Analysis of thermal properties of cement paste during setting and hardening

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Abstract. An experimental investigation is made in order to study changes of thermal properties of hardening cement paste. Using a hot disc principle for determination of thermal properties, specific heat capacity, effusivity and thermal conductivity are analyzed during first 4 days of hydration. Specific heat capacity value changed only slightly during hydration. Thermal conductivity decreased with the progress of hydration 20% compared to initial value. Hydration process was monitored using ultrasonic pulse velocity (UPV) test. A discussion of results is made taking into account porous nature of cement paste and transformation of liquid and hardened phases i.e. water and clinker minerals, into hardened structure.
The motivation for conducted research is improvement of numerical models for calculating temperature changes in mass concrete structures using hydration dependant thermal properties. Also, another field of application could be the quality control of cement based materials.

1. INTRODUCTION

Cement hydration can be defined as a sequence of chemical reactions initiated with the contact of cement and water. Progress of hydration process reflects itself at the macro level of observation as a change of cement based material properties. Different methods of testing, like measuring of the rheological properties, strength development or heat liberation can then serve as a tool for monitoring of the hydration process. Rate of chemical reactions significantly changes during hydration and can be divided into five stages: pre-induction, induction, acceleration, deceleration and diffusion [1, 2]. During the first few days of hydration the greatest portion of chemical reactions is finished. During that period changes of cement based material properties are also the greatest. In the early stage, hydration process is highly exothermal and generated heat may result in large temperature changes. Depending on the degree of external constraints, high tensile stresses may develop in relation to the actual tensile strength and harmful cracking is likely to appear. 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. In order to improve our understanding how cement based materials behave in early period of hydration it is necessary to gain more knowledge in how thermal and mechanical properties are connected to its governing process, i.e. the hydration of cement. Thermal conductivity variation during an early period of hydration is an input parameter for simulation of temperature and stress variations and evaluation of potential risk of cracking in young hardening concrete. For that reason in this paper an experimental investigation is made in order to study changes of thermal properties of cement paste during hydration. Thermal conductivity variation could also be a potential tool for monitoring of hydration process in concrete, which is a tool for estimating mechanical properties. The goal of this paper is to answer: How can changes of thermal properties of cement paste be monitored during hydration? How thermal properties are changing and how are they connected to the changes in the microstructure of cement paste?

2. TESTING METHODS USED

2.1 System for measuring thermal properties

In order to study changes of thermal properties during hydration it was necessary to use testing technique which will allow us to measure thermal properties in the small time intervals. For that purpose hot disk principle method was applied and the system used was Mathis TCi thermal conductivity analyzer (Figure 1). Mathis TCi system is comprised of a sensor, control electronics and computer software, where the sensor employs a one-sided, interfacial heat reflectance device that applies a constant current heat source to the sample. The interfacial sensor heats the sample by approximately 1-3°C during testing, the sample absorbs some of the heat, and the rest causes a temperature rise at sensor interface. Voltage drop on spiral heater is measured. Voltage data is then translated into the effusivity value of tested material. Conductivity is then calculated from the voltage data by iterative method and specific heat capacity can be calculated if density of material is known. During testing, the sensor does not physically alter or affect the sample being tested, reducing possible contamination as much as possible. Complete testing requires only 0.8 to 5 seconds what is only a fraction of the duration needed by some traditional methods [3, 4]. Sensor needs to come in contact with only one side of the sample, and has the capability of “seeing through” layers into the actual sample. For example, liquid samples can be tested in plastic bags, without the thermal value of the bag skewing the results. A sample of cement paste after mixing is placed in a low density polyethylene sheet 0.025 mm thick in order to preserve sensor from coming into direct contact with fresh cement paste. Placing of the specimen in the sheet allowed a continuous measurement of thermal properties.

2.2 Description of the ultrasonic setup

Beside the thermal properties measurements hydration process was monitored using ultrasonic pulse velocity (UPV) test. An experimental setup was made so that changes of the ultrasonic pulse velocity through cement paste sample can be continuously measured during the first few days of hydration. Measuring system (Figure 1)consists of a pulse generator which has a pulse repetition frequency of 1 pulse every 4 seconds. The pulse is converted to an ultrasonic wave through 54 kHz piezoelectric sensor. The wave is then transmitted through the material and picked up by a receiver, which is also 54 kHz piezoelectric sensor. Pulse generator is connected to a PC so that information about the speed of the ultrasonic wave is recorded. Sample of cement paste is placed in the mould after mixing and measurement is started. Results of time of flight are recorded to the computer every one minute and UPV is then calculated.

Figure 1. Mathis TCi Thermal Property Analyzer

Figure 2. Ultrasonic setup

2.3 Materials and preparation of cement paste

Cement paste used is made with CEM I type cement according to European standards. Investigation is conducted on cement paste with 0.3 w/c mass ratio. The paste was mixed according to a procedure given by the standard HRN EN 196-3. Properties of cement are shown in table I.

Table I. Properties of cement CEM I 42,5 R

Blaine (m^2/kg)	Mineral composition (%)				Setting time (h) w/c ratio = 0.3	
	C_3S	C_2S	C_3A	C_4AF	Initial set	Final set
353	59.86	11.94	8.36	8.82	2.33	3.00

3 ANALYSIS OF RESULTS

3.1 Development of UPV

Ultrasonic pulse velocity development can be used to describe the micro structural changes in the cement paste caused by hydration process [5, 6]. Development of the UPV can be divided into several consecutive stages. In the first stage, ultrasonic pulses transmitted through a fresh cement paste are not recorded by a measuring system, probably because of a large attenuation of the paste. After approximately 1.5 hours ultrasonic pulses are being recorded (figure 3). Initial UPV is at approximately 500 m/s. The reason for this low initial velocity is a large amount of very small air bubbles entrapped in the cement paste during mixing [4]. UPV has a constant increase up to about 1500 m/s which is attributed to the growth of ettringite crystals which fill out the capillary space and in that way reduce the distances between the cement particles. Another reason for the increase of the UPV is attributed to gravity effects and settling of cement particles which lead to improving the contact between them. It was presented by several authors [7, 8] that at the speed of ultrasonic wave of 1500 m/s cement paste, with w/c ratios varying from 0.3 to 0.6, transforms from liquid to a solid state, i.e. setting process is finished and a hardening process starts. The setting process of cement paste is caused by the increase in the connectivity of the cement particles. With the progress of hydration, connectivity increases and this causes increase of the UPV. At the same time water from capillary pores is consumed in the chemical reactions with cement and capillary spaces become partially filled with hydration products.

3.2 Development of thermal conductivity

In figure 3, changes of the thermal conductivity of the cement paste with a w/c ratio 0.3 are shown. Development of thermal conductivity is divided into three stages: first stage starts from the time zero (time of mixing), second stage starts approximately 4 hours after mixing and the third stage starts at the age of cement paste of 12 hours. By comparing the thermal conductivity and UPV development changes of the thermal conductivity can be connected to the micro structural changes in cement paste. In the first period, thermal conductivity decreases slightly and has a value between 1.4-1.5 W/mK. During that period mostly ettringite needles are formed in the paste. Greater decrease in thermal conductivity starts approximately at the age where UPV reaches a value of 1500 m/s so it can be attributed to the acceleration period of hydration and formation of C-S-H and CH. The value of thermal conductivity then drops to 1.2 W/mK. This can be caused by consumption of water from the capillary space. Capillary spaces in the paste which are not filled with hydration products are filled with air which has a lower thermal conductivity than water. At the age of 12 hours the third stage starts. Decrease of thermal conductivity continues but the slope is very small (figure 3). After the age of 24 hours there are practically no changes in thermal conductivity of the cement paste.

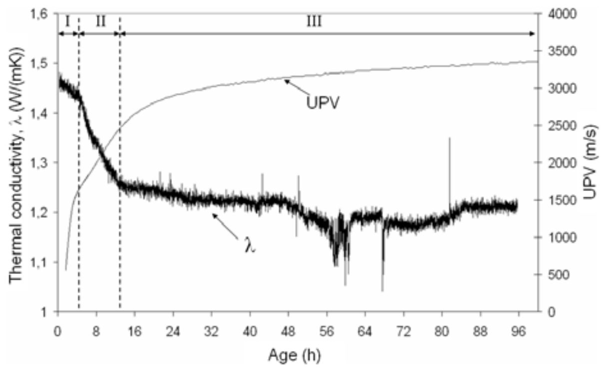

Figure 3. Changes of the thermal conductivity and UPV of cement paste

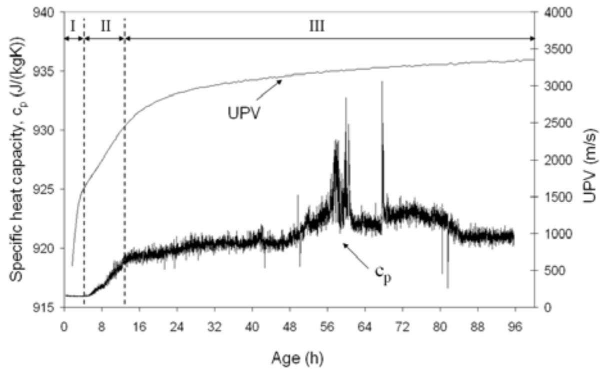

Figure 4. Changes of the specific heat capacity and UPV of cement paste

3.3 Development of specific heat capacity

In the figure 4, changes of the specific heat capacity of the cement paste are shown. Changes can also be divided into three stages. In the first stage its value remains constant. In the second period heat capacity increases slightly. And in the third stage its value shows a constant slow increase. Heat capacity of the cement paste changed during hydration within the limits from 916 to 920 J/kgK. Higher values recorded during measurement in the period between 48 and 80 hours of hydration (figure 4) are caused by the changes in the thermal bonding between the specimen and the sensor which is changed because sensor is connected to the cement paste sample through a thin layer of low density polyethylene sheet. During measurement, the entire system is surrounded by air and if air penetrates in either of the contact surfaces it will alter (reduce) the heat flow between the sample and the sensor. Reduced heat flow will result in reduced thermal conductivity (figure 3) and higher specific heat capacity (figure 4). Penetration of air is present at every measurement but the amount of air penetrated or, in other words, surface area contaminated by the penetration of air will determine its influence on the results.

4. CONCLUSIONS

Presented research showed how thermal properties can be monitored continuously during hydration of cement paste by the hot disc method. Specific heat capacity value changed only slightly during hydration while thermal conductivity decreased with the progress of hydration 20% compared to initial value. Decrease of the thermal conductivity of cement paste can be attributed to the loss of water from the pore space which slows down the heat transfer within the material. Applied hot disc technique could serve in the future not only for measuring thermal properties but also as a method for monitoring hydration of cement paste. Improvement of the hot plate method can be done through enhancing the contact between sensor and the specimen to ensure stable readings through all of the hydration process.

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LITERATURE

[1] Taylor, H.F.W. (1990) *Cement chemistry*, Academic Press, London

[2] Van Breugel, K. (1990) *Simulation of Hydration and Formation of Structure in Hardening Cement-Based Materials*, Delft Univ.Press, Delft

[3] Ramachandran, V.S.; Paroli, R.M.; Beaudoin, J.J.; Delgado, A.A. (2002) *Handbook of thermal analysis of construction materials*, William Andrew publishing, New York

[4] Bentz, D.P. (2007) *Transient plane source measurements of the thermal properties of hydrating cement pastes,* Materials and Structures vol. 40, pp 1073-1080

[5] Ye, G.; van Breugel, K. and Fraaij, A.L.A. (2003) *Experimental study and numerical simulation on the formation of microstructure in cementitious materials at early age*, Cement and Concrete Research, vol. 33 pp. 233–239.

[6] Voigt, T. and Shah, S.P. (2004). *Properties of early age Portland cement mortar monitored with shear wave reflection method*, ACI Materials Journal, vol. 101, n. 6, pp. 473-482.

[7] Trtnik, G.; Turk, G.; Kavčič, F. and Bokan Bosiljkov V. (2008) *Possibilities of using the ultrasonic wave transmission method to estimate initial setting time of cement paste*, Cement and Concrete Research vol. 38, pp. 1336–1342.

[8] Gabrijel, I. (2010) *Application of elastic waves for the determination of setting and hardening in cement composites*, Doctoral thesis, University of Zagreb, Zagreb