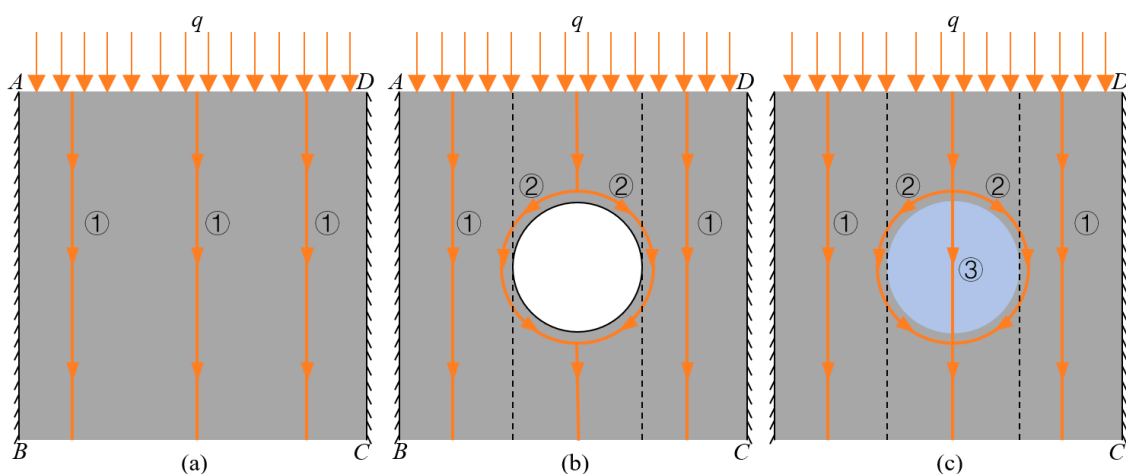


Figure 7. Microscopic heat transfer mechanism of three typical RVEs: (a) represents a homogeneous medium; (b) shows a homogeneous medium with an adiabatic circular void at the center; (c) depicts a homogeneous medium containing a central circular region composed of another homogeneous material.

The heat flux is transferred vertically downward, and the heat transfer mechanism can be analogized to the flow of water passing a circular obstacle. In a homogeneous medium, each heat flux stream flows vertically downward, exhibiting heat transfer mode ①, as shown in Figure 7a. In a homogeneous medium containing adiabatic circular inclusion, when the heat influx point lies outside the projected area of the circular inclusion, the heat flows vertically downward, still corresponding to mode ①. However, when the influx point is located within the projected area of the circular inclusion, the heat flux bypasses the adiabatic zone and continues downward, corresponding to heat transfer mode ②, which resembles the fluid flow circumventing an obstacle, as illustrated in Figure 7b. In Figure 7c, within the projected area of a non-circular void, the heat transfer mechanism remains mode ①. For projected areas of circular inclusion, two scenarios are observed: (1) if the thermal conductivity of the medium within the circular inclusion is higher than

that of the surrounding medium, the heat flux enters the circular region directly without detouring, resulting in heat transfer mode ③; (2) if the thermal conductivity of the medium within the circular inclusion is lower than that of the surrounding medium, part of the heat flux enters the region directly, while another part bypasses it before continuing downward, leading to combined heat transfer modes ② and ③.

The heat transfer mechanisms of MPCM-modified cement RVEs follow heat transfer ①, ②, and ③ because the thermal conductivity of medium is lower than that of cement, see Table 4. The thermal conductivity is inherently determined by the material properties, and the heat flux tends to flow in the vertical direction within the RVE. Thus, the concept of the columnar element is imported in the MPCM-modified cement RVE, see Figure 8. The columnar elements are categorized into two types. When the influx point is located within non-circular projection regions, i.e., $x \in [-d, r) \cup (-r, d]$, the corresponding columnar elements are classified as type-I, composed entirely of cement paste, see Figure 8a,b. When located within the circular projection area, i.e., $x \in [-r, r]$, the corresponding columnar elements are defined as type-II, with cement paste and MPCM, see Figure 8a,c. Analogous to the electrical circuit diagram, thermal circuit diagrams are abstracted for both types of columnar elements, as shown in Figure 8d–f. For type-I elements, heat flux flows vertically downward solely through the thermal resistance of the cement paste, as illustrated in Figure 8d. For type-II elements, when the heat flux reaches the upper boundary of the MPCM, it may either pass directly downward through the MPCM or bypass the MPCM by flowing through the adjacent cement paste, forming a parallel thermal resistance network. Whether this bypass occurs symmetrically on both sides or unilaterally depends on the position of the point, resulting in two possible thermal circuit configurations: one with two thermal resistances in parallel and the other with three parallel resistances, as shown in Figure 8e and f, respectively. The intersection point between the vertical centerline of a type-I columnar element and the x-axis is defined as point E , while the intersection between the vertical centerline of a type-II columnar element and the upper semicircle of the MPCM is defined as point F .

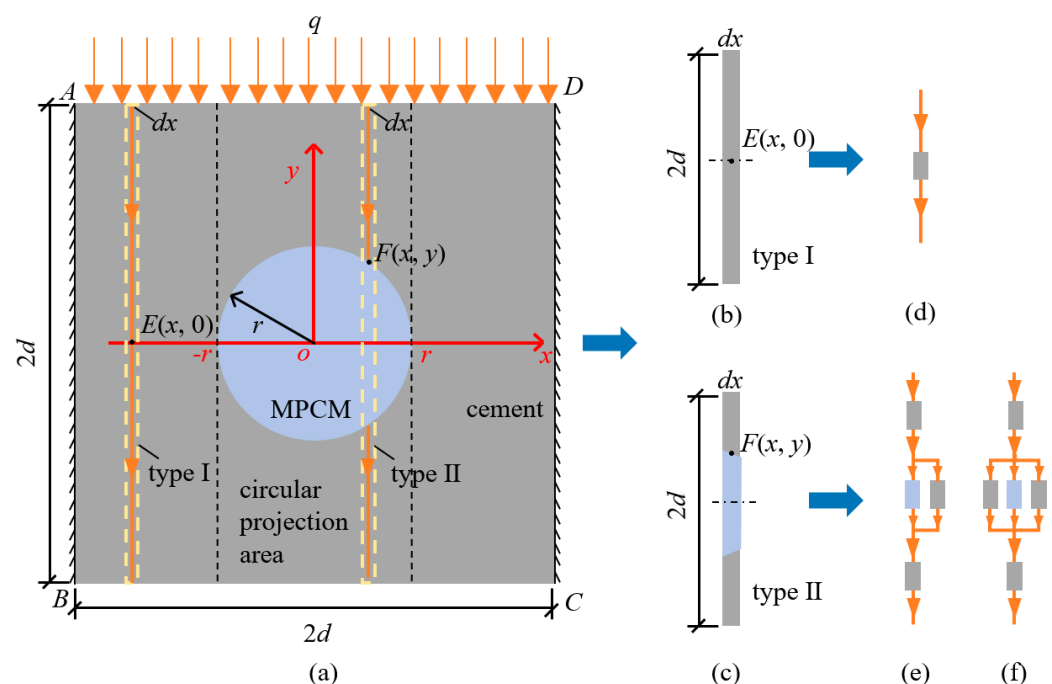


Figure 8. Conceptual model of heat flux transfer and types of columnar elements in MPCM-modified cement RVE: (a) method for constructing columnar elements within the RVE; (b) type-I columnar element; (c) type-II columnar element; (d) thermal circuit diagram for a type-I columnar element; (e) thermal circuit diagram for a type-II columnar element; (f) thermal circuit diagram for a type-II columnar element.

(e) thermal circuit diagram for a type-II columnar element; (f) alternative thermal circuit diagram for a type-II columnar element.

The thermal conductivity of cement paste is denoted as λ_c , and that of MPCM is λ_{PCM} . The thermal conductivity of the columnar element at a given point is represented as $\lambda(x)$, while the average thermal conductivity of RVE is denoted as $\bar{\lambda}_E$. $\lambda(x)$ is equal to λ_c in the non-circular projection regions. The length-weighted average method based on the proportions of cement paste and MPCM is adopted to calculate $\lambda(x)$ in the circular projection region, following

$$\lambda(x) = \frac{d-y}{d} \lambda_c + \frac{y}{d} \lambda_{PCM} \quad x \in [-r, r], \quad (9)$$

where y denotes the vertical coordinate of point F , see Figure 8a. Inserting $y = \sqrt{r^2 - x^2}$ into Equation (9) yields

$$\lambda(x) = \begin{cases} \lambda_c & x \in [-d, r) \cup (-r, d] \\ \frac{d-y}{d} \lambda_c + \frac{y}{d} \lambda_{PCM} & x \in [-r, r] \end{cases}. \quad (10)$$

The evolution of $\lambda(x)$ with x is shown in Figure 9.

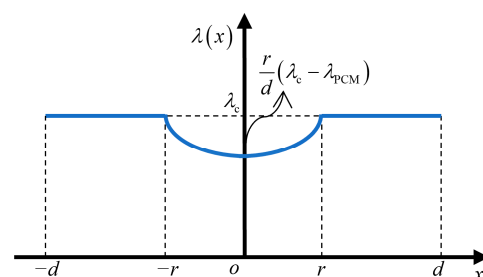


Figure 9. The thermal conductivity of columnar element changes with axis x .

Furthermore, based on Equation (10), the average thermal conductivity of MPCM-modified cement is calculated by the area-averaged method, following Equation (11)

$$\bar{\lambda}_E = \frac{1}{2d} \int_{-d}^d \lambda(x) dx = \left(1 - \frac{\pi r^2}{4d^2}\right) \lambda_c + \frac{\pi r^2}{4d^2} \lambda_{PCM}. \quad (11)$$

Meanwhile, the average thermal conductivity of the type-I columnar element ($\bar{\lambda}_1$) and type-II columnar element ($\bar{\lambda}_2$) follows Equations (12) and (13).

$$\bar{\lambda}_1 = \lambda(x) = \lambda_c \quad x \in [-d, r) \cup (-r, d]. \quad (12)$$

$$\begin{aligned} \bar{\lambda}_2 &= \frac{1}{2r} \int_{-r}^r \lambda(x) dx = \frac{1}{2r} \int_{-r}^r \left[\left(\frac{\lambda_{PCM} - \lambda_c}{d} \right) \sqrt{r^2 - x^2} + \lambda_c \right] dx \\ &= \left(1 - \frac{\pi r}{4d}\right) \lambda_c + \frac{\pi r}{4d} \lambda_{PCM} \end{aligned} \quad (13)$$

3.1.3. Micro-Macro Combinatorial Accumulation and Macroscopic Thermal Conductivity

The macroscopic thermal conductivity of MPCM-modified cement composites represents the combinatorial accumulation behavior of numerous RVEs. Considering the random stacking of n layers of RVEs, as shown in Figure 10, when a heat flux passes vertically from one layer to the next, it may enter either a type-I columnar element or type-II columnar element, as depicted in Figure 10a. According to the analysis in the previous section, the probabilities of the heat flux entering a type-I or type-II columnar element are $(d-r)/d$ and r/d , respectively, with the corresponding average thermal conductivities $\bar{\lambda}_1$ and $\bar{\lambda}_2$, respectively. Given that the side length of RVE is $2d$, the thermal resistances of the two columnar types are $2d/\bar{\lambda}_1$ and $2d/\bar{\lambda}_2$, respectively.

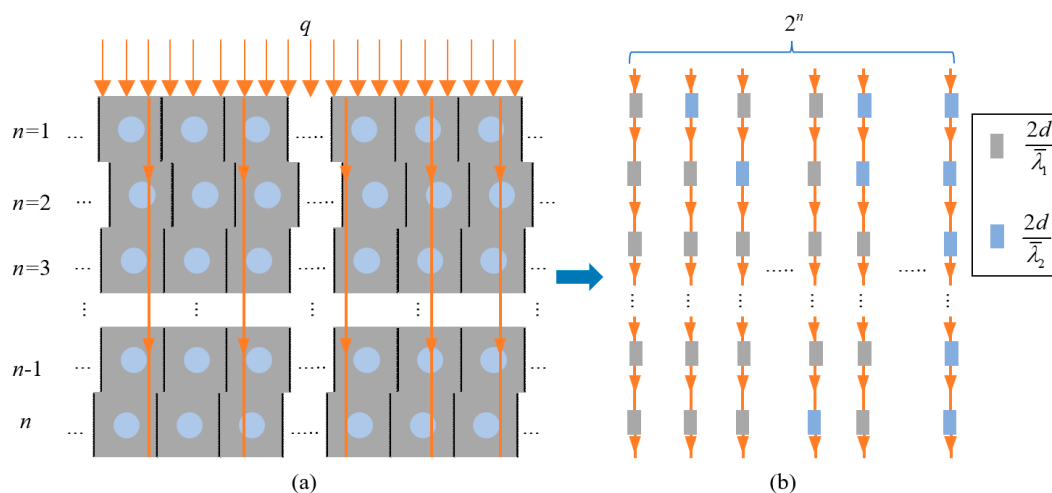


Figure 10. Schematic diagram of the stacking behavior of RVEs: (a) stacking behavior of n layer RVEs; (b) heat transfer network after n -layer stacking of RVEs.

A strip element passing through n layers of RVEs can thus be regarded as a series connection of n thermal resistances, see Figure 10b. Since each layer offers two possible resistances, there are 2^n possible heat passing paths, as illustrated in Figure 10b. The effective thermal conductivity of a strip element across n layers is determined by the minimum thermal conductivity among these layers. Because the experimentally measured λ_{PCM} is smaller than λ_c , Equations (12) and (13) indicate that $\bar{\lambda}_2$ is smaller than $\bar{\lambda}_1$. Therefore, if a strip element includes at least one layer of type-I columnar element, its average thermal conductivity equals $\bar{\lambda}_2$. Consequently, the average thermal conductivity of n stacked layers of RVEs ($\bar{\lambda}_n$) can be regarded as a probabilistic combination governed by different selection probabilities, following Equation (14).

$$\bar{\lambda}_n = \left(\frac{d-r}{d} \right)^n \bar{\lambda}_1 + \left[1 - \left(\frac{d-r}{d} \right)^n \right] \bar{\lambda}_2. \quad (14)$$

Substituting Equations (12) and (13) into Equation (14) yields Equation (15).

$$\bar{\lambda}_n = \left(\frac{d-r}{d} \right)^n \lambda_c + \left[1 - \left(\frac{d-r}{d} \right)^n \right] \left[\left(1 - \frac{\pi r}{4d} \right) \lambda_c + \frac{\pi r}{4d} \lambda_{\text{PCM}} \right]. \quad (15)$$

The stacked layer n is determined by the actual thickness (z) of the specimen and the size of RVE ($2d$), see Figure 6, following Equation (16) with the substitution from Equation (6).

$$n = \frac{z}{2d} = \frac{z}{\sqrt{\pi} \cdot r} \cdot f_{\text{PCM}}^{\frac{1}{3}}. \quad (16)$$

The thermal conductivity of MPCM is typically dependent on their phase state, which is determined by temperature (T). Therefore, the term λ_{PCM} can be replaced by $\lambda_{\text{PCM}}(T)$ in the above equations. $\lambda_{\text{PCM},s}$ and $\lambda_{\text{PCM},l}$ denote the thermal conductivities of MPCM in the solid and liquid phases, respectively. The variation of the thermal conductivity with temperature can be simply described by a piecewise function, as expressed in Equation (17) and shown in Figure 11. It should be noted that this treatment does not explicitly account for latent heat effects, variations in specific heat capacity, or transient heat-transfer behavior within the phase transition interval. Instead, it provides an engineering-level equivalent representation of the phase-dependent thermal conductivity, which enables tractable implementation of the proposed multiscale model.

$$\lambda_{\text{PCM}}(T) = \begin{cases} \lambda_{\text{PCM},s} & T < T_1 \\ kT + l & T \in [T_1, T_2], \\ \lambda_{\text{PCM},l} & T > T_2 \end{cases} \quad (17)$$

where k and l are linear fitting parameters.

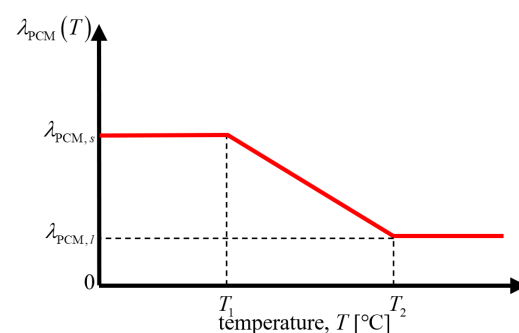


Figure 11. The evolution of thermal conductivity of PCM with temperature.

By substituting Equation (17) into Equations (11) and (15), Equations (18) and (19) are obtained

$$\bar{\lambda}_E = \left(1 - \frac{\pi r^2}{4d^2}\right) \lambda_c + \frac{\pi r^2}{4d^2} \lambda_{\text{PCM}}(T). \quad (18)$$

$$\bar{\lambda}_n = \left(\frac{d-r}{d}\right)^n \lambda_c + \left[1 - \left(\frac{d-r}{d}\right)^n\right] \left[\left(1 - \frac{\pi r}{4d}\right) \lambda_c + \frac{\pi r}{4d} \lambda_{\text{PCM}}(T)\right]. \quad (19)$$

When layer number n is large enough, $\left(\frac{d-r}{d}\right)^n$ approaches 0. Equation (19) can be simplified to Equation (20), following

$$\bar{\lambda}_n \approx \bar{\lambda}_2 = \left(1 - \frac{\pi r}{4d}\right) \lambda_c + \frac{\pi r}{4d} \lambda_{\text{PCM}}, \quad \left(\frac{d-r}{d}\right)^n \rightarrow 0. \quad (20)$$

3.2. Validation of MMCA Model

To validate the feasibility of the MMCA model, the theoretical thermal conductivity values predicted by the model were compared with experimental results and data reported in the literature.

3.2.1. Comparison with Experiments

The theoretical thermal conductivity under various experimental conditions was calculated based on the MMCA model. The diameter of the spherical MPCM ranged from 5

to 10 μm . Therefore, a representative diameter of 10 μm was adopted. The thickness of the specimen was 20 mm. The theoretical parameters of the specimens containing MPCM under different test conditions are listed in Table 5. The value of parameter n under different conditions are large; therefore, Equation (20) can be used to compute the theoretical thermal conductivity of the specimens.

Table 5. Parameter values for the MMCA model under different test conditions.

Volume Fraction of MPCM f_{PCM} [-]	C [-]	r [μm]	z [mm]	d [μm]	n [-]
0.000				-	-
0.065				11.0	905.9
0.122	1	5	20	8.9	1117.8
0.172				8.0	1254.6
0.217				7.4	1355.5

The theoretical thermal conductivity calculated by MMCA model (λ_p) was compared with the experimentally measured values (λ_M) to verify the feasibility of the MMCA model, see Figure 12. Furthermore, two statistical indicators, including the mean absolute error (MAE) and the mean absolute relative error (MARE) were employed to quantitatively evaluate the agreement between the theoretical and experimental results. The corresponding values are 0.013 W/(m·K) and 2.24%, respectively. To further enhance the statistical assessment of model performance, regression analysis between the predicted and measured values was conducted, and a 95% confidence interval was introduced, as shown in Figure 12. The coefficient of determination ($R^2 = 0.9672$) indicates a strong correlation between the MMCA predictions and the experimental results, and all data points fall within the 95% confidence interval. These additional statistical indicators provide a more comprehensive evaluation of model performance beyond conventional error metrics. The overall agreement between the theoretical predictions and the experimental measurements is satisfactory, confirming the rationality of the proposed MMCA model. This also indicates that the model can effectively reveal the internal heat transfer mechanism of MPCM-modified composites. The observed discrepancies primarily arise from unavoidable heterogeneity and incomplete compaction during specimen preparation, as well as from the simplification of PCM thermal conductivity variation during the phase transition process as a linear function.

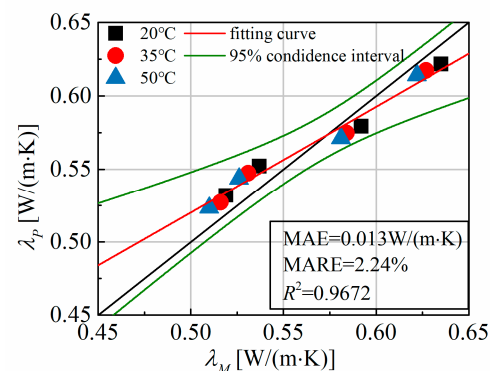


Figure 12. The comparison between the theoretical values predicted by the MMCA model and the experimental results.

3.2.2. Comparison with the Literature

The MMCA model was further validated using experimental data from the existing literature. Specifically, the thermal conductivities of MPCM-modified cement composites measured by Ricklefs et al. [56], Sam et al. [30], and Wang et al. [57] were adopted for validation. Relevant parameters of these three groups of experiments, along with the corresponding thermal conductivities predicted by the MMCA model, are summarized in Table A1. A comparison between the measured and predicted values is presented in Figure 13. The mean absolute error (MAE) and mean absolute relative error (MARE) were 0.094 W/(m·K) and 12.66%, respectively, confirming the feasibility of the MMCA model for predicting the thermal conductivity of cement matrices containing MPCM inclusions. Three factors contribute to the discrepancies between measured and predicted values: first, the MPCM inclusions are assumed to be spherical (shape factor = 1) in the three validation groups, whereas the actual shape of MPCM inclusions deviates from a perfect sphere; second, the temperature-dependent variation in the thermal conductivity of MPCM is not incorporated into the prediction; third, the interfacial thermal resistance is ignored.

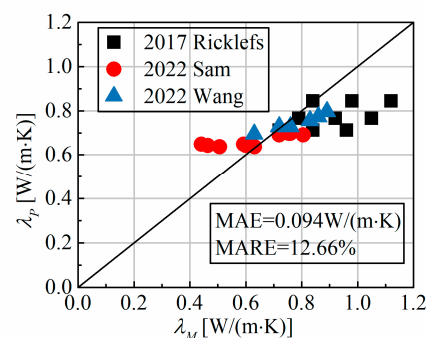


Figure 13. The comparison of measured thermal conductivity from the literature and values predicted by the MMCA model.

3.3. Comparison with Existing Models

The MMCA model developed in this study is compared with several existing analytical models for predicting the thermal conductivity of MPCM-modified cement composites, including the series model, parallel model, Maxwell model, and Hashin–Shtrikman (H–S) model. Their mathematical formulations, core assumptions, advantages, and limitations are summarized in Table 6. In addition, based on the experimental data reported by Jahalath et al. [49,58], evolutions of the predicted thermal conductivity results obtained using these analytical models, together with the measured values, is presented in Figure 14a. The mean bias error (MBE), MARE, and maximum relative error (erMAX) were calculated to quantitatively evaluate the predictive performance of these models, see Figure 14b. The average value of the upper and lower bounds defined by the H–S model is also illustrated in Figure 14a. According to the results presented in Table 6 and Figure 14, the thermal conductivity predicted by the series and parallel models is underestimated and overestimated, respectively, due to their oversimplified and idealized assumptions. The series model exhibits the largest MARE and erMAX values, reaching 42.82% and 68.22%, respectively. The Maxwell model provides predictions relatively close to the measured values, with an MBE and MARE of 0.093 W/(m·K) and 8.14%, respectively. However, its applicability is restricted to low inclusion volume fractions and spherical inclusions. The H–S model, derived from energy minimization theory, provides highly accurate estimations and exhibits the smallest MARE (3.3%) among the evaluated models. However, as a homogenization-based model, it mainly provides bounds or effective properties based on

global phase information and does not explicitly describe the heat-transfer pathways, inclusion interactions or geometry-dependent thermal evolution at the microscale. Although the MMCA model exhibits a higher MBE (0.170 W/(m·K)) and MARE (13.99%) than the H-S model, the prediction accuracy remains within an acceptable range for engineering estimation. More importantly, unlike conventional homogenization models, the MMCA model establishes an explicit connection between MPCM microstructural characteristics and macroscopic thermal conductivity by considering inclusion geometry, cumulative RVE effects, and localized heat-transfer interactions. More importantly, the proposed model demonstrates a superior capability to characterize the micro-to-macro heat transfer behavior between inclusions and the cement matrix. By considering localized energy dispersion and dissipation around the inclusions, the MMCA model is applicable to inclusions with various geometries and provides a more physically meaningful interpretation of the heat transfer mechanism. Therefore, the MMCA model is not intended to replace highly accurate homogenization bounds such as the H-S model but rather to provide a physically interpretable framework for understanding and designing MPCM-modified cement composites with different inclusion configurations. These advantages offer significant potential for the quantitative multiscale design and optimization of MPCM-modified cement composites. Furthermore, incorporating interfacial thermal resistance into the model in future studies is expected to further improve its prediction accuracy. The simplification of the particle size distribution may introduce minor deviations in predicted thermal conductivity, as particle dispersity can influence the local packing density and heat-transfer pathways within the RVE.

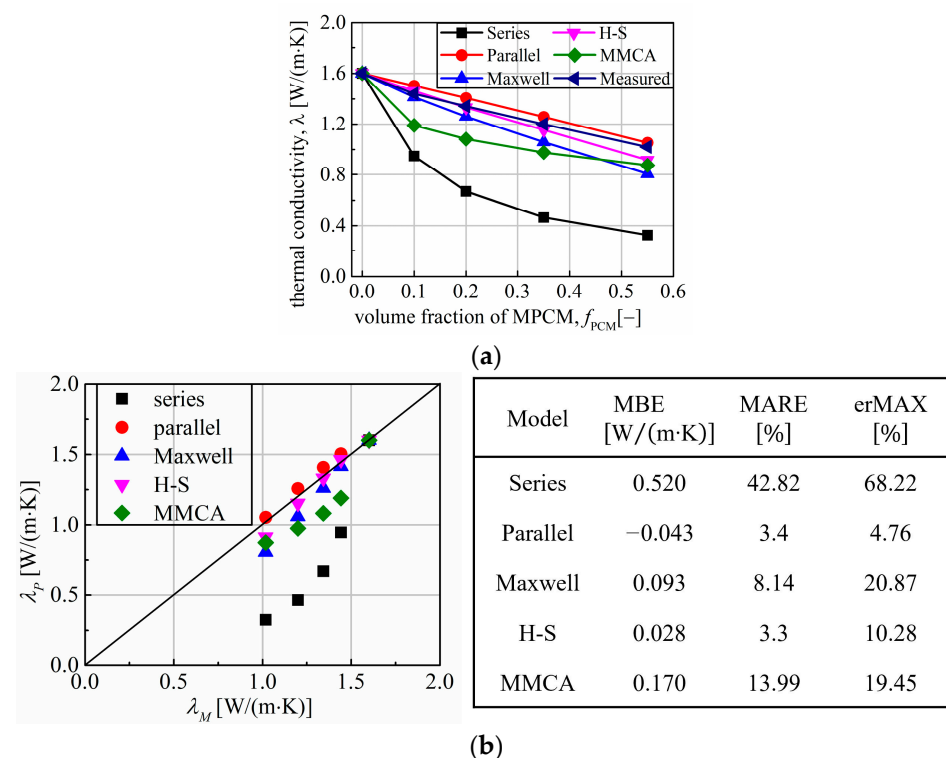


Figure 14. Comparison of thermal conductivity predicted by different models and experimental results: (a) predicted thermal conductivity versus MPCM volume fraction; (b) quantitative assessment of the agreement between model predictions and experimental measurements.

Table 6. Comparison of effective thermal conductivity analytical models.

Model	Mathematical Formulation	Core Assumptions	Advantages	Limitations
Series model	$\frac{1}{\lambda_{eff}} = f_m \frac{1}{\lambda_m} + f_i \frac{1}{\lambda_i}$	Heat flow is perpendicular to the phase interfaces; Phases are arranged in a series configuration.	Simple formulation; Providing the theoretical lower bound.	Idealized microstructure assumption; Tending to underestimate λ_{eff} .
Parallel model	$\lambda_{eff} = f_m \lambda_m + f_i \lambda_i$	Heat flow is parallel to the phase interfaces; Phases are arranged in a parallel configuration.	Simple formulation; Providing the theoretical upper bound.	Idealized microstructure assumption; Tending to overestimate λ_{eff} .
Maxwell model	$\lambda_{eff} = \lambda_m \frac{\lambda_f + 2\lambda_m + 2f_m(\lambda_f - \lambda_m)}{\lambda_f + 2\lambda_m - f_m(\lambda_f - \lambda_m)}$	Spherical inclusions are uniformly and sparsely dispersed in a continuous matrix; No particle–particle interaction; Perfect interface bonding.	More realistic for particulate composites; Reflecting the macro-transferring mechanism of inclusion–matrix.	Applicable only to low inclusion volume fractions and spherical particles; Ignoring interfacial thermal resistance.
H–S model	$\lambda_i + \frac{f_m}{\frac{1}{\lambda_m - \lambda_i} + \frac{f_i}{3\lambda_i}} \leq \lambda_{eff} \leq \lambda_m + \frac{f_i}{\frac{1}{\lambda_i - \lambda_m} + \frac{f_m}{3\lambda_m}}$	Two-phase isotropic composite; Statistically homogeneous distribution; No interfacial thermal resistance.	Providing the strictest theoretical bounds; Without requiring geometric details.	The output is not a single explicit value; The micro transferring mechanism of heat is unclear.
MMCA model (this study)	$\lambda_{eff} = \left(\frac{d-r}{d}\right)^n \lambda_m + \left[1 - \left(\frac{d-r}{d}\right)^n\right] \times \left[\left(1 - \frac{\pi r}{4d}\right) \lambda_m + \frac{\pi r}{4d} \lambda_i\right]$	Heat flow is perpendicular to the phase interfaces; No particle–particle interaction.	Reflecting the micro-to-macro transferring mechanism of inclusion–matrix; Applicability to inclusions with different geometries.	Idealized microstructure assumption; Ignoring interfacial thermal resistance.

Note: subscript m and i refer to the matrix and inclusion, respectively.

4. Discussion

4.1. The Effects of Specimen Thickness on Thermal Conductivity

The effects of specimen thickness on thermal conductivity were analyzed considering spherical inclusions, for which the shape factor function $f(C)$ was equal to 1. A representative particle size of 10 μm was adopted to characterize the MPCM inclusions, which is considered an equivalent size for the polydisperse distribution (5–10 μm) observed in the experiments. Based on the MMCA model, the variation in thermal conductivity of MPCM-modified cement composites with the number of layers (n) under different working conditions was analyzed, as shown in Figure 15. Subfigures (a–c) correspond to the solid, melting, and liquid phases, respectively. Under the same testing temperature, all volume fraction conditions exhibited a consistent trend: the average thermal conductivity decreased rapidly at first and then approached a stable value. When n ranged from 1 to 10, the decrease in thermal conductivity was significant, and the rate of decline gradually diminished with increasing n . When n exceeded 10, the thermal conductivity tended to stabilize. A higher MPCM volume fraction led to lower initial and stable values of the curve, as it directly affected the characteristic of RVE and the volume-fraction-weighted average in the approximate formula (Equation (20)).

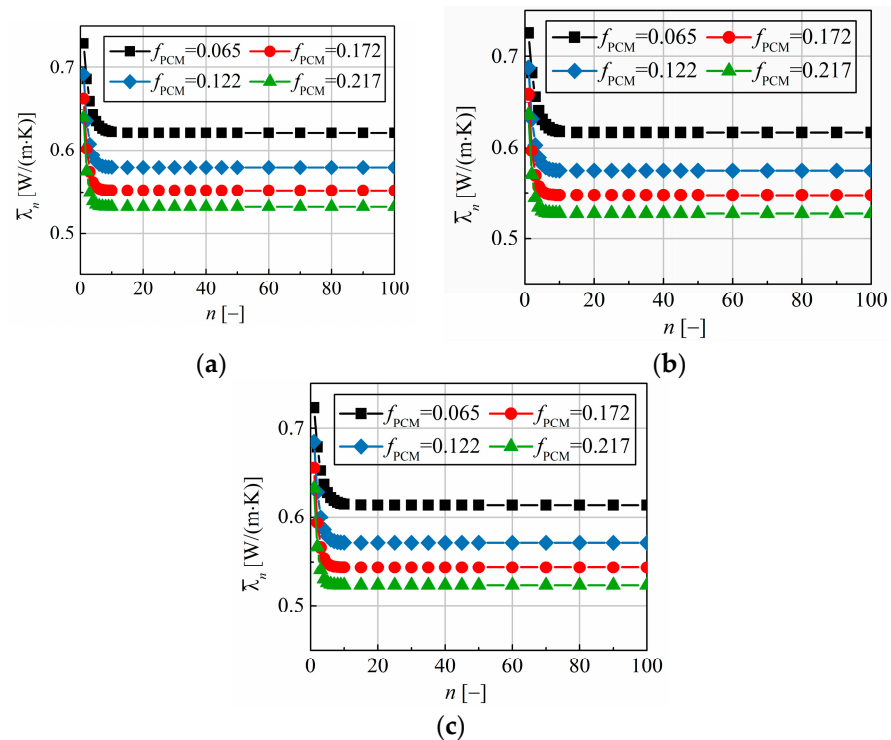


Figure 15. The variation in the average thermal conductivity with layers at different phases: (a) at solid phase, (b) at melting phase, and (c) at liquid phase.

The average thermal conductivities at $n=1$ and $n=\infty$ under various working conditions were plotted on the same graph, as shown in Figure 16. These two cases defined the lower and upper bounds of the thermal conductivity of the MPCM-modified composite, respectively. The thermal conductivities of the composites under different testing phases and thicknesses can all be located within the yellow-shaded region in the figure. This subsection further verifies that the proposed MMCA model can serve as a practical tool for guiding structural thickness design where the heat transfer characteristics of the material must be considered.

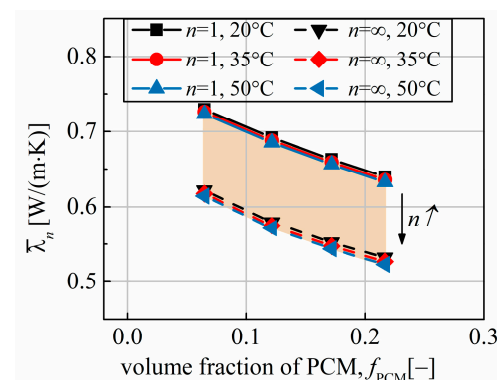


Figure 16. The variation in the average thermal conductivity at $n=1$ and $n=\infty$.

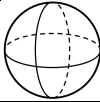
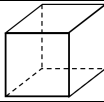
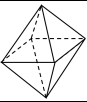
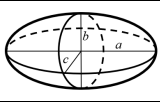
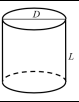
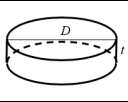
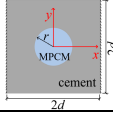
4.2. The Effects of MPCM Geometry on Thermal Conductivity

The influence of MPCM geometry on the thermal conductivity of MPCM-modified cement composites was evaluated using the MMCA model. Model coefficient β , introduced in the shape-factor function (Equations (6) and (7)), was first determined. Thermal conductivity data for composites with different MPCM geometries reported by Jahalath et al. [49] were used to calibrate this coefficient, and the calibration procedure is detailed

in Appendix B. Based on the computed results, an average coefficient of $\beta = -4$ is recommended for subsequent analyses.

A single RVE was considered in this analysis to isolate the effects of geometry, i.e., $m = 1$ in Equation (7). Six representative MPCM inclusion geometries with identical volumes (i.e., identical equivalent radius as defined in Equation (4)) were selected to examine their influence on the effective thermal conductivity: sphere, cube, octahedron, ellipsoid, cylinder, and platelet. The geometric parameters are summarized in Table 7. With the MPCM volume fraction fixed at 0.1, the RVE for each geometry was constructed according to Equation (6) of the MMCA model (see Table 7). The variations in half of RVE edge length d and the average RVE thermal conductivity with respect to geometric compactness C are presented in Figure 17 and Figure 18, respectively.

Table 7. Description of six typical geometries and corresponding RVEs.

Geometry	Sphere	Cube	Octahedron	Ellipsoid	Cylinder	Platelet
description of geometry						
	$C = 1.00$	$C = 0.88$	$C = 0.84$	$a:b:c = 2:1:1$ $C = 0.79$	$L:D = 2$ $C = 0.74$	$t:D = 0.2$ $C = 0.62$
RVE						
r/d	0.524	0.541	0.547	0.556	0.565	0.590

The more complex the inclusion geometry, the lower the compactness C . As shown in Figure 17, half edge length d decreases with decreasing compactness, indicating that the effective influence range of the matrix diminishes with the increasing geometric complexity of the inclusions. This behavior can be attributed to three factors: (1) the increased inclusion matrix interfacial area, which induces localized heat flux; (2) the enlarged equivalent thermal resistance; and (3) the dispersion and dissipation of energy in local regions, which weakens the heat transfer through the matrix. Jayalath et al. [49] also demonstrated that inclusion geometry plays an important role in determining the effective thermal conductivity of MPCM-modified cementitious composites. They reported that cylindrical MPCM inclusions exhibited a lower thermal conductivity than spherical inclusions, which was attributed to their larger surface area-to-volume ratios and the resulting enhanced interfacial effects. Collectively, these factors intensify the local temperature fields, reduce the effective influence zone of the inclusions, and consequently decrease the effective size of the RVE matrix domain. A fitted relationship between d and C is obtained as follows:

$$d = (0.5656C + 1.3496) \cdot r \quad R^2 = 0.9951. \quad (21)$$

These fundamental factors also affect the average thermal conductivity of the RVE, which decrease with the increasing inclusion complexity, as shown in Figure 18. As the compactness of inclusion geometry increased from 0.62 to 1, the average thermal conductivity of RVE increase from 0.645 W/(m·K) to 0.679 W/(m·K).

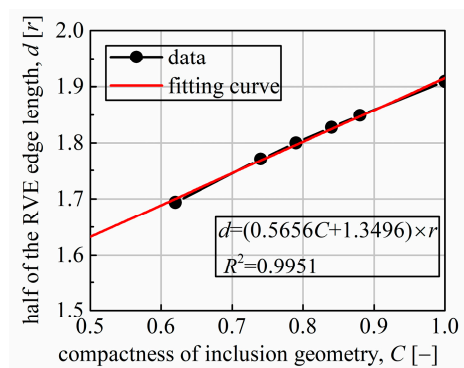


Figure 17. The evolution of half of the RVE edge length (d) with the compactness of inclusion geometry (C).

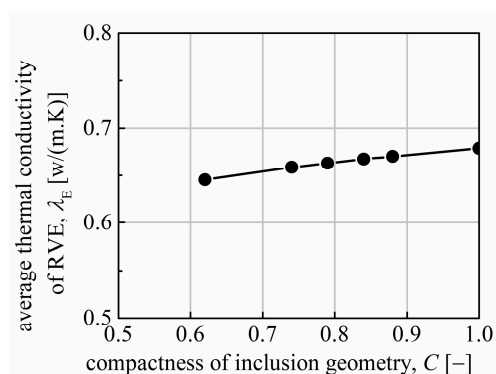


Figure 18. The evolution of the average thermal conductivity of RVE (λ_E) with the compactness of inclusion geometry (C).

5. Conclusions

In this study, the thermal conductivity of MPCM-modified cement composites was experimentally characterized, and a novel micro-macro combinatorial accumulation (MMCA) model was proposed to interpret and predict their multiscale heat transfer behavior. The main conclusions are as follows:

(1) The MMCA model was developed based on RVE construction, heat transfer theory, and combinatorial accumulation principles, incorporating diverse MPCM inclusion geometries and cumulative RVE effects. Model feasibility was verified through experimental results and literature comparisons. Compared with classical models, the MMCA model demonstrated enhanced capability in describing micro-to-macro heat transfer mechanisms and supporting the multiscale design of MPCM-modified cement composites.

(2) The effective thermal conductivity of MPCM-modified cement composites decreased with the increasing MPCM volume fraction. Specifically, when the MPCM volume fraction increased from 0 to 0.217, the thermal conductivity decreased from 0.802 to 0.519 W/(m·K), corresponding to a reduction of approximately 35.3%. In contrast, only minor differences were observed among the solid, melting, and liquid PCM phases.

(3) The average thermal conductivity exhibited a rapid initial decrease followed by stabilization as the number of accumulated RVEs increased. Meanwhile, the value of single RVE declined with the increasing inclusion geometric complexity, due to localized heat dispersion and dissipation effects. When the compactness of inclusions increased from 0.62 to 1.0, the average thermal conductivity of the RVE increased from 0.645 to 0.679 W/(m·K).

Overall, the MMCA model provides an effective approach for estimating the effective thermal conductivity of MPCM-modified cement composites and can assist in thermal performance optimization of energy-efficient cementitious materials for building and infrastructure applications. Although the inclusion geometry was considered, the interfacial thermal resistance was not quantitatively incorporated. Future work should focus on quantifying the interfacial thermal resistance and extending the model to multi-type inclusion systems. Furthermore, the proposed MMCA model will be extended to predict the thermal resistance of full-scale building components with practical structural configurations in future work.

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Data Availability Statement: Data are available on request from the authors.

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Abbreviations

The following abbreviations are used in this manuscript:

MPCM	Microencapsulated phase change material
PCM	Phase change material
PMMA	Polymethyl methacrylate
MMCA	Micro-macro combinatorial accumulation
RVE	Representative volume element
f_{PCM}	The volume fraction of MPCM
c	Cement
V	Volume
r	The equivalent radius of MPCM particle.
d	Half width of the rectangular element
β	The model coefficient
C	The shape compactness
E	Denoting the element
λ	Thermal conductivity
n	The layers of RVEs
z	The thickness of specimen

Appendix A

The key parameters from the experiments conducted by Ricklefs et al. [56], Sam et al. [30], and Wang et al. [57] are summarized in Table A1. Meanwhile, the thermal conductivity values of the composites predicted by the MMCA model are also included in this table.

Table A1. Experimental parameters from the studies of Ricklefs et al. [56], Sam et al. [30], and Wang et al. [57], and thermal conductivity values predicted by the MMCA model.

Ref.	Materials & Conditions	Volume Fraction of PCM f_{PCM} [%]	C [-]	r [μm]	z [mm]	d [μm]	n [-]	Thermal Conductivity of Matrix/PCM Inclusion [$W/(m \cdot K)$]	Measured Thermal Conductivity [$W/(m \cdot K)$]	Predicted Thermal Conductivity [$W/(m \cdot K)$]
2017 Ricklefs [56]	cement + PCM	10	1	10	38	19.09	995.1	1.14/0.42	0.98	0.84
		10	1	10	38	19.09	995.1		1.12	0.84
		10	1	10	38	19.09	995.1		0.84	0.84
		20	1	10	38	15.15	1253.8		0.92	0.77
		20	1	10	38	15.15	1253.8		1.05	0.77
		20	1	10	38	15.15	1253.8		0.79	0.77
		30	1	10	38	13.24	1435.2		0.84	0.71
		30	1	10	38	13.24	1435.2		0.96	0.71
		30	1	10	38	13.24	1435.2		0.72	0.71
2022 Sam [30]	cement + PCM; w/b = 0.45; 25 °C	20	1	10.4	25	15.76	793.1	0.9296/0.5	0.73	0.71
		40	1	10.4	25	12.51	999.3		0.59	0.64
	cement + PCM; w/b = 0.45; 45 °C	20	1	10.4	25	15.76	793.1	0.9296/0.5	0.73	0.70
		40	1	10.4	25	12.51	999.3		0.44	0.64
	cement + PCM; w/b = 0.4; 25 °C	20	1	10.4	25	15.76	793.1	0.9099/0.5	0.75	0.70
		40	1	10.4	25	12.51	999.3		0.60	0.64
	cement + PCM; w/b = 0.4; 45 °C	20	1	10.4	25	15.76	793.1	0.9099/0.5	0.76	0.70
		40	1	10.4	25	12.51	999.3		0.46	0.64
	cement + PCM; w/b = 0.33; 25 °C	20	1	10.4	25	15.76	793.1	0.8964/0.5	0.81	0.69
		40	1	10.4	25	12.51	999.3		0.63	0.63
	cement + PCM; w/b = 0.33; 45 °C	20	1	10.4	25	15.76	793.1	0.8964/0.5	0.72	0.69
		40	1	10.4	25	12.51	999.3		0.51	0.63
2022 Wang [57]	cement + micro-PCM	5	1	3.95	5	9.50	263.1	0.95/0.41	0.86	0.77
		10	1	3.95	5	7.54	331.5		0.72	0.73
		15	1	3.95	5	6.59	379.5		0.63	0.69
	cement + nano-PCM	5	1	0.27	5	0.65	3849.1	0.95/0.48	0.89	0.80
		10	1	0.27	5	0.52	4849.5		0.83	0.76
		15	1	0.27	5	0.45	5551.3		0.76	0.73

Appendix B

Jayalath et al. [49] reported the thermal conductivities of PCM-modified cement composites containing spherical and cylindrical inclusions, respectively. The geometric compactness values of the spherical and cylindrical inclusions were 1.00 and 0.47, with the latter corresponding to a length-to-diameter ratio of 3. According to the reference, four

test groups were defined by the number of RVE layers ($n = 2, 5, 10$, and 15). For each group, the average thermal conductivities of composites incorporating the two inclusion geometries were measured. The relevant parameters summarized from the reference are listed in Table A2, including the number of RVE layers (n), geometric compactness (C), thermal conductivity of matrix (λ_c), thermal conductivity of PCM (λ_{PCM}), and the test thermal conductivity (λ_{test}).

The calculation procedure of β based on the MMCA model is described as follows.

The term $\frac{2}{\sqrt{\pi}} f_{PCM}^{\frac{1}{3}}$ in Equation (6) is defined as A . By substituting Equations (6) and (7), A , λ_{test} , and $m=n$ into Equation (15), (A1) is obtained.

$$\lambda_{test} = \left(1 - A \cdot C^{1/(\beta n)}\right)^n \lambda_c + \left[1 - \left(1 - A \cdot C^{1/(\beta n)}\right)^n\right] \times \left[\left(1 - \frac{\pi}{4} A \cdot C^{1/(\beta n)}\right) \lambda_c + \frac{\pi}{4} A \cdot C^{1/(\beta n)} \lambda_{PCM}\right]. \quad (A1)$$

Based on Equation (A1), the value of A for each test group is first calculated under the condition of $C=1$. Subsequently, based on the obtained A , the value of β is determined using the Newton–Raphson method under the test condition of $C=0.47$. The calculated β values for all test group are summed up in Table A2. As the distribution of inclusions in the reference was not clearly described, leading to inconsistencies in β values across the groups, the average β value ($\beta=-4$) was considered more representative and thus used in the discussion of Section 4.1.

Table A2. Related parameters from the reference and the calculation results based on the MMCA model.

Test Group	Number of RVE Layers n [-]	Compactness C [-]	Thermal Conductivity of Matrix λ_t [W/(m·K)]	Thermal Conductivity of Matrix λ_{PCM} [W/(m·K)]	Test Thermal Conductivity λ_{test} [W/(m·K)]	$A = \frac{2}{\sqrt{\pi}} f_{PCM}^{1/3}$ [-]	β [-]
1	2	1	1.60	0.42	1.464	0.2932	-8.1284
		0.47			1.452		
2	5	1			1.463	0.2122	-4.7788
		0.47			1.456		
3	10	1			1.465	0.1718	-1.4429
		0.47			1.455		
4	15	1			1.461	0.1615	-2.1677
		0.47			1.457		
average			-			0.2097	-4

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