Water uptake/release by hydrates as source of hygrothermic coefficients and thermal expansion of cement paste

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Abstract:

The coefficient of thermal expansion of mature cement paste is an asymmetrical bell-shaped function of the internal relative humidity RH prevailing in the nanoscopic air-filled pores of the material. The maximum value of the coefficient of thermal expansion, occurring at RH ≈ 65%, is virtually twice as large as its minimum value, occurring at full water saturation, RH = 100%. Quasi-instantaneous expansion due to an increase of temperature (ΔT) goes hand in hand with a paradoxical increase of the internal relative humidity (ΔRH). The ratio ΔRH/ΔT, referred to as the hygrothermic coefficient, is another asymmetrical bell-shaped function of the internal relative humidity which prevails in the air-filled pores just before the temperature change. Hygrothermic coefficients are the smaller, the larger the initial water-to-cement mass ratio of cement paste. In order to gain insight into the underlying physical processes, multiscale engineering mechanics research is carried out, using microporomechanics and a three-scale representation of mature cement pastes.[1] Partially saturated gel and capillary pores are considered to be connected and spherical, with radii following exponential distributions. Corresponding characteristic radii are quantified by means of adsorption porosimetry, based on Brunauer-Xi adsorption isotherms. As regards multiscale modeling, it is accounted for that adsorbed water layers cover the surfaces of air-filled pores. Effective pore pressures depend on the size of the pores, because of the surface tension in liquid-gas interfaces. 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, and to quantify 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 initial water-to-cement mass ratios ranging from 0.50 to 0.70. It is concluded that nanoscopic cement hydrates release water upon heating and take up water upon cooling, in a quasi-instantaneous and reversible fashion. If the material is heated, the released water increases the Kelvin radius. Thus, the internal relative humidity increases. This results in a reduction of the average effective pore underpressure, and a poromechanical swelling of the material, in addition to the one resulting from the thermal expansion of the solid skeleton.

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[1] Wang, H., Hellmich, C., Yuan, Y., Mang, H., & Pichler, B. (2018). May reversible water uptake/release by hydrates explain the thermal expansion of cement paste? – Arguments from an inverse multiscale analysis. Cement and Concrete Research, 113, 13-26, https://doi.org/csgw.