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Early age properties of high-strength/high-performance concrete

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Abstract

Analyses and results of tests on heat of hydration and compressive strength of high-performance concrete cured in variable thermal conditions are presented in this paper. Investigations of hydration heat of cement were carried out in calorimeter, in adiabatic conditions. Test samples for strength tests were stored in isothermal conditions at temperature of $T = 8°\mathrm{C}$, 20°C, 35°C, and in adiabatic conditions at the temperature controlled by the temperature of the sample used in the hydration heat test. The purpose of the research was to determine a relation between the amount and kinetics of heat generation and the early age compressive strength of high-performance concrete cured in the massive structure, where the temperature in concrete changes continuously. The results for high-performance concrete are compared with respective values obtained for normal concrete. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Adiabatic conditions; Compressive strength; Curing conditions; Degree of hydration; Heat of hydration; High-performance concrete; Massive structures; Silica fume; Superplasticizer

1. Introduction

For calculation of the values of thermal stresses evolving from self-heating of large concrete masses as a result of exothermic process of cement hydration 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. The investigations of hydration heat of cement allow the determination of the distribution of temperature inside the mass of concrete. The investigations concerning the development of mechanical properties of concrete in the course of hardening, allow determining the level of effort in concrete and – consequently – the assessment of the level of risk of damage to the structures.

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 high-performance concrete where increased amounts of cement and silica fume are applied, self-heating is higher than in case of the normal concrete. This has been confirmed by temperature measurements in concrete while constructing different massive and medium massive structures [2–4]. 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. Significant effects upon the temperature distribution over the cross-section area of the structure in question have both the ambient temperature and the initial temperature of the concrete mixture [5]. Such a high temperature of the curing of concrete influences substantially not only the hydration process, but also the kinetics of the development of mechanical properties of early ages concrete and also its mechanical properties at latter ages.

Hegger [2], investigating self-heating of concrete mixes, found that in B85 concrete cured in the structure, a 10–15% drop of strength occurs in comparison with concrete hardening for 28 days at normal temperature of 20°C. He proposes to introduce a reducing coefficient for determining the characteristic strength of concrete. Masuda et al. [6], on the other hand, on the basis of concrete strength hardening for 28 days in normal conditions and for 90 days in massive structure, found that the diminution of concrete strength in a structure takes place, when the temperature of concrete exceeds 60°C. When the maximum temperature of concrete in structure does not exceed 60°C then its strength is higher than that of concrete hardening in normal conditions. The opinions of researchers that in high-performance concrete the hydration heat has much bigger influence on the thermal stresses by comparison to the normal concrete, have not been proved until now.

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The cement hydration process in the presence of superplasticizer and silica fume leads to the formation of a structure in high-performance concrete, which differs qualitatively from that found in normal concretes. 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). In study showed by Yogendran et al. [9], 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 the 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 et al. study [10]. They concluded that determination of degree of hydration in mixtures with supplementary cementitious materials from non-evaporable water content is more complicated and will require further study.

In massive structures the hardening process of concrete is proceeding in non-stationary conditions and the main problem is to define the relationships in the conditions that accompany the curing of concrete in structures. The measurements of the self-heating temperature of concrete carried out during construction of structures of this type indicate that inside concrete blocks exist quasi-adiabatic curing conditions. In view of this, the assessment and analysis of cement hydration heat in concrete and its compressive strength were carried out in own investigations in adiabatic conditions. This gave upper assessment of values of heat generated in concrete. Obtained results were compared with the strength of concrete cured in isothermal conditions assuming various initial temperatures of concrete mix. The aim of these investigations was to determine the relations between the amount and kinetics of the generated heat and development of compressive strength of high-performance concrete cured in varying thermal conditions as well as comparing the above with the relationships concerning normal concrete.

2. Experimental procedure

2.1. Assumptions

Temperature distribution in concrete caused by the influence of internal and external heat source can be described by Fourier–Kirchhof equation

$$\frac{\mathrm{d}T}{\mathrm{d}t} = a_\mathrm{T}\nabla^2 T + \frac{1}{c_\mathrm{b}\gamma}\frac{\mathrm{d}Q}{\mathrm{d}t}, \tag{1}$$

where T is the temperature at a given point in the concrete, t the time of the process, a_T the coefficient of temperature diffusion in concrete, c_b the specific heat of concrete, γ the concrete density, Q the heat of cement hydration in concrete and

$$\nabla^2 = \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right).$$

The second component of this equation concerns the internal heat source, i.e., it determines the temperature rise in concrete due to exothermic process of thermal hydration of cement. The kinetics of hydration heat emission is described by the – so-called – source function $W(t)$, defining the power density of hydration heat in concrete. The above function is bound up with the hydration heat by the following reaction:

$$Q(t) = \int_0^t W(t)\,\mathrm{d}t. \tag{2}$$

The values of the source function $W(t)$ depend on numerous parameters, such as time, curing temperature of concrete at a given point, quantity and kind of cement used, additives and admixtures. Suitable assumption of the form of source function has direct influence on the accuracy of the solution of the heat transfer equation; this, in turn, is conditioning on the correct determination of thermal stresses induced by the hydration heat in concrete.

The influence of temperature on the rate of physical–chemical reactions in concrete is described by the – so-called – temperature function $f(t)$:

$$f(T) = \frac{k_\mathrm{T}}{k_{T\mathrm{a}}}, \tag{3}$$

where k_T is the rate of physical–chemical changes in concrete at temperature T, $k_{T\mathrm{a}}$ the rate of physical–chemical changes in concrete at temperature T_a.

The reference temperature T_a is assumed to be the usual temperature of concrete curing $T_\mathrm{a} = 20°\mathrm{C}$. The relationship between the constant reaction rate and the temperature can be described by Arrhenius equation

$$k_\mathrm{T} = A\exp\left(-\frac{E_\mathrm{A}}{RT}\right), \tag{4}$$

where E_A is the activation energy, R the universal gas constant, $R = 8314$ J/(mol K) and A is the constant.

Determining the rate of reaction at reference temperature T_a using Eq. (5)

$$k_{Ta} = A \exp\left(-\frac{E_A}{RT_a}\right) \tag{5}$$

the temperature function can be presented in the form (6)

$$f(T) = \frac{k_T}{k_{Ta}} = \exp\left[-\frac{E_A}{R}\left(\frac{T_a - T}{T_a T}\right)\right]. \tag{6}$$

Temperature function in this form is often assumed in analyses of the influence of curing temperature on the strength of concrete. The notion of maturity coefficient of concrete hardening in variable temperature, or – otherwise – "equivalent concrete curing time" is connected with temperature function. It denotes the time needed by concrete cured at reference temperature T_a to attain the same properties as concrete cured at variable temperature T during time t.

$$t_e = \int_0^t f(T)\,dt. \tag{7}$$

Assuming temperature function in the form (7), time t_e can by expressed by Eq. (8)

$$t_e = \int_0^t \exp\left[-\frac{E_A}{R}\left(\frac{T_a - T}{T_a T}\right)\right] dt. \tag{8}$$

Ekerfors et al. [11], define the equivalent concrete curing time in variable temperature using Eq. (9)

$$t_e^* = \int_0^t \beta_T^*\,dt, \tag{9}$$

where

$$\beta_T^* = \begin{cases} \exp\left[Q^*\left(\frac{1}{T_{ref}} - \frac{1}{T_k}\right)\right] & \text{for} \quad T_k > 263\ \text{K}, \\ 0 & \text{for} \quad T_k \leqslant 263\ \text{K}, \end{cases}$$

where

$$Q^* = Q_{ref}\left(\frac{30}{T_k - 263}\right)^{\kappa},$$

β_T^* is the mixed rate effect of temperature and relative humidity, T_k the concrete temperature, T_{ref} the reference temperature, $T_{ref} = 293$ K, Q^* the "activation temperature" regarded as dependent on the temperature and Q_{ref}, κ is the constants obtained from fitting of test data.

Results presented in paper [11] have been obtained by investigating the hydration heat of concrete cured in semi-adiabatic conditions, concrete strength – on the other hand – cured in isothermal conditions. In RILEM report [12] Arrhenius equation was also used in describing the influence of temperature on the rate of hydration reaction. The value of the activation energy in relation to the type of cement is proposed in this equation as follows:

For portland cements:

$$\frac{E_A}{R} = \begin{cases} 4000 & \text{for} \quad T \geqslant 20^\circ\ \text{C}, \\ 4000 + 145(20 - T) & \text{for} \quad T < 20^\circ\text{C}. \end{cases} \tag{10}$$

For slag cements:

$$\frac{E_A}{R} = 6000.$$

Jonasson et al. [13] assumed the value of activation energy of hydration process of portland cements produced in Sweden according to the relationship (11):

$$\frac{E_A}{R} = 5300\left(\frac{30}{T + 10}\right)^{0,45}. \tag{11}$$

Determining the influence of temperature on the source function is essential, as the temperature, variable during the curing of concrete, is affecting the rate of progress of the hydration reaction in cement, and therefore the structure of concrete and its mechanical properties formed in these conditions.

2.2. Methods of investigations

In order to determine the influence of temperature on the course of high-performance concrete hardening process in massive structure, concurrent investigations of hydration heat and compressive strength of concrete cured in adiabatic conditions have been carried out, giving the upper evaluation of the amount of heat generation in concrete. The measurements were carried out in special calorimeter apparatus, the schematic diagram of which is shown in Fig. 1.

Cylindrical test samples measuring 240 mm × 300 mm were used in hydration heat tests. The temperature of the sample was recorded continuously during 7 days of concrete curing. Compressive strength was tested on 100 mm × 100 mm × 100 mm cubes stored in calorimeter container at temperature controlled by the temperature of the sample used for testing hydration heat in adiabatic conditions. Compressive strength tests on samples of concrete cured in isothermal conditions were also carried out, assuming variable initial temperatures of concrete mixes. Samples were tested after 8, 12, 20 h and after 1, 2, 3, 7 days of curing in adiabatic conditions as well as after 8, 12, 20 h and 1, 2, 3, 7, 28 days of curing at temperatures of 8°C, 20°C and 35°C.

2.3. Materials

Test results of high-performance concrete B80 ($w/c = 0.31$) were compared with the results of tests on normal concrete B40 $w/c = 0.42$) and B20 ($w/c = 0.53$). Notation and composition of selected mixes are presented in Table 1.

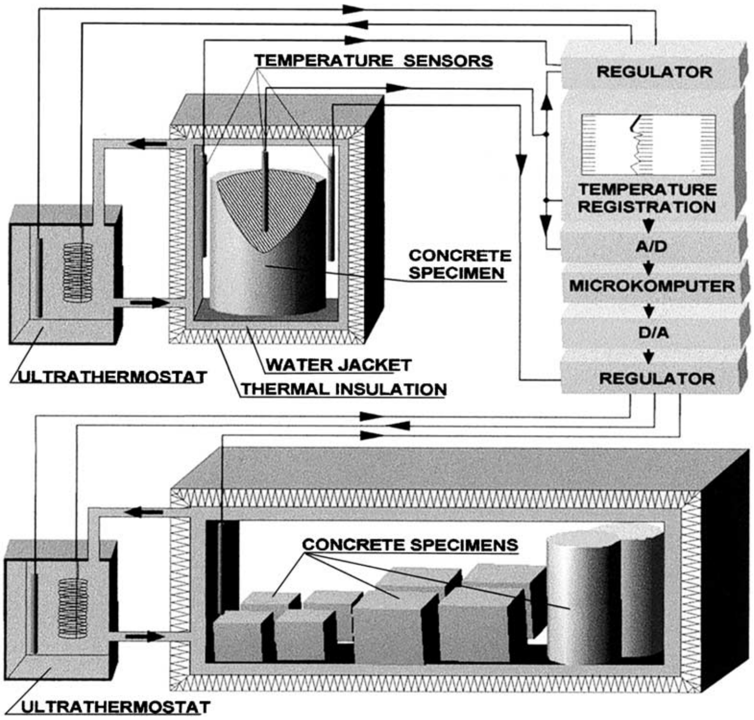

Fig. 1. Schematic diagram of the test stand.

Table 1
Concrete mixture notation and composition

Concrete type	Cement [kg/m^3]	Aggregate [kg/m^3]	Water [l/m^3]	Silica fume [kg/m^3]	Superplasticizer [l/m^3]
B80	500	1725	155	50	10
B40	435	1788	185	–	–
B20	300	1975	158	–	–

To determine the influence of different initial temperatures on both the cement hydration thermal effects and concrete strength the following initial temperatures of the concrete mixtures were assumed: $T_0 = 20°\mathrm{C}$ (mixtures B80/20, B40/20 and B20/20), and $T_0 = 8°\mathrm{C}$ (mixtures B80/8, B40/8 and B20/8), and $T_0 = 35°\mathrm{C}$ (mixtures B80/35, B40/35 and B20/35), as the characteristic temperatures prevailing in autumn/winter and summer concrete pouring periods, respectively.

3. Results of investigations

3.1. Determining the temperature function of the tested concrete

On the ground of the compressive strength test results of concrete cured in isothermal conditions at 8°C, 20°C and 35°C, a constant value of activation energy of hydration process, satisfying the Arrhenius equation, was determined. This allowed to establish the relation between concrete strength and equivalent curing time, based upon formulae (8) and (9). The constant value of activation energy of the process in Eq. (8) was determined comparing the instantaneous rates of increase of concrete strength in variable temperatures at the same level of strength. Adopting the rate of the process $\mathrm{d}\alpha/\mathrm{d}t$ on the basis of Eq. (3) as the rate of strength increase at temperatures T and T_a, the instantaneous increase of concrete strength at these temperatures is described by Eqs. (12) and (13):

$$v(t,T) = \frac{\mathrm{d}f_\mathrm{c}(T)}{\mathrm{d}t} = k_\mathrm{T} f(f_\mathrm{c}) = A \exp\left(-\frac{E_\mathrm{A}}{RT}\right) f(f_\mathrm{c}), \tag{12}$$

$$v(t,T_\mathrm{a}) = \frac{\mathrm{d}f_\mathrm{c}(T_\mathrm{a})}{\mathrm{d}t} = k_{T\mathrm{a}} f(f_\mathrm{c}) = A \exp\left(-\frac{E_\mathrm{A}}{RT_\mathrm{a}}\right) f(f_\mathrm{c}). \tag{13}$$

Activation energy was determined from the graph of the rate of strength increase (logarithm) at various temperatures, at the same strength in function of inverse of temperature $1/T$.

$$\ln\frac{v(t,T_{\mathrm{a}})}{v(t,T)} = \frac{E_{\mathrm{A}}}{R}\left(\frac{1}{T}\right) - \frac{E_{\mathrm{A}}}{RT_{\mathrm{a}}}. \tag{14}$$

Equation of a straight line $y = ax + b$ was obtained ($y = \ln[v(t,T_{\mathrm{a}})/v(t,T)], x = 1/T$), inclined to the X-axis at an angle, the tangent of which was $\mathrm{tg}\beta = E_A/R$. Using the least square method, constant value of the activation function of the cement hydration process and the equivalent curing time have been determined. For the investigated concrete B80, the following formula was obtained

$$E_{\mathrm{A}} = 42.93\ \mathrm{kJ/mol},$$
$$t_{\mathrm{e}} = \int_0^t \exp 5167\left(\frac{T-293}{293T}\right)\mathrm{d}t. \tag{15}$$

In Eq. (9) the constants Q_{ref} and κ have been determined using the method of least squares, comparing the equivalent curing time of concrete in variable temperatures, needed to attain the same strength. The following equation was obtained for the equivalent curing time of the B80 concrete investigated:

$$t_{\mathrm{e}} = \int_0^t \exp\left[5273\left(\frac{30}{T-263}\right)^{0.25}\left(\frac{T-293}{293T}\right)\right]\mathrm{d}t. \tag{16}$$

Compressive strength of B80 concrete cured in isothermal condition at temperatures of 8°C, 20°C and 35°C in function of the real curing time, and in function of the equivalent curing time, calculated using formula (16) – is shown in Fig. 2.

As can be seen from the graph in Fig. 2, the relationship (16) accepted in calculation of the equivalent curing time of B (80) concrete is describing very well the influence of variable curing temperature on the growth of strength of concrete in the range of temperatures adopted. In further considerations the temperature function in the form (6) was accepted, with coefficients established on the basis of tests for the given grade of concrete.

3.2. Hydration heat and strength development in 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 $W(t)$ were calculated. The characteristic values derived from the research on the concrete self-heating $\Delta T_{\max}$, generated amount of hydration heat $Q_{\max}$, the maximum value of the source function $W_{\max}$, as well as the time $t_{w_{\max}}$ are summarized in Table 2.

In the case of B20 concrete 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 the development and maximum values of the source function. After 7 days of the research the concrete self-heating effect was almost at the same level $T_{\max} = 35$°C regardless of the initial temperature. However, the different self-heating temperature reached in the hydration exothermic process $T_{\max} = 41.3$°C, $T_{\max} = 55.4$°C, $T_{\max} = 70.6$°C significantly influenced both the heat emission kinetics and concrete strength increase [14].

In the case of B80 concrete it was found out that both the kinetics and amount of generated hydration heat depend equally upon the concrete mixture initial temperature. Fig. 3 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.

The HPC self-heating reached clearly higher values than in case normal concrete and diversification dependent on the concrete mixture initial temperature $\Delta T_{\max} = 46.8$–57.0°C, and the higher values concrete maximum temperature $T_{\max} = 66$–80°C, regardless of the fact that the amounts of generated specific heat, i.e.,

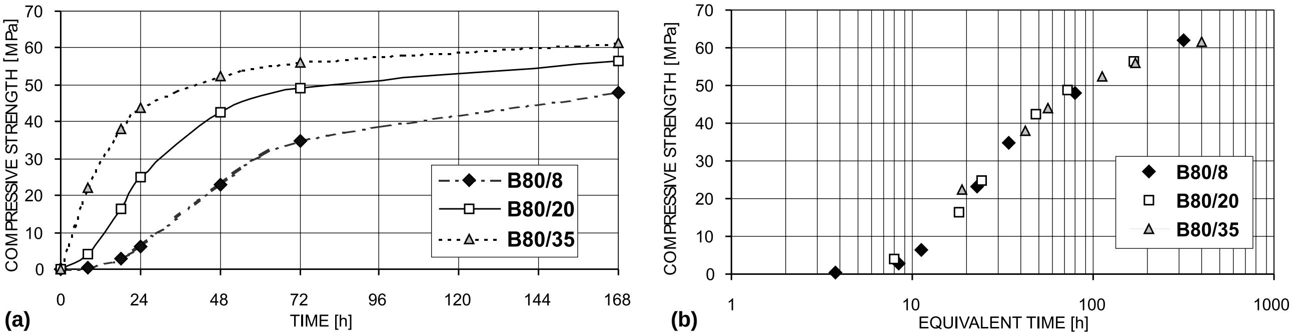

Fig. 2. Compressive strength of B80 concrete cured under isothermal conditions for varied initial temperatures vs. time and equivalent time.

Table 2
Values characteristic for self-heating of concrete specimens

Concrete mixture	T_0 [°C]	T_{max} [°C]	ΔT_{max} [°C]	Q_{max} [kJ/kg]	W_{max} [W/kg]	t_{wmax} [h]
B80/8	9	66.0	57.0	280	10.4	16
B80/20	22	74.7	52.7	259	12.8	9
B80/35	33	79.8	46.8	230	16.2	5
B40/8	11	65.0	54.0	300	7.1	15
B40/20	21	72.0	51.0	283	8.3	10
B40/35	33	78.2	45.2	251	10.0	5
B20/8	7	41.3	34.3	276	1.8	48
B20/20	20	55.4	35.4	285	4.0	16
B20/35	35	70.6	35.6	286	8.5	7

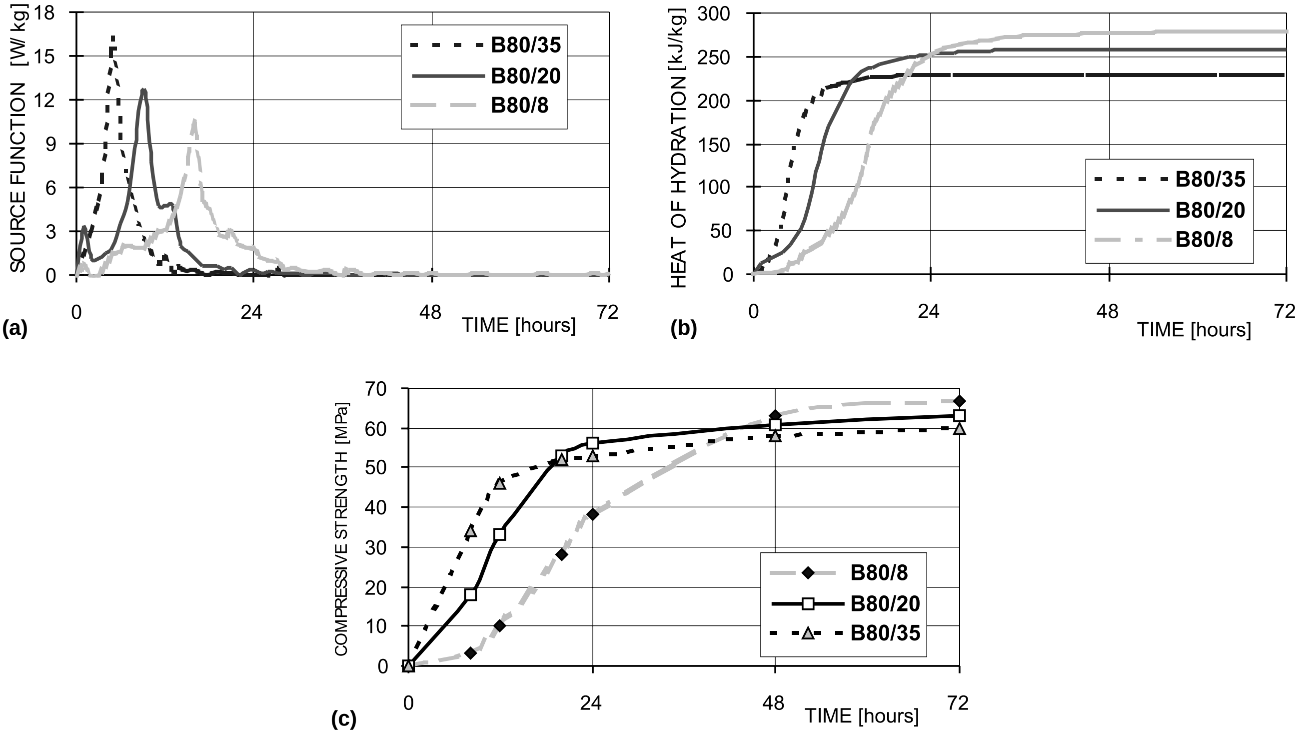

Fig. 3. Source function, heat of hydration and compressive strength of B80 concrete for varied initial temperature.

per 1 kg binder were not greater than those valid for normal concrete. Similar values of the self-heating for high-performance concrete were registered during construction of structures [2–5].

Adopting the temperature function to Eq. (16) and having a continuous temperature distribution over the time for solidifying of concrete, the distribution being recorded while examining the hydration heat, the equivalent time for concrete curing at varying temperatures has been computed, assuming 1-h intervals of integration. Fig. 4 shows amounts of the hydration heat and the compressive strength of B80 concrete at different initial temperatures of the concrete mixture versus the equivalent curing time.

The tests have revealed that the adopted temperature function reflects well the temperature effect on the concrete strength, which permits the assessment of the strength of concrete that is cured at varying temperatures across a structure.

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 have been determined. Fig. 5 provides a comparison of the functions $f_c = f(Q)$ for the B80 and B20 concretes with relation to the initial temperature of concrete mixtures.

Mean values of $f_c = f(Q)$ function in B20, B40 and B80 concretes are presented in Fig. 6.

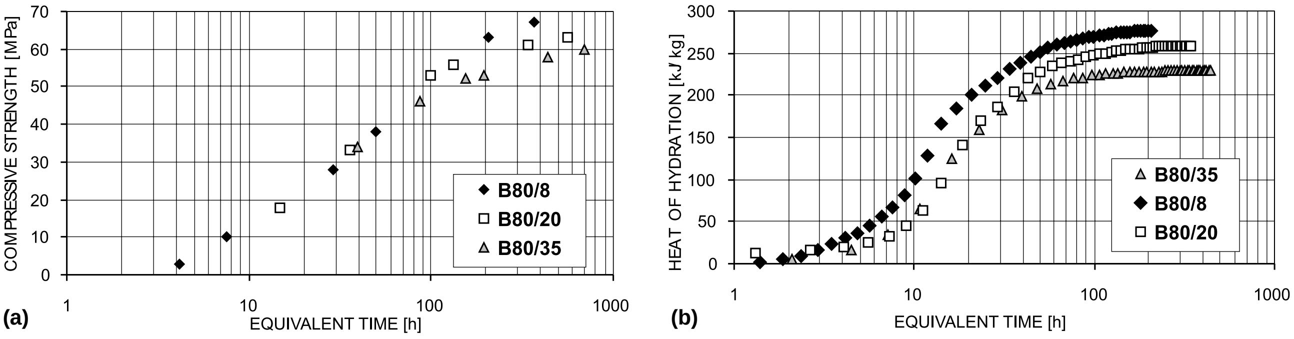

Fig. 4. Heat of hydration and compressive strength of B80 concrete cured under adiabatic conditions vs. equivalent time.

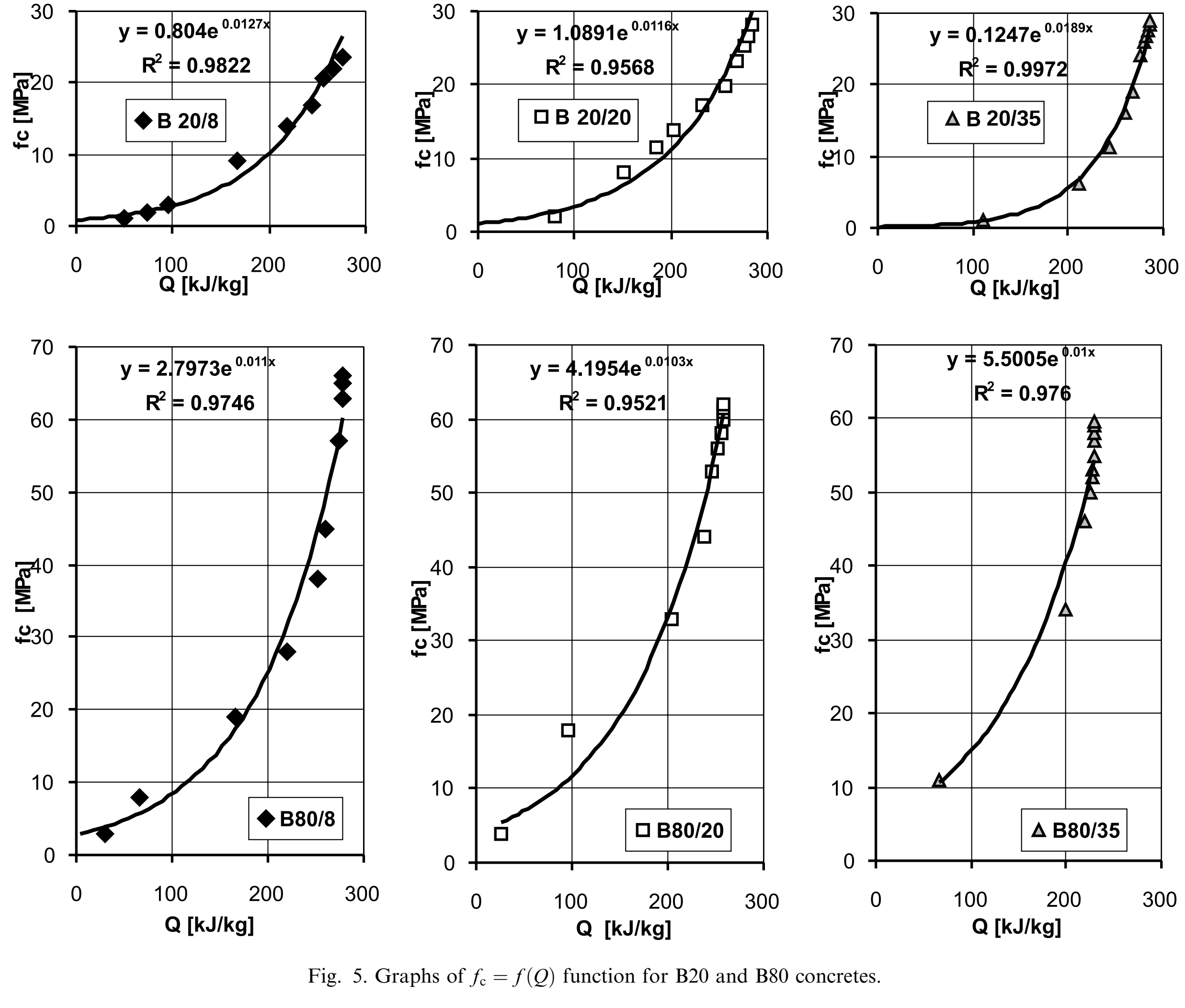

Fig. 5. Graphs of $f_c = f(Q)$ function for B20 and B80 concretes.

At a given amount of generated 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. Investigations also proved that independent of the initial temperature of concrete mix and class of concrete, the strength growing process is slower than the hydration heat remittance process in concrete, Kaszyńska [15].

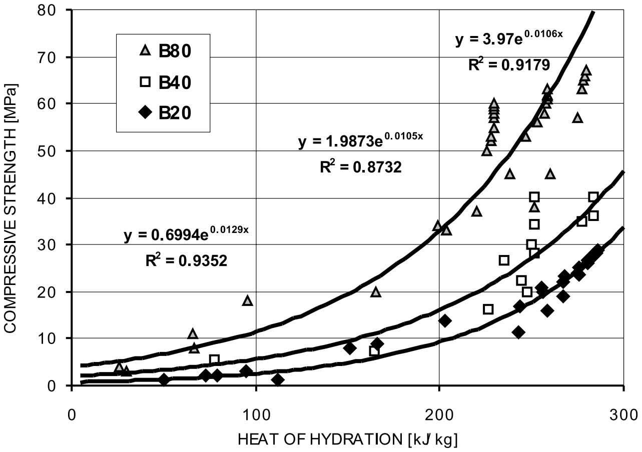

Fig. 6. Graphs of mean values of $f_c = f(Q)$ function in B20, B40 and B80 concretes.

3.3. Degree of hydration

The degree of hydration of cement in concretes cured in the adiabatic conditions has been determined by the formula

$$\alpha(t) = \frac{Q(t)}{Q_{\max}}, \tag{17}$$

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

Comparison of the degree of hydration of the B80 and B20 concretes hardening under adiabatic conditions is shown in Fig. 7.

In Fig. 8 the relation between the degree of hydration HPC and the equivalent curing time is shown.

4. Conclusions

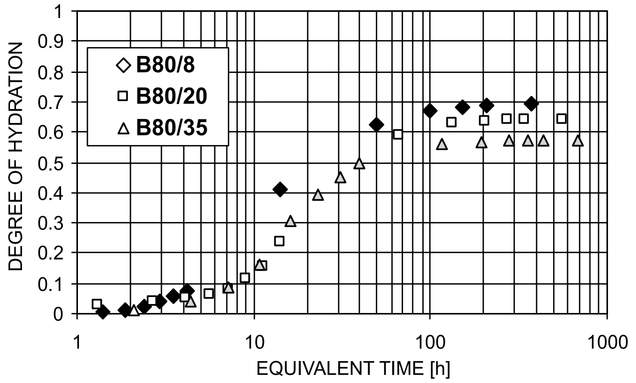

Fig. 8. The degree of hydration of B80 concrete vs. equivalent time.

Investigations carried out proved that a close relation exists between the advancement of hydration process, expressed by the amount of the generated 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 cement per 1 m^3. of concrete; on the other hand, the amount of heat generated per 1 kg of binder is similar or lower than those generated in normal concrete. A low *w/c* ratio results in an incomplete hydration due to lack of water required for that process. The concrete temperature increase depends on the amount of hydrated cement but does not depend on the total amount of cement present in the concrete mixture.

Investigations proved great influence of the initial temperature of concrete mix on the course of heat generation 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.

In massive structure, concrete hydrates in conditions completely different from those that prevail in the standard specimens used to control its properties in

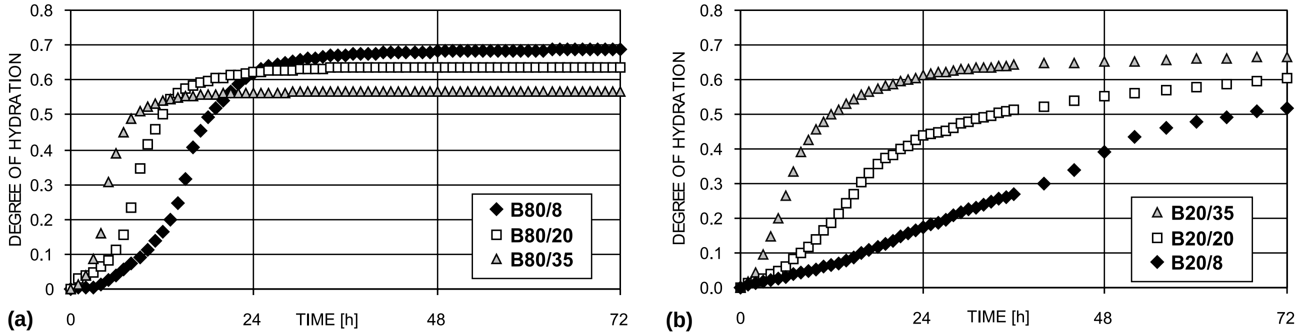

Fig. 7. The degree of hydration of cement in concretes B80 and B20.

laboratory. The special calorimeter apparatus used for investigations has enabled the simulation of thermal conditions, which occur in given period of concrete curing, at various points of a concrete block. Simultaneous investigations into the kinetics of hydration heat generation and into development of mechanical properties of hardened concrete allow the selection of the correct values of concrete properties in analytically solving the problem of thermal stresses in mass concrete.

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