

Transient plane source measurements of the thermal properties of hydrating cement pastes

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Abstract A transient plane source measurement technique is applied to assessing the heat capacity and thermal conductivity of hydrating cement pastes in their fresh state and during the course of 28 d of hydration at 20°C. Variables investigated include water-to-cement mass ratio (w/c – 0.3 or 0.4) and curing conditions (sealed or saturated curing). The heat capacity data for the fresh cement pastes are compared to a simple law of mixtures, and analytical expressions are developed to estimate the heat capacity as a function of degree of hydration for the two curing conditions. The measured thermal conductivities of the fresh pastes along with the known thermal conductivity of water are used to estimate the thermal conductivity of the original cement powder via application of the Hashin-Shtrikman (H-S) bounds. Hydration is seen to have only a minor influence on the measured thermal conductivity. Extension of the law of mixtures for heat capacity and the H-S bounds for thermal conductivity to predicting

the corresponding properties of concretes are discussed.

Résumé Une technique basée sur une source de chaleur pulsée est utilisée pour déterminer la capacité calorifique et la conductivité thermique de pâtes de ciment à l'état frais et pendant les 28 premiers jours d'hydratation à 20°C. Les variables étudiées sont le rapport eau-ciment en masse (e/c 0.3 ou 0.4) et les conditions de cure (éprouvettes scellées ou dans l'eau). Les mesures de capacité calorifique des pâtes de ciment fraîches sont comparées avec la simple loi des mélanges. Des expressions analytiques ont été développées pour estimer la capacité calorifique en fonction du degré d'hydratation pour les deux conditions de cure. La conductivité thermique de la poudre de ciment utilisée est estimée à l'aide des valeurs de conductivité thermique mesurées et de la conductivité thermique de l'eau par la méthode des limites Hashin-Shtrikman. Le degré d'hydratation semble avoir une influence mineure sur la valeur de la conductivité thermique mesurée. L'utilisation de l'extension de la loi des mélanges pour la capacité calorifique et des limites H-S pour la conductivité thermique afin de prédire les propriétés correspondantes du béton est discutée.

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1 Introduction

As cement hydrates and concrete cures in the field or in a pre-cast plant, there is always a risk of early-age cracking that might compromise the longer term performance of the in-place product. Of the various sources of stresses that can influence such cracking, thermal stresses can be one of the more significant contributors. For this reason, various models to predict the distributions of temperature [1–3] and stress [4] in hardening concrete have been developed in recent years. Whether a simplified one-dimensional or a fully developed three-dimensional heat transfer model is utilized, critical inputs for these computations are the thermophysical properties of the concrete as a function of time, including its density, heat capacity, and thermal conductivity. These properties will be determined by the concrete's mixture proportions, the thermophysical properties of the aggregates that it contains, and those of its hydrating cement (binder) paste component. While the necessary densities are generally either well known or easily measured, less information is readily available on the heat capacities and thermal conductivities, particularly those of the hydrating cement paste. In this paper, a transient plane source (TPS) method is applied to measuring heat capacities and thermal conductivities of hydrating cement pastes cured under both saturated and sealed conditions at room temperature.

Previous measurements of heat capacity (specific heat) and thermal conductivity (thermal diffusivity) for cement-based materials were conveniently summarized by De Schutter and Taerwe in 1995 [5]. Since that time, several additional studies have been published [6–14]. However, while most of these recent studies have focused on thermal conductivity, the obtained values for this property for hydrated cement paste still exhibit considerable scatter, as illustrated in Table 1. For the heat capacity of hydrating cement pastes, two previous studies [5, 15] have measured the heat capacity of water-to-cement mass ratio ($w/c = 0.5$) cement pastes of two different cement types during hydration, obtaining values in good agreement with one another. In addition, in [13], a heat capacity of 1.6 J/(g K) is reported for a hardened $w/c = 0.4$ cement paste.

Table 1 Literature values for the thermal conductivity of hydrating cement pastes

Method [reference]	Paste details	k [W/(m K)]
Transient (thermal diff.) [15]	$w/c = 0.5$, $T = 30^\circ\text{C}$	0.88 (early)
	rapid hardening	0.78 (late)
Transient probe [7]	$w/c = 0.4$, $T = 20^\circ\text{C}$	Wet -1.16
	Type V cement	Dry -0.77
TPS [6]	Density = 2100 kg/m ³ crushed	2.85
Laser flash (thermal diff.) [8]	Density = 2010 kg/m ³	0.53
	$w/c = 0.35$, 28 d	
Dual hot wire [12]	$w/c = 0.348$	Fresh -1.0
	Type I cement	28 d - 1.07
Two-linear parallel probe [13]	$w/c = 0.4$	1.013
	24 h	

The current study will supplement these previous data by performing measurements on hydrating cement pastes with $w/c = 0.3$ and $w/c = 0.4$, using the TPS technique.

2 Experimental

All cement pastes were prepared using Cement and Concrete Reference Laboratory (CCRL) cement proficiency sample 152 [16]. Specimens with w/c of 0.3 and 0.4 were prepared. Water and cement were mixed for several minutes in a temperature-controlled high-speed blender. After mixing, small disks of cement paste (about 5–6 mm thick and 47 mm in diameter) were cast in pre-weighed plastic Petri dishes and “consolidated” by tapping the dish numerous times on a laboratory counter top. The specimens were covered, weighed, and then placed in an environmental chamber at 20°C where they were cured under either sealed or “saturated” (small volume of distilled water on top) conditions. At ages of 8 h and (1, 2, 3, 8, 15, and 28) d twin specimens of similar mass were selected and removed from their dishes. The specimens cured under sealed conditions were easily removed, due to their ongoing autogenous shrinkage, while for those cured under saturated conditions (which had actually expanded slightly during hydration due to water imbibition), it was usually necessary to break open the bottom Petri dish in order to remove the disk specimen. The mass of each specimen was measured upon removal. Each specimen was then inverted and

placed back in a bottom Petri dish, but now being placed on top of a rubber o-ring spacer so that the top of the specimen was slightly higher than the top rim of the Petri dish. These specimens were then placed directly into the Hot Disk Thermal Constants Analyzer¹ for evaluation of their thermal conductivity.

The basic experimental configuration for measuring the thermal properties of cement paste specimens using the thermal constants analyzer is provided in Fig. 1. The thermal constants analyzer consists of a variety of transient plane source probes connected to a computerized control unit. The transient plane source measurement technique has been previously described in detail by Gustafsson and Log [17, 18] and theoretical considerations have been summarized recently by He [19]. For the current study, a 6.403 mm radius probe (Ni foil encased in Kapton) was selected. The probe was sandwiched horizontally between the cast sides of the twin hardened cement paste specimens in a holding frame and the entire setup was placed in a small closed chamber (to minimize the influence of air currents, etc.). After an equilibration time of at least 45 min in a laboratory nominally maintained at 23°C, measurements were obtained with a power of 0.3 W applied for a measurement time of 10 s. The measured response of the probe/sensor was analyzed using the built-in software to determine the thermal conductivity of the specimens, after providing the heat capacity value that was determined in a separate experiment (described below). The analyzer samples 200 points during the 10 s measurement time and points 75–200 were used in the quantitative analysis. Fresh cement pastes were also analyzed separately using a 6.631 mm radius Ni/Kapton probe (0.3 W for 10 s) that was placed vertically into a 35 mm inner diameter plastic cup holding about 50 g of fresh cement paste (height of about 25 mm). In this case, both the thermal conductivity and the heat capacity of the fresh

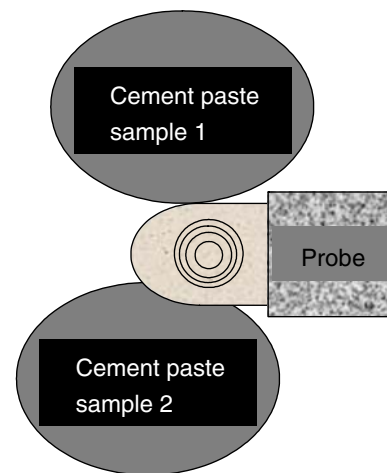


Fig. 1 Schematic of experimental configuration for measuring the thermal properties of a pair of (twin) cement paste specimens

cement pastes were estimated in a single probe measurement. According to the manufacturer, the thermal conductivity measurements made in this way are reproducible within $\pm 2\%$.

For the separate heat capacity experiments on the hydrated cement pastes, after their thermal conductivity measurements were completed, a small piece of one of the disks of known mass (typically 1.5–3.0 g) was broken off and placed in the Hot Disk heat capacity unit, consisting of a special probe attached to the base of a gold pan/lid. For the measurements, the gold pan with its lid is surrounded on all sides by polystyrene insulation, in an attempt to minimize energy loss. First, a reference measurement is made with an empty pan, followed by the measurement with the specimen placed in the pan. For these heat capacity measurements, a power of 0.1 W was applied for a measurement time of 160 s. In this case, points 100–200 (of the total 200 sampled in the 160 s) were used in the quantitative analysis. Knowing the mass of the specimen, its heat capacity in units of J/(g K) can be easily determined. For the analysis employed in this paper, any heat generation due to the ongoing cement hydration reactions during the 160 s of measurement time was ignored, as even for the earliest 8 h specimen, the maximum (heat) power generation due to hydration was estimated to be 0.005 W. The heat capacity measurements of the hydrating cement paste were facilitated by

¹ Certain commercial products are identified in this paper to specify the materials used and procedures employed. In no case does such identification imply endorsement by the National Institute of Standards and Technology, nor does it indicate that the products are necessarily the best available for the purpose.

placing the (flat) cast surface of the specimen in the bottom of the pan to produce a high quality (thermal) contact between pan and sample. Additionally, the thickness of the specimens was such that the top of the specimen did not contact the bottom surface of the gold lid, as recommended in the Hot Disk User's Manual. According to the manufacturer, the heat capacity measurements made in this way are reproducible within $\pm 2\%$.

After breaking one of the disks to obtain a specimen for the heat capacity measurement, the remainder of the (broken) disk was crushed to a fine powder for measurement of its degree of hydration via loss-on-ignition (LOI) analysis. For this purpose, the non-evaporable water content (w_n) of each sample was determined as the mass loss between 105°C and 1000°C divided by the mass of the ignited sample, corrected for the LOI of the unhydrated cement powder, determined in a separate LOI measurement. Previously, the expanded uncertainty in the calculated w_n has been estimated to be 0.001 g/g cement, assuming a coverage factor of 2 [20]. The values of w_n were then converted to estimated degrees of hydration based on the phase composition of the cement and published coefficients for the non-evaporable water contents of the various cement clinker phases [21]. Based on a propagation of error analysis, the estimated uncertainty in the calculated degree of hydration is 0.004.

3 Results

3.1 Heat capacity

For the fresh cement pastes, heat capacities of 1.55 J/(g K) and 1.73 J/(g K) were measured for the $w/c = 0.3$ and $w/c = 0.4$ fresh cement pastes, respectively. Using the known heat capacity of water [22] (4.18 J/(g K) at 23°C) and a value of 0.75 J/(g K) for cement powder (based on the measured values for tricalcium silicate and dicalcium silicate [23]), the heat capacity of a fresh cement paste at 23°C can be estimated using a simple law of mixtures [5] as:

$$\begin{aligned} C_p^{(\text{freshpaste})} &= 4.18M_f^{\text{water}} + 0.75M_f^{\text{cem}} \\ &= 0.75 + 3.43M_f^{\text{water}} \end{aligned} \quad (1)$$

where M_f^{water} is the mass fraction of water in the fresh paste, and $M_f^{\text{cem}} = 1 - M_f^{\text{water}}$ is the mass fraction of cement powder. When this equation is applied for $w/c = 0.3$ ($M_f^{\text{water}} = (0.3/1.3) = 0.231$) and $w/c = 0.4$ ($M_f^{\text{water}} = (0.4/1.4) = 0.286$), estimated heat capacities of 1.54 J/(g K) and 1.73 J/(g K) , respectively, are obtained, in excellent agreement with the measured values provided above. For a $w/c = 0.5$ cement paste, Eq.1 would predict a heat capacity of 1.89 J/(g K) , while a value of $1.92 \pm 0.05 \text{ J/(g K)}$ at 1.5 h maturity has been obtained previously [15]. The value of about 1.7 J/(g K) reported for a $w/c = 0.4$ fresh cement paste in [13] is also in good agreement with the values measured experimentally and calculated according to Eq. 1 here.

The measured heat capacities for the hydrating cement pastes cured under sealed and saturated conditions are provided in Fig. 2. For both w/c under sealed curing conditions, the heat capacity is observed to decrease rapidly at early hydration and then level off to a nearly constant value. Apparently, as the pore water becomes chemically and physically bound within the (gel) hydration products during the early stages of hydration, its heat capacity decreases significantly. For bulk water, a significant contribution to its unusually high heat capacity is the energy consumed in the breaking and bending of hydrogen bonds. It is possible that less bending and breaking will occur in "more restricted bound" water, leading to a

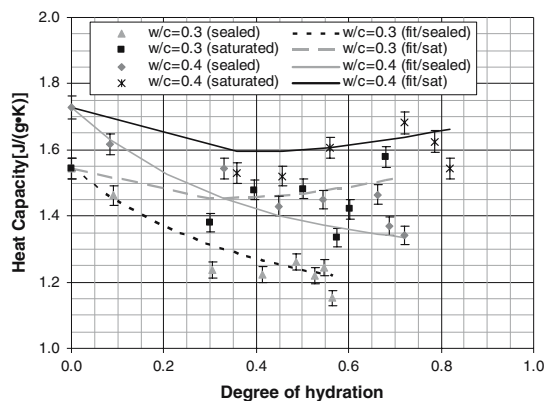


Fig. 2 Measured heat capacities of hydrating cement pastes as a function of degree of hydration for curing under saturated and sealed conditions. Error bars indicate a reproducibility of $\pm 2\%$

lower heat capacity. The heat capacity of ice is about one half of the value of liquid water [24], supporting this hypothesis that as the water molecules become less mobile during cement hydration, their heat capacity would decrease.

Previously, Hansen et al. [15] have plotted measured heat capacities vs. the log of maturity (in h), while De Schutter and Taerwe [5] have hypothesized a linear (decreasing) relationship between heat capacity and degree of hydration. Here, to adequately capture the observed initial rapid decrease in measured heat capacity, the data obtained in this study for hydration under sealed conditions were fitted to a relationship as a function of the measured degree of hydration, α , of the form:

$$C_p^{\text{sealed}}(\alpha) = C_p^{(\text{freshpaste})} * \{1 - A * [1 - \exp(-B\alpha)]\} \quad (2)$$

with the obtained fitting constants $A = 0.26$ and $B = 2.9$ for both $w/c = 0.3$ and $w/c = 0.4$ cement pastes hydrated under sealed conditions. The observed rapid decrease in heat capacity during initial hydration followed by a leveling off with continued hydration as described by Eq. 2 would be consistent with the previously measured development of the surface area of hydrating cement paste by neutron scattering techniques [25].

For the specimens hydrated under saturated conditions, the experimentally measured heat capacities soon bifurcate from those measured under sealed conditions. For the $w/c = 0.3$ pastes, the capillary pores depercolate after a few days hydration [26], so that it is not possible to easily maintain saturation for the 5 mm to 6 mm thick disks employed in this study. Thus, in Fig. 2, the heat capacity values for these pastes reach a local maximum after 3 d of hydration (degree of hydration = 0.5) and then return towards those measured for sealed curing conditions, before increasing once more. In support of this hypothesis concerning depercolation and saturation, the measured masses of water “drawn into” these “saturated” specimens follow the same trend as the presented heat capacities. This same decreasing trend in heat capacities at later ages is observed for the saturated $w/c = 0.4$ pastes

hydrated for 8 d, 15 d, and 28 d (the last three data points of their data set in Fig. 2), in agreement with the expectation that this higher w/c paste would achieve depercolation of its capillary pores somewhere between 7 d and 14 d of hydration [26].

Prior to depercolation of the capillary porosity, the maintenance of saturated conditions results in a set of relatively large water-filled capillary pores remaining in the hydrating cement paste microstructure; under sealed curing conditions, these pores will be the first to empty due to self-desiccation [20, 27]. Since the heat capacity of “free” water is 4.18 J/(g K), the imbibition and subsequent presence of this pore water would be expected to increase the heat capacity of the composite relative to that achieved under sealed curing conditions, as is observed in Fig. 2. An additional effect of this extra curing water is that the degree of hydration of the saturated specimens are increased relative to those achieved by the sealed specimens at the same hydration age [20, 27]. In Fig. 2, an attempt has been made to apply the law of mixtures to the heat capacity obtained for the saturated specimens, by considering them to be a mixture of a sealed specimen and (extra) imbibed water. Knowing the chemical shrinkage (CS) of the cement used at complete hydration (0.073 g of water per 1 g of cement), the amount of imbibed water per gram of original cement *paste* can be conveniently estimated as $\alpha CS/(1 + w/c)$. Then, applying the law of mixtures results in:

$$C_p^{\text{sat'd.}} = \frac{C_p^{\text{sealed}}(1 + \frac{w}{c}) + \alpha CS * C_p^{\text{imbibed_water}}}{1 + \frac{w}{c} + \alpha CS} \quad (3)$$

Equation 3 was found to provide a reasonable fit to the experimental data only when the heat capacity of the imbibed water was assumed to be 9 J/(g K), about twice the value of 4.18 J/(g K) for bulk water. This would suggest that the presence of the additional imbibed water and the maintenance of “saturated” conditions also increase the heat capacity of the remainder of the (original) water in the hydrated cement paste, relative to its value in an equivalent sealed system. Under sealed conditions, due to the

chemical shrinkage and self-desiccation that accompanies the hydration [28], large internal stresses are generated within the pore water that might further decrease its mobility and thus, its heat capacity, as discussed above.

To extend these heat capacity measurements to concrete at various ages, the law of mixtures could again be applied [3]:

$$C_p^{\text{concrete}} = C_p^{\text{paste}} M_f^{\text{paste}} + C_p^{\text{fineagg}} M_f^{\text{fineagg}} + C_p^{\text{crseagg}} M_f^{\text{crseagg}} \quad (4)$$

where C_p^{paste} represents the heat capacity of the hydrating cement paste at the age (degree of hydration) of interest and can be estimated using either Eq. 2 or Eq. 3 for sealed or saturated curing conditions, respectively.

3.2 Thermal conductivity

While the thermal conductivity of liquid water (k_1) is well known [22], that of cement powder (k_2) could not be found in the literature. An estimate, however, can be readily determined based on the measured thermal conductivities of the fresh $w/c = 0.3$ and $w/c = 0.4$ cement pastes and application of the Hashin-Shtrikman (H-S) bounds for the thermal conductivity of a two-phase (cement particles in water) material. For $k_2 \geq k_1$, the Hashin-Shtrikman lower (k_l) and upper (k_u) bounds for the thermal conductivity of a two-phase composite, with volume fractions of water (x_1) and cement powder ($x_2 = 1 - x_1$), are given by [29]:

$$k_l = k_1 + \frac{x_2}{\frac{1}{k_2 - k_1} + \frac{x_1}{3k_1}} \quad (5)$$

$$k_h = k_2 + \frac{x_1}{\frac{1}{k_1 - k_2} + \frac{x_2}{3k_2}} \quad (6)$$

Figure 3 provides a plot of these bounds along with the measured data for the two fresh cement pastes utilizing thermal conductivity values of 0.604 W/(m K) and 1.55 W/(m K) for water and the cement powder, respectively. The latter value for the cement powder provides H-S bounds that encompass both of the experimental data points for the fresh cement pastes.

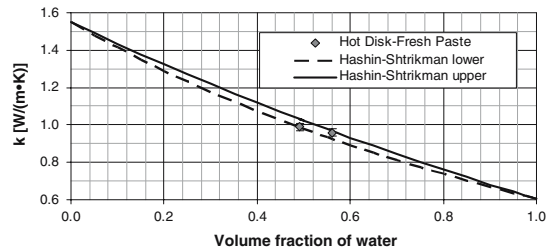


Fig. 3 Measured thermal conductivities of fresh cement pastes as a function of initial water volume fraction. Error bars indicate a reproducibility of $\pm 2\%$

The measured thermal conductivities as a function of degree of hydration are provided in Fig. 4. Within the reproducibility of the measurements, there is little variation in the thermal conductivity with degree of hydration and nominally a value of 1.0 W/(m K) would provide a reasonable estimate for both w/c pastes and both curing conditions at all evaluated degrees of hydration. This value is in reasonable agreement with several of the previously measured values that were summarized in Table 1 (those ranging from 0.77 W/(m K) to 1.16 W/(m K), for example), and especially with the values provided recently in [12] for a $w/c = 0.348$ cement paste and [13] for a $w/c = 0.4$ cement paste. However, the previously measured data for crushed cement paste specimens (2.85 W/(m K)) [6] and that obtained using the laser flash diffusivity technique (0.53 W/(m K)) [8] are both significantly different from the values obtained in this (and the other previous) studies. Furthermore, in [8], a heat capacity of 0.736 J/(g K) is reported for a $w/c = 0.35$ cement paste hydrated at 100% RH for 28 d, also in considerable disagreement with

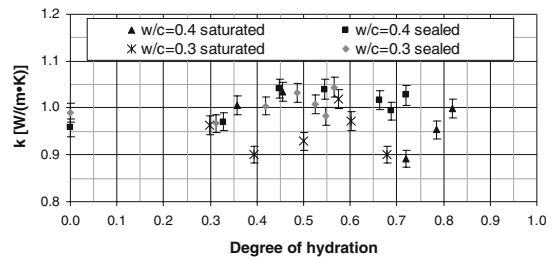


Fig. 4 Measured thermal conductivities of hydrated cement pastes as a function of measured degree of hydration. Error bars indicate a reproducibility of $\pm 2\%$

the values measured in the present (see Fig. 2) and other previous studies.

The H-S bounds can also be applied in extending thermal conductivity predictions to concrete [6], by considering it to be a two-phase composite consisting of aggregates in hydrated cement paste (effectively ignoring any air entrainment). Then, knowing the thermal conductivity of the specific aggregates [30] and assuming a value of 1.0 W/(m K) for the hydrated cement paste, Eq. 5 and 6 can be applied to determine upper and lower bounds for the thermal conductivity of any concrete composite of known mixture proportions, typically considering cement paste as phase 1 and aggregates as phase 2, since the thermal conductivity of most aggregates is higher than the cement paste's nominal value of 1.0 W/(m K) and Eqs. 5 and 6 require $k_2 \geq k_1$. (Lightweight aggregates with their much lower thermal conductivity could be an exception to this; in that case, the aggregates could be considered as phase 1 and the higher thermal conductivity cement paste as phase 2.) Finally, a reasonable estimate of the thermal conductivity of the concrete of interest could be taken as the mean of these upper and lower bounds. As an example, Figure 5 shows the computed H-S bounds for a concrete containing limestone aggregates ($k_2 \approx 3$. W/(m K) [7, 31]). For the typical cement paste volume fraction of 30–35%, the concrete would be expected to have a thermal conductivity of (2.1–2.2) W/(m K). While the H-S bounds are fairly tight in Fig. 5, for siliceous aggregates such as quartz with their higher thermal conductivity (≈ 5 . to 8. W/(m·K) [6, 7, 30]),

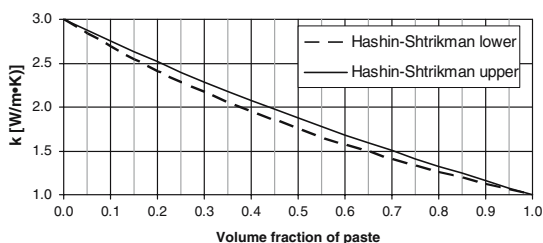


Fig. 5 Estimates based on the H-S bounds for the thermal conductivity of a concrete as a function of the volume fraction of paste, assuming that the cement paste has $k_1 = 1$. W/(m K) and the (limestone) aggregate has $k_2 = 3$. W/(m K)

the H-S bounds will be wider and the inaccuracy of using the mean H-S value as an estimate for the concrete will increase.

4 Conclusions

The transient plane source method has been applied to measuring the heat capacity and thermal conductivity of hydrating cement pastes as a function of w/c , curing conditions, and degree of hydration. The obtained results are in reasonable agreement with a majority of the previous measurements in the literature. A simple law of mixtures and the Hashin-Shtrikman bounds are useful in estimating heat capacities and thermal conductivities, respectively, both for hydrating cement pastes and ultimately for concrete mixtures.

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