

Atomistic simulations, Meso-scale analyses and Experimental validation of Thermal properties in ordinary Portland cement and Geopolymer pastes

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Abstract

Ordinary Portland Cement (OPC)- and alternative binder-based materials have been widely used in Thermal Energy Storage (TES) applications due to their excellent TES capacities, good mechanical properties and low-cost. In this attempt, this work proposes an upscaling procedure to model the TES properties of two hydrated pastes made of OPC and a Hybrid cement (i.e., an alternative binder H-Cement), the latter employed for a GEopolymer-based composite (GEO). Firstly, an atomistic approach based on energy minimization and molecular dynamics is employed for modelling the thermal behaviors and heat storage capacities of CSH (calcium silicate hydrate) and NASH (sodium aluminosilicate hydrate) phases, being those the main phases for OPC and GEO, respectively. Then, an up-scaling optimization procedure and meso-scale FEM homogenization techniques are proposed to link the TES parameters of the atomistic main phases of OPC and GEO with the homogenized upper meso/macro scale values. To this end, the results of an experimental program on both OPC and GEO pastes have been considered as benchmark to calibrate/validate the numerical tools. Promising simulations at several scales and up-scaling procedures are demonstrated in terms of homogenized temperature-dependent heat capacity and thermal diffusivity, showing a good agreement with the experimental data of the analyzed mixtures.

Keywords: Atomistic simulations, thermal properties, CSH, NASH, OPC, geopolymers, ReaxFF, phonons, vibrational states, finite-element-based homogenization, optimization.

1. Introduction

Energy-efficiency in construction and building materials has become a major challenge for both science and industry [1]. It is driven by the urgent need to strongly reduce the emissions of greenhouse gases and to cut-back on the inefficient usage of the worldwide primary energy. The building stock is actually responsible for over one-third of the global energy consumption and with this, for nearly 40% of total direct and indirect CO₂ emissions, making it the largest EU energy consumer [2]. Therefore, a major leap in energy-saving is vital to protect our environment and to boost the EU's green economy [3, 4].

In this attempt, cement-based materials, like concrete, represent the most employed construction materials worldwide. Their basic ingredients match the ones of the Earth's crust and are abundantly available and at low cost [5]. Combining the low-cost nature of cementitious materials, together with the possibility of manipulating their inner

multi-scale structures, make them very attractive for shaping their thermal properties and to achieve highly thermal-energy storage and saving applications, as urgently needed in new and/or existing buildings [6, 7].

Despite their practical importance, the origin of the thermal properties of cementitious systems is still at an incipient stage [8]. Most of the existing literature has focused on macroscopic experimental measurements and numerical tools, where the connection to the intrinsic properties of the constituents is lost, mainly focused on specific applications like fire resistance (high temperatures) [9], thermal insulation (mid temperatures) [10], early-age processes [11], heat exchangers [12], geothermal energy applications [13], and/or studying the effects of special components such as waste glass aggregates and nanosilica [14], micro-encapsulated phase change materials [15], nano-particles [16], etc.

Thermal properties are one-to-one related to the vibrational atomic states, and how these vibrational states are

activated as a function of the temperature [17, 18]. More specifically, phonons are the physical particles in which mechanical vibration is responsible for the transmission of sound and heat [19]. Atomistic simulations can help in understanding how these vibrational modes are excited and predicting valuable parameters like (specific) heat capacity, thermal conductivity and thermal-energy storage parameters in general sense [20, 21, 22].

Nevertheless, until the advent of sufficient computational capacity, the estimations of the Vibrational Density of States (VDOSs) in physics have resorted to simplified models like the Debye model [23] that gives satisfactory results in certain cases. For instance, the Debye model is able to estimate quite well the heat capacity of polycrystalline materials, under low temperature regimes (i.e., temperatures lower than the so-called T_{Debye} temperature). T_{Debye} lies above the room temperature for most of the crystalline phases present in cementitious materials (namely, C2S, C3S or CH). This is the reason why the use of this simple model has been successfully exploited by Bernard et al. [24] to predict the heat capacities of $w/c = 0.45$ cement paste and the corresponding mortar, measuring a c_p of $870 J/(kg \times K)$ for the well-hydrated cement paste and $742 J/(kg \times K)$ for the mortar. However, the Debye model fails to capture both the low energy extra vibrational states of amorphous materials [25] and, as expected, the thermal properties when the temperature starts being not negligible with respect to the Debye temperature [26]. In these two cases, the use of accurate atomistic simulation models is an indispensable must.

In this scenario, the works of Qomi et al. [27] and Zhou et al. [18] have recently disclosed the right theoretical methodology for elucidating the physical origins of thermal properties in cement systems. Indeed, they reported studies of properties of some basic constituents of Ordinary Portland Cement (OPC) pastes (i.e., analysing phases like CH, CSH, C2S and C3S) at room temperatures. As a salient result that directly targets to the limits of Debye model, they noticed the existence of the so-called Boson peak for the CSH gel (see Dolado et al. [28]). This peak, reflected in a deviation with respect to the quadratic frequency dependence of VDOS, is a hallmark in many glassy materials [29], though its origin is still unclear. Dolado [30] has extended the methodology to explore the thermal properties at high temperature, comparing the properties of some crystalline structures present in OPC and those made of calcium aluminate cement pastes.

This paper aims at sharing ongoing works on this topic, reporting new simulations and experiments that have been done for studying the thermal properties of cement-based and alternative binders materials. In particular, based on an extension of the previous work by Dolado [30], this work includes the analysis of temperature-dependent thermal properties of poorly crystallized structures like CSH and NASH. The latter represent the key ingredients of OPC and geopolymer-based cement pastes, respectively. The heat capacity and thermal conductivity of CSH and

NASH have been estimated through atomistic simulations in the temperature range that goes from room temperature (300 K) till 600 K. In parallel, some experiments (at both experimental and numerical up-scaling standpoints) over OPC and geopolymer-based cement pastes have been also carried out for comparative purposes.

After this general introduction Section, the paper is structured as follows. Section 2 summarizes the experimental tests and data on OPC and geopolymer pastes, investigated in this work and used as benchmark for the numerical activities. Section 3 presents the atomistic modelling procedure for analyzing the thermal properties of CSH and NASH structures. They are considered as the key ingredients of OPC and geopolymer-based cement pastes, respectively. Then, Section 4 discusses the atomistic results while a discussion in Section 5 is provided to link the nano-scale analyses with homogenized (up-)macro-scale results. Then, meso-scale numerical simulations compared against both experimental data, and the homogenized atomistic simulations are presented in Section 6 with the aim to verify the soundness and capabilities of the presented nano-to-meso scale methodology. Finally, some concluding remarks are made in Section 7.

2. Experimental tests and data

2.1. Materials

Two hydrated pastes were investigated in this work: i) an OPC made of cement (namely, CEM II-42.5R) and ii) a Hybrid Cement (H-Cement, see Martauz et al. [31]), the latter employed for a geopolymer-based paste (with a label GEO). Table 1 and 2 provide the chemical ingredients of the considered binders. They were mixed with distilled water (provided by Sigma-Aldrich Lab) by considering a water-to-cement(binder) ratio of 0.4 and 0.6 by weight, respectively. Specimens were then cast in a cylindrical mold (38 mm diameter \times 15 mm height) and sealed. After 24 hours, the sample discs were moved to a hermetically closed desiccator, under controlled humidity (i.e., 100 % RH) and kept at 20 °C during 28 days.

Table 1: Chemical composition of cement CEM II-42.5R.

Chemical composition [% weight]	SiO ₂	Al ₂ O ₃	CaO	MgO	SO ₃	Na ₂ O	K ₂ O	TiO ₂	Fe ₂ O ₃
CEM II-42.5R	19.31	4.31	61.08	2.38	2.96	0.29	0.86	0.14	2.28

Table 2: Chemical composition of the H-cement by Martauz et al. [31].

Chemical composition [% weight]	CaO	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	SO ₃	K ₂ O	Na ₂ O	L.O.I.
H-Cement	22.55	43.55	17.52	5.86	2.68	3.85	2.74	2.49	1.51

2.2. Methods

2.2.1. Differential scanning Calorimetry

Modulated Differential Scanning Calorimeter (DSC), by using a TA Instrument Q2000, was performed to determine the reversible part of the specific heat of the samples (having weights of 25 mg circa). Aluminum pans were used for all the samples. Measurements were performed with an average heating rate of 3.0 K/min and amplitude of modulation ± 0.48 K, with a period of $t_p = 60$ s. Samples were previously pre-heated at 105°C during 1 hour. Finally, data were collected in the temperature range between 50 °C to 300 °C (with an interval step of 50 °C).

2.2.2. Thermal conductivity

LFA 457 Microflash (from NETZSCH Company) was used for determining the thermal diffusivity in all mixtures. Specimens were pellet discs of pastes having a diameter of 10 mm and height of 2 mm. The samples were spray-coated with graphite, on both sides, in order to enhance light absorption and infrared thermal response. The investigation was carried out at representative temperatures of 25, 100, 200, 300, 400, 500, and 600 °C.

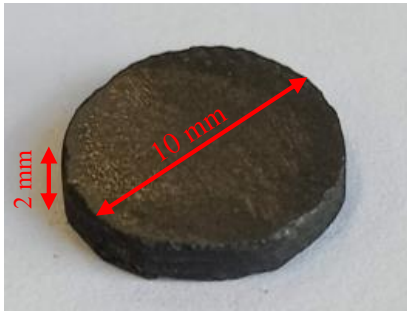


Figure 1: Pellet discs of pastes having a diameter d of 10 mm and height h of 2 mm.

2.3. Measurements

The thermal properties of both OPC and geopolymers are reported in this section. Particularly, Figure 2 shows the results in terms of c_p measurements ($J/(g \times ^\circ C)$) under rising temperatures. The comparison between OPC and GEO highlights the fact that the ordinary Portland cement pastes have a lower specific heat capacity, for each level of temperature, than the corresponding GEO data. The behavior of both OPC and GEO is characterized to have a clear temperature dependency between c_p and the increasing values of the considered temperatures. However the c_p rise (mostly linear) is much more evident for the GEO than for the OPC pastes.

Figure 3 shows the results in terms of thermal diffusivity measurements (mm^2/s) at different temperatures. The comparisons between OPC and GEO show that the OPC pastes have quite higher thermal variation, at each T measurements, than the GEO ones. The thermal diffusivity in both OPC and GEO is characterized to have a clear linear

temperature dependency against the considered temperature levels. This mostly linear tendency shows reduction of the thermal diffusivity with a similar trend for both OPC and GEO.

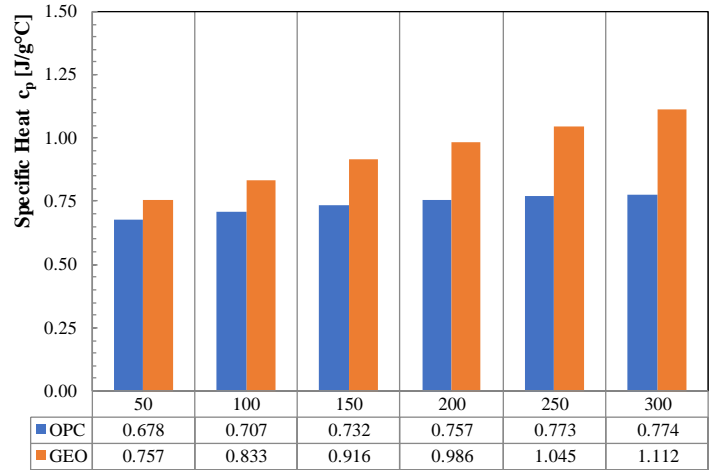


Figure 2: Specific heat of OPC pastes and GEO pastes for several Temp = 50, 100, 150, 200, 250 and 300 °C.

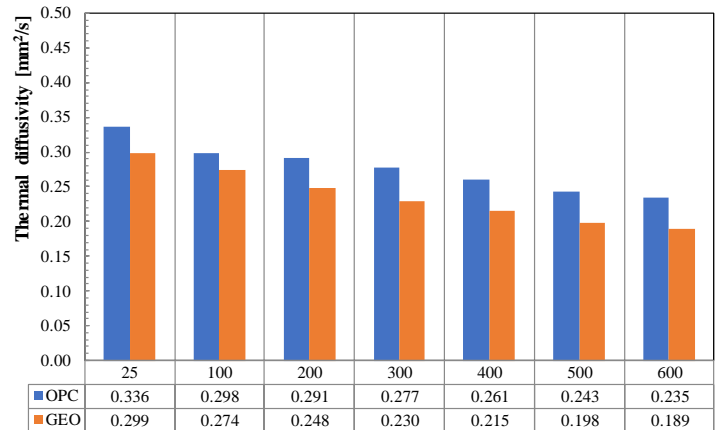


Figure 3: Thermal diffusivities of OPC pastes and GEO pastes for several Temp = 25, 100, 200, 300, 400, 500 and 600 °C.

3. Atomistic modelling and nanoscale description

3.1. Atomistic structures

This section is paying the attention to CSH and NASH structures, considered as the key ingredients of OPC and geopolymer-based cement pastes, respectively.

On the one hand, the structure of CSH is developed according to the procedure described by Qomi et al. [27], based on an improvement of the original procedure proposed by Pellenq et al. [32]. In this context, the structure of Tobermorite 14 Å (with C/S=0.83) is taken as the starting point (see Figure 4-a), modifying its structure by

firstly removing the water molecules (see Figure 4-b). Afterwards, some bridging silicate groups are also randomly removed to get the targeted C/S ratio. Finally, to avoid charge unbalances and get the right water content, some Ca-ions and water molecules are randomly added into the inter-laminar space (see Figure 4-c). The built structure is finally equilibrated by performing an energy minimization and molecular dynamics simulations with the Reactive Force Field (ReaxFF) by Van Duin et al. [33]. Details of ReaxFF can be found in Duque Redondo [34]. Present study focuses on the C/S=1.7, which is the average value found in C-S-H gel. The chosen C-S-H configuration actually corresponds to a very large system (a orthogonal cell with sizes a=26.08 Å, b=30.84 Å and c=25.88 Å) and whose exact stoichiometry is $(CaO)_{254}(SiO_2)_{152}(H_2O)_{306}$.

On the other hand, a realistic NASH model has been constructed following a protocol akin to the one recently proposed by Lolli et al. [35]. In particular, the starting structure has been the experimental sodalite ($Na_8[Al_6Si_6O_{24}]Cl_2$), a structure given by Hassan et al. [36] (see Figure 5-a), to which it has been replaced the Cl atom with an hydroxyl ion (see Figure 5-b). Afterwards, the Gran Canonical Monte Carlo (GCMC) protocol has been applied to introduce water into its structure (see Figure 5-c). As result, the final structure turned to be $(Na_2O)_4(Al_2O_3)_3(SiO_2)_6(H_2O)_{10}$.

3.2. Optimization and relaxation of the structures

The GULP code [37] is used to perform the atomistic calculations. In this approach, the initial structures are optimized to the local energy values that minimise lattice energy, while allowing cell parameters and atomic positions to vary. A quasi-Newton-Raphson minimisation procedure, i.e. an update of the Hessian variation on the Broyden-Fletcher-Goldfarb-Shannon scheme, is employed. In the case of NASH structure, the GCMC protocol uses a chemical potential of -0.082eV. The used force field has been the implementation based on Manzano et al. [38] for the ReaxFF. The obtained lattice constants of the CSH and NASH structure can be found in Table 3.

Table 3: Stoichiometry and Lattice constants of the studied CSH and NASH structures.

	CSH	NASH
Composition	$(CaO)_{254}(SiO_2)_{152}(H_2O)_{306}$	$(Na_2O)_4(Al_2O_3)_3(SiO_2)_6(H_2O)_{10}$
a (Å)	26.08	9.53
b (Å)	30.84	9.06
c (Å)	25.88	9.05
α (°)	90.00	92.12
β (°)	90.00	90.79
γ (°)	90.00	88.45

3.3. Thermal properties

The heat capacity $((C)_V)$ can be directly extracted from GULP by its definition

$$(C)_V = \left(\frac{\partial U_{\text{vib}}}{\partial T} \right)_V \quad (1)$$

where

$$U_{\text{vib}} = \int_0^\infty \hbar\omega \left(n(\omega) + \frac{1}{2} \right) d\omega \quad (2)$$

and by plugging the computed VDOS, $g(\omega)$, into $n(\omega) = g(\omega)f_{BE}(\omega)$, where

$$f_{BE}(\omega) = \left(e^{-\hbar\omega/k_B T} - 1 \right)^{-1} \quad (3)$$

the latter being the so-called Bose-Einstein probability distribution, while $\hbar\omega$ is the phonon energy, \hbar is the reduced Planck's constant, and k_B is the Boltzmann constant.

The thermal conductivity of cement/binder-based materials has been obtained within the framework of lattice dynamics, where the thermal conductivity reads as shown in the following equation

$$k = \frac{1}{V} \sum_i^{\text{modes}} C_i(T) D_i \quad (4)$$

being V the cell volume, $C_i(T)$ the heat capacity of the mode i at temperature T , and D_i the mode diffusivity. While accurate results can be obtained by solving the so-called Boltzmann transport equations for phonons, this work will resort to the Allen-Feldman theory [39], as it provides reasonable good values at much lower computational costs.

In this model the thermal conductivity is decomposed in two terms, the contribution of the diffusive modes (diffusons) and of propagating modes (propagons). While the first term (namely, diffusive one) can be computed in its totality, the second contribution (i.e., propagating contribution) is only computed above a cut-off frequency, being the low frequency contribution approximated by analytic formulae that describe the quadratic nature of the density of states as it tends to zero frequency.

As previously done by Zhou et al. [18] and Dolado [30], an appropriate cut-off frequency has been taken. Educated values around 3 THz were taken for both the CSH and NASH gels. Moreover, and to avoid size effects when accounting for the low frequency contributions, big simulations cells have been employed ($1 \times 1 \times 1$ and $2 \times 2 \times 1$ supercells for CSH and NASH, respectively).

4. Atomistic results and discussion

4.1. Heat capacity

In the Figure 6, the specific heat capacities of CSH and NASH structures are plotted as functions of the temperature. It can be seen that the simulated specific heat capacities of NASH phase exceeds those found for CSH phase,

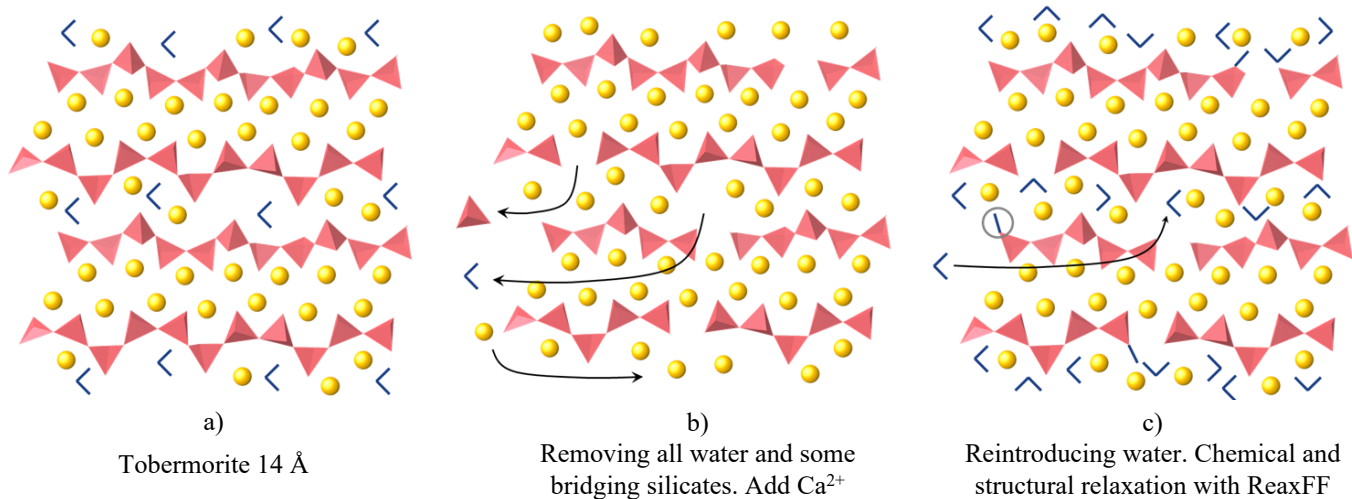


Figure 4: The structure of CSH.

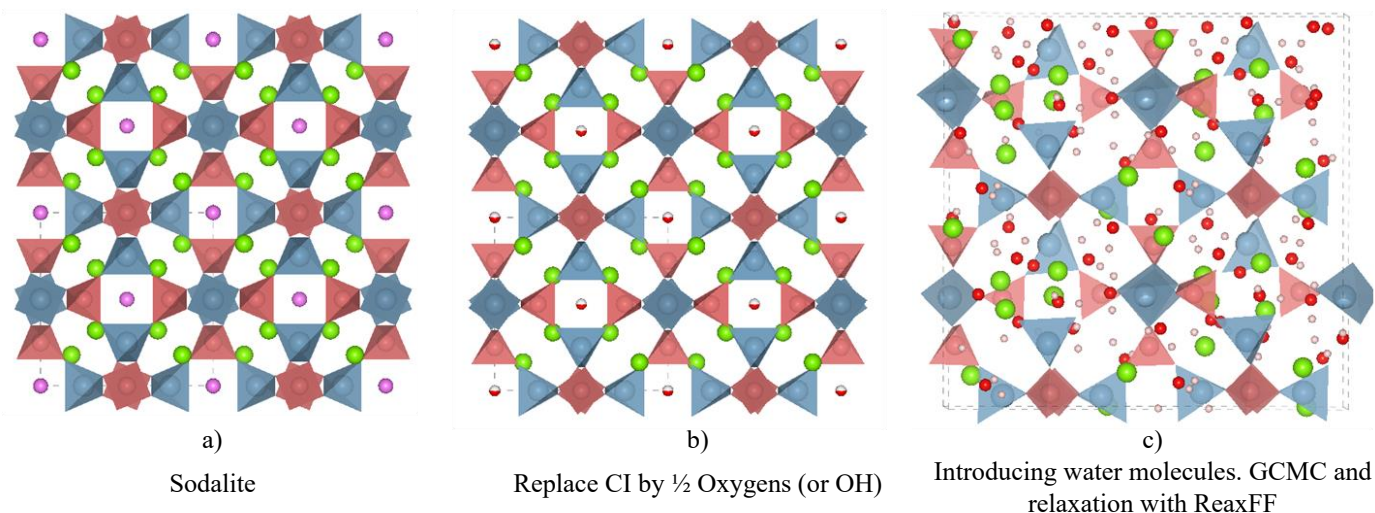


Figure 5: The structure of NASH.

capturing well the trend observed in the experimental values measured over OPC and GEO pastes, respectively (i.e., as in Figure 2). This result can be explained in terms of the larger content of water that the NASH structure can host in comparison to the CSH phase. It is also worth noting that for a better comparison against the experimental values, the effect of the porosity together with the rest of the cementitious phases, present in the hydrated pastes, should be included in the simulations.

4.2. Thermal diffusivity

The thermal diffusivity λ is defined according to the following equation

$$\lambda = \frac{k}{\rho c_p} \quad (5)$$

being k the conductivity [$W/(m \times K)$], ρ is the density [g/m^3], and c_p is the specific heat [$J/(K \times g)$].

Firstly, the thermal diffusivities of CSH and NASH phases, arising from the atomistic simulations, are shown in Figure 7. It can be observed that temperature changes do not sustainably affect the diffusivity, showing only a slight decrease as long as the temperature raises. Moreover, as expected, the thermal diffusivities for the NASH phase are lower than those for the CSH. As a rule of the thumb, the higher the heat capacity the lower the thermal conductivity and vice-versa.

5. Jumping between atomistic simulations and the meso/macro scale

5.1. Proposed approach

Information regarding the main phases of OPC and GEO pastes (i.e., CSH and NASH, respectively), it is desirable to find other phases (including voids and humidity) that allow to upscale, from the atomistic simulations

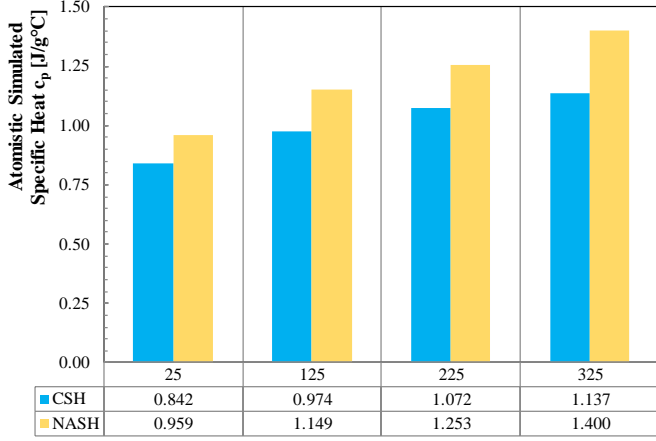


Figure 6: Specific heat of CSH and NASH obtained through atomistic simulations for several Temp = 25, 125, 225 and 325 °C.

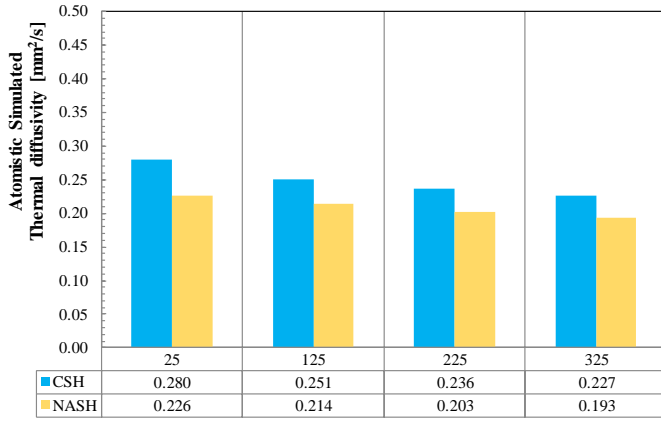


Figure 7: Thermal diffusivities of CSH and NASH obtained through atomistic simulations for several Temp = 25, 125, 225 and 325 °C.

properties to the experimental macro ones, i.e., the effective diffusivity and specific heat capacity obtained by the experimental procedures explained before.

In this sense, an optimization procedure is proposed to match the experimental data with some analytical model. It mainly consists in a iterative process to find a “second generic” phase that best matches simultaneously the experimental diffusivity and specific heat. Recourse is made to the simple mixture law [40], to calculate the effective heat capacity per unit volume, while the Maxwell model [41, 42] is used to calculate the effective thermal conductivity, and with that, the thermal diffusivity. Further, Genetic Algorithms (GAs) are used to solve the optimization problem.

5.2. Mixture law model

Under the assumption of no chemical interaction between the components, the effective specific heat of the OPC and GEO pastes can be determined as

$$c_{p\text{eff}}^{\text{OPC}} = c_p^{\text{CSH}}(1 - \theta^{2\text{pOPC}}) + c_p^{2\text{pOPC}}\theta^{2\text{pOPC}} \quad (6)$$

and

$$c_{p\text{eff}}^{\text{GEO}} = c_p^{\text{NASH}}(1 - \theta^{2\text{pGEO}}) + c_p^{2\text{pGEO}}\theta^{2\text{pGEO}}, \quad (7)$$

respectively, where the superscript 2pOPC and 2pGEO correspond to the second generic phases that conform the OPC and GEO pastes, while θ represent the mass fraction of these phases.

Since the optimization procedure deals with determining the thermal diffusivity, it is convenient to work in terms of effective heat capacities, and consequently the mixture rule is based on volumetric fractions of each phase. Hence, they can be calculated as

$$C_{\text{eff}}^{\text{OPC}} = \rho c_p^{\text{CSH}}(1 - \phi^{2\text{pOPC}}) + \rho c_p^{2\text{pOPC}}\phi^{2\text{pOPC}} \quad (8)$$

and

$$C_{\text{eff}}^{\text{GEO}} = \rho c_p^{\text{NASH}}(1 - \phi^{2\text{pGEO}}) + \rho c_p^{2\text{pGEO}}\phi^{2\text{pGEO}}, \quad (9)$$

for OPC and GEO pastes, respectively; ϕ represents the volumetric fraction of the second phases.

Following the same idea, it is also possible to determine the effective density of the composites, i.e.,

$$\rho_{\text{eff}}^{\text{OPC}} = \rho^{\text{CSH}}(1 - \phi^{2\text{pOPC}}) + \rho^{2\text{pOPC}}\phi^{2\text{pOPC}}, \quad (10)$$

and

$$\rho_{\text{eff}}^{\text{GEO}} = \rho^{\text{NASH}}(1 - \phi^{2\text{pGEO}}) + \rho^{2\text{pGEO}}\phi^{2\text{pGEO}}. \quad (11)$$

By combining Eqs. (8), (9), (10) and (11), respectively, it is possible to obtain a new expression for the specific heat in terms of volumetric fraction of the second phase, such as

$$c_{p\text{eff}}^{\text{OPC}} = \frac{C_{\text{eff}}^{\text{OPC}}}{\rho_{\text{eff}}^{\text{OPC}}}, \quad (12)$$

and

$$c_{p\text{eff}}^{\text{GEO}} = \frac{C_{\text{eff}}^{\text{GEO}}}{\rho_{\text{eff}}^{\text{GEO}}}. \quad (13)$$

5.3. Maxwell model

Under the same previous assumption of no interaction between components, and considering that the second phase is embedded as spherical particles in a matrix of either CSH or NASH, the effective thermal conductivity can be determined by using the Maxwell model for composite materials, i.e.,

$$k_{\text{eff}}^{\text{OPC}} = k^{\text{CSH}} \left[1 + \frac{3\phi^{2\text{pOPC}}}{\left(\frac{k^{2\text{pOPC}} + 2k^{\text{CSH}}}{k^{2\text{pOPC}} - k^{\text{CSH}}} \right) - \phi^{2\text{pOPC}}} \right] \quad (14)$$

and

$$k_{\text{eff}}^{\text{GEO}} = k^{\text{NASH}} \left[1 + \frac{3\phi^{2\text{pGEO}}}{\left(\frac{k^{2\text{pGEO}} + 2k^{\text{NASH}}}{k^{2\text{pGEO}} - k^{\text{NASH}}} \right) - \phi^{2\text{pGEO}}} \right]. \quad (15)$$

These equations are only valid for volumetric fraction values less than 0.25 [42].

Once the effective heat capacity and thermal conductivity are determined, it is possible to calculate the corresponding effective thermal diffusivity of OPC and GEO composites as

$$\lambda_{\text{eff}}^{\text{OPC}} = \frac{k_{\text{eff}}^{\text{OPC}}}{C_{\text{eff}}^{\text{OPC}}}$$

and

$$\lambda_{\text{eff}}^{\text{GEO}} = \frac{k_{\text{eff}}^{\text{GEO}}}{C_{\text{eff}}^{\text{GEO}}}. \quad (17)$$

5.4. Optimization problem

In order to obtain the thermal properties of the second phases, the following constrained optimization problem is solved to minimize the error between the experimental data and the results from the previously defined analytical models, i.e.,

$$\min f(\mathbf{x}) \quad (18)$$

$$\text{subject to } \mathbf{Ax} \leq \mathbf{b} \quad (19)$$

$$\mathbf{A}_{\text{eq}}\mathbf{x} = \mathbf{b}_{\text{eq}}, \quad (20)$$

$$\mathbf{l}_b \leq \mathbf{x} \leq \mathbf{u}_b, \quad (21)$$

where f is the function to be minimized, \mathbf{x} is the vector of design variables, \mathbf{A} and \mathbf{b} are the matrix and vector of inequality constraints, \mathbf{A}_{eq} and \mathbf{b}_{eq} the matrix and vector of equality constraints, and \mathbf{l}_b and \mathbf{u}_b the vectors defining the lower and upper bounds of the box constraints, all to be explained below.

5.4.1. Design variables

The vector \mathbf{x} is in turn composed of three other vectors containing the thermal conductivity, the specific heat and density, and a scalar defining the volumetric fraction, all representative of the second generic phase, i.e.,

$$\mathbf{x} = [\mathbf{k} \ \mathbf{c}_p \ \rho \ \phi]^T. \quad (22)$$

being T the transpose vector operator.

The lengths of \mathbf{k} , \mathbf{c}_p and ρ can be selected at will, and depend on the quantity of data to be matched. In the current case, it is desired to match the thermal diffusivity and specific heat (of either OPC or GEO) at four different temperatures, $T_{\text{eval}} = [25 \ 125 \ 225 \ 325]^T$ expressed in degrees Celsius. By this way, the vector of design variables for the current case of analysis has a length of 13 values and stands as

$$\mathbf{x} = [k^{25}, \dots, k^{325}, c_p^{25}, \dots, c_p^{325}, \rho^{25}, \dots, \rho^{325}, \phi]^T. \quad (23)$$

5.4.2. Objective function

The objective function measures the error between, the calculated effective diffusivity and specific heat (i.e., from either OPC or GEO), and the corresponding experimental values (exp), at the four previously defined temperatures, i.e.,

$$f = \left\{ \sum_{i=1}^N \frac{0.5}{N} \times \left[\left(\frac{\lambda_{\text{exp}}^{(i)} - \lambda_{\text{eff}}^{(i)}}{\lambda_{\text{exp}}^{(i)}} \right)^2 + \left(\frac{c_{p\text{exp}}^{(i)} - c_{p\text{eff}}^{(i)}}{c_{p\text{exp}}^{(i)}} \right)^2 \right] \right\}^{1/2}, \quad (24)$$

where the superscript (i) indicates the temperature at which each property is calculated or measured, i.e., the index of vector T_{eval} . The length of this vector is thus equal to four, being $N = 4$.

5.4.3. Inequality constraints

These constraints are defined in order to guarantee that k and c_p of the second phase increase (or stay constant) under temperature rises, which means that

$$k^{25} \leq k^{125} \leq k^{225} \leq k^{325}, \quad (25)$$

and

$$c_p^{25} \leq c_p^{125} \leq c_p^{225} \leq c_p^{325}. \quad (26)$$

This hypothesis is based in assuming that properties of the second phase behave like the ones of the CSH and NASH phases (see c_p increasing with temperature in Figure 6). The latter can be imposed by defining the matrix \mathbf{A} and vector \mathbf{b} (i.e., Eq. (19)) as

$$\mathbf{A} = \begin{bmatrix} 1 & -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & -1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 1 & -1 & 0 & 0 & 0 & 0 & 0 \end{bmatrix},$$

and

$$\mathbf{b} = [0 \ 0 \ 0 \ 0 \ 0 \ 0]^T.$$

5.4.4. Equality constraints

In this case, the constraints guarantee that the density of the second phase stays constant with changes in the temperature, i.e.,

$$\rho^{25} = \rho^{125} = \rho^{225} = \rho^{325}. \quad (27)$$

To do so, it is defined the matrix \mathbf{A}_{eq} and the vector \mathbf{b}_{eq} of Eq. (20) as

$$\mathbf{A}_{\text{eq}} = \begin{bmatrix} 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & -1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & -1 & 0 \end{bmatrix},$$

$$\mathbf{b}_{\text{eq}} = [0 \ 0 \ 0]^T,$$

respectively.

5.4.5. Box constraints

These are defined so the search of the second phase conducts to physical-sound results, i.e., close to typical phase values that can be found for either OPC or GEO pastes. In the case of thermal conductivity, close values to the thermal conductivity (in $W/(m \times K)$) of air and $\beta-C_2S$ (belite [27]) are used for the lower and upper bounds, respectively. For the specific heat (in $J/(kg \times K)$), close values to those of C_3S (alite [27]) and water. For the density (in kg/m^3), those again of water and alite. Finally, for the volumetric fraction, it is adopted a minimum value of 0.05 and a maximum one of 0.30. Based on this assumption, the vectors for the lower and upper bounds are given as

$$\mathbf{l}_b = [0.026, \dots, 0.026, 680, \dots, 680, 1000, \dots, 1000, 0.05]^T,$$

and

$$\mathbf{u}_b = [3.5, \dots, 3.5, 4182, \dots, 4182, 3600, \dots, 3600, 0.30]^T,$$

respective, with a length of 13 values.

5.4.6. Optimization solver

In order to solve the optimization problem (Eqs. (19)-(21)) recourse is made to GAs, which have proven to be robust in solving optimization problems with non-linear objective functions, as it is the case of Eq. (24). For its implementation, it is used the algorithm developed by Deep et al. [43].

For the setting of GAs, the parameters in Table 4 were selected.

Table 4: GA algorithm settings.

Parameter	Value
Number of individuals	200
Number of generations	10000
Elite individuals	5%
Selection	Stochastic universal sampling
Crossover method	Scattered
Crossover probability	80%
Mutation method	Adaptive

5.5. Results of the proposed approach

The results of the optimization procedure for the OPC and GEO pastes are those detailed in the Tables 5 and 6, respectively. These second phases are representative of homogenized (smeared) thermal properties of a multi-phase system that could be composed by a blend of alite (C_3S), water and air for the OPC pastes, and a blend of calcium silicate hydrate (CSH), water and air for the GEO pastes. With those values it is possible to determine the thermal diffusivity of OPC and GEO pastes by using Eqs. (16) and (17), respectively. As it is depicted in Figures 8 and 9, the properties of the second generic phases conduct to results that match the experimental data with low error, for both OPC and GEO.

Table 5: Parameters arising from the GA optimization procedure for OPC pastes.

2 nd phase for OPC modelling			
Temp [°C]	k [W/(m·K)]	c_p [J/(g·°C)]	Density [Kg/m ³]
25	0.650	0.681	1883.660
125	0.650	0.681	
225	0.660	0.681	
325	0.660	0.681	

Table 6: Parameters arising from the GA optimization procedure for GEO pastes.

2 nd phase for GEO modelling			
Temp [°C]	k [W/(m·K)]	c_p [J/(g·°C)]	Density [Kg/m ³]
25	0.530	0.680	1165.250
125	0.530	0.680	
225	0.530	0.680	
325	0.530	0.681	

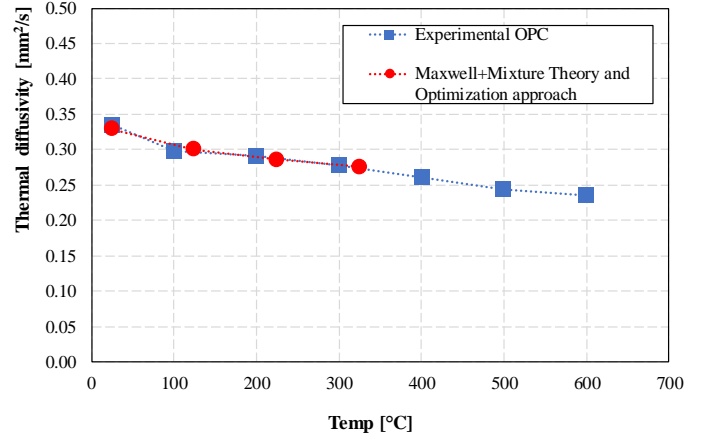


Figure 8: Thermal diffusivity of OPC: experimental data vs. proposed analytical approach.

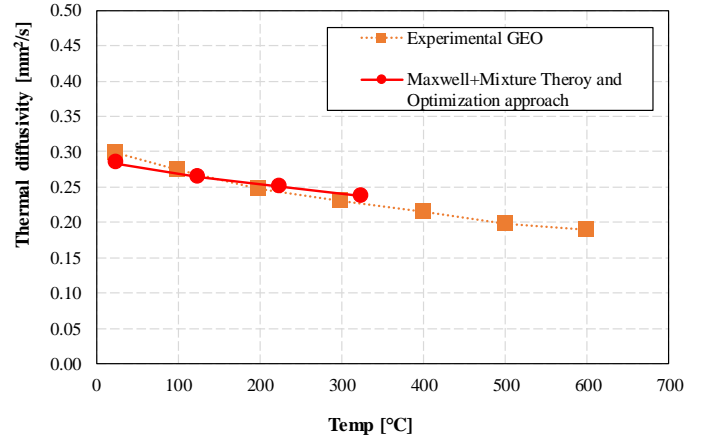


Figure 9: Thermal diffusivity of GEO: experimental data vs. proposed analytical approach.

Regarding the specific heat, it is possible to calculate it by using Eqs. (12) and (13). As it is clearly shown in Figures 10 and 11, the temperature dependency trends and the predicted specific heats are quite good. However, the proposed approach do not exactly match the experimental data. One of the reasons of this could be that the CSH (or NASH for GEO) presented in the hydrated OPC (or H-cement for GEO) could be different from the one obtained by atomistic simulations. Also, it can be noticed that the specific heat of the OPC (or H-cement for GEO) is much lower than the corresponding one of CSH (NASH), which means that the second generic phase must have a lower specific heat than the OPC (or H-cement for GEO). The latter is directly deducted from the mixture laws of Eqs. (6) and (7), and explains why the optimization procedure, in both cases, leads to results that are close (almost equal) to the lower bounds of the specific heat box constraints.

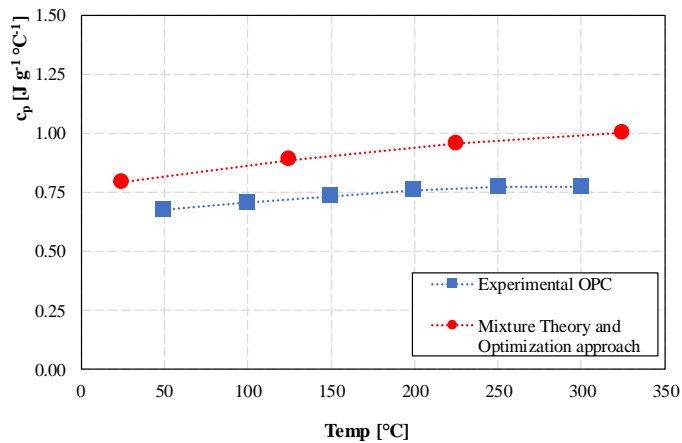


Figure 10: Specific heat of OPC: experimental data vs. proposed approach.

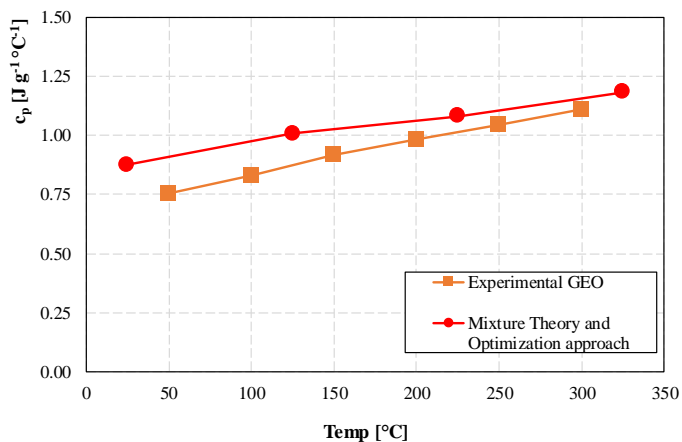


Figure 11: Specific heat of GEO: experimental data vs. proposed approach.

6. Computational homogenization at the macro-scale

Assumptions and validations of Section 5 are based on the mixture law and Maxwell model. However their soundness and accuracy must be tested, not only against experimental data, but also against more accurate methods based on the homogenization of the effective thermal properties. Regarding the mixture law, it is proven to be an appropriate method for obtaining properties like the effective heat capacity. On the contrary, in the case of the thermal conductivity, the Maxwell model is only valid for volumetric fractions lower than 0.25. As the results of the optimization procedure give values of 0.30 for the volumetric fraction, recourse is made to the Finite Element (FE)-based homogenization technique to obtain the effective thermal conductivity of OPC and GEO pastes, respectively.

By using an ad-hoc code in Matlab, the FE mesh of the representative volume element (RVE) of OPC and GEO pastes is generated. Inside the domain, 50 spheres defining the second phases are randomly distributed. Considering an unitary value for the diameter of these spheres, the size of the RVE is iteratively adjusted in order to match the desired volumetric fraction of the inclusions. Figure 12 depicts the RVE characterizing the micro-structure of either OPC or GEO pastes, showing the second phases in red and the matrix (either CSH or NASH phase) in gray.

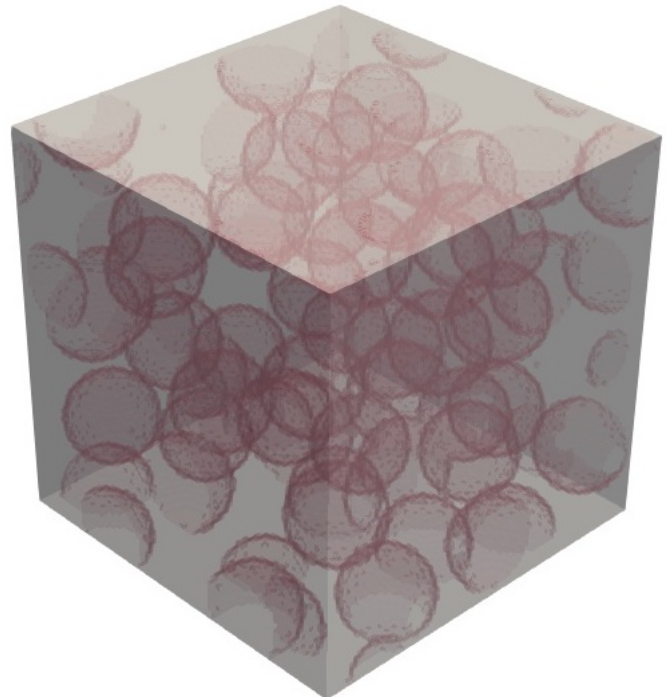


Figure 12: Representative volume element of either OPC or GEO pastes. Red spheres represent the second generic phase embedded in a matrix of CSH or NASH. The volumetric fraction of the second phase is 0.30.

The computation homogenization methodology pro-

posed by Yvonnet [44] is used to compute the effective thermal conductivity of the paste whose microstructure is defined by the RVE shown in Figure 12. Taken this RVE as the domain of analysis Ω , the temperature $\mathbf{T}^{(i)}$ in all the nodes $\mathbf{x}_j \in \Omega$ under a prescribed macroscopic temperature gradient $\mathbf{G}^{(i)} = \mathbf{e}_i$ (where \mathbf{e}_i , $i = 1, 2, 3$ is a canonical vector) is determined by solving the discretized heat conduction equation

$$\mathbf{K}\mathbf{T}^{(i)} = \mathbf{0} \quad (28)$$

subject to the periodic boundary conditions

$$T_{\alpha}^{(i)} - T_{\beta}^{(i)} = \mathbf{G}^{(i)} \cdot (\mathbf{x}_{\alpha} - \mathbf{x}_{\beta}) \quad (29)$$

where \mathbf{K} is the global conductivity matrix, and $(\mathbf{x}_{\alpha}, \mathbf{x}_{\beta})$ stands for each couple of opposite boundary nodes.

Once $\mathbf{T}^{(1)}$, $\mathbf{T}^{(2)}$, and $\mathbf{T}^{(3)}$ are known, the effective thermal conductivity tensor $\bar{\mathbf{k}}$ is defined by:

$$\bar{\mathbf{k}} = \frac{1}{|\Omega|} \int_{\Omega} \mathbf{k}_{\mu} \mathbf{B} \begin{bmatrix} \mathbf{T}^{(1)} & \mathbf{T}^{(2)} & \mathbf{T}^{(3)} \end{bmatrix} d\Omega, \quad (30)$$

where \mathbf{k}_{μ} is the microscopic thermal conductivity in the RVE, and $B_{ij} = \partial N_j / \partial x_i$, such that $\mathbf{B}\mathbf{T} = \nabla T$.

Since the observed anisotropy in the analyzed examples of OPC and GEO pastes is low, it is defined an effective isotropic (scalar) thermal conductivity as

$$k_{\text{eff}} = \frac{\bar{k}_{11} + \bar{k}_{22} + \bar{k}_{33}}{3}. \quad (31)$$

Now, the effective thermal conductivities of OPC and GEO pastes are calculated for the different temperatures, and the results are depicted in Figures 13 and 14 for OPC and GEO, respectively. As it can be appreciated, the results perfectly match with a extremely low scatter the results from the Maxwell models, confirming that the latter approach can be considered appropriate for the determination of the properties of second phases in OPC and GEO, as well as for the determination of the homogenized thermal energy storage properties of the composites under consideration.

7. Concluding remarks

In this work recent progresses on the atomistic description of the thermal properties of cementitious materials, along with some of the concomitant experimental analyses, have been reported. Particularly, two hydrated pastes were investigated, such as a ordinary Portland cement (OPC), and a hybrid cement (an alternative binder called H-Cement) employed for a geopolymer-based paste (GEO).

Based on the achievements and results arising from this work, the following conclusions can be itemized:

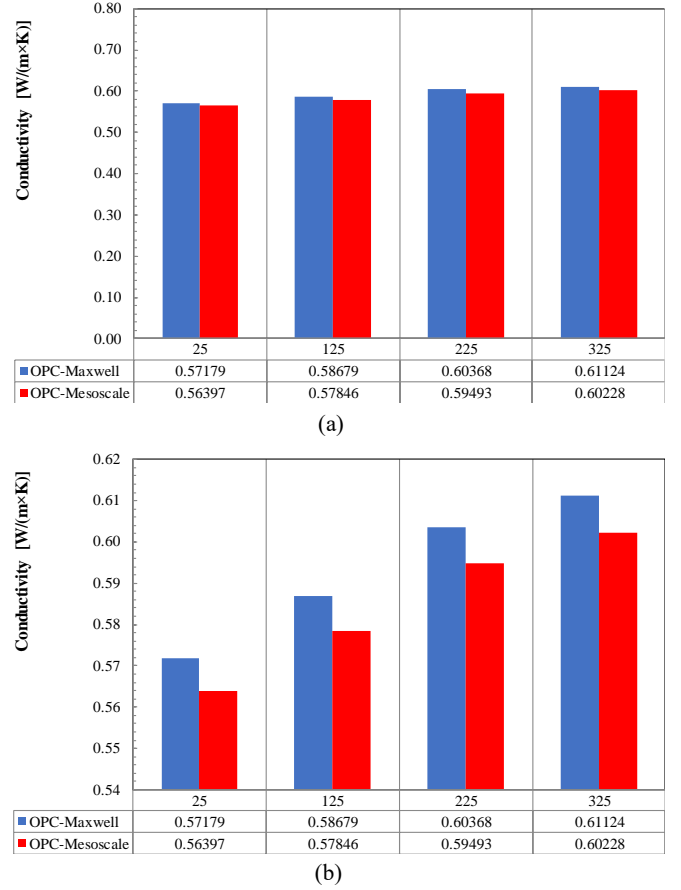


Figure 13: Conductivity of OPC: (a) experimental data vs. meso-scale FEM simulation and (b) zoom view.

- The thermal response of hydrated pastes depends on the thermal activation of vibrational states. In this context, analytical models, like the Debye model, can provide simple descriptions of the vibrations of a solid, though quite satisfactory for (poly)crystalline materials at the low temperature limit (i.e., values much lower than the well-known Debye Temperature). However, complex amorphous materials (like CSH and NASH gels) require a more accurate description that is only attainable via atomistic simulations, as shown in this work.
- Heat capacity of CSH and NASH structures have been thus atomistically calculated in a range of temperatures ranging from room temperature to 600K. Energy minimization and molecular dynamics simulations, by adopting the Reactive Force Field, were performed to regulate the aforementioned structure.
- The atomistic simulations well captured the trend observed in the related experiments, in both over OPC and GEO pastes as well. On the one hand, the heat capacity values increase with the rise of the temperature. On the other hand, the NASH structure seems to be able to absorb more heat than the CSH phase.

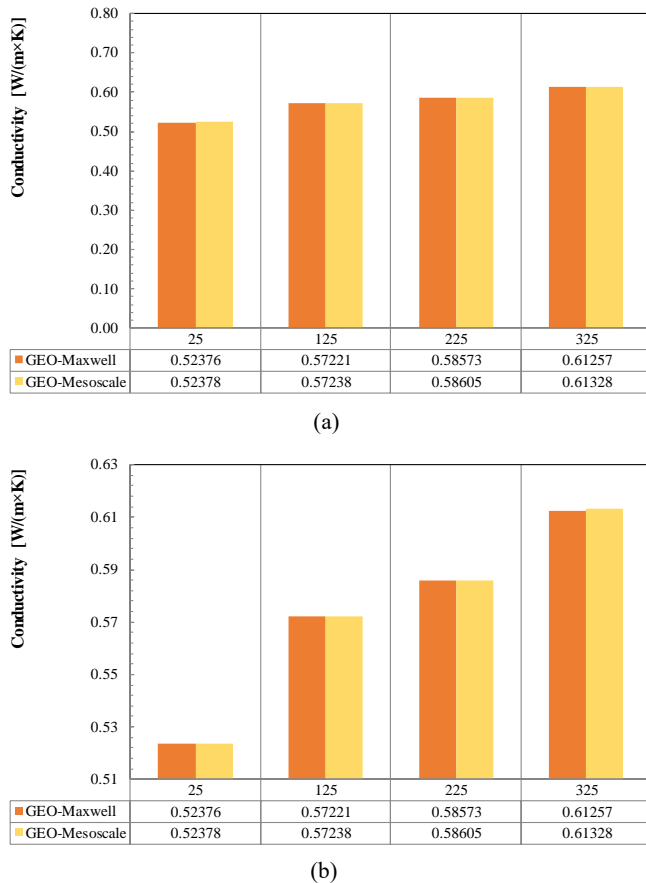


Figure 14: Specific heat of GEO: (a) experimental data vs. meso-scale FEM simulation and (b) zoom view.

- By modelling also the thermal diffusivity, it can be stated that the atomistic simulations reproduce quite well the slight decrease of this thermal variable as a function of the temperature. Besides, and contrary to what happened with the specific heat capacities, the thermal diffusivities of CSH (and OPC pastes) are larger than those found in the NASH (and GEO pastes). Finally, in spite of the crude undertaken approximations, the simulations provide reasonable comparisons with the experimental values.
- Analytical up-scaling (i.e., by employing the mixture theory for c_p and $\rho \times c_p$ and Maxwell rules for k) and numerical tools (based on meso-scale FEM homogenization) were proposed to link the thermal energy storage parameters of the atomistic phases of OPC and GEO pastes with the homogenized meso/macro scale values.

Future research on this topic should explore, in deep detail, the impact of other phases together with voids and water content on the vibrational modes and phonon thermal properties of general binder-based composites. It is the ambition of the authors to make use of vibration of phonons, atomistic-to-building scale simulations and

meta-optimization tools to achieve nearly-zero conductive media and to use them in designing thermal diodes.

Acknowledgments

This work has been carried out under the umbrella of the Transborder laboratory LTC Green Concrete (<https://greenconcretelab.com>). We acknowledge the computing resources of the Donostia International Physics Center (DIPC). We also acknowledge the financial supports of: i) the grant RTI2018-098554-B-I00 of ECRETE project, funded by MCIN/AEI/10.13039/501100011033 and by "ERDF A way of making Europe"; ii) the grant PCI2019-103657 of POROCM project, funded by MCIN/AEI/10.13039/501100011033 and co-funded by the European Commission; iii) the European Union's Horizon 2020 research and innovation program under the grant agreement No: 870114; iv) the National Scientific and Technical Research Council (CONICET) of Argentina through the project "Computational design of functional thermal metamaterials in transient regime taking advantage of phase changes" (PIP 11220200101018CO), v) the National Agency for the Promotion of Research, Technological Development and Innovation (AGENCIA) of Argentina through the project "Computational design of metamaterials applied to the development of thermal diodes for building envelopes" (PICT 2020 SERIE A 03765), vi) the National Technological University (UTN) of Argentina, through the grant PID MAUTNFE0007745, and vii) the Technical University of Darmstadt for the "Future Talent (Guest Stay)" and "Career Bridging" Grants, both given to the second author of this work.

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