HEAT OF HYDRATION AND STRENGTH DEVELOPMENT
IN HIGH-PERFORMANCE CONCRETE

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Abstract
The paper deals with the effect of concrete maturing conditions on early age cracking, due to thermal and shrinkage stress. This is a concern about high performance concrete subjected to higher temperatures induced by exothermic hydration, and the effect of increased temperatures on the strength growth as well as volumetric changes in the initial stage of setting and hardening. Tests were carried out to determine the hydration heat of cement binders with pozzolanic additives and chemical admixtures. The results are presented for the cement paste specimens hardened in a calorimetric apparatus under isothermal conditions as well as concrete specimens with the same w/b ratio as those made of cement paste and hardened in calorimetric apparatus under adiabatic conditions. The purpose of the presented research is to determine the relationship between the amount and kinetics of heat generation and the early age compressive strength of high performance concrete cured in a real structure, with continuously changing concrete temperature.

1. Introduction
The issues relating to the self-heating effect of concrete due to the exothermic process of the hydration are well known in case of normal concrete [1]. In the high-performance concrete where increased amounts of both higher grade cement and silica fume are used, more heat is generated than in case of the normal concrete, and this has been confirmed by temperature measurements in concrete while constructing different massive and medium massive structures [2,3,4,5]. The registered maximum temperatures of the concrete’s self-heating across a structure are close to +80°C, the ambient temperature being +10°C to +15°C. Therefore, opinions of researchers on a much-increased influence of the hydration heat upon the thermal stresses in high performance concrete, compared with normal one, have been ambiguous.

The prolonged period of action of elevated temperature due to self-heating of concrete is influencing the rate of hydration process and therefore the development of mechanical properties of early-age concrete and – in consequence – its properties in later periods. In a structural element, concrete hydrates in conditions completely different from those that prevail in the small specimens used to control its properties. For calculation of the values of thermal stresses evolving from self-heating it is necessary to establish the properties of early age concrete in such conditions as will actually accompany the process of setting and hardening in a structure. If thermal stresses are greater than the strength of early age concrete it leading to microcracking already in construction stage. The strength gain of any hydrated cement paste is always associated with the release of heat and a contraction of the solid volume, and vice versa.
Aitcin [6] introduced the name “Bermuda Triangle” : strength – heat – volumetric contraction to illustrate this fact. The concrete evolves within the “Bermuda Triangle” and it is impossible for any concrete to reach strength without exhibiting two concomitant phenomena.

The microcracks in the early stage of hardening of high performance concrete may be caused by high autogenous shrinkage, too. Autogenous shrinkage increases with decreasing water-cement ratio in concrete and in high performance concrete is much higher than in normal concrete. Therefore the proper curing is necessary in high-performance concrete to minimize this shrinkage and to hydrate as much as possible the cement present in the mix. The purpose of curing is to protect the hardening concrete till it has reached a certain degree of hydration or certain level of maturity so that the desired properties may develop. The development of concrete strength is directly related to the degree of hydration, which is the ideal parameter for curing requirement measurement.

The hydration rate of the cement binders can be determined using several methods, such as measurement of the amount of chemically bounded water, or the amount of calcium hydroxide or measurement of the cement hydration heat. Results of the relevant tests related to normal concrete can be relatively easy analysed, while in case of the tests concerning high-performance concrete (HPC) determination of the cement hydration rate is much more difficult and complicated due to the presence of additives and admixtures in the concrete mixture. Hydration process and reactivity of the pozzolanic additives is considerably affected in HPC by temperature of the concrete hardening. Therefore, it is difficult to interpret mechanisms and effects of pozzolanic reactions on cement hydration process in high performance concrete.

Relationships between the strength of the HPC and the development of the relative hydration (ratio of the hydrated water and the mixing water content in the concrete) are presented by Persson [7]. He calculated the degree of hydration from the chemically bound water content. It has been found out that for concrete without silica fume, the degree of hydration increases continuously, but for concretes with silica fume the degree of hydration decrease after approximately 90 days. Meng and Schiessl [8] showed the results of investigations on the reaction mechanisms of silica fume in combination with cement. They reported that thermogravimetry is unable to differentiate the bound water, which results from the other involved reactions (CSH gel or silica gel). According to Kurdowski and Nocuń [9], addition of the reactive silica fume and decreasing of Ca²⁺ concentration in the solution considerably accelerate reaction Ca₃A with water and, therefore, leads to the decay of inductive period in a curve illustrating kinetics of the heat realise. They express opinion that a large surface of silica gel is a decisive factor because of acceleration of calcium ionic bond into the hydration, which is the ideal parameter for curing requirement phase C-S-H. In study showed by Yogendran et al. [10], the hydration process of cement/silica fume paste was followed from the estimation of hydration heat tested in isothermal conduction calorimeter. The study indicated that the hydration reaction of the cement is altered due to presence of silica fume. The relationship between non-evaporable water content, compressive strength and degree of hydration in high performance concrete was discussed in Hobbs & al. study [11]. They concluded that determination of degree of hydration in mixtures with supplementary cementitious materials from non-evaporable water content is more complicate and will require further study.

The purpose of the research presented in this paper was to determine the degree of hydration in high-performance concrete and the relation between the amount and kinetics of heat generation and the compressive strength of HPC when cured in varying thermal conditions.
2. Experimental procedure

The test results concerning hydration heat of cement binders with pozzolanic additives and chemical admixtures are presented based on the investigations of cement paste specimens hardened in calorimetric apparatus under isothermal conditions as well as concrete specimens with the same w/b ratio like the paste ones, hardened in calorimetric apparatus under adiabatic conditions to simulate real conditions of concrete curing inside a massive structure.

Two values of the water/cement ratio, characteristic for normal concrete, namely w/c = 0.55 and w/c = 0.43, have been applied, while a constant values of the water/binder ratio, w/b = 0.28, characteristic for HPC, has been applied. All notations and material proportioning concerning the paste and concrete are listed in Table 1 and 2.

Table 1: Cement pastes proportions

<table>
<thead>
<tr>
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<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>P20</td>
<td>30</td>
<td></td>
<td></td>
<td>16.5</td>
<td>-</td>
<td>0.55</td>
</tr>
<tr>
<td>P30</td>
<td>30</td>
<td></td>
<td></td>
<td>12.9</td>
<td>-</td>
<td>0.43</td>
</tr>
<tr>
<td>PS80/A</td>
<td>27,3</td>
<td>2.7</td>
<td></td>
<td>8.5</td>
<td>0.5</td>
<td>0.28</td>
</tr>
<tr>
<td>PSF80/A</td>
<td>19,1</td>
<td>2.7</td>
<td>8.2</td>
<td>8.5</td>
<td>0.5</td>
<td>0.28</td>
</tr>
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</table>

Table 2: Concrete mixture proportions

<table>
<thead>
<tr>
<th>Concrete Type</th>
<th>Cement [kg/m³]</th>
<th>Silica Fume [kg/m³]</th>
<th>Fly Ash [kg/m³]</th>
<th>Water [l/m³]</th>
<th>Sp [l/m³]</th>
<th>Aggregate [kg/m³]</th>
<th>w/b ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>B20</td>
<td>273</td>
<td>-</td>
<td>-</td>
<td>150</td>
<td>-</td>
<td>808</td>
<td>0.55</td>
</tr>
<tr>
<td>B30</td>
<td>435</td>
<td>-</td>
<td>-</td>
<td>185</td>
<td>-</td>
<td>715</td>
<td>0.43</td>
</tr>
<tr>
<td>BS80/A</td>
<td>500</td>
<td>50</td>
<td>-</td>
<td>155</td>
<td>10</td>
<td>453</td>
<td>0.28</td>
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<tr>
<td>BSF80/A</td>
<td>350</td>
<td>50</td>
<td>150</td>
<td>155</td>
<td>10</td>
<td>435</td>
<td>0.28</td>
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</table>

The cement hydration test in isothermal conditions have been performed under constant temperature, 20°C, in the calorimetric apparatus Wexham Developments. The assessment and analysis of cement hydration heat in concrete were carried out in the calorimetric apparatus under adiabatic conditions. The apparatus allows determining the upper bound of the heat released in concrete. A constant initial temperature, 20°C, of the concrete mixture has been applied in the first part of investigations. All the measurements have been carried out up to the stabilization of the temperature in the concrete tested.

Compressive strength was tested on specimens stored in calorimeter container at temperature controlled by the temperature of the sample used for testing hydration heat in adiabatic conditions and on specimens hardening in laboratory conditions (T = 20°C).

3. Results of Investigations

3.1 Hydration heat under isothermal and adiabatic conditions

On the basis of the temperature vs. time curves recorded during the tests, the amounts of heat of hydration of cement in concrete $Q(t)$ and the values of the source function $W(t)$ (rate of heat evolution) were calculated. Comparison of the test results concerning the amount of the kinetics of generated hydration heat in the cement pastes (P) hardening under isothermal
conditions as well as in concretes (B) hardening under adiabatic conditions for normal and HPC concrete are presented in Fig. 1.

Fig.1. Hydration heat and rate of heat evolution in cement pastes (P) and in concretes (B)
The characteristic values derived from the research on the concrete self-heating are summarized in Table 3.

<table>
<thead>
<tr>
<th>Concrete Type</th>
<th>$T_{\text{max}}$ [$^\circ\text{C}$]</th>
<th>$\Delta T_{\text{max}}$ [$^\circ\text{C}$]</th>
<th>$Q_{\text{max}}$ [kJ/kg]</th>
<th>$W_{\text{max}}$ [W/kg]</th>
<th>$t_{w_{\text{max}}}$ [h]</th>
</tr>
</thead>
<tbody>
<tr>
<td>B20</td>
<td>54.4</td>
<td>34.8</td>
<td>313</td>
<td>313</td>
<td>5.0</td>
</tr>
<tr>
<td>B30</td>
<td>67.1</td>
<td>47.8</td>
<td>266</td>
<td>266</td>
<td>5.9</td>
</tr>
<tr>
<td>BS80/A</td>
<td>75.8</td>
<td>56.0</td>
<td>275</td>
<td>250</td>
<td>6.8</td>
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<tr>
<td>BSF80/A</td>
<td>62.8</td>
<td>43.2</td>
<td>294</td>
<td>187</td>
<td>6.7</td>
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</tbody>
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Investigations has shown that the amount of the hydration heat generated at the initial period of hydration process is considerably higher in concretes hardened under adiabatic conditions than in the cement pastes hardened under the constant temperature $T=20^\circ\text{C}$. Relatively high temperature resulting from the exothermal nature of hydration process leads to acceleration of the heat generated in concrete hardened under adiabatic conditions.

### 3.2 Degree of hydration

The tests performed by various researchers [7,8,9,10,11] show that determination of the cement hydration degree in the cement pastes with pozzolanic additives is very difficult and sometimes controversial. When a superplasticizer is also added, the problem becomes more and more complicated, especially if the cement hydration process in concrete is analysed.

Waller [12] calibrated the following formulae for the cement degree of hydration in the presence of silica fume and fly ash (Eq. 1):

$$h_c = 1 - \exp[-3.38(w/c - \delta)]$$

where:

$\delta = \exp(1.63w/c) \frac{0.6h_{sf} sf}{c}$ in the presence of silica fume

$\delta = \exp(1.63w/c) \frac{0.42h_{fa} fa}{c}$ in the presence of fly ash

$\delta = \exp(1.63w/c) \frac{0.60h_{sf} sf + 0.42h_{fa} fa}{c}$ in the presence of silica fume and fly ash

$h_c$ – the final degree of hydration of the cement,

$h_{sf}$ – the degree of consumption of silica fume,

$h_{fa}$ – the degree of consumption of fly ash.

For calculating the total heat released it is necessary to evaluate the heat released by one unit mass of each particular binder. Waller [6] measured heat of hydration by performing adiabatic tests on mixtures of pozzolan, lime and water, with an excess of lime to attain a maximum transformation of the pozzolans into hydrates. The values obtained in his tests for silica fume and fly ash are following: $Q_{sf} = 870 \text{ kJ/kg}$, $Q_{fa} = 570 \text{ kJ/kg}$.

The total heat released by concrete with Portland cement, silica fume and fly ash in Waller model is the sum of the heats released by the various binders, weighted by their degrees of hydration/transformation and is expressed by the formulae (Eq. 2):
\[ Q = \left(510 \cdot t_{C,3} + 260 \cdot t_{C,9} + 1100 \cdot t_{C,4} + 410 \cdot t_{C,AF} \right) \frac{h_c}{100} + 870h_{sf}sf + 570h_{fa}fa \]  

(2)

where:

- \( Q \) – the concrete heat of hydration, \([kJ/m^3]\),
- \( c, sf, fa \) – amount Portland cement, silica fume and fly ash in concrete, \([kg/m^3]\),
- \( t \) – stands for the percentage of clinker phases of cement

The final adiabatic temperature rise of concrete \( \Delta \theta \) is the ratio of the heat released (from Eq.2) to the heat capacity \( C^{th} \), (Eq. 3).

\[ \Delta \theta = \frac{Q}{C^{th}} \]  

(3)

In these investigations the degree of hydration of cement in concretes cured in the adiabatic conditions has been determined by the formula (Eq. 4):

\[ \alpha(t) = \frac{Q(t)}{Q_{max}} \]  

(4)

where:

- \( \alpha(t) \) - degree of hydration,
- \( Q(t) \) - heat of cement hydration in concrete,
- \( Q_{max} \) - maximum amount of heat emitted during the full hydration determined based upon the cement mineral composition.

Comparison the degree of hydration of the concretes hardening under adiabatic conditions has been shown in Fig.2.

**Fig. 2. The degree of hydration cement in concrete**

The degrees of the hydration heat and final adiabatic temperature rise of concrete obtained from the tests and calculated using the Waller’s model are compared to each other in Table 4. Almost the same values of the degree of hydration and temperature rise of concrete have been obtained for three-component binder cement/silica fume/fly ash.
3.2. Hydration heat and strength development in isothermal and adiabatic conditions

To determine the influence of different initial temperatures on both the cement hydration thermal effects and concrete strength in the second part of investigations the following initial temperatures of the concrete mixtures were assumed: \( T_0 = 20^\circ C \) (mixtures \( B80/20 \) and \( B20/20 \)), and \( T_0 = 85^\circ C \) (mixtures \( B80/8 \) and \( B20/8 \)), and \( T_0 = 35^\circ C \) (mixtures \( B80/35 \) and \( B20/35 \)), as the characteristic temperatures prevailing in autumn/winter and summer concrete pouring periods, respectively.

On the ground of the compressive strength test results of concrete cured in isothermal conditions at 80\(^{0}\) C, 200\(^{0}\) C and 350\(^{0}\) C, a constant value of activation energy of hydration process, satisfying the Arrhenius equation, was determined. This allowed the establishment of the relation of concrete strength in function of equivalent curing time. The following equation was obtained for the equivalent curing time of the B80 concrete investigated:

\[
t_e = \int_0^t \exp \left[ \frac{5273}{T - 263} \cdot \left( \frac{1}{T - 293} \right) \cdot \frac{T - 293}{293 - T} \right] dt
\]  

(5)

Compressive strength of B80 concrete cured in isothermal condition at temperatures of 8\(^{0}\) C, 20\(^{0}\) C and 35\(^{0}\) C in function of the real curing time, and in function of the equivalent curing time, calculated using formula (5) – is shown in Fig.3.

As can be seen from the graph in Fig.3, the relationship (5) accepted in calculation of the equivalent curing time of B80 concrete is describing very well the influence of variable curing temperature on the growth of strength of concrete in the range of temperatures adopted.

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Table 4: The theoretical and experimental values degree of hydration and temperature rise

<table>
<thead>
<tr>
<th>Concrete type</th>
<th>( \alpha )</th>
<th>( h_c ) (Eq.1)</th>
<th>( \Delta T_{\text{max}} )</th>
<th>( \Delta \theta ) (Eq.3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B20</td>
<td>0.70</td>
<td>0.84</td>
<td>34.8</td>
<td>42.2</td>
</tr>
<tr>
<td>B30</td>
<td>0.60</td>
<td>0.77</td>
<td>47.8</td>
<td>59.3</td>
</tr>
<tr>
<td>BS80/A</td>
<td>0.56</td>
<td>0.54</td>
<td>56.0</td>
<td>66.0</td>
</tr>
<tr>
<td>BSF80/A</td>
<td>0.42</td>
<td>0.42</td>
<td>43.2</td>
<td>45.2</td>
</tr>
</tbody>
</table>
Figure 4 presents the test results on the amount and kinetics of generated hydration heat and on compressive strength concerning the B80 concrete cured in adiabatic conditions for varied initial temperatures.

In the case of normal concretes the tests revealed that different initial temperatures of the concrete mixture did not affect the total amount of the hydration heat emission rate, but they had an impact on rate of heat evolution. After 7 days the concrete self-heating effect was almost at the same level $\Delta T_{\text{max}} = 35^\circ\text{C}$ regardless of the initial temperature, [13].

In the case of high performance concrete it was found out that both the kinetics and amount of emitted hydration heat depend equally upon the concrete mixture initial temperature. The HPC self-heating reached clearly higher values and diversification dependent on the concrete mixture initial temperature $\Delta T_{\text{max}} = 46.8 \div 57.0^\circ\text{C}$, and the higher values concrete maximum temperature $T_{\text{max}} = 66^\circ\text{C} \div 80^\circ\text{C}$, regardless of the fact that the amounts of generated specific heat, i.e. per 1 kg were not greater than those valid for normal concrete.

Having a continuous temperature distribution over the time for solidifying of concrete, the distribution being recorded while examining the hydration heat under adiabatic conditions, the equivalent time for concrete curing at varying temperatures has been computed, assuming 1-hour intervals of integration. In Fig. 5 the degree of hydration HPC in a function of the equivalent curing time has been shown.

Based upon the obtained results, the relationships between the amount of hydration heat emitted in the concrete and its compressive strength at a specific instant of its solidifying has been determined. Fig. 6 provides a comparison of the functions $f_c = f(Q)$ for the B80, B40 and B20 concretes. At a given quantity of emitted heat, B80 concrete attains the highest strength, taking into account that the same values of this function are reached by individual concretes after different curing periods.
4. Conclusion

Investigations carried out proved that close relation exists between the advancement of hydration process, expressed by the amount of the emitted heat and the development of mechanical properties of concrete, hardening in variable thermal conditions. Self-heating of high-performance concrete attains appreciable values in connection with high content of high class cement per 1 cu.m. of concrete; on the other hand, the quantities of heat emitted per 1kg of binder is lower than in normal concrete.

The maximum temperature reached within a high-performance concrete does not depend on the amount of cement used to make the concrete but rather on the amount of cement that actually hydrated. The test results shown that the cement degree of hydration decreases when pozzolanic additives are used.

Investigations proved great influence of the initial temperature of concrete mix on the course of heat emission process and on the growth of strength in high-performance concrete. In view of
the influence of self-heating in high-performance concrete on its strength in structures, it is most advantageous to use concrete mixes with their temperature lowered and concreting during low ambient temperatures. At high initial temperature and its subsequent rapid growth due to self-heating of concrete, the growth of strength is inhibited.

5. References


KASZYNNSKA, „Heat of Hydration” 10/10

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