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Dependence of the Kinetics of Cement Concrete Hardening from the Heat Treatment Temperature

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Abstract: Using the theory of transfer kinetic constants of hardening were calculated for cement concretes on the basis of cement from six different cement plants of Russia with different content of alite (43-65%) and C_3A (4-12%) hardened at a temperature of 20 to 70°C. It is shown that the initial curing rate increases monotonically with increasing temperature of the medium, while the drag coefficient in time is at a minimum at 40°C, with the exception of the cement of plant Volskcement, for which this ratio decreases linearly with increasing temperature. It is suggested that this feature of the influence on the drag coefficient is due to the maximum solubility of gypsum at 40°C. Apparent activation energy of curing of concrete class B15 was calculated and it was shown that the activation energy of the initial rate of hardening is close to the activation energy of the hydrogen bond and the drag coefficient is 4.4 kJ/mol, which is close to the value of the Van der Waals force.

Key words: Heat treatment · The initial rate of hardening · Drag coefficient of the hardening · The apparent activation energy of the hardening · Kinetics of concrete hardening · Kinetics of heat generation of concrete

INTRODUCTION

Heat treatment is one of the most effective ways to speed up the hardening and increase the grade strength of cement concrete, so it is widely used in the construction industry all over the world.

However, it requires extra expenditure of heat-carrying agents, that results in a substantial increase in the cost of concrete products and structures. To optimize the heat treatment process it is necessary to learn the relations between hardening of cement systems and temperature.

In recent decades in the Russian Federation and abroad intensive studies of energy-saving modes of heat treatment of building products of hydration hardening are carried out [1]. In many countries in recent years treatment with heat-carrying agents with temperature of 40°C is used, that is much lower than is commonly practiced (80-90°C) [2]. However, the scientific basis for the use of such a regime is not available [3]. This work is devoted to this issue.

Main Part: As the initial data experimental results obtained by L.I. Chumadova during the study of six different portland cements at the Leningrad Polytechnic Institute were used [4]. Table 1 shows the results of her research on the determination of the level of adiabatic specific heat generation of cements in concretes. Concrete mixes were made with consumption of cement of 330 kg/m^3 at a water-cement ratio W/C = 0.45 and 2 cm slump. Heat generration was determined at a temperatures 20, 40, 70 and 80°C in a hardening time ranging from 5-18h, finishing 36-168 hrs. Also calculations according to the article "Energy-efficient modes of heat technologies of concrete and methods of their implementation" by S.M. Trembitskogo were made [5]. This is due to the fact that it considers kinetics of cement stone hardening from 1°C to 80°C and shows high quality experimental data with no missing points and unnatural bends in the curve.

Effect of temperature on the kinetics of any physico-chemical processes can be described by the Arrhenius equation:

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Table 1: The adiabatic heat generation of cements in concrete, kJ/kg

Temperature of hardening,°C	Time of hardening, hours	Cements					
		Alekseevka cement	Belgorod cement	Leningrad cement	Volsk cement	Sebrakov cement	Pikalevo cement
20	18	69,9	121,8	86,7	71,2	66,9	70,3
	24	94,2	137,8	110,5	92,5	84,6	93,8
	48	141,1	185,1	148,6	135,7	128,1	164,5
	72	161,2	213,1	176,7	164,9	144	193,5
	96	178,4	233,6	198,9	183,8	190,1	212,7
	120	191,3	252,1	217,3	203,5	209,4	229
	144	198	267,5	225,3	-	-	244,5
	168	209,4	285,6	242,4			260
40	6	59,5	108	96,7	54,4	64,5	100,1
	18	140,7	197,6	200,9	141,5	142,4	184,6
	24	161,2	219,8	231,1	162,9	169,2	213,1
	48	210,2	272,2	293,9	218,1	220,7	270,5
	72	239,1	308,2	328,3	249,1	246,2	299,4
	96	263,4	329,5	355,1	274,7	262,9	321,6
	12	240,3	339,1	367,6	290,6	275,5	335,8
	144	297,3	348,8	380,6	304,4	285,9	349,2
	168	311,9	356,3	396,9	311,9	296	362,2
70	5	89,6	151,9	114,3	73,7	88,8	-
	9	144	196,8	167,5	151,6	139,4	515,2
	18	195,9	253,7	215,6	211,9	178,8	215,6
	24	213,1	217,3	231,1	231,9	198	238,7
80	5			133,1			66,2
	9			195,5			160,8
	18			255,4			232,4
	24			276,8			257,5
	36			189,3			278,4

$$U = U_{\infty} \cdot \exp(\frac{-E}{R \cdot T}) \quad (1)$$

Where U is a speed of the process,

U_8 Is a pre-exponential factor, which is equal to the speed of the process at an infinitely high temperature,

E - activation energy,

R - Universal gas constant,

T - The absolute temperature.

From this equation it follows that:

$$\ln U = \ln U_{\infty} - \frac{E}{R \cdot T} \quad (2)$$

From this equation it follows that the logarithm of the speed of hardening depends linearly from the inverse temperature (T^{-1}). When using this equation it should be borne in mind that U characterizes the speed of physico-chemical interaction between the components of the system. At the same time it is known that in the first hours hardening of cement paste and concrete is a heterogeneous complex process that depends on the physical and chemical similarity of the reactants, in this case – cement and water. In fundamental period of hardening the process is under diffusion control, it depends on the diffusion of water molecules and products of reaction of hydrate neoplasms. The temperature of dependence of the kinetic and diffusion factors of hardening are quantitatively very different. To overcome this difficulty, we offer to use the technique described in [6], where the kinetics of the corrosion process is described using the radiation transfer equation:

$$\frac{\tau}{\sigma} = \left(\frac{\tau}{\sigma}\right)_0 + k_1 \cdot \sigma \quad (3)$$

$$\frac{t}{s} = \left(\frac{t}{s}\right)_0 + k_2 \cdot t \quad (4)$$

where τ – hardening time (hydration), days; σ – compressive strength, MPa; $(\tau/\sigma)_0$ – the inverse of the initial rate of hardening (hydration), days/MPa; k_1 and k_2 – drag coefficients of hardening process (hydration).

Table 2: The mineral composition of used cements

Cement	The content of clinker minerals,%			
	C_2S	C_3S	C_3A	C_4AF
Alekseevka cement	27	52	5,5	15,5
Belgorod cement	29	46	12	13
Leningrad cement	18	55	10	13
Volsk cement	21	65	4	15
Sebrakov cement	12	64,9	5,3	15
Pikalevo cement	31,01	43,51	11,26	12,04

In the derivation of these equations, it was assumed that U_0 – is the maximum rate of hardening, which is observed in the first ten hours, when the film of hydrated tumors do not have a significant effect on the speed of the process. Meanwhile the rate of hardening is determined only by physical and chemical activity of the interaction of cement with water [7]. In this period, the diffusion inhibition has no significant effect and the process is under kinetic control [8]. The coefficients k_1 and k_2 reflect the impact of the diffusion inhibition on the hardening process. It follows that the use of the Arrhenius equation to account the influence of temperature factor on the kinetics of hardening we should examine the initial rate of hardening U_0 and drag coefficient K_t separately.

Table 2 shows the mineral compositions of used cements [9].

Examination of the mentioned data shows that by a wide range of cements was used in this research.

The kinetics of heat generation of cement samples at 20°C, 40°C, 70°C was studied [10]. Concrete mixes were made at a rate of cement 330 kg/m^3, water-cement ratio W/C = 0.45 and 2 cm slump. Kinetics of heat generation samples made from studied cements is shown in Figure 1.

Calculation of kinetic constants of the initial velocity U_0, drag coefficient K_{tor} and correlation coefficient K_{kor} produced by the equations of the theory of the transfer equation [3, 4].

Based on these data graphs of relations between initial velocity U_0 and drag coefficient K_{tor} and also graphs of relations between as the correlation coefficient K_{kor} and temperature of hardening of cements of different manufacturers were drawn (Figures 1, 2, 3).

Analysis of these graphs (Fig. 2, 3, 4) shows that the initial rate of hardening of all studied cements increases almost proportionally to the temperature with temperature increase from 20°C to 70°C.

Figure 3 shows relations between the drag coefficient and temperature. Examination of this graph shows that for all cements except Wolski, drag coefficient has minimum value at 40°C. The minimum value of Wolski cement monotonically decreases from 20 to 70°C.

It is known that the greatest influence on the ultimate strength of concrete samples has drag coefficient. In this regard from the Figure 2 it follows that 40°C is the optimum temperature of heat treatment for the majority of cements.

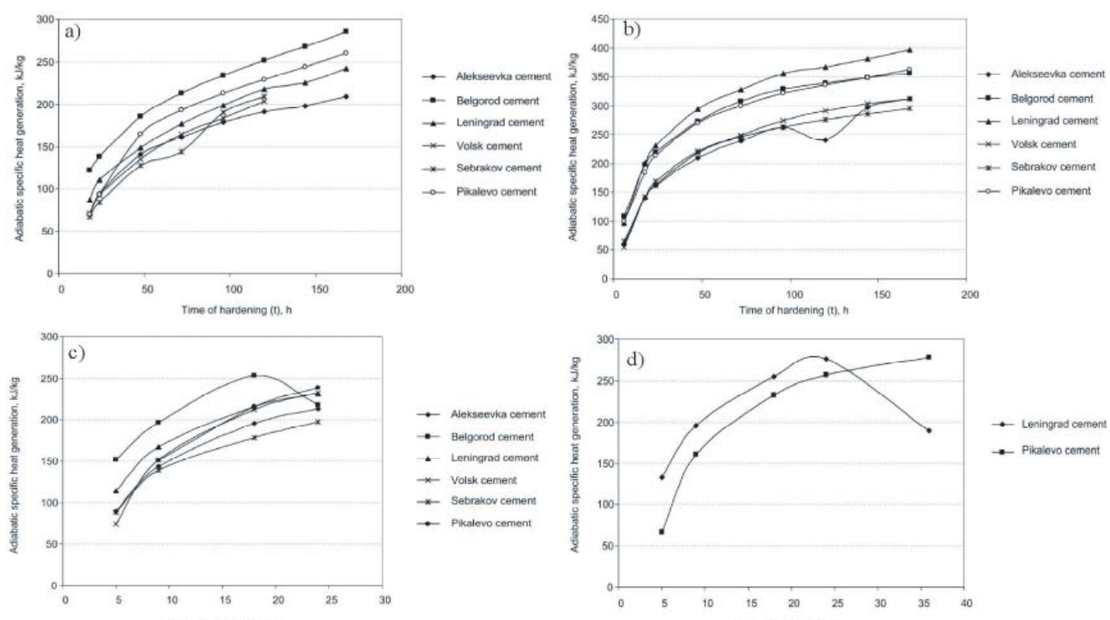

Fig. 1: Adiabatic specific heat of cements in concrete temperatures: a) at 20 0 C and b) at 40 0 C and c) at 70 0 C, d) at 80 0C.

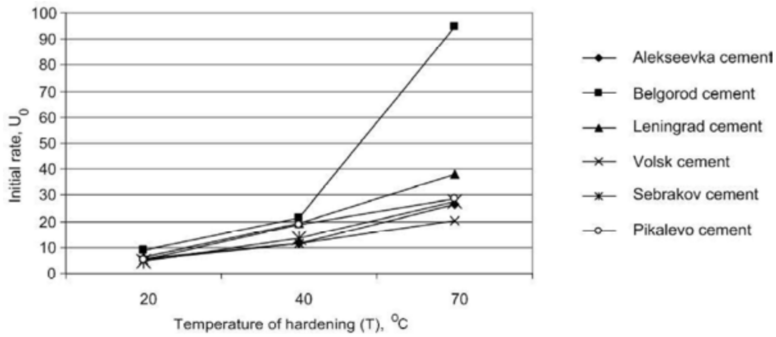

Fig. 2: Relations between the initial rate (U_0) and the hardening temperature (°C) of cements

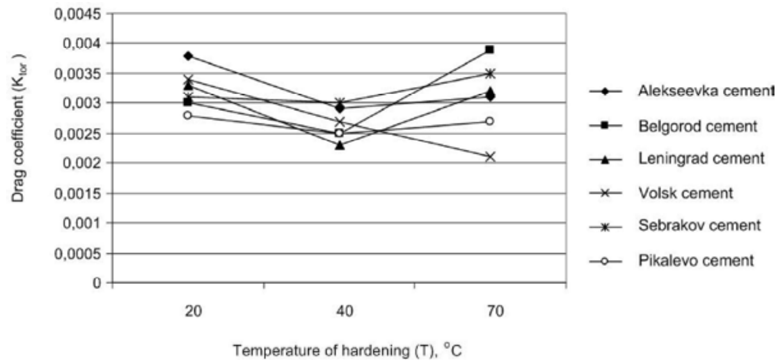

Fig. 3: Relations between the drag coefficient (K_{tor}) and the hardening temperature (°C) of cements

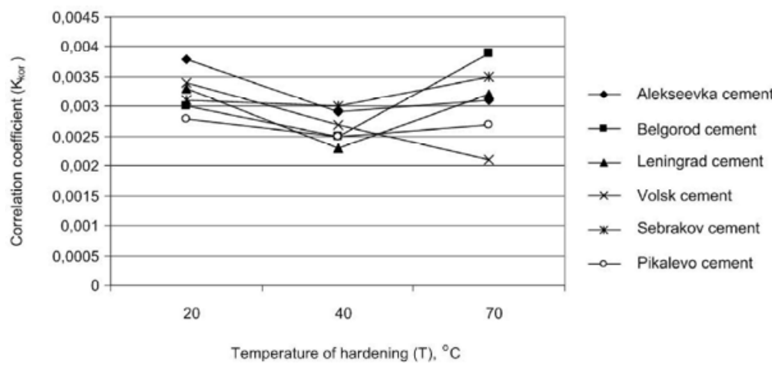

Fig. 4: Relations between the correlation coefficient (K_{kor}) and the hardening temperature (°C) of cements

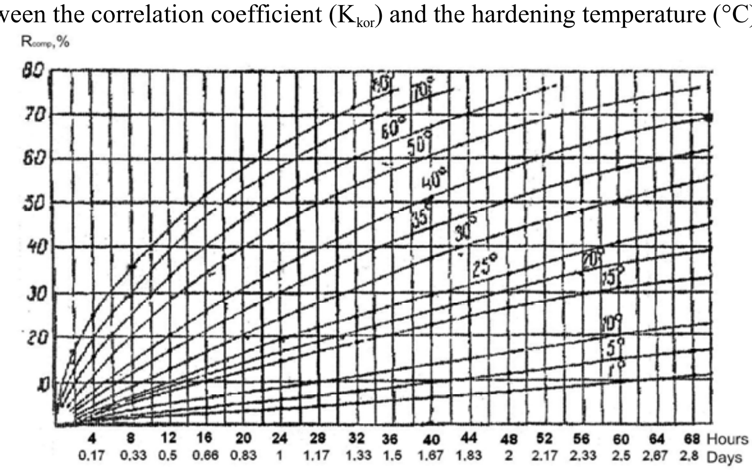

Fig. 5: Graphs of changes in strength of concrete B15 (M200) on portland cement PC 400 D0, in% from the grade strength at different temperatures of curing

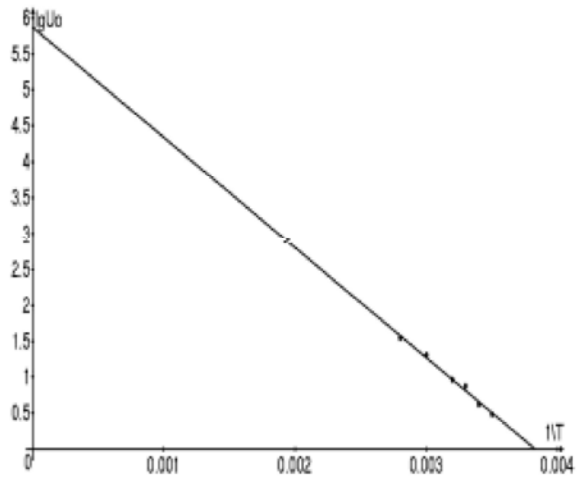

Fig. 6: Graph of the Arrhenius equation with respect to the initial rate of hardening U_0

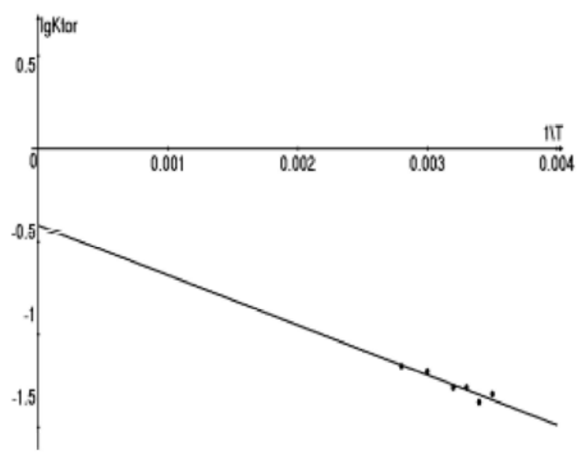

Fig. 7: Graph of the Arrhenius equation with respect to the drag coefficient K_{tor}

Also the experiment according to the data from the article “Energy-efficient modes of concrete heat technologies and methods to implement them” by S.M.Trembitskiy was carried out [4]. Figure 4 shows the graph of the changes in strength of concrete at temperatures from 1°C to 80°C.

Calculation of kinetic constants of the initial velocity U_0, drag coefficient K_{tor} and correlation coefficient K_{kor} is produced according to the equations of the theory of transference (equations 3, 4).

Using the Arrhenius equation [6], based on Figures 6 and 7 activation energies of the curing process were calculated, which were as follows: for the initial rate of hardening – 32.9 kJ/mol and for a drag coefficient – 4.4 kJ / mol.

Summary. Summarizing the material, we can note the following:

- It is shown that the effect of temperature on the kinetics of hardening of concrete can be described with a fairly high degree of accuracy using the equation based on the theory of transference and the Arrhenius equation;
- The activation energy of the initial rate of hardening is equal to 28.9 kJ/mol and the drag coefficient of 4.4 kJ/mol. It follows that the increase in temperature accelerates the hardening is much stronger in the first period than in the past. Thus, the strength of products subjected to heat treatment become less dependent on the temperature with the increase of hardening time.
- Analysis of the numerical values of the activation energy of the initial rate of hardening shows that they are close to the level of hydrogen bond energy (20-25 kJ/mol) and drag coefficient that is associated with the processes of diffusion of ions and molecules and is close to dispersion forces. This indicates that diffusion of ions occurs at the relay mechanism. This may be due to the OH^- ions and H_3O^+.
- Analysis of these graphs (Fig. 2, 3) shows that the initial rate of hardening of all studied cements with temperature increase from 20°C to 70°C increases almost proportionally to the temperature.
- Figure 2 shows the dependence between the drag coefficient and the temperature. Examination of this graph shows that for all cements, except for Volsk cement, braking ratio is minimal at 40°C. The braking rate of Volsk cement monotonically decreases to 70°C.
- It is known that the greatest influence on the ultimate strength of concrete samples has drag coefficient. In this regard from Figure 2 it follows that 40°C is the optimum temperature of heat treatment for the majority of cements.

CONCLUSIONS

Possible reason of described regularities of influence of curing temperature on the kinetics of hardening of cement systems may be the fact that the solubility of calcium sulfate in water has a maximum value at 40°C. This can have a significant effect on the kinetics of formation of hydrosulfoaluminate phases and hardening of cement stone. This gives a basement to suggest that the cement of Volsk plant has a minimum amount of gypsum.

The advantage of the proposed technology of considering temperature factors compared with the current is that used curing constants U_0 and K_{tor}, as well as E_a and K_0 refer to any term of hardening and not only for the grade strength. In addition, the activation energy of hardening also refers to any temperature at which the system solidifies. In this regard, the use of this technique allows to simplify the accounting of temperature- time factor for hardening of cement systems.

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