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Measuring thermal properties of hydrating cement pastes

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ABSTRACT

Critical inputs for heat transfer computations in concrete are the thermo-physical properties of the material as a function of time, including its density, heat capacity, and thermal conductivity. It is widely accepted that the conductivity and the heat transfer coefficient have an influence on temperature gradient along the concrete structure. Meanwhile, the exothermic phenomenon during the hardening process is mainly affected by the specific heat and density of concrete. While thermal and mechanical properties of the hardened concrete have been investigated in detail, only few studies of thermal properties fresh and young hardening concrete have been performed. Measurements of thermal properties of cement materials as heterogeneous, wet and porous materials by conventional steady-state methods can produce large errors. In order to avoid water migration during the long run-time of the steady thermal tests, transient measurement methods are preferable. 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.

1. INTRODUCTION

One of the challenges in the design of mass concrete structures is to avoid the initiation of cracks regardless of the concrete element size, concreting procedure, weather conditions and material properties. Temperature and stress analysis due to the hydration of concrete is highly non-linear problem because a vide variety of time-dependent boundary conditions and strongly time and temperature dependent thermal and mechanical properties of early-age concrete. Modeling the generation and transfer of heat in early-age concrete is essential to understanding the behavior of concrete block as a whole. Thermal gradients can cause internal stresses which can lead to cracking on a microscopic or macroscopic scale (Mehta, 2006). Hence, the temperature of concrete during hardening is a major design consideration, especially since the time-temperature history affects both strength and durability (De Schutter, 2001).

Various models to predict the distributions of temperature (Bošnjak, 2000; Mikulić, 2007) and stress (Milovanović, 2009) in young hardening concrete have been developed in recent years. Critical inputs for these computations are the thermo physical properties of the concrete as a function of time, including its density, heat capacity, and thermal conductivity. As important input variables in the heat conduction model, the thermal conductivity and heat capacity need to be determined depending on time or the maturity of concrete.

It is widely accepted that conductivity and heat capacity have an influence on temperature gradient along the concrete structure and also that it could be taken into the model with the value of hardened concrete or even the values of aggregates used to make concrete mixture. Thermal conductivity values of concrete range from 1.98 to 2.94 W/(mK) in accordance with different aggregates, as reported by the ACI Committee 207 or even wider range reported for normal concretes, from 1.20 up to 3.00 W/(mK) (Bošnjak, 2000).

However, thermal properties of concrete are depended by the concrete's mixture proportions, the thermo physical properties of the aggregates that it contains, and those of its hydrating cement (binder) paste component, (Bentz, 2007; Bentz, 2011). While the necessary densities are generally well known and easily measurable, less information is available on the heat capacity and thermal conductivity, particularly those of the hydrating cement paste.

Previous measurements of thermal conductivity for cement-based materials were conveniently summarized by (De Schutter, 1995). Since that time, several additional studies have been published (Morabito, 2001; Demirboga, 2003; Kim, 2003). Obtained values from these studies still exhibit considerable scatter of thermal conductivity and heat capacity (Bentz, 2007).

Contradictory results on thermal conductivity of concrete at early ages can be summarized as shown in the figure 1. An analytical evaluation of the effect showed a slight increase of the conductivity with age. Substantial increase of the conductivity with age has been found by Marechal and Sassedateljev, whereas Hundt *et al.* and Brown *et al.* reported decreasing conductivity by 20-30% during hardening (RILEM Report 15, 1998).

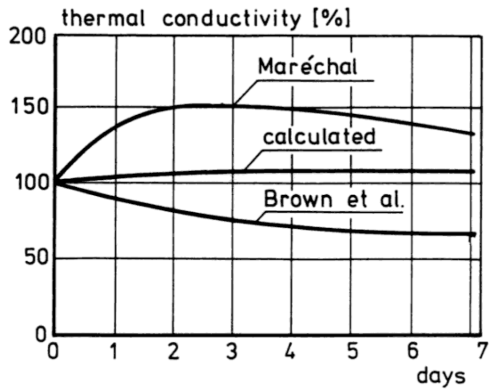

Figure 1. Development of thermal conductivity at early ages according to different authors

It is well known that thermal properties of building materials depend strongly on temperature of the material and moisture conditions, thus it can be assumed that thermal properties of concrete will vary during the hydration since temperature and moisture condition is constantly changing.

At maximal rate of hydration, hydration degree of about 30%, and temperature of about 85 °C, some authors documented 40% and 36% higher thermal conductivity than that of a fresh cement paste and hardened paste (degree of hydration, α~0.55), respectively (Mounanga, 2004). On the other hand, (Bentz, 2007) documented a little variation in thermal conductivity with degree of hydration by applying transient plane source measurement technique on small semi-isothermal specimens.

In this paper an experimental investigation is made in order to study changes of thermal properties of cement paste during hydration. Thermal properties were measured on cement paste due to the heterogeneity of concrete and the limitations of the measuring device, small plane source.

2. EXPERIMENTAL SETUP

Measurements of thermal properties of cement materials as heterogeneous, wet and porous materials by conventional steady-state methods can produce large errors. In order to avoid water migration during the long run-time of the steady thermal tests, transient measurement methods are preferable (Ukrainczyk, 2010). The transient techniques, measure a response as a heat signal is sent into the sample, and the sample response is monitored. Therefore, these techniques are distinguished mainly by the short time required to obtain the desired results.

In this paper, a transient plane source (TPS) method is applied to measure heat capacities and thermal conductivities of hydrating cement pastes cured under both saturated and sealed conditions at room temperature, Figure 2.

Figure 2. Mathis TCi Thermal Property Analyzer

The sensor (Figure 3) employs a one-sided, interfacial heat reflectance device that applies a constant current heat source to the sample.

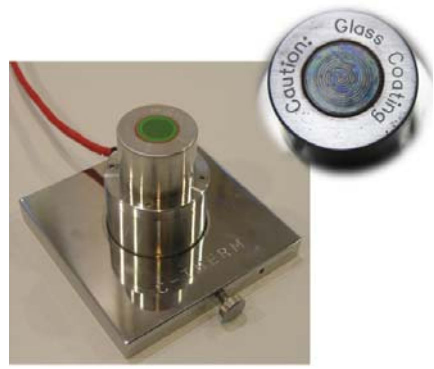

Figure 3. Plane source sensor

The interfacial sensor heats the sample by approximately 1-3°C during the testing. The sample absorbs some of the heat, and the rest causes a temperature rise at the sensor interface. The voltage drop on the spiral heater is measured before and during the transient. The voltage data is then translated into the effusivity value of the tested material. The conductivity is calculated from the voltage data by iterative method. Sensor does not physically alter or affect the sample being tested, reducing possible contamination as much as possible. As a result, samples remain intact, undisturbed, and reusable. Complete testing requires only 0.8 to 5 seconds what is only a fraction of the duration needed by some traditional methods. In addition, by varying the test time, materials can be evaluated at their surface or to a range of depths. There are practically no restrictions on sample size, the external sensor can obtain accurate readings from samples as small as 17 mm diameter, with a minimum thickness of 0.5 mm, in this case only a good contact needs to be achieved. The maximum sample size and thickness is unlimited as long as material is homogenous.

Cement paste specimens used were made of standard consistency and w/c mass ratios of 0.3, 0.4, 0.5 and 0.6. They were prepared with CEM I and CEM III type cements according to European standards. The pastes were mixed according to a procedure given by the standard HRN EN 196-3. Chemical composition of cements used is shown in table 1.

Table 1. Chemical composition of investigated CEM I 42,5 R

Oxides	CEMENT CEM I 42.5 R	CEMENT CEM III/B 32.5 N SR-LH
CaO	64.36	48.37
SiO_2	20.32	29.36
Al_2O_3	5.62	9.2
Fe_2O_3	3.08	1.74
MgO	2.9	6.11
SO_3	2.4	2.77
K_2O	1.03	0.57
Na_2O	0.42	0.29
MnO	0.21	0.32
Cl-	0.007	0.071
SUM	100.347	98.801

After mixing, cement paste was placed into standard Vicat mould and "consolidated" by tapping the mould on the counter top. The fresh pastes were tested at temperature 20 °C during the period of 0.5 - 1.0 hours after mixing. Then the specimens were weighed, covered, and then placed in an environmental chamber at 20°C, 90% RH where they were cured under either sealed or unsealed conditions. At ages of 8 hours and 1, 3, and 7 days twin (sealed and unsealed one) specimens of the same mixture were weighted and tested.

The measurements of the hydrating cement paste were facilitated by placing the (flat) cast surface of the specimen on the sensor to produce a high quality (thermal) contact between the sensor and sample. The sensor has a solid surface optimally engineered for the testing of fluids.

When measuring solids a contact agent is required as there is some contact resistance that may significantly affect the results if not addressed within the measurement protocol. The quality of contact and therefore the heat transfer depends on many parameters such as type of material, surface quality and the degree of wetting.

According to the manufacturer, the best contact agent available is water, since it has a relatively high thermal conductivity (~0.6 W/mK), low viscosity, and is easy to apply and clean. Water can be used in a limited temperature range though, from ~5°C to ~70°C. At temperatures lower than 5°C and higher than 70°C alternative contact agents like glycol and glycerin are needed. Measurements of fresh cement paste were done without any additional contact agent since paste itself contains water, water was used when paste turned to solid, for measurements after 8 hours and beyond.

3. RESULTS

While the thermal conductivity of liquid water (λ_w) is well known λ_w=0,60 W/(mK), that of cement powder (λ_c) could be found in the literature as values varying from 0.30 W/(mK) (Kim, 2003) up to 1.55 W/(m K) (Bentz, 2007) regardless on the type of cement and without any reference, what was the bulk density of the sample when conductivity was measured. To determine the value of thermal conductivity of cement used and to remove the influence of bulk density of cement powder, thermal conductivity of the cement was tested on clinker. The value of thermal conductivity gained for clinker was 1,85 W/(mK)

An estimation of the thermal conductivity of the cement paste can be determined based on the measured thermal conductivities of the water and cement powder and application of the Hashin-Shtrikman (H-S) bounds for the thermal conductivity of a two phase (cement particles in water) material. For $\lambda_c \geq \lambda_w$, the H-S lower (λ_l) and upper (λ_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 equations 1 and 2, respectively.

Equation 1

$$\lambda_l = \lambda_w + \frac{x_2}{\dfrac{1}{\lambda_c - \lambda_w} + \dfrac{x_1}{3\lambda_w}}$$

Equation 2

$$\lambda_u = \lambda_c + \frac{x1}{\dfrac{1}{\lambda_w - \lambda_c} + \dfrac{x_2}{3\lambda_c}}$$

Figure 4 provides a plot of these bounds along with the measured data for the two fresh cement pastes utilizing thermal conductivity values of 0.60 W/(m K) for water and 1.85 W/(m K) for cement clinker. The latter value for the cement clinker provides H-S bounds that encompass experimental data points for the fresh cement pastes.

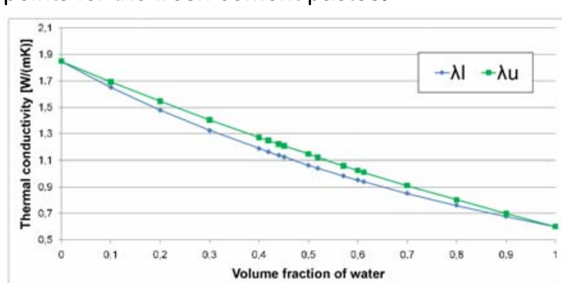

Figure 4. Measured thermal conductivities of fresh cement pastes as a function of initial water volume fraction

Measured values of thermal conductivity for fresh cement pastes were corrected to correspond relatively well with theoretical value boundaries gained from simple law of mixtures (Hashin-Shtrikman bounds).

Mean value from theoretical upper and lower values of thermal conductivity was used to calibrate the sensor when fresh cement paste was measured and in further research this values are presented as thermal conductivity of the fresh cement paste. Other values, those of hardened cement paste were measured with calibration for a ceramic material in thermal conductivity range from 1,1 to 29,0 W/(mK) and with water as a contact agent, as given by the manufacturer of the sensor.

The measured thermal conductivities as a function of degree of hydration are provided in Figures 5 - 8. Within the reproducibility of the measurements, there is some variation of the thermal conductivity of the cement pastes in time.

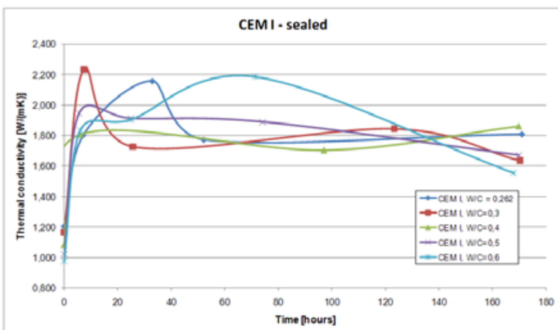

Figure 5. Measured thermal conductivities as a function of time for CEM I - sealed

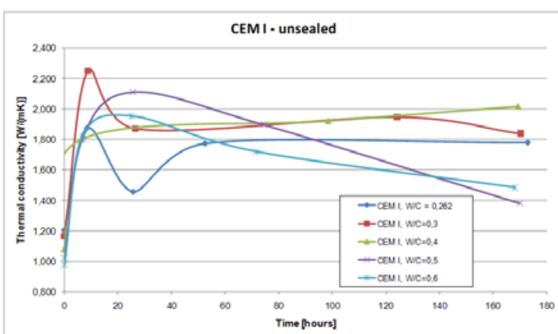

Figure 6. Measured thermal conductivities as a function of time for CEM I - unsealed

Generally, it can be said that cement pastes made with CEM I have greater water to cement ratios than those made with CEM III, respectively. There can be noted a similar tendencies on all of the tested samples made with CEM I and CEM III, there is a great increase of thermal conductivity in first 8 hours, after which a decrease can be noted until thermal conductivity reaches a constant value.

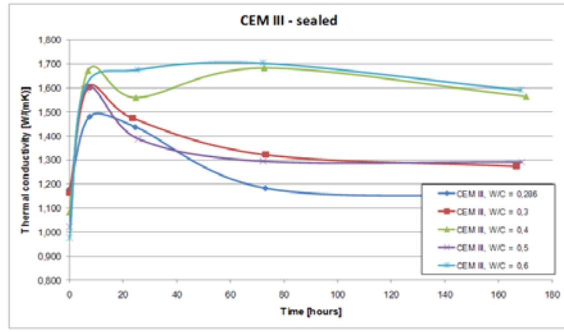

Figure 7. Measured thermal conductivities as a function of time for CEM III-sealed

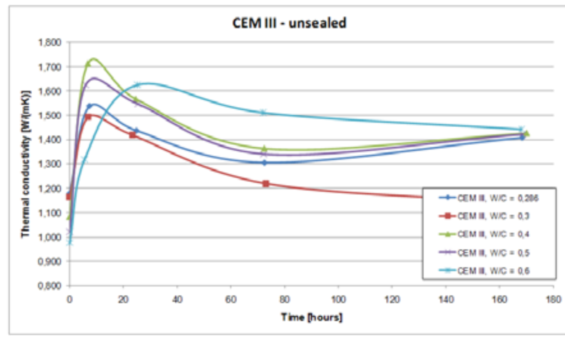

Figure 8. Measured thermal conductivities as a function of time for CEM III-unsealed

The samples made with CEM III indicate that the initial gain of thermal conductivity is smaller. This should be noted because CEM III is cement with a large content of slag which could influence the described thermal conductivity peak and also a smaller final value of thermal conductivity of hardened cement pastes.

From the results obtained it is interesting to stress the following. As the volume fraction of the solids (components having the highest thermal conductivity) increases and the free water volume fraction decreases during hydration, the expected increase in thermal conductivity occurs.

Afterwards, during the hydration, volume fractions of unreacted cement and free water components decrease while the fractions of formed hydration products increase but this is more than compensated by the formation of the internal porosity (filled with air and water vapor in case of sealed conditions) due to chemical shrinkage.

4. CONCLUSIONS

Measurements of thermal properties evolution during hydration are quite a challenge because during the cement setting and hardening, microstructure of material and amounts of individual phases (hydraulic cement minerals, water and formed hydrates) are changing continuously.

A simple law of mixtures and the Hashin-Shtrikman bounds are useful in estimating thermal conductivities of fresh cement pastes.

The obtained results show that there is an increase in the thermal conductivity of cement pastes in first 8 hours after mixing and then thermal conductivity is decreasing to a constant value. This constant value can be accepted as 1,80 W/(mK) for CEM I, and 1,40 W/(mK) for CEM III.

It was also found that the conductivities of the cement paste are affected by the types of cement used, while the influence of water to cement ratio still cannot be determined.

ACKNOWLEDGMENTS

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