A multi-scale micromechanical investigation on thermal conductivity of cement-based composites

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Abstract. Cement-based composites (CBCs) are one of the most widely used materials in construction. An appealing characterization of thermal conductivity of CBCs plays an essential role to evaluate the energy consumption in buildings and to facilitate the development of novel thermal insulation materials. Based on Eshelby equivalent inclusion principle and multi-scale methodology, this paper attempted to present a generalized multi-scale micromechanical model in terms of thermal performance of the CBCs, which covers some classic models for thermal conductivity estimation. A Mori-Tanaka homogenization method was applied to investigate the thermal conductivity of the CBCs of different compounds, water-to-cement ratios and curing ages. In addition, saturation degree factor was considered. The results of this model are in good agreement with the experimental value, showing that the multi-scale model developed in this paper is able to evaluate the thermal conductivity of the CBCs in different conditions.

1. Introduction

Cement-based composites (CBCs) are one of the most extensive used construction materials in the world. Increasing demands of the CBCs and requirements of reducing energy conservation provide both scientific and engineering incentives for evaluating the thermal conductivity of the materials.

Many factors may influence the thermal conductivity of the CBCs [1, 2], including types and volume fractions of aggregates and raw binder materials, mineralogical characters of hydrates, water-to-cement ratios and saturation degrees. Although numerous previous studies have been conducted on experimental methods and calculation models of the thermal conductivity of the CBCs, these methods mostly depend on mix proportion and petrographic composition of aggregates, therefore the proposed methods are generally empirical. Alternatively, effective-medium-theory based models, with clear physical meanings, can predict the thermal conductivity of the CBCs, because the structures of the materials generally conform to the inclusion-matrix type. For example, concrete can be treated as a two-phase composite material made up of cement mortar (continues phase) and aggregates (dispersed phase). The models [3, 4] include the simple series and parallel models, Maxwell-Eucken type model, Bruggeman type model, and Hasselman-Johnson model. Note that these models are remaining on a single scale, while the CBCs are typical composites structured in multi scales.

Recent and ongoing studies of the CBCs by different experimental methods allow mineralogical and structural understanding of the materials on different scales in depth. In microscale, the CBC can be treated as a porous inorganic material with calcium-silicate-hydrate (C-S-H) matrix, calcium hydrate (CH) crystals, unreacted cement clinkers and micro gel pores. In mesoscale, the CBC can be regarded as a composite consisting of a cement paste matrix and sands surrounded by interfacial
transition zones (ITZs). Therefore, multiscale method might be suitable for predicting the thermal conductivity of the CSCs, as the method has been widely used in analysis of thermal and mechanical property of other composite materials [5].

Based on the principle of the effective medium theory and the multi-scale nature of the CBCs, this study attempted to evaluate the thermal properties of the materials. A multi-scale micromechanical model was developed and the modelled results were compared to the data from experimental measurements.

2. Micromechanical model of the thermal conductivity

2.1. Multi-scale nature of CBCs

The macro properties of CBCs are associated with their structural nature that can be characterized in multi-scales. By connecting the physical and mechanical properties of each scale, a systematic understanding of the nature of the materials can be established.

Generally, one can model a CBC with four elementary levels based on the microstructures of the material (see Figure 1) [6]:

- **Level I** ($10^{-8}$-$10^{-6}$m): The main solid phase in this scale is the C-S-H, the main hydration product of C$_2$S and C$_3$S. It has now established that the C-S-H exists in two different forms, named the low density (LD) and high density (HD) C-S-Hs. In this case, an amorphous colloidal structure of the C-S-H (about 5 nm) is constructed by ‘globules’ that are composed of basic building blocks and an intra-globules porosity (about 2 nm) [7].

- **Level II** ($10^{-6}$-$10^{-4}$m): The C-S-H matrix, together with the large CH crystals, cement clinker and micro capillary pores, forms the cement paste. The cement clinker may contain C$_2$S, C$_3$S, C$_3$A and C$_4$AF. In this scale, the micro and meso capillary porosity is strongly related to the w/c.

- **Level III** ($10^{-4}$-$10^{-2}$m): This scale refers to mortar, which is a three phase composite material composed of cement paste, sand particle inclusions, and ITZs.

- **Level IV** ($10^{-2}$-$10^{-1}$m): Concrete is considered as a three phase material composed of aggregates embedded in a mortar matrix and ITZs in this scale.

According to the four elementary levels of the CBCs, admixtures can be embedded in the materials in different scales. For instance, nanoparticles can be placed in Level I, fly ash in Level II and the glazed hollow bead in Level III or IV depending on their sizes. This interpretation can help to access the thermal and mechanical properties of the CBCs blended with different admixtures.

2.2. Multi-scale model of thermal conductivity of composite materials

According to Fourier’s law, the amount of the heat flux through a material is proportional to the negative gradient of temperature, which gives:
\[ \dot{Q} = -K \frac{dT}{dx} = -K \cdot \nabla T \]

Where \( \dot{Q} \) is the heat flux, \( K \) is the thermal conductivity, and \( \nabla T \) is the temperature gradient.

Based on the mean-field theory, a consistent mechno-physical framework can associate the homogenized thermal conductivity, \( K_{\text{hom}}(X) \) at level \( i+1 \) to \( K_i(x) \) at level \( i \), where \( X, x \) are position vectors at level \( i+1 \) and level \( i \), respectively. In micromechanics, continuum points can be characterized by temperature gradients, namely:

\[
\text{Level } i: \ \mathbf{g} = \nabla \tau; \ \text{Level } i+1: \ \mathbf{G} = \nabla T
\]

Where \( \mathbf{G} \) and \( \mathbf{g} \) are temperature gradients at level \( i+1 \) and level \( i \), respectively. The temperature gradient and heat flux at level \( i+1 \) are essentially the average of these variables in level \( i \):

\[
\mathbf{G} = \left\langle \mathbf{g} \right\rangle_v; \ \dot{Q} = \left\langle \dot{q} \right\rangle_v
\]

Where \( \left\langle y \right\rangle_v = \frac{1}{V} \int y(x)\,dV \) is the volume average of representative volume element (RVE), and \( \dot{Q} \) and \( \dot{q} \) are the heat flux at level \( i+1 \) and level \( i \), respectively. Furthermore, temperature gradients at two levels can be linked via a linear localization condition:

\[
\left( \mathbf{g} \right)_x = \mathbf{A}_x \cdot \mathbf{G}_x
\]

Where \( \mathbf{A}_x \) is a second order localization tensor that satisfies the compatibility condition:

\[
\left\langle \mathbf{A}_x \right\rangle = \mathbf{I}
\]

For a heterogeneous material composed of homogeneous phases, it is convenient to introduce a linear phase concentration of the form:

\[
\left\langle \mathbf{A}_x \right\rangle_{\nu} = \left\langle \mathbf{g} \right\rangle_{\nu} \cdot \mathbf{G}(x)
\]

\[
\sum_{s=1}^{n} f_s \left\langle \mathbf{A}_x \right\rangle_{\nu_s} = \mathbf{I}
\]

Where \( f_s \) is the volume fraction of each phase. The constitutive relation of thermal conduction with two scales can be exploited to relate \( \dot{q} \) and \( \dot{g} \):

\[
\dot{q}(x) = K_i(x) \cdot \mathbf{g}(x) = K_i(x) \cdot \mathbf{A}_x \cdot \mathbf{G}(X)
\]

By spatially averaging the former identity, the homogenized thermal conductivity is expressed as:

\[
K_{\text{hom}}(X) = \left\langle K_i(x) \cdot \mathbf{A}_x \right\rangle_{\nu}
\]

This is the generalized multi-scale model of thermal conductivity tensor of composite materials. In scope of linear mechanics, the strain localization tensor is constant for an ellipsoidal inclusion embedded in an infinite matrix. Similarly, \( \mathbf{A}_r \), for heat conduction can be given by [8]:

\[
\mathbf{A}_r = \left[ \mathbf{I} + S : (K_M^{-1} R K_I R^T - \mathbf{I}) \right]^{-1}
\]

Where \( S \) is the Eshelby-like tensor, \( \mathbf{I} \) is the unit tensor, and \( K_M, K_I \) are the thermal conductivity of the matrix and inclusion, respectively. The rotation matrix \( R \) is used to transform the local to global coordinate systems.

The above model for a two-phase matrix-inclusion system can be extended to incorporate a multiphase system. The thermal conductivity of the volume around the inclusion phase needs to be considered. The localization tensor is written as:

\[
\mathbf{A}_s = \left[ \mathbf{I} + S_s : (K_r^{-1} R K_s R^T - \mathbf{I}) \right]^{-1} \left[ \mathbf{I} + S_s : (K_0^{-1} R K_s R^T - \mathbf{I}) \right]^{-1}
\]

Where \( S_s \) is the Eshelby-like tensor (\( s=1, 2...n \), \( n \) is the number of the phase), \( K_s \) is the thermal conductivity of each phase.
According to the Mori-Tanaka scheme [9], the reference medium is chosen to be the matrix phase \( (K_0 = K_M) \). In this case, the localization tensor can be written as

\[
A_s = \left[ I + S_s : (K_M^2 R K_s R^T - I) \right]^{-1} \left[ I + S_s : (K_M^2 R K_s R^T - I) \right]^{-1} I
\]  

(12)

For the spherical inclusions, \( S = 1/3trI \). With the absence of preferential orientation for inclusions, the rotation matrix is reduced to \( R = I \). Using the above equation in (12), the localization tensor reduces to [10]:

\[
A_s = A_s I = \frac{3K_M}{2K_M + K_s} I
\]  

(13)

Combining Eqs (9) and (13), it was obtained that the Mori-Tanaka based micromechanical model of the thermal conductivity:

\[
K_{MT} = \frac{f_M K_M + \sum_{i=1}^{n} f_s K_i A_s}{f_M + \sum_{i=1}^{n} f_s A_s}
\]  

(14)

Where \( f_M, f_s \) are the volume fraction of the matrix and inclusions, respectively, \( n \) is the number of the inclusion phases, \( K_M, K_s \) are the thermal conductivity of the matrix and inclusions, respectively.

When \( A_s = 1 \), the multi-scale model is in accordance with parallel model. When \( A_s = K_M / K_s \), this model is in accordance with series model. Benveniste and Miloh [11] proved that the Mori-Tanaka method with thermal boundary resistance is identical to the Hasselman-Johnson model. It indicates that this generalized multi-scale micromechanical model is able to recover some classic models for estimating thermal conductivity of composites.

3. Application to CBCs

3.1. Cement paste

Cement paste can be simplified to be a two-scale model from level I to level II (see Figure 1). However, it still needs homogenization two times for calculating the effective thermal conductivity. It was adopted that a classical hydration model (e.g., Ref. [12]) to estimate the volume fractions of solid phases. For simplification, in this study, the aluminate phases, such as C_3A and C_4AF, are equivalent to C_3S and C-S-H, yielding the Max. and Min. estimations of the thermal conductivity of the cement paste. The density and thermal conductivity of C_2S, C_3S, CH, C-S-H are respectively 3.55, 3.57, 2.25, 2.40 g/cm\(^3\) and 3.45, 3.35, 1.32, 0.98 W/m·K [10]. The thermal conductivity values of water and air are 0.6 and 0.026 W/m·K under ambient condition.

![Figure 2. Plots of predicted thermal conductivity of cement pastes against hydration degree](image-url)
(a) with w/c ratio of 0.3; (b) with w/c ratio of 0.4. The shaded region presents the Max. and Min. estimations of the thermal conductivity of the cement paste. The experimental data were adopted from Ref. [14].

Figure 2 displays the predicted thermal conductivity of the cement pastes with different w/c ratios against hydration degree. It was found that the thermal conductivity of the cement pastes decreases with increasing the hydration degrees. This is reasonable as the thermal conductivity values of the C-S-H and CH are lower than those of the clinker phases. The result is in agreement with the experimental data of [13]. Another indication obtained in this study is that the thermal conductivity values of the cement pastes decrease with increasing the w/c ratios, which is consistent with the experimental observations in Ref. [15]. An important reason is that the thermal conductivity of water is heavily lower than those of other solid phases. Figure 2 also presents the predicted and measured thermal conductivity of the cement paste with w/c ratio of 0.3 and 0.4 in Ref. [14]. The experimental values are close to the max values in the region of the low hydration degrees. It may suggest that the thermal conductivity values of the aluminates hydrates are close to that of C₃S. Note that, in this study, it was neglected the effect of self-desiccation that is especially severe for the cement pastes of lower w/c ratios. The differences between the measured and predicted data presented in Figure 2 are thus acceptable.

![Figure 2](image_url)

**Figure 2.** Predicted and measured thermal conductivity of the cement paste with different w/c ratios against hydration degree.

Figure 3 presents the comparison between the predicted and measured thermal conductivity data of the dried and saturated cement pastes with w/c ratios of 0.36, 0.44, 0.58 and 0.8. The experimental mix proportion and material parameters were adopted from Ref. [16]. It was observed that the thermal conductivity values of the saturated cement pastes are obviously higher than the dried ones. Again, higher thermal conductivity of water than the air accounts for the observation. Another indication from Figure 3 is that the relative errors between the predicted and measured values of the dried cement pastes increase with increasing the w/c ratio. This maybe because the classical hydration model used in this study cannot fully consider the actual microstructure and mineral distribution of the cement pastes that vary with the w/c ratios, curing ages, and moisture conditions.

![Figure 3](image_url)

**Figure 3.** Predicted and measured thermal conductivity of dried and saturated cement pastes with different w/c ratio; the experimental data were adopted from Ref. [16].

3.2. Concrete

Concrete has more complex structures with four-level representative scales (see Figure 1). The thermal conductivity of quartz, granite, limestone and cement pastes calculated above are 4.45, 2.50-2.65, 2.29-2.78 and 1.094 W/m·K. The density of cement pastes, sands and gravels are 3.15, 2.55 and 2.58 g/cm³. The experimental data is selected from Ref. [17], where the mix proportion and curing conditions can be found therein. Figure 4 presents the comparison between the measured and predicted thermal conductivity data of the dried concrete with different volume fractions of coarse aggregates. Clearly, the proposed multi-scale model can capture the experimental data with relatively low errors (<5%). Note that the distribution of the coarse aggregates may be much more complex than the simple
sphere particles presented in Figure 1, so it could be safe to conclude the promised accuracy of the established model for predicting the thermal conductivity of the CBCs.

![Figure 4](image1.png)

**Figure 4.** Relative errors between the measured and predicted thermal conductivity of the dried concrete with different volume fractions of coarse aggregate; the experimental data were adopted from Ref. [17].

For further examination of the robustness of the model, the thermal conductivity of the concretes with different types of aggregates under both dried and saturated conditions was calculated. Figure 5 shows the experimental and predicted values of the thermal conductivity of the concretes. It is found that the predicted values are in a good agreement with the experimental results for both the dried and saturated concretes. The deviations of the predicted the thermal conductivity of the dried concretes from the measured ones are in the range of (0.5%, 16.3%), while those of the saturated concretes are in the range of (5.9%, 22.2%). The relatively large errors between the predicted and measured thermal conductivity of the saturated concretes can be due to the fact that for the very high water saturation case, the spatial distribution of the pore fluids that may percolate through the material is beyond the Eshelby equivalent inclusion principle. Further investigation is deserved in the future for the water effect on the thermal conductivity of complex composites.

![Figure 5](image2.png)

**Figure 5.** Experimental and predicted values of thermal conductivity of (a) dried and (b) saturated concrete with three different types of coarse aggregates (basalt, limestone and siltstone) and two types of fine aggregates (sand type I: reddish land quarried quartz sand and sand type II: greyish river sand); the experimental data were adopted from Ref. [18].

4. Conclusions
Based on Eshelby equivalent inclusion principle and multi-scale nature of the microstructure of the CBCs, this study attempted to evaluate the thermal conductivity of the materials by the multi-scale
micromechanical approach. With a Mori-Tanaka homogenization method, a multi-scale micromechanical model was developed to capture the thermal conductivity of the CBCs.

- The multi-scale model captures the influences of the cement pastes, fine and coarse aggregates on the thermal conductivity of the concretes in different scales. Generally, the multi-scale model can predict the thermal conductivity of the pastes and concretes in relative good accuracy.

- The Eshelby equivalent inclusion principle and Mori-Tanaka homogenization method oversimplify the effects of water confined in pores that may percolate the materials spatially. This causes the relative large errors between the predicted and experimental values of the thermal conductivity of the cement pastes and concretes for the saturated conditions. Further study is needed in this aspect in the future.

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