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May reversible water uptake/release by hydrates explain the thermal expansion of cement paste? — Arguments from an inverse multiscale analysis

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ABSTRACT

Quasi-instantaneous thermal expansion of cement pastes is governed by the relative humidity (*RH*) within their air-filled pores and by the decrease/increase of this internal *RH* resulting from a temperature decrease/increase. The latter effect is traced back to quasi-instantaneous water uptake/release by cement hydrates, using microporomechanics and a three-scale representation of mature cement pastes. Partially saturated gel and capillary pores are considered to be connected and spherical, with radii following exponential distributions. The Mori-Tanaka scheme provides the scale transition from effective pore pressures to eigenstrains at the cement paste level. This modeling approach, together with considering mass conservation of water, allows for downscaling macroscopic thermal expansion coefficients, so as to identify the molecular water uptake/release characteristics of the hydrates. The latter characteristics are mixture-independent, as shown by their use for predicting the thermal expansion coefficients of different mature cement pastes, with *w*/*c*-ratios ranging from 0.50 to 0.70.

1. Introduction

External heating/cooling of a millimeter-to-decimeter-sized sample of partially saturated (drained) cement paste actives two transport processes. Heat transport provides the transition between two different isothermal states [1-3]. This takes typically from minutes to hours, depending on the size of the specimen and on the magnitude of the temperature change, ΔT. The increase/decrease of temperature goes hand in hand with both thermal expansion/contraction of the cement paste sample *and* an increase/decrease of its internal relative humidity. The latter change activates a moisture transport process between the open porosity of the specimen and the ambient air. This takes typically from days to weeks. The corresponding deformation partly recovers the thermal expansion/contraction [1,2,4]. In saturated (or close to saturated) conditions, delayed deformations under constant temperature have been attributed to macroscopic water transport caused by overpressure of water expanding more than the solid skeleton, see Ref. [5].

The coefficient of thermal expansion of mature cement paste ranges from $8 \cdot 10^{-6}\,\mathrm{K}^{-1}$ to $22 \cdot 10^{-6}\,\mathrm{K}^{-1}$ and appears as an asymmetrical bell-shaped function of relative humidity which prevails in the air-filled pores just *before* the applied temperature change, see Refs. [6-10] and Fig. 1. Knowledge of such thermal expansion coefficients is important for practical applications in concrete construction, see, e.g. Ref. [11]. In this context, it is noteworthy that concrete aggregates have typically smaller thermal expansion coefficients, ranging between $4 \cdot 10^{-6}\,\mathrm{K}^{-1}$ and $12 \cdot 10^{-6}\,\mathrm{K}^{-1}$, depending on the mineral composition [9,12,13]. Therefore, subjecting concrete to a temperature change, yields a mismatch of thermal eigenstrains. This results in thermal (micro-)stresses, which may even cause microcracking [14-16], reducing the durability of concrete structures.

Quasi-instantaneous expansion due to the temperature increase ΔT goes hand in hand with an *increase* of the internal relative humidity ΔRH, see, e.g. measurements documented in Refs.[2,10,17-19]. These experimental data suggest that the ratio $\Delta RH/\Delta T$, referred to as the hygrothermic coefficient [3], is a nonlinear function of the internal relative humidity which prevails in the air-filled pores just *before* the temperature change, see Fig. 2. In addition, the hygrothermic coefficient is considered to depend on the initial water-to-cement mass ratio [3,19], but the underlying physical processes are still not fully understood.

The ongoing scientific discussion regarding the origin of hygrothermic coefficients mainly concerns the redistribution of liquid water. In this context, Bažant [2] attributed hygrothermic coefficients to water migration from gel pores to capillary pores, considering that increasing

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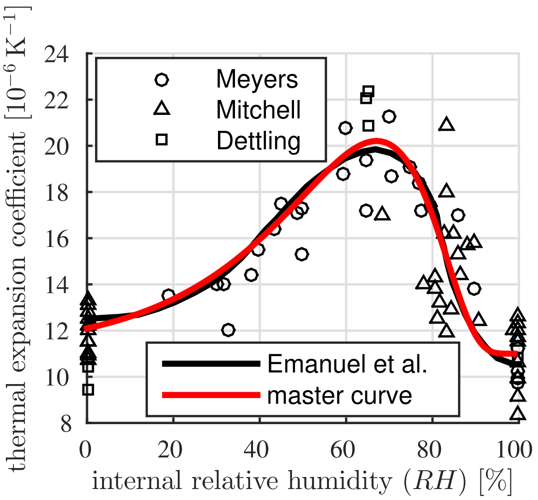

Fig. 1. Relation between the coefficient of thermal expansion and the internal relative humidity which prevails in the air-filled pores, just *before* the temperature change: experimental data from Meyers [6], Mitchell [7], and Dettling [8], measured on mature cement pastes with initial water-to-cement mass ratios $w/c \in [0.12; 0.40]$; the curve described by Emanuel et al. [9]; and the "master curve" given in Eq. (3).

temperature causes a chemical potential difference between the gel and the capillary water. Grasley et al. [10] and Radjy et al. [19] estimated temperature-induced changes of relative humidity *RH*. For that, they used Kelvin's equation, considered that the surface tension at liquid-gas interfaces decreases with increasing temperature according to measurements [20], and treated the radius of the corresponding meniscus between pore water and air as a constant. The correspondingly estimated increase of relative humidity underestimates the measured hygrothermic coefficients. Therefore, Grasley and Lange proposed water expansion in ink-bottle pores to be responsible for the aforementioned measured values of hygrothermic coefficients [10]. This indicates that the radius of the meniscus between the pore water and the air increases with increasing temperature. Wyrzykowski and Lura [21] obtained hygrothermic coefficients by means of water activity and sorption measurements. The two independent methods associated with the aforementioned measurements delivered consistent results. Using a model linking capillary pressure to elastic deformation [22-24], Wyrzykowski and Lura related the measured early-age evolution of the hygrothermic coefficients to the measured coefficients of thermal expansion. They did so for samples aged between 1 and 7 days [21], when the measured relative humidity decreased from full saturation to values, ranging between 85% and 94%. Still, modeling of hygrothermic coefficients of mature cement pastes in the regime of intermediate relative humidities from 25% to 85% remains an open research question.

Existing models for thermal expansion of cement paste are of hygrothermoporoelastic and macroscopic nature. They typically consider two contributions: (i) thermal expansion of the solid skeleton, α_{cp}^{sol}, and (ii) hygrothermic expansion resulting from pore pressure changes [2,10,21,25], α_{cp}^{hyg}:

$$\alpha_{cp}^{mod} = \alpha_{cp}^{sol} + \alpha_{cp}^{hyg}. \tag{1}$$

As regards the latter, the Kelvin-Laplace equation is used to quantify capillary pressure from knowledge on temperature and relative humidity. Increasing temperature and the associated increase of internal relative humidity result in a decrease of capillary pressure Δp_c and an increase of the saturation ratio ΔS_r. The resulting hygrothermic expansion $\Delta\varepsilon_{hygro}$ is typically quantified as [10,21,24]

$$\Delta\varepsilon_{hygro} = \frac{\Delta p_c\, S_r + p_c\, \Delta S_r}{3}\left(\frac{1}{k_{\mathrm{hom}}} - \frac{1}{k_s}\right), \tag{2}$$

where k_{hom} and k_s, respectively, are the bulk moduli of the porous material and of the solid skeleton. Eq. (2) is theoretically rigorous for liquid saturation, i.e. for $S_r = 100\%$, see Refs. [21,24], and it is of approximate nature in case of partial saturation [24,26]. While Eq. (2) could be shown to be reliable for saturation degrees $S_r \geq 80\%$, it underestimates the hygrothermic expansion at smaller saturation degrees [21,24].

In the present paper, hygrothermic coefficients and thermal expansion of mature cement pastes are explained by quasi-instantaneous uptake or release of water by the hydrates. This is an effect for which no physical measurements were available at the time of submitting the present manuscript. However, such measurements were reported shortly thereafter [27]. In the present context of modeling, the hydrates are, in the sense of a reductionist approach, not subdivided explicitly into different hydration products, such as calcium-silicate-hydrates (C-S-H), portlandite, and ettringite. Still, it is noteworthy that water (H) in the C-S-H can be considered to be at least partly mobile [28,29], while the water chemically bound in crystalline products, such as portlandite and ettringite, cannot be considered as at least partially mobile.

Methods of microporomechanics [26,60] in combinations with the mass conservation law are used to identify the quasi-instantaneous uptake or release of water by hydrates, with focus on mature cement pastes and on the central regime of relative humidities ranging from 25% to 85%. To this end, unhydrated clinker grains, hydrates, capillary pores, and gel pores are introduced as elementary constituents in a three-scale representation of mature cement pastes. The pores are considered to be well connected and spherical. They are either filled by water or by air, following the Kelvin-Laplace equation. Thin layers of adsorbed water are taken into account at solid surfaces, including the surfaces of "air-filled" pores [30]. The size distributions of gel and capillary pores are modeled by exponential distributions, following Huang et al. [31]. These distributions are identified such that the model-predicted adsorption isotherms agree as well as possible with

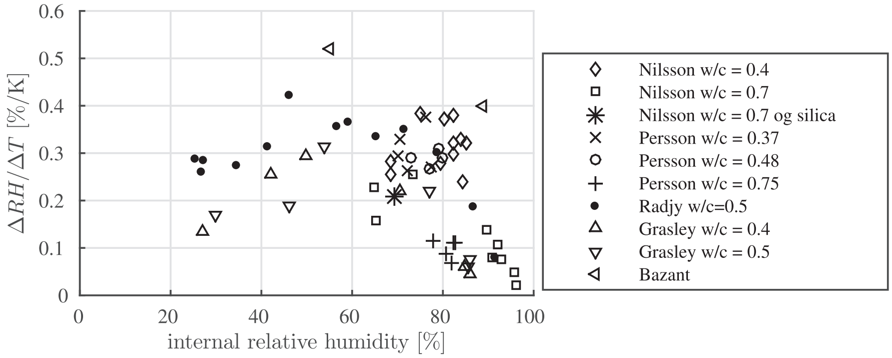

Fig. 2. Hygrothermic coefficient of cement paste as a function of the internal relative humidity, prevailing just *before* the temperature change: test results from Nilsson [17], Persson [18], Radjy et al. [19], Grasley et al. [10], and Bažant [2].