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# Multiscale estimation of the thermal properties of cement-based materials at early-age

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**ABSTRACT:** The prediction of the thermal response of concrete structures depends on the adequate determination of the thermal properties of concrete. Especially at early-age, these properties depend on the evolution of the microstructure and the multiscale character of cement-based materials. In this paper, heat capacity, thermal conductivity and coefficient of thermal expansion (CTE) are estimated by means of analytical homogenization techniques from the composition of the material. Mori-Tanaka and Generalized Self-consistent schemes are combined to represent cement paste, interface transition zone (ITZ), mortar and concrete microstructures. The evolution of the clinker and hydrates phases are accounted for at the cement paste scale. At the mortar scale, the ITZ is considered. Finally, concrete effective properties are obtained. CTE is estimated within an ageing linear viscoelasticity framework. The estimations are compared to the final values obtained experimentally in previous tests.

## 1 INTRODUCTION

The prediction of the thermal response of concrete structure depends on the adequate determination of the thermal properties of concrete. Heat capacity, thermal conductivity and coefficient of thermal expansion (CTE) are particularly important in the determination of the early-age behaviour (Bentz, 2008). These properties evolve at early age with the changes in the microstructure of the cement-based materials. Generally this aspect is not explicitly taken into account in simulations or even experimentally. However, different authors report an impact of the variation of these properties on the structural response. For instance, Briffaut et al. (2012) performed simulations, at the structure level, in which the heat capacity and the thermal conductivity evolved with respect to the degree of hydration. In their simulation the evolution of the heat capacity impacted the stress response more strongly than the evolution of the thermal conductivity. Lura and van Breugel (2001) reported that a given variation of the heat capacity may lead to a variation of the same order in the computed temperatures and stresses. These authors also communicated that up to 5% of variation in the thermal conductivity, an almost negligible effect is observed on the temperature and stress responses, and that the CTE affects actively the thermo-chemo-mechanical response. On the other hand, Hilaire (2014) reported a not very strong impact of the CTE evolution on the mechanical response at early-age.

These thermal properties depend on different factors including the type of aggregate, the temperature, the water content and the age of the material (Bentz, 2007; Cruz and Gillen, 1980; Hansen et al., 1982; Lura and Van Breugel, 2001; Marshall, 1972; Morabito, 2001). At early-age, due to hydration processes, the thermal properties are expected to evolve as a function of the extent of hydration. For instance, Hansen et al. (1982) reported a decrease of thermal conductivity from 0.88 to 0.78 W.m.K during hydration of rapid hardening Portland cement, w/c=0.5 at T = 30 °C, while Mounanga (2003) obtained an increase.

Despite the importance of such properties in the early-age analysis, there is a lack of experimental data especially concerning the hydration products. Experimental difficulties to measure these properties include their moisture dependence and the fact that heat sources provoke moisture gradients (Marshall, 1972). This aspect highlights the importance of modeling approaches to determine the thermal properties.

In this paper, we propose a multiscale estimation of the thermal conductivity, heat capacity and CTE at early age based on homogenization theory. The representation of the microstructure is presented and the evolution of the volume fraction of products and reactants are obtained. In order to estimate the CTE, upscaling methods based on ageing linear viscoelasticity are employed following the ones developed previously to estimate mechanical properties (Honorio, 2015; Honorio et al., 2015; Sanahuja, 2013a).

In the following the properties of C-S-H are used for estimating the ones of the hydration products which are unknown. Thermal conductivity and CTE are considered as isotropic. No effects of convection and radiation are accounted for: gas and liquids are assumed transparent to radiation and the emitted radiation is considered as totally absorbed by the solid part. No temperature and jumps effects are considered either (Vargaftik, 1993). Additionally, we assume that a percolated structure exists at the different levels, which limits the scope of applicability of this work to periods after the solid percolation threshold.

## 2 MULTISCALE ESTIMATION OF THERMAL PROPERTIES

### 2.1 Representation of the microstructure

Analytical homogenization is used to estimate the properties at the cement paste up to concrete scale. We employ inclusions-matrix morphologies (Figure 1) to represent the [material from](#) hydration products up to concrete scale, as similarly proposed previously by e.g. (Bary and Béjaoui, 2006; Stora et al., 2009). At cement paste level (Level 1), the hydrating particle is embedded in a high density (HD) products layer (Level 0a) which is, in turn, embedded in a low density (LD) products layer (Level 0b). At mortar scale (Level 2), the sand particle is embedded in an ITZ layer (Level 0c) which is, in turn, embedded in a cement paste layer. At concrete scale (Level 3), the coarse aggregate is embedded in a mortar matrix, no ITZ is considered at this scale. The GSC scheme is used to obtain the homogenized properties of the cement paste, mortar and concrete. MT scheme is used to estimate the properties within each coat of the cement paste. The formulations of the schemes in ageing linear viscoelasticity are presented in (Honorio, 2015; Sanahuja, 2013a).

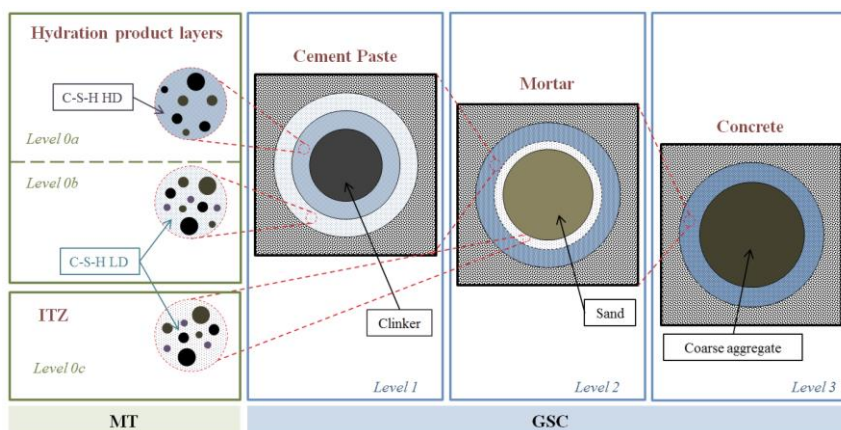


Figure 1 Multiscale representation of cement-based materials from C-S-H up to concrete scale.

The evolution of the volume fraction at the hydration products scale (Levels 0a, 0b and 0c) is obtained by means of a simplified model of hydration kinetics (Honorio et al., submitted) coupled with hydration balance equations (Tennis and Jennings, 2000). The evolutions of the volume fractions of the phases at the cement paste scale are shown in Figure 2.

The values of thermal properties used in the estimations are shown in Table1. [For air thermal conductivity, no convection and radiation effects are considered here. Further improvements in order to account for these effects are envisioned.](#)

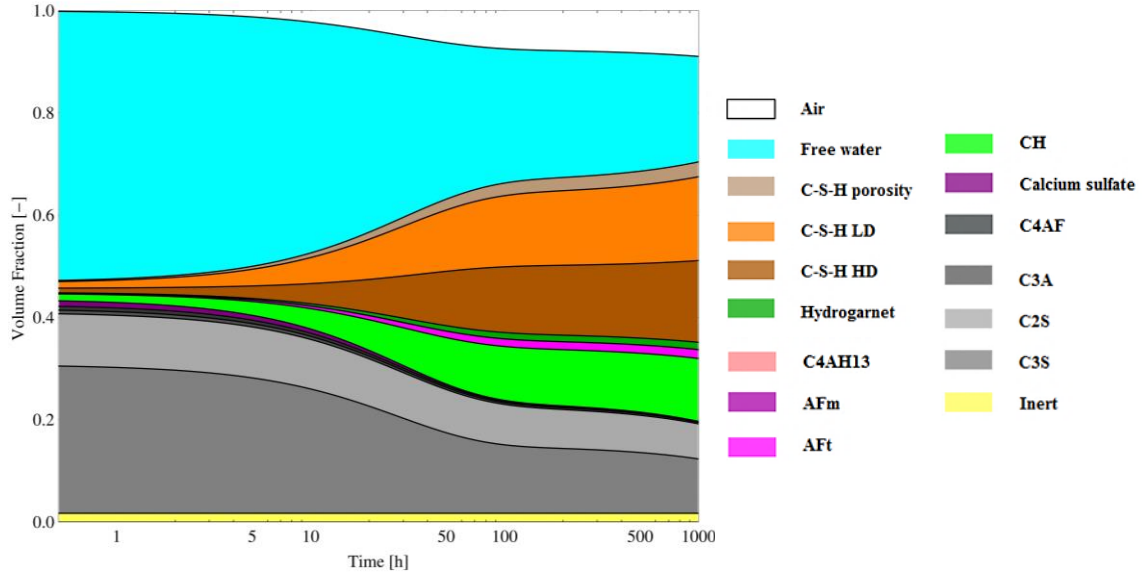


Figure 2 Evolution of volume fraction at cement paste scale, w/c = 0.4, cement composition as in (Craeye, 2010; Honorio, 2015).

Table 1. Thermal properties used in the simulations.

Compound	Specific heat [J/(kg.K)]	Thermal conductivity (volumetric) [W/m.K]	CTE $\times 10^{-6} [^{\circ}\text{C}^{-1}]$
Clinker	750 (1)	1.55 (1) (estimated)	45(4)
C-S-H HD and LD	920 (4)	0.98 (4)	45(4)
Gypsum	1080.4 (3)	0.66 (2)	-
Water	4183 (free water) (18)	0.604 (1)	300
Air	1005	0.025 (7)	3430
CH	1140 (4)	1.32 (4)	99.1 (4)
Limestone aggregates	908 (5)	3.15 (5)	10.2 (6)

(1)(Bentz, 2007) ; (2)(Cerny and Rovnanikova, 2002); (3)(Ukrainczyk and Matusinović, 2010); (4)(Abdolhosseini Qomi et al., 2015) (molecular simulations); (5) (Marshall, 1972); (6) (Wong and Brace, 1979); (7) (Holman, 2009)

## 2.2 Thermal conductivity

Mori-Tanaka estimations of the coefficient of thermal conductivity for a n-phase composite is given by (Benveniste, 1987):

$$\lambda^{MT} = \lambda_0 \left( 1 + 2 \sum_{r=1}^n \left( \frac{\lambda_r - 1}{\lambda_0} f_r^v \right) \right) / \left( 1 - \sum_{r=1}^n \left( \frac{\lambda_r - 1}{2 + \lambda_r} f_r^v \right) \right) \quad (1)$$

where  $\lambda_r$  is the thermal conductivity of the phase ( $r$ ); with  $r=0$  referring to the phase considered as the reference medium (matrix).

For spherical inclusions, it can be shown that MT solution coincides with the solution for a composite sphere embedded in an effective medium with volume fraction  $v_s$ , provided  $0 \leq f^v \leq 1$ . The 2-phases estimation is then given by (Benveniste, 1986):

$$\lambda^{2GSC} = \lambda_1 \frac{\lambda_2(1 + 2f_1^v) + 2\lambda_1(1 - f_1^v)}{(2 + f_1^v)\lambda_1 + \lambda_2(1 - f_1^v)} \quad (2)$$

The 3-phases estimation can be obtained by applying iteratively the 2-phases formula above.

### 2.3 Heat capacity

For small changes in strain and temperature in a thermoelastic n-phase composite, from the Helmholtz free energy it can be shown that the heat capacities at constant stress and strain, respectively, are given for an isotropic material (Chen et al., 2014):

$$\begin{aligned} \overline{C_p} &= \langle C_v \rangle + \frac{T_0}{\langle \rho \rangle} f(f_r^v, \alpha_r, k_r, \mu_r) \\ \overline{C_v} &= \langle C_v \rangle + \frac{T_0}{\langle \rho \rangle} g(f_r^v, \alpha_r, k_r, \mu_r) \end{aligned} \quad (3)$$

where  $\langle x \rangle = \frac{1}{V} \int_V x dV$  is the volume average operator,  $T_0$  is the reference temperature;  $\alpha_r, k_r$  and  $\mu_r$  are the coefficient of thermal expansion, bulk modulus and shear modulus, respectively, of phase ( $r$ ). For  $k_r, \mu_r \ll \langle C_v \rangle \langle \rho \rangle / \alpha_r$  as in the present case, we obtain:

$$\overline{C_p} \approx \langle C_v \rangle \approx \overline{C_v} \quad (4)$$

Multiscale approaches based on Rosen–Hashin bounds (Wyrzykowski and Lura, 2013) have been used to estimate the CTE of cement-based materials. Viscous aspects are generally not taken into account. The viscoelastic behaviour is itself generally sensitive to thermal aspects. But with the adoption of a thermorheologically simple behaviour of each one of the involved phases, the temperature dependence can be incorporated into the time-scale for viscoelastic response (e.g. Schapery, 1968).

### 2.4 CTE

Assuming perfect bonded phases, the CTE can be estimated by means of Levin (1967) equation:

$$\boldsymbol{\alpha}^{hom} = \sum_{p=1}^N (f_p^v \mathbb{A}_p^T \cdot \boldsymbol{\alpha}_p) \quad (5)$$

where  $\boldsymbol{\alpha}^{hom}$  is the homogenized tensor of thermal expansion which is directly connected to the strain localization tensor  $\mathbb{A}_p^T$  and the tensor of thermal expansion of phases  $\boldsymbol{\alpha}_p$ . This formula can be applied for both Mori-Tanaka and self-consistent schemes by adopting the corresponding localization tensor (Siboni and Benveniste, 1991).

In ageing linear viscoelasticity following Volterra correspondence principle (Salençon, 2009; Sanahuja, 2013a), we can write:

$$\boldsymbol{\alpha}^{hom} = \sum_{p=1}^N \left( f_p^v \mathbb{A}_p^T \overset{\circ}{\hat{}} \boldsymbol{\alpha}_p \right) \quad (1)$$

Following the extension of Bazant's (1977) solidification theory to a tensorial ground (Sanahuja, 2013b), it is possible to derive the CTE of a solidifying solid in ageing linear viscoelasticity. To do so, we assume no thermo-activation on the viscous effects. Massive filling is adopted for the hydration product layers and concentric inwards filling is adopted in the cement paste scale, as in (Honorio, 2015).

### 3 RESULTS AND DISCUSSION

The evolution of the specific heat capacity is shown in Figure 3a for cement paste, ITZ, mortar and concrete. Within the first 3 days the most part of the evolution of the specific heat capacity occurs for mortar and cement paste. In the paste and ITZ, a slight evolution still takes place after that time. The evolution is almost linear in all cases with respect to the degree of hydration. For the studied concrete, the specific heat capacity measured at late ages is 1000 kJ/kg.K (Craeye, 2010), which corresponds to the estimations provided here. Note that the variation of the heat capacity within the first days may play a non-negligible role on the thermo-chemo-mechanical response of concrete structures.

The estimation of the thermal conductivity is shown in Figure 3b for cement paste, ITZ, mortar and concrete. Within the first 2 days the most part of the evolution of the thermal conductivity occurs for all materials. But even in the very early ages the evolution is not very pronounced. Again, the evolution is almost linear in all cases with respect to the degree of hydration. Thermal conductivities ranging from 0.7 to 1.0 W/m.K were experimentally determined for cement pastes with different w/c and temperatures by Mounanga (2003). A similar evolution with a slight increase in the thermal conductivity with time was also observed. The asymptotic thermal conductivity measured experimentally by Craeye (2010) for concrete is 1.8 W/m.K and is in agreement with the value obtained in the multiscale estimation.

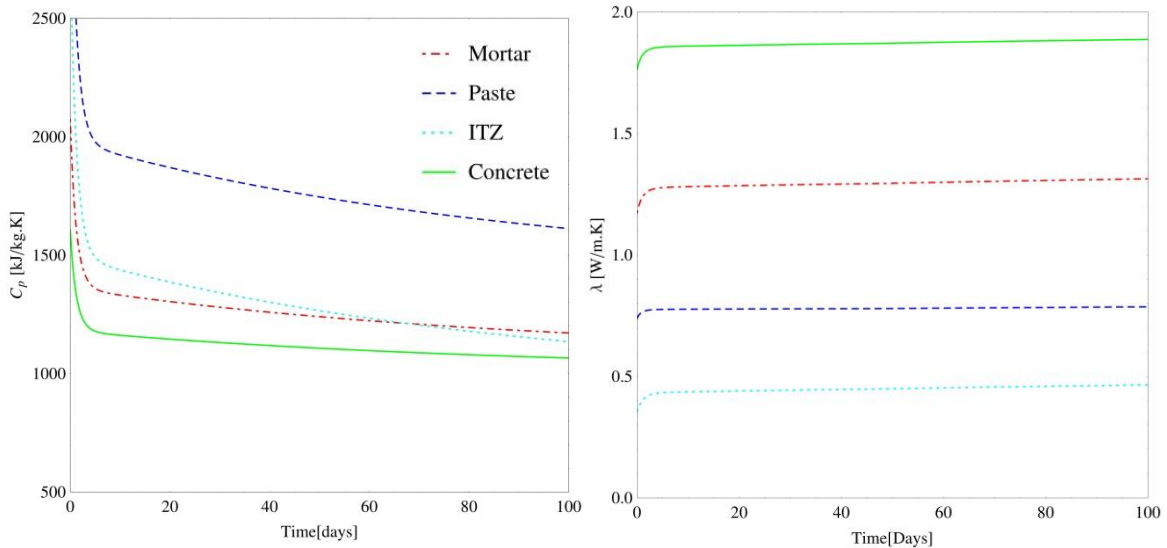


Figure 3. Evolution of the heat capacity (left) and thermal conductivity (right) of the cement paste, ITZ, mortar and concrete as a function of time, w/c = 0.4.

The estimations of the CTE of cement paste, ITZ, mortar and concrete are shown in [Figure 4](#). Except for the ITZ after about 2 days, the estimations do not evolve monotonously with time: a local maximum is obtained by 3 days at cement paste, mortar and concrete scales. Such kind of behavior can also be observed for some formulations, as for example in Wyrzykowski and Lura (2013) for cement paste and mortar. Similarly, as supported experimentally, asymptotic behaviors are observed in all cases after about 400 h. The obtained values of the concrete CTE are close to the experimental value found for the concrete modules of  $\alpha = 11 \times 10^{-6} \text{ } ^\circ\text{C}^{-1}$ . Cement paste CTE is higher than the value currently reported in the literature 10 to  $-60 \times 10^{-6} \text{ } ^\circ\text{C}^{-1}$ . Note, however, that a higher CTE (close to water CTE) would be expected for the very early-age. Further investigations are necessary in order to better account for the effects of water/moisture in the CTE estimations.

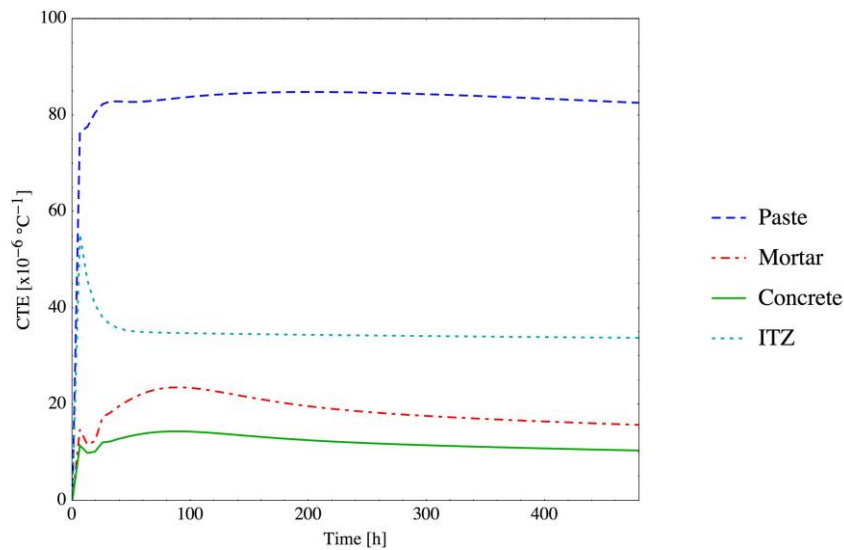


Figure 45. Evolution of the CTE of the cement paste, mortar, ITZ and concrete, w/c = 0.4.

#### 4 CONCLUSIONS AND PERSPECTIVES

The thermal properties of cement-based materials – namely, heat capacity, thermal conductivity and CTE – are estimated by means of multiscale methods. Note that for all cases, some assumptions were made about the behaviour of the phases at the cement paste scale due to lack of data, especially concerning thermal properties of hydrates.

Adequate estimations of the asymptotic values of the heat capacity, thermal conductivity and CTE of concrete were obtained. The thermal conductivity showed only a small variation within the very first days which corroborates, for instance, the choice of a constant value of thermal conductivity for early-age analysis. On the other hand, the heat capacity and CTE varied in a more pronounced way within the first 3 days, which indicates that precise early-age modelling would need to take into account such evolutions.

The confrontation of the modelling approach developed here with a more exhaustive experimental campaign may validate it in a more comprehensive way. Again, the non-consideration of a solid percolation threshold limits the range of applicability of the estimations. Further researches in this direction could be interesting. An approach accounting for the dependency of the temperature on the mechanical (including viscous) and thermal properties in a multiscale framework is also to be developed.

Moreover, in a mechanism-based description of the evolution of thermal properties, some aspects regarding the structuration of C-S-H, the main hydration product, is not generally taken into account. Space filling is reported to drive key process related to hydration kinetics (Bishnoi and Scrivener, 2009; Muller et al., 2012; Powers, 1960; Scrivener et al., 2015), and consequently, to the evolution of mechanical properties (Do, 2013; Honorio et al., 2015, in preparation). To our knowledge, no effects of such process have been considered in multiscale estimation of thermal properties of cement-based materials.

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