Multi-Scale Study of High-Strength Low-Thermal-Conductivity Cement Composites Containing Cenospheres

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Abstract

Cenosphere particles are hollow, but due to their hard shells, they can be used in cementitious composites to produce ultra-lightweight cement composites (ULCC) with high strength and low thermal conductivity. This study integrates thermal conductivity with mechanical experimental research, microscopic investigation, and numerical simulations to provide new insights into the behavior of these advanced composites. The microstructure of ULCC samples was characterized using synchrotron high-resolution microtomography, transmission electron microscopy and scanning electron microscopy. Composite models were used to predict the thermal conductivity of the cenospheres based on the experimental results of ULCC thermal conductivity and the porosity of the samples.

1 Introduction

In 2010, U.S. buildings were responsible for 7% of global energy consumption. This represents 41% of total U.S. energy consumption. Furthermore, heating and cooling of U.S. buildings are responsible for 37% of the country's energy consumption [1]. Similarly, buildings in the European Union (E.U.) were responsible for approximately 40% of the total energy consumed in that region, with 43% of the E.U.'s energy being used for air heating and cooling [2]. As expected, in tropical countries, the energy used only for air conditioning in buildings jumps to approximately 50%, and another 20% is consumed for ventilation [3]. Therefore, there is great interest in reducing the thermal conductivity (TC) of materials used in the building envelope. Compared to other construction materials, concrete has low TC, but this already low TC can be further reduced by increasing the concrete's porosity. However, an increase in porosity often leads to changes in the mechanical properties of the concrete and thus requires modification of the structural design. Wang et al [4] summarized the following methods of introducing air voids in concrete: a) use of porous aggregates with a wide range of sizes; b) introduction of voids in the cement paste; and c) reduction or even elimination of fine aggregates to create voids between the coarse aggregate particles.

The use of cenospheres, a byproduct of thermal power plants' coal combustion, is becoming attractive for the production of ultra-lightweight cement composites (ULCC) with compressive strengths greater than 60 MPa [4] and very low thermal conductivity. Cenosphere particles are hollow but have a stiff shell made mostly of silica and alumina. Morphologically, the hollow cenospheres have diameters between 10 and 300 μm [5], while the thin shell typically has a thickness of 2.5-10.5% of the diameter [6]. The strong shell minimizes the losses in strength and elastic modulus caused by the increase in the porosity of the ULCC samples. Although cenospheres can be reactive, they can last a very long time if the composite material is cured at ambient temperature. Cenospheres have low water absorption and positive effects on the packing factor, resulting in a material with very good flow in its fresh state [7].

Recent studies have evaluated the effects of cenospheres on thermal and mechanical performance [6], [8]–[12], acoustic properties [13], influence on concrete durability (crack propagation [14]), water transport [15], and alkali-silica reaction [16]. There have also been innumerable studies of cenospheres themselves (e.g., [17]) and of cenosphere coatings and composites [18]–[20]. While progress has been made in the use of cenospheres in cementitious materials, there is a need for more information on the 3D pore structure of the matrix. This work characterizes the microstructure of ULCC samples with synchrotron high-resolution microtomography and scanning electron microscopy (SEM). Experimental thermal conductivity results were used to validate existing composite models and numerical simulations were performed to determine why the use of porous cenospheres does not significantly reduce the compressive strength of the ULCC samples.

2 Materials and methods

2.1 Materials and sample preparation

The cenospheres used in this research (QK 300, Sun Microspheres) had an average particle density of 908 kg/m^3 ; most particles were in the range of 10 to 300 microns in diameter. The cenospheres had low CaO content (less than 1%) but high combined SiO_2 and Al_2O_3 content (approximately 90%). X-ray diffraction analysis of the cenosphere material indicates that it contains a large amount of amorphous material with only small amounts of quartz and mullite crystals, as previously described in [16].

The samples were made from ASTM Type I ordinary Portland cement (OPC), undensified silica fume, shrinkage reducing admixture (SRA) (Eclipse® Floor, W.R. Grace Asia Pte Ltd), polycarboxylate superplasticizer (SP) (ADVA 181, W.R. Grace Asia Pte Ltd) and a viscosity modifying admixture (VMA) (V-MAR@ 10P, W.R. GRACE Asia Pte Ltd). Mix proportions of two ULCCs and their corresponding cement pastes (CP) are given in Table 1. Water/cementitious material ratios (w/cm) of the composites were approximately 0.35 and 0.45, calculated considering the SRA and the water in the SP. Cement pastes with comparable w/cm and mix proportions were also prepared. These mixes were presented previously in [12].

The materials were added to a Hobart mixer and carefully blended. Workability of the fresh mixtures was determined using a flow table method according to BS EN 1015-3. The flow

values of ULCC 1, ULCC 2 and CP1 were controlled to be approximately 200 mm. The flow value of CP2 was only 160 mm because VMA was used to adjust the consistency of CP2 at the high w/cm value of 0.45.

Table 1 Mix proportions of ULCC and cement pastes (CP).

	w/cm	Water (kg)	OPC (kg)	Silica fume (kg)	Cenosphere (kg)	SRA (kg)	SP (L)	VMA (g)	Flow (mm)
ULCC1	0.35	302	837	73	348	10.5	4.9	0	200
ULCC2	0.45	282	606	53	442	9.7	6.7	176	195
CP1	0.35	499	1356	117	-	14.9	1.3	0	200
CP2	0.45	561	1180	102	-	16.9	0	912	160

Six cubes (100-mm side length) were prepared to measure the compressive strength at 7 and 28 days. Three cylindrical specimens (100-mm diameterx200-mm height) were cast to measure the elastic modulus and two specimens (300-mm diameterx50-mm height) were cast for the thermal conductivity test. The specimens were cured in a fog room with temperatures ranging from 28 to 30°C until the time of testing.

After 28 days of curing, the specimens for the thermal conductivity test were dried in air for two weeks and later dried in an oven at 105°C to constant weight because the thermal conductivity of CP and of ULCC strongly depends on their moisture content.

X-ray diffraction (XRD) tests were conducted for a) cenospheres, b) ULCC samples after 7 days of curing, and c) ULCC samples after 2 years of curing. The samples were ground to a fine powder and placed into a 20-mm diameter holder.

The microstructural characterization using SEM with energy dispersive X-ray analysis (SEM-EDX) was conducted using 200 µm-thick slices of hardened ULCC, dried via solvent exchange using propanol before being resin-impregnated with EPO-TEK 301-2 (from Epoxy Technology). The resin-impregnated pastes were then ground and polished using Dayton Micro-3µ and ¼ µ sand paper until level and smooth. The samples were then carbon-coated to a thickness of approximately 15 nm to prevent charging under the electron beam. The anhydrous material was placed on a carbon film for the same reason.

For the 3D microtomography analysis, a sample of ULCC with a w/cm of 0.35 and similar mix proportion as ULCC1 (Table 1) was prepared in plastic pipettes and removed from the pipettes after 24 hrs. The sample was cut into small pieces and placed in a fog room for curing. The sample was taken out of the fog room after approximately 1 month and placed in an empty bottle until examination at the age of approximately 2-3 months. The sample was analyzed in its natural state, that is, no drying or other sample preparations were made prior to imaging, assuring that no artifacts were present as a result of sample preparation.

2.2 Techniques

The thermal conductivity of the ULCC was determined according to ASTM C 518 [21] using a heat flow meter (HFM 436/3, NETZSCH-Gerätebau GmbH). The higher thermal conductivity

of the cement pastes was measured using guarded hot plate equipment (GHP 300, Holometrix Micromet) according to ASTM C 177 [22].

The X-ray diffraction (XRD) tests were conducted using PANalytical X'Pert PRO cobalt K α radiation ($\lambda=1.5418$ Å), operated at 40 kV and 40 mA. The sample was spun at 30 revolutions per minute, with continuous collection at a scan speed of 0.0042°/sec and a step size of 0.0170° between 5 and 65° 2 θ , yielding 3529 steps, at a count time of 0.6 seconds. The fixed divergence and scatter slits were set to 0.5° and the receiving slits to 0.1 mm.

SEM image and EDX data collection were conducted using a Zeiss EVOMA10 SEM, equipped with a EDAX TSL energy EDX detector from AMETEK and EDAX Genesis software for imaging and X-ray analysis, at an accelerating voltage of 15 kV and beam current of 850 pA.

The microtomography experiments were run at beamline 8.3.2 of the Advanced Light Source (ALS) at the Lawrence Berkeley National Laboratory, utilizing an X-ray beam with energy of 36 keV at a ring current of 500 mA. A PCO.edge sCMOS camera (2560x2160 pixels) was used with a 2x lens, giving a 3.32 μm / pixel size with up to 8.3 mm field of view. This resolution facilitated the study of microstructural behavior. A total of 1025 images were captured (~1.7 mm-thick section), reconstructed using the software Octopus®, and visualized with FIJI. The final 3D rendering and segmentation were performed with Avizo®.

3 Results and discussion

3.1 Mineralogy and morphology characterization of cenospheres and ULCC

The XRD pattern of the anhydrous cenospheres (**Figure 1**) is, as expected, similar to the pattern of anhydrous fly ash [23], where both mullite and quartz are present along with an amorphous phase between 20 and 37°. When the pattern of anhydrous material is compared to that of hydrated pastes in **Figure 1**, the formation of calcium hydroxide (CH) can be clearly observed. Anhydrous phases remain present even after two years of hydration. As **Figure 1** indicates, there is substantially more CH present in two-year-old paste than in seven-day-old paste. Wang et al [1] observed that the pozzolanic reactivity of cenospheres was limited at room temperature. Due to the limited pozzolanic reactivity of cenospheres and increase in the degree of cement hydration of the paste, the consumption of CH was not detected after two years of hydration.

Figure 1 XRD pattern of anhydrous material and the two pastes set to the same scale.

The anhydrous cenospheres were imaged in secondary electron mode (Figure 2) to assess homogeneity and size of the spheres. The results indicate that the range was approximately 200 μm to 25 μm , with the majority being approximately 100 to 150 μm . Figure 3 shows backscattered images of ULCC with cenospheres after 7 days of hydration, while Figure 4 presents the same after 2 years of hydration. With time, the presence of holes is still clear, while the presence of shells is less evident because they react.

Figure 2 Secondary electron image of anhydrous cenospheres (a) and of a broken anhydrous cenosphere.

Figure 3 Backscattered electron image of cenospheres in OPC samples after 7 days hydration.

Figure 4 Backscattered electron image of cenospheres in OPC samples after 2 years hydration.

3.2 3D characterization of ULCC

The ULCC sample scanned with micro-CT was reconstructed in three dimensions and visualized (Figure 5a). To avoid excessive computing time and minimize edge effects, a region of interest (ROI) of 2380x2350x1060 mm inside the volume of the sample, where the composite is more homogeneous, was used. Figure 5 shows the raw reconstructed sample and a slice of the sample, highlighting the region of interest where the analysis was focused.

Figure 5 Reconstructed slice of the sample. Highlighted area is the Region of interest (ROI).

In the reconstructed image, different materials with different densities can be identified by their gray scale represented in Figure 6 (which is the ROI analyzed) and are labeled as follows: a) unreacted anhydrous cement grains, the brightest phase due to its having the highest density; high absorption of X-rays; b) hydrated cement paste, light gray; c) product of the cenospheres' reaction, darker grey (this could also be hydrated cement paste above the cenosphere or void, with lower density); d) unreacted cenospheres, dark grey; e) porosity, the darkest phase; little absorption of X-rays.

Figure 6 (a) Slice and (b) reconstructed volume of the ROI. Labels refer to the different identified material phases.

The image processing was kept to a minimum in order to maintain the image information close to its raw form. Light smoothing was applied to reduce contrast and soften edges and a 3D median filter with one iteration was used to minimize noise. Artifacts were eliminated by smoothing the boundaries, connecting close particles and filling the holes inside the particles.

Different densities were isolated by thresholding the entire ROI volume by considering the different grey levels according to the previously assigned labels and by using the volume histogram (Table 2). Note that any holes filled with air or water are labeled as voids because their x-ray attenuations at the energy used in the experiment are very similar, making it impossible to distinguish between them. Additionally, entrapped air and holes inside the cenospheres cannot be distinguished because both have the same density, so both are included in the estimated total void volume. This is considered as part of the error in the quantification of the results. The previously described five different phases can be identified in the entire segmented volume shown in Figure 7. Different colors are related to the different materials, as follows: a) Purple: air voids, b) Yellow: cenospheres; c) Blue: reaction products; d) Green: cement paste; e) Light pink: unhydrated cement grains.

Table 2 Thresholding limit values for each material in the image reconstruction.

Material	Thresholding limit values
Purple: air voids	0-68
Yellow: cenospheres	69-100
Blue: reaction products	101-140
Green: cement paste	141-209
Light pink: unhydrated cement grains	210-260

Figure 7 Image segmentation showing the different materials identified through thresholding. (a) volume rendering, (b) slice image and (c) slice segmentation. Image slice 700x700 μ m. The colors indicate the following: purple: air voids; yellow: cenospheres; blue: reaction products; green: cement paste; light pink: unhydrated cement grains.

Quantification of each phase in the reconstructed 3D image gives a good approximation of the volume fraction of the initial materials in the mixing paste. It is assumed that there are hydrated and unhydrated cenospheres and that the reaction products are spread around the

initial boundaries in the cement paste. The reaction products observed here were also described by Lanzón et al (2012), who attributed this region to the formation of supplementary cementitious components in the form of a gel, due to the pozzolanic nature of cenospheres, and indicated the densification of the transition zone, thus reducing the degree of open porosity.

In the initial mix proportion, the volume fraction of cement paste was 54.80%, while, for cenosphere plus air voids, it was 45.20% (38.95% of cenospheres and 6.25% of entrapped air void). By calculating the surface area and volume of each individual patch, the image reconstruction, after thresholding, indicates that approximately 50% of the volume is related to the sum of cenospheres, air, and reaction products. This also considers the natural porosity of the paste, thus providing a reasonable approximation compared to the initial state. The ratio of each component observed by thresholding is described in Table 3.

Table 3 Volume ratio of materials from image reconstruction thresholding.

Material	Volume ratio (%)
Purple: air voids	17.2
Yellow: cenospheres	13.3
Blue: reaction products	20.4
Green: cement paste	47.9
Light pink: unhydrated cement grains	1.2

The rendered image indicates a uniform distribution of cenospheres in the volume (Figure 8a). It is also possible to observe that some parts of the cenospheres have already reacted and Figure 8b shows the reaction products around that same area. The image of the reaction products shows the high packing density and shows that this material was not restricted to the initial boundaries of the cenospheres but instead has spread over the matrix. Air voids have uniform distribution as well, and in addition to the voids from the cenospheres, there are smaller air voids that are related to the entrapped air voids in the cement paste itself (Figure 8c).

Figure 8 3D images showing the distribution of (a) cenospheres; (b) reaction products; and (c) air voids in the volume. Subvolume size 400x700x700 μm .

The volume of each empty space for both air voids and cenospheres was measured. Volumes are presented in Table 4 and refer to the volume remaining after the mixing and curing of the sample.

Table 4 Observed volumes of individual air voids and cenospheres.

Material	Smaller (μm^3)	Bigger (μm^3)	Average individual volume (μm^3)
Air voids	1.47E+03	9.65E+06	9.82E+04
Cenospheres	1.47E+03	2.33E+07	1.19E+05

Values observed for the volume of cenospheres are lower than for the volume of the bulk particles. However, these values are fitting given the values for the diameter and thickness of cenospheres referenced in the literature [7], [17]–[20].

At this resolution, it is not possible to identify different phases from the cement hydration or cenospheres' pozzolanic reactions, as discussed in previous studies [24]. However, some features can be observed: some small needles are formed inside the original boundary of

the cenospheres and, while they are present in some slices, they did not appear in the entire volume. Arrows in Figure 9 indicate selected needles. Their grey level matches either the levels established for the cenosphere's hydration products or for the cement paste, confirmed by image thresholding (Figure 11). This phenomenon could be due to cracks in the cenosphere and leakage of cement paste inside, or it could be attributed to the cenosphere's reaction products because this type of material is expected in both the cement paste and the cenosphere's reaction products.

Figure 9 Different slices of the same region, showing several needles.

Looking in detail at one of the cenospheres in different slices, it is clear that the needles are not present in the whole volume of the sphere. However, these needles appear in many consecutive slices, indicating a considerable thickness (Figure 10).

Figure 10 Details of one cenosphere with needles, which appear in different slices, over the x-y (top) and y-z (bottom) axes.

Figure 11 (a) Slice with image segmentation, showing the cenosphere with “needles”. The different materials identified by the same colors (introduced above) show that the “needles” have compositions in accordance with the cement paste. (b) 3D image of the cenospheres with “needles” showing the surface of each material. RP refers to reaction products surrounding the cenosphere particle. CP refers to cement paste, filling some space in this cenosphere. Subvolume size 250x160x130 μ m.

A recent research [25] has used X-ray microtomography to study the microstructure of mortars with low-density additions (expanded perlite, expanded glass and cenospheres) and reported that samples containing cenospheres had the smallest open pores, as well as low capillary water absorption when compared to the other additions. Barbare et al [15] measured the uptake and loss of water in a cement composite material containing cenospheres and the results confirmed that the pore size for water penetration in concrete with cenospheres was smaller than in normal concrete because the pores are not connected.

3.3 Thermal and mechanical properties of ULCCs

Table 5 presents the experimental results for density, compressive strength, elastic modulus, and thermal conductivity. The ULCC had 28-day cube compressive strength in the range of 40 to 70 MPa and corresponding wet density in the range of 1200 to 1470 kg/m³. The structural efficiency (compressive strength/density) of the ULCC is similar to that of normal weight concrete with compressive strength of 80-115 MPa and density of 2400 kg/m³. However, as expected, the ULCCs had lower elastic modulus compared with that of normal weight concrete. The thermal conductivity of the oven dried ULCCs was 0.31 to 0.40 W/m.K.

Table 5 Experimental results

	w/cm	1-day density (kg/m ³)	Oven dry density (kg/m ³)	28-day Cube compressive Strength (MPa)		Elastic modulus (GPa)	Thermal conductivity (W/m.K)
				7-day	28-day		
ULCC1	0.35	1471	1303	57.8	69.4	17.0*	0.40

ULCC2	0.45	1196	1042	32.0	40.9	12.0*	0.31
CP1	0.35	2000	1715	52.5	63.1	21.6*	0.84
CP2	0.45	1854	1479	37.8	51.3	16.5**	0.80

* determined at the age of 70 days due to the breakdown of the test equipment

** determined at 28 days.

Blanco et al [8] also investigated the thermal conductivity of lightweight cement composites with cenospheres. However, the composites they developed presented lower compressive strength (22-33 MPa) and higher thermal conductivity for oven dried specimens (0.43 to 0.50 W/m.K). It is not clear, however, if the density they reported was based on wet or oven dried specimens. The thermal conductivities of the ULCC, as shown in Table 5, are comparable to those of lightweight concretes with similar densities (made with blast furnace slag as aggregate) [26], but substantially lower than those of normal weight concrete [27], [28]. However, no information was available on the compressive strength of the lightweight and normal weight concretes in these references. In general, the thermal conductivity of normal weight concrete is mainly affected by the TC of aggregate, and may not be affected significantly by the concrete strength level. The thermal conductivities of the oven dried cement pastes with w/cm of 0.35 and 0.45 were 0.84 and 0.80 W/m.K, respectively.

3.4 Finite element model

One point that needs to be addressed is the reason for the fairly small decline in mechanical properties when cenospheres are used even though the particles introduce a large porosity into the matrix because they are hollow (difference observed on samples with w/cm 0.45). To explore the mechanical response when cenospheres are introduced into the matrix, a numerical simulation based on the Finite Element Method (FEM) was performed. The main hypothesis to be tested is the assumption that the stiff shell of the cenospheres can have a significant effect on the overall mechanical properties of the ULCC samples under load. A simplified three-dimensional model is used in which eight spheres, with the radius of 150 μm are uniformly distributed in the matrix with the dimension of 1x1x1 mm³ (see **Figure 12**). Shell layers with the thickness of 30 μm are generated, which is approximately 10% of the diameter of the cenosphere. As a qualitative test, the number of spheres can be arbitrarily decided. However, the choice of the size of the spheres and of the thickness of the shell layer is suggested by [18]. The whole geometry is discretized by four-node tetrahedral elements. The mechanical parameters of the three phases in the sample are listed in **Table 6**; the reason for choosing 1 (N/mm²) instead of 0 as Young's modulus of the cenosphere interior is to avoid numerical problems. In the numerical test, the lower surface of the sample is fixed and a tensile displacement-controlled boundary condition is prescribed on the top surface. The stress distributions in y and z directions with and without the shell layer are shown in **Figure 13**. It is clear that stress concentrations occur at the shell layer. The force-displacement curves indicate that, due to the presence of the stiff shell, the overall stiffness of the specimen increases, thus fully compensating for the presence of the holes. Because this is a linearly elastic model, only stiffness (and not strength effects) is captured.

Figure 12 Phases in the numerical model (left) the whole specimen (b) cut through the x-z plane across the midplane of four spheres.

Table 6 Parameters used in the numerical model.

	Young's modulus (N/mm ²)	Poisson's ratio
Cement Paste	17,460 [37]	0.2 [29]
Cenosphere interior	1.0 [29]	0.0 [29]
Shell	80,000 [29]	0.2 [20]

(a1)

(a2)

Figure 13 Stress distributions (a1) along y without shells (a2) along z without shells (a3) along y with shells (a4) along z with shells.

Figure 14 Force-displacement curves.

4 Analytical estimates and bounds for thermal conductivity of cement paste with cenospheres

Physical properties of materials obtained through experiments in laboratories rely on the assumption that materials are homogeneous. However, most materials are heterogeneous with physical properties that vary throughout their microstructures, e.g., in this work, we examine composite paste with cenospheres randomly distributed in cement paste. Obviously, conventional experiments are not able to account for effects of the microscopic heterogeneity of materials. However, it is impossible to obtain exact analytical solutions of effective or macroscopic properties of materials that completely characterize macroscopic behaviors. Through the analytical homogenization procedure, one can obtain estimates and bounds for macroscopic properties of heterogeneous materials [30,31]. The subject of

analytical homogenization aims at understanding the relationship between microstructures and macroscopic behaviors of materials, as measured through experiments. The objective of this section is to calculate analytical estimates and bounds for thermal conductivity of a cement composite with cenospheres through well-known approaches. We do not aim at developing a new method here, as the scope of this paper is centered on experimental methods.

Analytical estimates include, e.g., the Maxwell (MW) model, the Self-Consistent (SC) model and the Differential (DF) model. The MW model, developed by Maxwell [30], explicitly provides the thermal conductivity of the heterogeneous material as a function of the thermal conductivities of its components and of their volume fractions. Conversely, the SC model, developed by Bruggeman [31], offers implicit equations. In this model, each component of the material is treated symmetrically; hence, the result is invariant to the simultaneous interchange of the thermal conductivities of components and of their volume fractions. The DF model in [31] does not treat each component symmetrically. However, both the SC and DF models adopt the idea of incremental homogenization. More specific details about analytical estimates for the thermal as well as the mechanical problem can be found in [32] and [33]. The Reuss-Voigt bounds (RV) and Hashin-Shtrikman bounds (HS) were derived from variational methods; see [32] for more details.

Analytical thermal homogenization has been widely applied for various materials. For instance, Maxwell [30] calculated the effective conductivity of a dispersion of dilute spheres. Dasgupta and Agarwal [34] adopted two-scale asymptotic homogenization schemes to calculate the orthotropic thermal conductivity of plain-weave fabric-reinforced composite laminates. Sadeghi et al [35] developed a compact analytical model for determining the effective thermal conductivity of a gas diffusion layer in a fiber-reinforced composite, which accounted for thermal conduction in both the solid fibrous matrix and in the gas phase. The spreading resistance associated with the contact area between overlapping fibers was also taken into account. Staicu et al [36] calculated analytical bounds for nuclear materials with various microstructures and compared them with experiments. Henon et al [37] identified the thermal conductivity of potassium geopolymers foams via analytical homogenization, where the quantitative characterization of the pore volume fractions was accomplished by image analysis.

Table 7 presents analytical estimates of MW, SC and DF models for a two-phase particulate microstructure, where particles are randomly embedded in the matrix. k^* indicates the estimate of effective thermal conductivity. $k^{(I)}$ and $v^{(I)}$ denote the thermal conductivity and the volume fraction of component I respectively, where $I = 1$ states for the matrix and $I = 2$ represents the particle. Note that the following assumptions are supposed to be satisfied: a) Macroscopically isotropic; b) Linearly conducting; c) Spherical particles.

Table 7 A summary of analytical estimates for the effective thermal conductivity of a two-phase particulate microstructure (d represents the number of spatial dimensions).

Model	Estimate
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k_{MW}^*	$\frac{k^* - k^{(1)}}{k^* + (d-1)k^{(1)}} = v^{(2)} \frac{k^{(2)} - k^{(1)}}{k^{(2)} + (d-1)k^{(1)}}$
k_{SC}^*	$\sum_{I=1}^2 v^{(I)} \frac{k^{(I)} - k^*}{k^{(I)} + (d-1)k^*} = 0$
k_{DF}^*	$\frac{dk^*}{dv^{(2)}} = \frac{k^* d}{1 - v^{(2)}} \left[\frac{k^{(2)} - k^*}{k^{(2)} + (d-1)k^*} \right]$

4.1 Estimates

In the following sections, we provide more details on the background of the various analytical estimates.

4.1.1 MW model

Figure 15 Scheme related to the MW model.

In the MW model, it is assumed that an infinite homogeneous matrix with the thermal conductivity $k^{(1)}$ contains a spherical inclusion of radius R_0 and the thermal conductivity of $k^{(1)}$ (see Figure 15). In turn, the spherical inclusion is assumed to contain N smaller spheres with the radius R and the thermal conductivity $k^{(2)}$. A constant temperature gradient g_0 is prescribed at infinity to the matrix. The volume fraction of small spheres $v^{(2)}$

$$v^{(2)} = N(R/R_0)^d \quad (4.1)$$

is sufficiently small, such that interactions among spheres can be neglected. The small size of the sphere $I = 2$ means that the thermal field $g(\mathbf{r})$ at the radial position $\mathbf{r}$ in Figure 15 can be simply assumed to be the superposition of the thermal field $g(\mathbf{r}) = g_0 + \frac{v^{(2)} R_0^d \beta_{21}}{r^d} [d\mathbf{n} \otimes \mathbf{n} - \mathbf{I}] \cdot g_0$ (4.2)

where β_{21} is the polarizability defined by

$$\beta_{21} = \frac{k^{(2)} - k^{(1)}}{k^{(2)} + (d-1)k^{(1)}} \quad (4.3)$$

If the large sphere were homogeneous with effective thermal conductivity of k^* , it would be

$$g(\mathbf{r}) = g_0 + \frac{R_0^d \beta_{e1}}{r^d} [d\mathbf{n} \otimes \mathbf{n} - \mathbf{I}] \cdot g_0 \quad (4.4)$$

where β_{e1} is given by

$$\beta_{e1} = \frac{k^* - k^{(1)}}{k^* + (d-1)k^{(1)}} \quad (4.5)$$

Equations (4.4) and (4.5) yield

$$\beta_{e1} = v^{(2)} \beta_{21} \quad (4.6)$$

By using Equations (4.3), (4.5) and (4.6), the equation for k^* is given by

$$\frac{k^* - k^{(1)}}{k^* + (d-1)k^{(1)}} = v^{(2)} \frac{k^{(2)} - k^{(1)}}{k^{(2)} + (d-1)k^{(1)}} \quad (4.7)$$

For the case of $k^{(2)}k^{(1)} = \infty$, indicating that spheres are superconducting relative to the matrix, the thermal estimate follows as

$$\frac{k^*}{k^{(1)}} = \frac{1+(d-1)v^{(2)}}{1-v^{(2)}} \text{ if } k^{(2)}k^{(1)} \rightarrow \infty \quad (4.8)$$

The opposite situation $k^{(2)}k^{(1)} = 0$, where the spheres are perfectly insulating relative to the matrix, leads to

$$\frac{k^*}{k^{(1)}} = \frac{(d-1)(1-v^{(2)})}{d-v^{(1)}} \text{ if } k^{(2)}k^{(1)} = 0 \quad (4.9)$$

More details about the MW model can be found in [32].

4.1.2 SC model

In the SC model, a macroscopically isotropic material is assumed to be composed of M different types of spherical inclusions with volume fractions $v^{(1)}, \dots, v^{(M)}$ and thermal conductivities $k^{(1)}, \dots, k^{(M)}$. The SC model relies on the assumption that all components outside a type j inclusion are homogeneous and have effective thermal conductivity k^* , which is the unknown to be calculated [32]. Because perturbations to a uniform field on average are zero, it is

$$\sum_{j=1}^M v^{(j)} \beta_{je} = \sum_{j=1}^M v^{(j)} \frac{k^{(j)} - k^*}{k^{(j)} + (d-1)k^*} = 0 \quad (4.10)$$

As mentioned previously, the SC model treats each phase symmetrically. Therefore, it is invariant to the simultaneous interchange of phase conductivities and volume fractions. Concerning a two-phase material, phase 1 is treated as the matrix and phase 2 is considered as an included spherical phase. The estimate of thermal conductivity for the two-phase material is given by

$$k^* = \frac{\alpha + \sqrt{\alpha^2 + 4(d-1)k^{(1)}k^{(2)}}}{2(d-1)}$$

with

$$\alpha = k^{(1)}(dv^{(1)} - 1) + k^{(2)}(dv^{(2)} - 1) \quad (4.11)$$

If the spherical phase is superconducting, it is

$$\frac{k^*}{k^{(1)}} = \frac{1}{1-dv^{(2)}} \text{ if } k^{(2)}k^{(1)} \rightarrow \infty \quad (4.12)$$

On the other hand, if the spherical phase is perfectly insulating relative to the matrix, the estimate of the SC model gives

$$\frac{k^*}{k^{(1)}} = 1 - \frac{d}{d-1}v^{(2)} \text{ if } k^{(2)}k^{(1)} = 0 \quad (4.13)$$

A detailed overview of the SCE model is given in [38].

4.1.3 DF model

Unlike the SC model, the DF model does not treat each phase symmetrically. However, both SC and DF models adopt the idea of incremental homogenization. In the DF model, it is assumed that the effective thermal conductivity at one value of $v^{(2)}$ is known. First, $k^*(v^{(2)})$ is considered to be the host thermal conductivity of the material. Secondly, after a small fraction $\Delta v^{(2)}/(1-v^{(2)})$ is replaced by inclusions of phase 2, $k^*(v^{(2)} + \Delta v^{(2)})$ represents the effective thermal conductivity of the material. By using the dilute-limit result [32], it is

$$k^*(v^{(2)} + \Delta v^{(2)}) - k^*(v^{(2)}) = k^*(v^{(2)}) \left[\frac{k^{(2)} - k^*(v^{(2)})}{k^{(2)} + (d-1)k^*(v^{(2)})} \right] \left[\frac{\Delta v^{(2)}}{1-v^{(2)}} \right] d \quad (4.14)$$

The limit case $\Delta v^{(2)} \rightarrow 0$ yields the differential equation

$$(1 - v^{(2)}) \frac{dk^*}{dv^{(2)}} = k^* \left[\frac{k^{(2)} - k^*}{k^{(2)} + (d-1)k^*} \right] d \quad (4.15)$$

with the initial condition $k^*(v^{(2)} = 0) = k^{(1)}$. Integrating Equation (4.15) yields

$$\frac{k^{(2)} - k^*}{k^{(2)} - k^{(1)}} \left(\frac{k^{(1)}}{k^*} \right)^{1/d} = 1 - v^{(2)} \quad (4.16)$$

In terms of the two limit cases (superconducting and perfectly insulating), the estimates of the DF model are given by

$$\frac{k^*}{k^{(1)}} = \frac{1}{(1-v^{(2)})^d} \text{ if } k^{(2)}k^{(1)} \rightarrow \infty \quad (4.17)$$

and

$$\frac{k^*}{k^{(1)}} = (v^{(1)})^{d/(d-1)} \text{ if } k^{(2)}k^{(1)} = 0 \quad (4.18)$$

Figure 16 Estimates of thermal conductivity of MW, SC and DF models when spheres are superconducting relative to the matrix. ($k^{(2)} / k^{(1)} \rightarrow \infty$)

Figure 16 and Figure 17 display estimates of effective thermal conductivities for a two-phase material composed of spheres (phase 2) in the matrix (phase 1), as a function of the volume fraction of phase 2 for two limit cases: $k^{(2)} / k^{(1)} \rightarrow \infty$ and $k^{(2)} / k^{(1)} = 0$. Clearly, for the case of $k^{(2)} / k^{(1)} = 0$, all models predict the effective thermal conductivity to decrease as the volume fraction of phase 2 increases. A nontrivial percolation threshold is predicted by the SC model, while the MW and DF models imply that phase 1 remains connected until $v^{(2)}$ is reached.

Figure 17 Estimates of thermal conductivity of MW, SC and DF models when spheres are perfectly insulating relative to the matrix ($k^{(2)} / k^{(1)} = 0$).

Table 8 Thermal conductivities and volume fractions of cement composite and cenospheres.

Component	Thermal Conductivity	Volume Fraction (%)
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	(W/mK)	
Cement Paste	$k^{(1)} = 0.8$	$v^{(1)} = 61$
Cenospheres	$k^{(2)} = 0.08$	$v^{(2)} = 39$

Table 9 Analytical estimates of thermal conductivity for cement paste with cenospheres.

Estimate	k_{WM}^* (W/mK)	k_{SC}^* (W/mK)	k_{DF}^* (W/mK)
Value	0.4563	0.4157	0.4236

Table 8 presents thermal conductivities and volume fractions of cement composites and cenospheres. Analytical estimates of thermal conductivity for cement composite with cenospheres can be found in Table 9. The results for the three models are similar, and agree with the results from the experiments, of 0.4 W/m.K (Table 5). The SC model results in the closest value for thermal conductivity compared to the experimental data.

4.2 Bounds

Table 10 illustrates a summary of analytical bounds of thermal conductivity for the two-phase particulate microstructure, where phase 1 is the matrix and phase 2 is the sphere. Table 11 displays the calculated bounds of thermal conductivity for the cement paste with cenospheres.

Table 10 A summary of analytical bounds of effective thermal conductivity for cement composite with cenospheres, where the thermal conductivity of the cenospheres $k^{(2)}$ is smaller than that of the cement paste $\langle k \rangle = v^{(1)}k^{(2)} + v^{(2)}k^{(1)}$.

Bounds	Value
$k^{(1)}$	0.08
k^{RV-}	$\langle k^{-1} \rangle^{-1} = \left(v^{(1)}(k^{(1)})^{-1} + v^{(2)}(k^{(2)})^{-1} \right)^{-1}$

k^{HS-}	$\langle k \rangle - \frac{v^{(1)}v^{(2)}(k^{(2)}-k^{(1)})^2}{\langle k \rangle + (d-1)k^{(2)}} \text{ (if } k^{(2)} < k^{(1)} \text{)}$ $\langle k \rangle - \frac{v^{(1)}v^{(2)}(k^{(2)}-k^{(1)})^2}{\langle k \rangle + (d-1)k^{(1)}} \text{ (if } k^{(2)} > k^{(1)} \text{)}$
k^*	k^*
k^{HS+}	$\langle k \rangle - \frac{v^{(1)}v^{(2)}(k^{(2)}-k^{(1)})^2}{\langle k \rangle + (d-1)k^{(1)}} \text{ (if } k^{(2)} < k^{(1)} \text{)}$ $\langle k \rangle - \frac{v^{(1)}v^{(2)}(k^{(2)}-k^{(1)})^2}{\langle k \rangle + (d-1)k^{(2)}} \text{ (if } k^{(2)} > k^{(1)} \text{)}$
k^{RV+}	$\langle k \rangle = v^{(1)}k^{(1)} + v^{(2)}k^{(2)}$
$k^{(2)}$	0.8

Table 11 Analytical bounds of thermal conductivity for cement composite with cenospheres.

Bound	k^{RV-} (W/mK)	k^{HS-} (W/mK)	k^{HS+} (W/mK)	k^{RV+} (W/mK)
Value	0.1774	0.2857	0.4563	0.5192

The order of analytical bounds is given by

$$\begin{aligned}
 & k^{RV+} < k^{(2)} \\
 & k^{HS+} < k^{RV+} \\
 & k^{HS-} < k^{E2} < k^{E1} < k^{HS+} \quad (4.19) \\
 & k^{RV-} < k^{HS-} \\
 & k^{(1)} < k^{RV-}
 \end{aligned}$$

where k^{E1} and k^{E2} are measured experimental results for ULCC1 and ULCC2 samples, respectively (see Table 5). It is observed that not only the estimates but also the experimental results lie within the analytical bounds.

5 Conclusions

From the energetic point of view, the ULCC presents extremely satisfactory performance, with a significant reduction in the thermal conductivity compared to the cement paste samples: 48% for w/c = 0.35 and 39% for w/c = 0.45. This happened along with a small decrease or even an increase in compressive strength. The elastic modulus suffered a

reduction of less than 30% for both samples. At the same time, the reduction of at least 25% in the dry density allows its use in lightweight structures without compromising performance.

Microtomography image reconstruction shows the dispersion of the cenospheres in the cement paste, as well as the distribution of pores and the products formed from the reaction of cement and cenospheres. Image analyses provide data on the volume fractions of the materials, which are in accordance with the initial quantities in the mixing paste. Different materials can be identified through image rendering, and parts of cenospheres that have already reacted can be differentiated from the still unreacted shells. That is, it is possible to identify the parts of the shell that have already reacted as well as the unreacted parts. Air voids from the cement paste cannot be differentiated from those produced by the addition of the hollow spheres. They can, however, be counted with the decrease in the thermal conductivity of this material.

Analytical homogenization is carried out to obtain estimates and bounds for the effective thermal conductivity of cement composites. A good agreement between analytical estimates and experimental results is found. However, the shell is not accounted for in analytical homogenization, due to the lack of information on its thermal conductivity. Future work could focus on measuring the thermal conductivity of the shell through experiments and on developing a new model for analytically calculating the effective thermal conductivity of cement composites with three phases: cement matrix, cenospheres and shells. Also, numerical thermal homogenization is planned for future studies, which will use randomly distributed spheres embedded in the homogeneous matrix to represent the microstructure of cement paste and cenospheres.

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