MICROSTRUCTURE DEVELOPMENT DURING EARLY PORTLAND CEMENT HYDRATION

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Abstract

Two main properties of concrete are most important on the construction site: the setting time and the hardening time. The setting determines the workability and casting period of the mixture. The hardening is responsible for the strength developments and controls the necessary time point to demould concrete.

In this study five different Portland cements were examined by using ultrasonic wave propagation techniques and thermal calorimetry measurements. The aim is to find a better understanding of the early hydration kinetics to enhance the forming material properties of concrete. The focus is put on the chemical and physical factors of the early hydration mechanism. Ultrasonic pulse velocity offers a possibility to follow in situ and non-destructive the developments of the microstructure. Isothermal conduction calorimetry determines the overall chemical reactivity. With the help of these methods the end of the dormant period could be clearly defined and the diversity of the acceleration processes were documented of the single Portland cements.

1. INTRODUCTION

The time period when concrete is workable is very important, it determines the transportability and casting time of it. Primary accountable for the time being concrete workable is the dormant period or so called induction period. Following the heat flow measured by isothermal conduction calorimetry the single evolution steps of hydration can be determined (see fig.1). Typically, the reaction of Portland cement (PC) starts with a strong exothermic peak (pre-induction period, stage 1). Easy dissolvable components go into solution and the first hydration products precipitate. Hereafter the heat flow decreases within one hour to a limited level (dormant period, stage 2). The reaction remains at this level for some time period until its controlling factors are overcome and pass into the acceleration period, stage 3. In stage 4 and 5 the reaction rate decelerates again.

Concrete is workable until the initial setting is reached. Numerous models are presented in literature to explain the events which take place during the dormant period, but until now there is no definitive consensus on the issue. The focus is set on the controlling factors of the
dormant period which lead into the settlement of the paste. The connection between the chemical and physical reaction of the cement and water system is searched. Earlier work on ultrasonic wave reflection technique could show the connection between initial and final settlement by determining changes in ultrasonic velocity [1]. These results were in nice agreement with standard testing of pin penetration [2]. Numerical modelling showed that the increase of ultrasonic velocity can be associated by the increasing interconnectivity of the cement grain [3].

This paper spotlights the early hydration kinetic of five Portland cements from five different production kilns. The aim is to find a better understanding of the dormant period and influencing factors on the settlement of the paste. The Portland cements are type I cements according to CEN-EN 197-1 and are here coded cement D, E, G, M, and P. These cements were detailed determined by mineral and chemical composition, including by their particle size distribution. Later the hydration reaction was followed by isothermal conduction calorimetry and ultrasonic pulse velocity.

![Figure 1: Stages during the early Portland cement hydration](image)

2. METHODS

2.1 Material characterisation

First the five different cements were thoroughly characterized. The mineral compositions were determined at three independent locations through X-ray diffraction (XRD) with Rietveld refinements (two by Brucker and one by PANalytical instrument). The chemical analysis were completed with x-ray fluorescence (Philips PW 2404 x-ray spectrometer). Free lime content was determined by glycol extraction. Finally particle size distributions (PSD) were measured using a Malvern Mastersizer.

2.2 Isothermal conduction calorimetry

To evaluate the different hydration stages a TAM Air machine measured the heat flow in milliwatt range under isothermal conditions at 20 °C. A water cement to ratio (w/c) of 0.5 was applied. Special effort was put to obtain repeatable results during the first hour after mixing.
For this purpose the cement was placed in small glass ampoules and water was added by using syringes. Beforehand the sample could thermally adjust for 2 hours. Next the paste was mixed manually with a small propeller device for one minute. As reference water filled glass vessels were applied with same heat capacity as the sample [4].

2.3 Ultrasonic pulse velocity

Five Portland cements were chosen to be study the kinetics of hydration by ultrasonic pulse velocity (UPV). The experiments were performed on cement pastes with a w/c of 0.4. The mix was kept at constant temperature of 20 °C using a cooling steel jacket. Software controlled the experiment temperature with an accuracy of ΔT of 0.1 °C and automatically recorded the hydration time and the ultrasonic pulse transition time at least every 6 minutes.

The cement paste was cast into a steel mould with the dimension of 50x150x200 mm³ (thickness x height x length). The steel mould was coated with a lubricant (grease) to prevent adhesion on the wall and the sensor opening was closed with a thin plastic membrane. The ultrasonic measurement was conducted using a portable ultrasonic digital indicating tester (Pundit Plus®). In order to avoid the influence of the wall of the steel mould on the ultrasound propagation, two holes with 54 mm diameters were made in the wall. The transmitting and the receiving transducer are fixed at opposite sides of the specimen with a distance between the transducer of 50 mm. Both transducers were coupled with the specimen directly through a piece of plastic membrane. Four springs adjusted the transducer's contact pressure in order to guarantee good contact with the specimen. The springs were not released until 6~8 hours after casting, when the material was sufficiently hard to withstand their pressure.

3. RESULTS

3.1 Material characterisation

The five different cements were coded D, E, G, M and P. The quantitative mineral analyse showed that cement D had a high alite content reaching almost 70 %, followed by cement M with 65 %. Cement M stood out by its large ferrite amount of 11 %. Cement P featured the lowest alite content and proportionally a larger belite amount. Taking a look on the aluminate phase this bared that cement E had a great amount of cubic aluminate. All cements had sulphate oxide contents between 2.5 and 3.5 %, which was determined by XRF. Cement D, E and M had more hemihydrate than dihydrate. Cement G showed a very low hemihydrate content and in cement P no hemihydrate was detected. The particle size distribution illustrates the diversity in fineness of the five cements (fig.2). The distribution displayed that cement D is the finest grained cement, followed by cement E. Cement G and P had a very similar spreading. Cement M appeared to have the coarsest PSD. The results of the material characterisation are combined in table 1. Additional a surface area value was calculated from the laser diffraction data [5]. The surface area of the cements varied between 190 and 370 m²/kg.
Table 1: Material properties of the five Portland cements

<table>
<thead>
<tr>
<th></th>
<th>Cement D</th>
<th>Cement E</th>
<th>Cement G</th>
<th>Cement M</th>
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<td>Aluminate orth. [%]</td>
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<tr>
<td>Ferrite [%]</td>
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<td>Anhydrite [%]</td>
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<td>Hemihydrate [%]</td>
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<td>Gypsum [%]</td>
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<td>0.1</td>
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<td>290</td>
<td>280</td>
<td>190</td>
<td>280</td>
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</table>

Figure 2: Particle size distribution of the five Portland cements

3.2 Observed hydration kinetic

The isothermal calorimetry results of the five cements for with a w/c of 0.5 are plotted for the first 24 hours in figure 3. All five cements showed a first burst of heat during the pre-induction period. The calorimetry data could illustrate that this initial reaction was rather strong. Cement D and E presented the strongest heat release and reached after 60 minutes 23.3 and 21.5 J/g. In contrast cement M showed the lowest value of thermal energy with 7.6 J/g after one hour reaction, while Cement G and P were in-between located.
Hereafter the effects of this first exothermic reaction were overcome and the thermal energy stayed at a more or less constant level. This is characteristic of the second or dormant stage, a period of low reactivity. During the dormant stage Cement D and M had an elevated value of heat flow, but cement D, E and G stayed the shortest in the dormant period.

Each Portland cement developed an unique acceleration kinetic. Cement M and P weakly accelerated to the next stage, whereas cement D demonstrated the strongest acceleration of the reaction. Cement E and G are intermediate situated during stage 3. After 24 hours cement D reached the highest thermal energy with 232 J/g, followed by cement G, E and P. Cement M reached the lowest value of thermal energy with 148 J/g.

3.3 Observation of the microstructure development

The ultrasonic analyse demonstrated that the five Portland cement relatively fast increased during the first 24 hours of reaction. However the individual cements illustrated different velocity developments (fig. 4). The starting speed of the ultrasound wave was about 100 to 250 m/s and reached 2000 to 3000 m/s after 24 hours. All 5 cements illustrated two turning points in the evolution of the velocity increase rate. The strongest increase in wave propagation was recognized after the pre-induction period, close to the minimal thermal power and lasted until 4 to 8 hours depending on the cement variety. In comparison cement D illustrated the strongest ultrasonic velocity and cement M the lowest.
Figure 5: Relation between ultrasound velocity and heat flow of cement D

Figure 6: Relation between ultrasound velocity and heat flow of cement E

Figure 7: Relation between ultrasound velocity and heat flow of cement G

Figure 8: Relation between ultrasound velocity and heat flow of cement M

Figure 9: Relation between ultrasound velocity and heat flow of cement P
4. DISCUSSION

The cement hydration is a complex process. The chemical reaction results into formation of a physical microstructure by changing the cement and water suspension into a solid hydration structure. The beginning of the set is reached when one cannot mix anymore the paste or concrete without permanently altering the microstructure. After final setting the mix is not any more plastic and achieved certain stiffness. With the help of ultrasonic wave propagation the connectivity of the solid phase of a material can be defined. During the dormant period the paste has the properties of a suspension and the measured ultrasound speed is dominated by the liquid phase. Later the particle cluster transforms to a connecting network and the propagation path becomes governed by the solid. The velocity is directly associated to the stiffness and strength of the measured material. Here the focus is put on the evolution steps monitored by ultrasonic pulse velocity and thermal calorimeter to follow the kinetic steps of the early Portland cement hydration.

In figure 5 to 9 are the evolution of ultrasound velocity and thermal power of the single cements visualized. During the dormant period the cement suspension results in a relatively low wave velocity controlled by the liquid phase. The first turning point of the ultrasonic velocity slope illustrates a strong increase in velocity (fig. 5-9). It is assumed that this point indicates the first continuous solid path, which becomes the dominate one of wave propagation. Hereafter this network is growing and more connections are built among one another. This development adds up to a define increase of velocity. The first turning point could be earlier determined as initial set [1].

The here found initial set coincides in time (±15 min) with the minimum of heat flow determined by isothermal conduction calorimetry for all five Portland cements (fig. 5-9). Earlier studies showed similar coincidences of the initial set determined by ultrasonic wave reflecting and the beginning of stronger exothermic reaction [2]. The minimum of the heat flow indicates the beginning of the acceleration period and the turning point of the chemical reaction. The creation of a solid network overlaps with the beginning of the acceleration of the chemical reaction. This overlap illustrates that from here on a new mechanism starts. At this time point new hydration products are formed and result into more interconnectivity of the microstructure. The formed microstructure involves a higher ultrasound speed.

It is here noted that two different water to cement ratios are used in the calorimetry and ultrasound investigation, but nevertheless other calorimetry studies showed that the position of the maximal reaction barley shifted by the w/c ratio. With respect of this information the following interpretation was still possible. Further investigations are planed to additionally exclude this aspect of the w/c. During the acceleration period the ultrasound velocity and the thermal energy develop independently. It is noticeable that the second turning point of the ultrasonic pulse velocity is reached before the maximal thermal acceleration rate is accomplished. At the second turning point the ultrasonic pulse velocity exceeded the optimum rate and builds subsequently a less steep gradient. An earlier study demonstrated that the second inflection point of ultra sonic wave propagation can be defined as final set. Öztürk confirmed that the minimum ultrasonic wave reflection index coincident in time with the final setting by needle penetration [2]. At final set the velocity reaches between 1300 and 1450 m/s, except cement M which reach a much lower value. This appears to be in good correlation of the empirical determined final set by Rheinhardt [1], who stated a velocity of 1500 m/s.
The five studied Portland cements have large diversity in mineral composition as well in particle size distribution. It is highly expected that the material composition of the cements have an influence on the hydration kinetics. The ultrasonic pulse velocity and thermal reactivity showed unique developments of the single cements over time. On important factor of the microstructure growth is the C-S-H and calcium hydroxide formation after the initial set, which slowly interlocks the existing structure. The main constituent in this process are the calcium silicates. The comparison of the amount of the main clinker components alite and belite together with the time of final set could demonstrate that with increasing alite amount the final set appears earlier; while an increasing belite amount reduces the speed of microstructure formation (see fig. 10).

The detected ultrasonic velocity appeared to be in correlation of the PSD of the single Portland cements. The reached ultrasound speed after 24 hours clearly showed that the cement with the highest surface area reached the fastest propagation (cement D) and the cement with the lowest available surface area reached the slowest propagation (cement M) (fig. 4). Cement E, G and P meanwhile are intermediate located. In figure 11 the achieved ultrasound velocity are illustrated against the specific surface area of the single cements at four time steps. After the final set dependency of the ultrasound speed and particle size distribution becomes visible. Regarding this aspect it can be learned that the early strength trends highly depends on the particle size distribution and grain properties of the starting material.

5. CONCLUSION

Five different Portland cements were observed by ultrasonic pulse velocity and isothermal conduction calorimetry. With the help of these techniques the following early hydration kinetic aspects were resolved. The end of the dormant period was clearly determined by coincident in time of the turning points of ultrasonic wave propagation and thermal power. A new reaction mechanism begins at this time point. The heat flow reached a minimum, which implied that the chemical reaction began to accelerate, while the ultrasound technique determined the initial set of the paste.
The evaluation of the single material properties on the hydration kinetic illustrated that the alite, belite ratio influenced the final setting time. With increasing alite amount the final set was earlier reached. Whereas the particle size distribution influenced the absolute value of ultrasound velocity at early age. It could be demonstrated that with increasing surface area a higher speed was accomplished.

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REFERENCES