Thermal properties of cement-based materials: Multiscale estimations at early-age

Tulio Honorio [a,b,*], Benoit Bary [a], Farid Benboudjema [b]

[a] CEA, DEN, DPC, SECR, Laboratoire d'Etude du Comportement des Bétons et des Argiles, F-91191 Gif-sur-Yvette, France
[b] LMT (ENS Cachan, CNRS, Université Paris Saclay), 94235 Cachan, France

ARTICLE INFO

ABSTRACT

The prediction of the thermomechanical response of cement-based materials depends on the adequate determination of the thermal properties. At early-age, these properties depend on the evolution of the microstructure due to hydration processes and the multiscale nature of CBMs. In this paper, the heat capacity, the thermal conductivity and the coefficient of thermal expansion of cement-based materials are estimated by means of analytical homogenization. Estimates at the scales of cement paste, mortar and concrete are provided. At cement paste scale, the evolution of the volume fractions of clinker minerals and hydrates are taken into account. Interface Transition Zone (ITZ) is considered at mortar scale. A discussion about the effective properties of the "pore phase" and C-S-H as well as their influence on the effective behaviour is provided. A formulation accounting for the mechanical coupling in the determination of the heat capacity is used. Finally, the model estimations prove to be consistent with experimental data from the literature.

1. Introduction

The prediction of the thermomechanical response of cement-based materials (CBM) depends on the adequate determination of the thermal properties of such materials. Heat capacity, thermal conductivity and coefficient of thermal expansion (CTE) are particularly important in the early-age behaviour of massive concrete structures [1] or in the thermal performance of cement-based building envelopes [2]. At early age, these thermal properties evolve with the changes in the microstructure due to cement hydration processes. This evolution is due to an interplay between the thermal properties of the new forming phases (i.e. cement hydration products) and the thermal properties of the original phases.

Generally such age dependency is not explicitly taken into account in early-age structural analysis. However, a non-negligible impact of variations of these properties on the structural response is reported. Briffaut et al. [3], comparing simulations with time-dependant heat capacity and thermal conductivity with simulations in which these thermal properties are kept constant,

obtained higher total stresses developed in the former case, especially due to the variations of the heat capacity of concrete. Lura and van Breugel [4] reported that variations in the heat capacity may lead to a variation of the same order of magnitude in the computed temperatures and stresses. The same authors also found that up to 5% of variation in the thermal conductivity, only a minor effect is observed on the temperature and stress responses, and that the CTE affects actively the thermo-chemo-mechanical response (a variation of 16% in the CTE is reported to increase the cracking risk by about 15%) [4]. On the other hand, Hilaire [5] reported a not very pronounced impact of the CTE evolution on the mechanical response at early-age. These examples highlight the importance of properly understanding the evolution of the thermal properties in order to predict the performance of cement-based materials and structures more accurately.

In general, the thermal properties of materials depend on environmental, structural and composition aspects [6].

Environmental aspects, for CBM, include mainly moisture content and temperature dependence. After Morabito [7], the thermal conductivity decreases when the temperature increases, whilst the heat capacity increases with the temperature rise. Marshall [8] reported an almost linear evolution with the temperature up to about 30 °C and an increase in the heat capacity with the temperature. Cruz and Gillen [9] also reported a dependency of

* Corresponding author. Current address: Université Paris-Est, Laboratoire Modélisation et Simulation Multi-Echelle, MSME UMR 8208 CNRS, 94010 Créteil cedex, France.
E-mail address: tulio.honorio-de-faria@u-pec.fr (T. Honorio).

the thermal conductivity of CBM on the temperature. Similar variations with the temperature are observed for the heat capacity [8] and CTE [4]. For applications in ambient temperatures, however, it seems reasonable to neglect the dependence on the thermal properties of the temperature.

Microstructural aspects include the crystallinity and imperfections of constituent phases. In general, higher conductivity is observed in crystals since the mean free path of phonons is longer than in disordered or amorphous solids [6]. The different clinker minerals and hydrates phases own different structures. Specific studies on the influence of these structural aspects (which are beyond the scope of this paper) are needed to better understand the behaviour of the constituent phases of reactants and products in CBM especially under different humidity conditions. Hereafter, these constituent phases are considered as homogeneous with respect to a representative elementary volume of cement paste. Also, no further considerations about the internal structure of aggregates are made. In the presence of aggregates, an Interface Transition Zone (ITZ) embedding aggregates is reported to affect the behaviour of CBM [10]. Some works point out the impact of this zone on diffusivity [11] and mechanical properties [12,13] of CBM. The particular effect of this zone on the thermal properties is explored in this paper.

Composition aspects include the proportioning of reactive system (clinker composition, water/cement (w/c) ratio, presence of supplementary cementitious materials) and the nature of aggregates. Water and air thermal properties are quite different from the thermal properties of the solid phases in cement systems (see Table 1). In this sense, the changes in the porosity combined with the consumption of water, directly affect the evolution of the thermal properties at early age. The (free) water content seems to play a major role in the thermal properties [14]. At early-age these changes in porosity and the free-water content itself are related to the w/c ratio [15]. With variations in the water content from 4 to 8% of the concrete weight, Marshall [8] reported a decrease in thermal conductivity and an increase in the heat capacity. The thermal properties of the aggregates generally differ from that of cement paste matrix. Although the aggregates are not the percolating phase, their high proportion in formulations of mortars and concretes leads to a significant impact of their behaviours on the overall behaviour of the material. Related to microstructural aspects, mineral composition, as well as rock structure and texture affect the thermal properties of the aggregates [16]. Marshall [8] observed variations up to 42% in the thermal conductivity and 8% in the heat capacity according to the type of aggregates tested. The combination of homogenization techniques with hydration kinetics and phase assemblage models allows estimating the thermal properties accounting explicitly to the composition of the material. This is the core contribution of this paper.

Despite the importance of the thermal properties in the early-age analysis, there is a lack of experimental data especially in an ageing context and concerning the most fundamental phases such as hydration products. Tables 1 and 2 gather some values found in the literature for the constituents of cement-based materials. These values correspond to temperatures around 20 °C. Note that experimental difficulties in measuring these properties at early age are reported. For example, heat sources often used in the experimental devices provoke moisture gradients [8], which can affect the determination of the properties since the properties are moisture dependent. These aspects highlight the importance of modelling approaches, especially multiscale-based strategies, in the study and estimation of thermal properties. Atomistic approaches combined to homogenization tools have been recently used to determine the thermal properties of some hydration products [17]. This kind of development leaves room to multiscale studies up to (macroscopic) scale of industrial applications. Upscaling tools allow estimating with a single set of intrinsic material properties (i.e. the property to be homogenized of the elementary constituents) the macroscopic properties of composites with constant microstructures. The same tools can be used for composites with evolving microstructure but only for properties of the elementary phases that are instantaneous (such as the elastic response in aging viscoelasticity [18]) or not time-dependent.

In this paper, we propose a multiscale estimation of the heat capacity, coefficient of thermal expansion and thermal conductivity of CBM at early age. We use mean-field thomogenization in an extension of the work developed in Ref. [19]. Estimations at scales of cement paste, mortar and concrete are provided. At cement paste scale, the evolution of the microstructure due to hydration is accounted for by means of a simplified kinetics model [20] combined with hydration balance equations [21]. ITZ is further considered at mortar scale. A discussion about the effective properties of C-S-H and "pore phase" as well as their influence on the overall behaviour is provided. A formulation accounting for the mechanical coupling, in an elastic ground, in the determination of the heat capacity is used. Finally, the model estimations are confronted with experimental data from the literature.

Some simplifying hypotheses are adopted. Thermal conductivity, CTE and elastic properties are considered as isotropic at micro and macro scales. No creep/relaxation effects, which may affect especially the CTE [22], are accounted for. No temperature jumps effects are considered either [23].

Table 1
Some typical values of the thermal properties of the constituents of cement paste gathered from the literature for temperatures close to 20 °C.

Compound		Specific heat [J/(kg.K)]	Thermal conductivity (volumetric) [W/m.K]	Volumetric CTE $\times 10^{-6}[°C^{-1}]$
(Free) Water		4183 [24]	0.608 [14,15,23]	200 [25]
Clinker, clinker phases, gypsum	Clinker	750 [14]	1.55 [14]	
	C_3S	745 [26]	–	49.5 [17]
	C_2S	741 [26]	–	49.9 [17]
	C_3A	768 [26]	–	–
	C_4AF	813 [26]20 °C	–	–
	Gypsum	1080.4 [27]	0.66 [28]	–
			1.26 [29]	
Hydration products	C-S-H	950 [28]	0.978 [17]	42 [30]
		722 [26]		45 [17]
	CH	1150 [17]	1.32 [17]	70 [31]
				99.1 [17]
	AFt	1502 [26]	–	–
	AFm	888.3–1114.8 [32]	–	–
	Hydrogarnet	666-1121 [33]	–	–