EFFECT OF TEMPERATURE UPON THE STRENGTH DEVELOPMENT RATE AND UPON THE HYDRATION KINETICS OF CEMENTS

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The effects of temperatures upon the properties and upon the hydration kinetics of three kinds of cements (Portland cement CEM I, blended cements CEM II/B and CEM III/A) have been undertaken and reported in this work. The rate at which the compressive strength increases depends on the ratio clinker/blast furnace slag and on temperature. Then, a new criterion "Index of temperature strength development" was introduced in order to characterise the rate at which the compressive and flexural strength increase with temperature and with time. Two types of calorimeter were used; the first one to determine the values of hydration heat under isothermal conduction, while the second was used to investigation the influence of temperatures upon the flow of hydration heat and subsequently to calculate the apparent activation energy. The activation energy ($E_{CEM\,I} = 10.24 \pm 0.36\ kJ\ kmol^{-1}$, $E_{CEM\,II/B} = 11.95 \pm 0.97\ kJ\ kmol^{-1}$, $E_{CEM\,III/A} = 17.33 \pm 0.60\ kJ\ kmol^{-1}$) of different cement was found strongly depending on the replacement ratio of blast furnace slag.

INTRODUCTION

Cementitious materials based on Portland cement are used under different climatic conditions according to seasons and regions. The resulted physical and mechanical properties change, not only according to the cement type, but also according the temperatures and other weather conditions such as humidity, atmospheric pressure and wind velocity. The energy and materials consumption with ecological and social corollary of cement production has motivated the cement industry to develop new kind of cements. These cements, so-called "Blended cements"[1] or "Low-energy cements"[2-4] or "Cements with Low-emission of CO_2" [5] are produced under EN 197-1 that has set 27 types of cements depending on clinker content and number of admixtures [1]. The production of blended cements is considered as alternative to OPC for many reasons: environment protection (depletion of CO_2, large scale use of industrial wastes and by-products), energy savings (reduction of clinker part in cement) and technical requirements (low hydration heat, durability of concrete, sulphate resistance etc.) [6]. The massive use of these

cements has encountered some practical problems due to the influence of climatic ups downs. The main factors influencing the properties of cement pastes or concretes are curing period and the temperature at which they are prepared and used. Many studies [7-9] have reported the behaviours of concretes under different temperatures. The main schools resulting from these investigations are that the temperature activates hydration process at the same manner like chemical reactions by Arrhenius law [10]. Indeed, hydration of pure Portland cement is a multi-stage and heterogeneous chemical reaction of individual clinker minerals with water in the presence of gypsum to form stable crystallohydrates causing setting and hardening of cement pastes or concrete. This complex process involving dissolution of primary minerals, nucleation, crystal growth of crystallohydrates is globally exothermic. The microstructure of cement paste or concrete resulting from this exothermic process is responsible for chemical, physical and mechanical properties of construction and buildings. Temperature is one of the keys factors that play important role during this chemical and physical process. The blended cements are anymore complex that pure Portland cement denoted

as CEM I. Portland composite cements of type CEM II /A-S and CEM II /B-S, or CEM II /L-A and CEM II/ L-B [1] are world wide commercialised and used under different climatic conditions. If limestone is considered as inert fillers, some authors have reported its influence upon the hydration of C_3S and C_3A. The authors have demonstrated that finely ground limestone can actively participate to the hydration by forming crystallohydrates like calcium monocarboaluminate [11]. Slag Portland cements are the most investigated and worldwide used among blended cements. Slag alone is hydraulically latent. The combination of limestone and slag at different ratio in one blended cement or blast furnace cements (III/A, B, C) are now in investigating course.

The present work was undertaken to investigate the sensitivity of mechanical and physical properties of new kind of blended cements with different content blast furnace slag (BFS) and limestone to the temperature change. The findings could give practical recommendations on use of different kind of cements under different weather. Also, the behaviours of well-known CEM I, as reference sample, have been investigated under the same conditions.

EXPERIMENTAL

Materials

Three industrial cements CEM I 42.5 R, CEM II /B-S 42.5 N and CEM III/A from cement PCLA Ladce (Slovakia) were used in these investigations. Blast furnace slag (BFS) from US Steel Košice, limestone with $CaCO_3$ content about 90 ± 2 % and natural gypsum combined with gypsum by-product were used in the preparation of cement and blended cements. Table 1 is reporting the composition of cement samples. The chemical composition of cement samples are reported in Table 2.

Calorimeter methods

The course of hydration heat was monitored by two calorimeters. The first one with limited possibility of temperature manipulations is the isothermal calorimeter TAM (Thermal Activity Monitor) instrument manufactured by Thermometric AB, Sweden equipped with eight-channels. Six grams of dry sample powder were loaded into the glass ampoule and then hermetically closed by a plastic plug. A calculated amount of water (water-cement ratio = 0.5) is then added by using syringe and the sample is stirred inside the calorimeter in order to start the hydration process. Heat evolved causes temperature rise. To maintain the isothermal condition, an electric power is generated to cool calorimeter to constant room temperature. The electric power (mW) generated is proportional to the heat evolved and is continuously monitored and recorded. The time integration of power signals multiplied by a calibration coefficient gives the heat evolution and the total heat Q, associated with a hydration process. Unfortunately, this calorimeter cannot operate under different temperatures. The data of heat flow rate were collected and heat evolution of hydration was determined in a period up to 7 days.

The second calorimeter used is a conduction calorimeter described in [12,13] and modified in order to follow hydration heat under temperatures up to 90°C. The results recorded at different temperatures (20°C, 30°C, 40°C and 50°C) were used to calculate the activation energy.

Fabrication and curing of specimen

The mortars with cement to standard sand ratio of 1:3 by weight and w/c= 0.5 were prepared and fresh mixtures were casted in steel prism tree-gang mould ($40 \times 40 \times 160$ mm^3). Mortar specimens were stored under different temperatures (10°C, 20°C and 30°C). These temperatures have practical meaning in construction as cements is used under different weathers.

Table 1. Composition of cement samples, specific surface and predicted strength class.

Type of Cement sample	Clinker + clinker (wt.%)	BFS (wt.%)	Limestone (wt.%)	Specific surface (m^2/kg)	Strength class
CEM I	95	5	-	375	42,5 R
CEM II/B-S	70	25	5	465	42,5 N
CEM III/A	40	55	5	415	32,5 N

Table 2. Chemical analysis of used cements (wt.%).

Component	Ignition loss	SiO$_2$	Al$_2$O$_3$	Fe$_2$O$_3$	CaO	MgO	SO$_3$	NP	Cl	Na$_2$O ekv.
CEM I 42.R	2.07	20.90	5.21	4.1	59.1	2.69	3.8	2.36	0.069	0.51
CEM II/B-S 42.5N	3.87	23.73	6.42	2.75	53.38	3.76	2.39		0.068	0.39
CEM III/B 32.5N	2.69	29.02	5.38	3.59	50.01	4.76	2.16	2.78	0.059	0.35

Mechanical properties (compressive strength and flexure strength) were tested according to the European Standard EN 196-1 [14] under three temperatures $T_1 = 10 \pm 1°C$, $T_2 = 20 \pm 1°C$ and $T_3 = 30 \pm 1°C$ after 1 day, 2 days, 7 days and 28 days (the one-day and 7-day tests were done in order to follow the strength development). Likewise, the normal consistency and the course of setting of cement paste recorded by automatic Vicat apparatus were according to EN 196-3 [15]. The automatic Vicat apparatus allows investigating the influence of temperatures by continuous monitoring and recording the dept from bottom, at which the needle stops. Also, specific surface according to Blaine method and setting and hardening time were ascertained by standard method EN 196-3.

RESULTS AND DISCUSSION

Influence of temperature upon the mechanical strength development

The compressive and flexural strength development of CEM I with temperatures is depicted in Figure 1. It is clear that the temperatures have a positive influence upon the strength development, but not at the same rate in time period. The influence of temperatures upon the rate of compressive strength decreases proportionally with time. It is evident from Figure 1 that the gap between the strengths at same time but under different temperatures reduces with curing time. The influence of temperature upon the flexural strength is negligible at one-day or 28-days of curing, but it affects greatly the 2-day and 7-day values. As CEM I 42.5 R is a pure clinker with
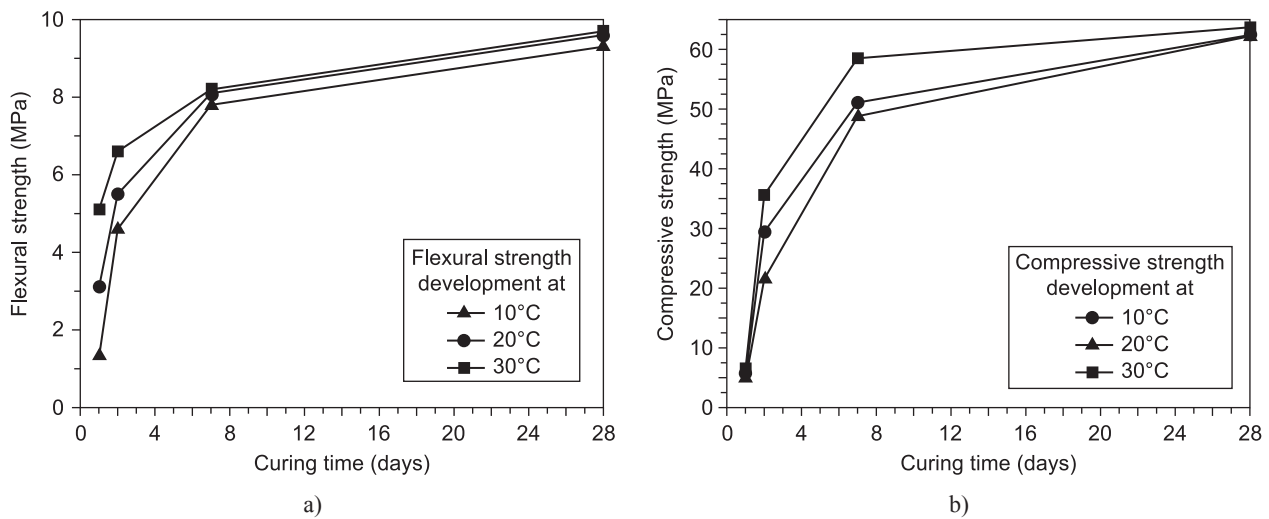

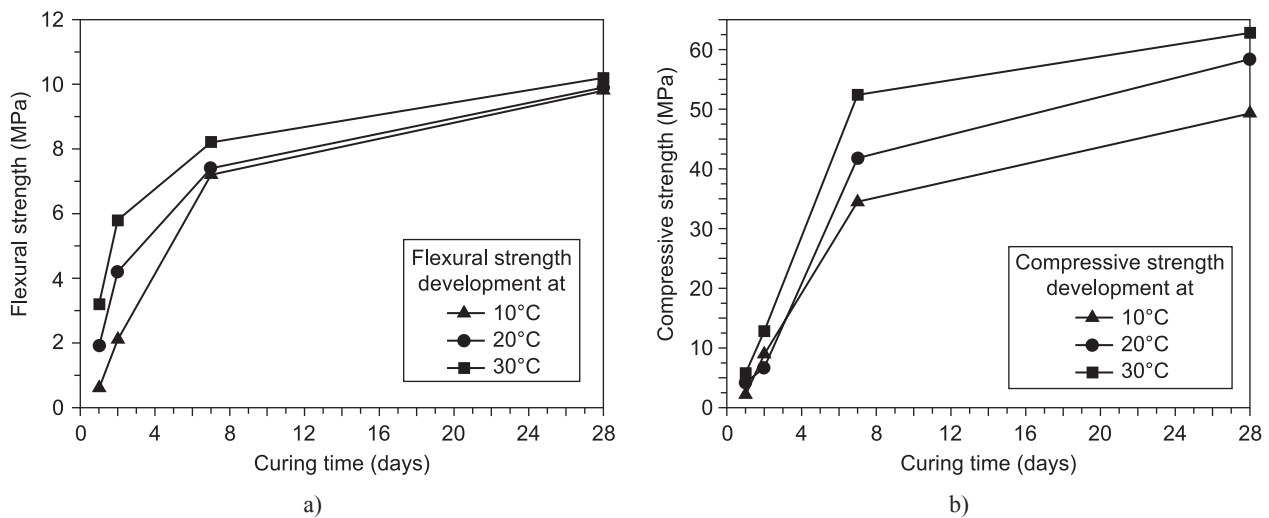Figure 1. Strength development of CEM I under different temperatures.

Figure 2. Strength development of CEM II (containing 25 wt. % BFS and 5 wt.% limestone) under different temperatures.

gypsum as set regulator, its hydration is highly dependent on mineralogical composition. The formation of CSH and ettringite is accelerated at the early period leading to the rapid strength development. Then, the progress in hydration is achieved due to the lack of clinker minerals. Many studies [8,9,16,17] have reported that at higher temperatures the degree of hydration initially develops faster exhausting thus all minerals for following chemical reaction. As corollary, the later strength development is slightly retarded.

CEM II is cement with 25 wt.% of slag and 5 wt.% of limestone. The behaviour of compressive strength development under different temperatures has the same characteristics as those of CEM I. The influence of temperatures upon the compressive strength is more pronounced within the first two days, while this influence is negligible at later ages of curing (Figure 2). The change in temperature influence upon the flexural strength is evidenced. Temperature influences negligibly the flexural strength within the first two days, but this influence is more pronounced in the later period. Also, it is evident that the trend is strength development at later age declines more slightly.

The characteristics of strength development of the last blended cement (CEM III/A) are different from those of the two first samples. At first glance, it is evident that temperature has negligible effect on the mechanical strength within the first two days of curing. As it can see in Figure 3, the temperatures have a great influence upon the mechanical strength at later ages. Compressive and flexural strength increase almost linearly with temperatures. Although the values of mechanical strength of CEM III/A are lower than those of the two first samples, the influence of temperature and curing time will continue after 28-days of curing. From the practical point of view, it should recommended to use CEM III/A during the warming period with increasing temperatures.

Determination of "index of cement strength development" as function of temperatures

A new criterion „Index of temperature strength development" is introduced in order to characterise the rate at which the compressive or flexural strength increases or decreases with temperature rise within a given period. The cement paste, mortars or concrete paste or concrete that was made at 10°C and has gained a one-day strength under this temperature is submitted to rising temperature to 20°C on second day with 2-day strength. The increasing temperatures have a positive effect on compressive strength, but the sensitivity of compressive strength development to the temperature change within a determined period is here evaluated for different kind of cement samples. The practical meaning of this "index" or "coefficient" is to enable to determine the compressive or flexural strength and their corresponding temperatures at any curing time within a given period. The Figure 4 illustrates the methodology to evaluate the "index of temperature compressive strength development". This "index" can be determined as linear coefficient or as the slope of straight line that illustrates the compressive strength P (MPa) as function of temperature T (°C) and time t (day). The temperature T is function of time t.

$$\alpha = \frac{P_2^{20} - P_1^{10}}{\Delta t \cdot \Delta T} \tag{1}$$

where α is index of temperature strength development, P_2^{20} is the two-day compressive at 20°C (MPa), P_1^{10} is the one-day compressive strength at 10°C (MPa), Δt is time interval (day) and ΔT is temperature interval (°C).

The results of *index of temperature strength development* for different cement samples are reported in Table 3 and 4. As a matter of fact, this coefficient varies with period and with the type of cement. At early period, the "index of temperature strength development" of CEM I
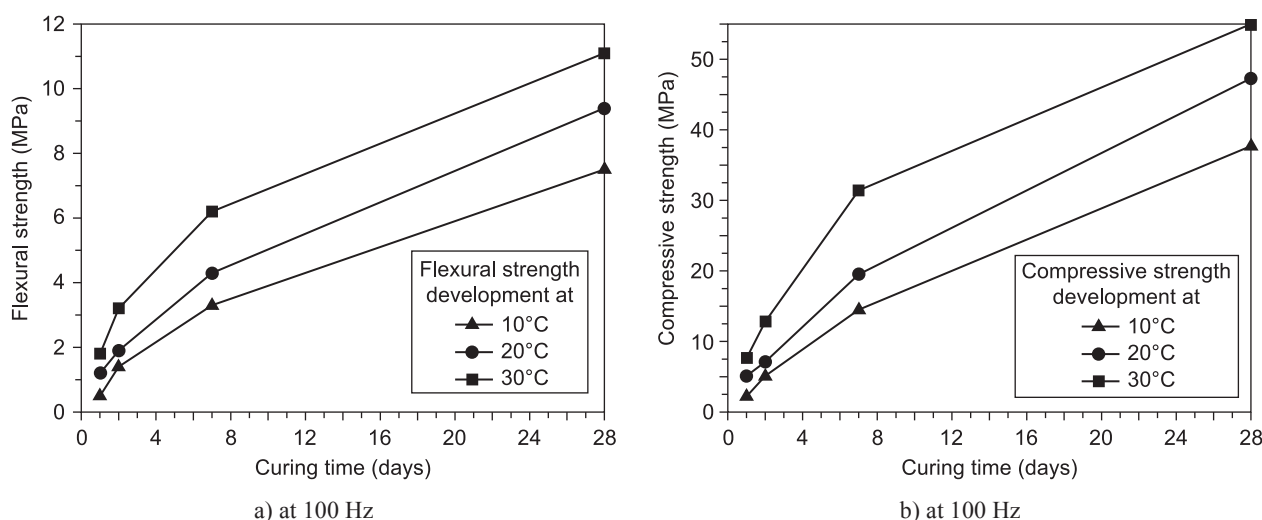

a) at 100 Hz

b) at 100 Hz

Figure 3. Temperature dependence of dielectric constant ε_r and dielectric loss $tg(\delta)$ of $0.935(Bi_{0.5}Na_{0.5})TiO_3$ -$0.065BaTiO_3$ ceramics sintered at different temperatures at 100 Hz.

is the highest between 10°C and 20°C or between 20°C and 30°C, and decreases with BSF content. CEM II has the highest index of strength development in middle period under both temperature differences. The value of this index is highest with CEM III at later ages in both temperature differences.
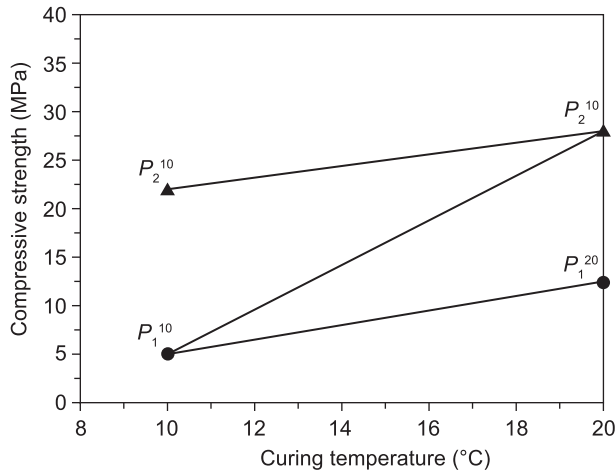

Figure 4. Methodology to determine the „Index or coefficient of temperature strength development".

Table 3. Index of temperature compressive strength development.

	Period	CEM I	CEM II	CEM III
	1-2	2.48	1.34	0.49
10-20	2-7	0.59	0.658	0.288
	7-28	0.064	0.113	0.156
	1-2	2.25	1.75	0.77
20-30	2-7	0.582	0.646	0.486
	7-28	0.06	0.1	0.15

Table 4. Index of temperature flexural strength development.

	Period	CEM I	CEM II	CEM III
	1-2	0.42	0.36	0.14
10-20	2-7	0.07	0.106	0.058
	7-28	0.0072	0.017	0.088
	1-2	0.35	0.39	0.2
20-30	2-7	0.054	0.08	0.088
	7-28	0.0076	0.013	0.032

The influence of temperature upon the setting and hardening process

The curves describing the dependence of setting process on temperature for CEM I are depicted in Fig. It is clear that the temperature strongly influences the setting time. The higher the curing temperatures, the shorter is the beginning of setting time. At 30°C, the beginning of setting is 180 minutes, at 20°C 210 minutes and at 10°C is 330 minutes. Also, curing temperatures markedly influences the hardening time.

The influence of temperature upon the setting and hardening time for cement sample CEM II show the same characteristics as those of CEM I, but the process is more retarded with decreasing temperatures. If we consider that hydration reaction is one of the most important keys that govern the setting and hardening of cement paste, one can confirm that this reaction obeys also to Arrhenius law. These curves could be explored to evaluate the activation energy in the future.

Contrary to the two first cement samples, one can see an important difference between 20 °C and 30°C. The replacement of clinker by 55 wt.% of BFS submitted to 30°C accelerates the setting time. With decreasing temperatures is the retardation of setting process more pronounced. CEM II is more sensitive to temperature than CEM CEM II and I.
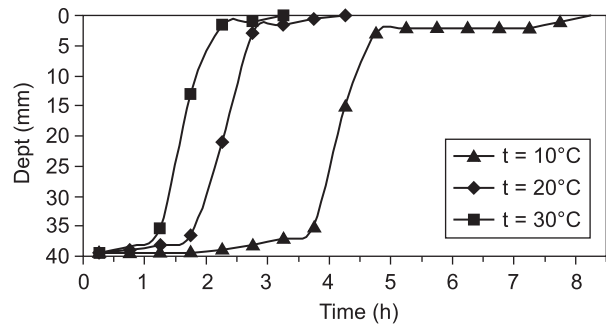

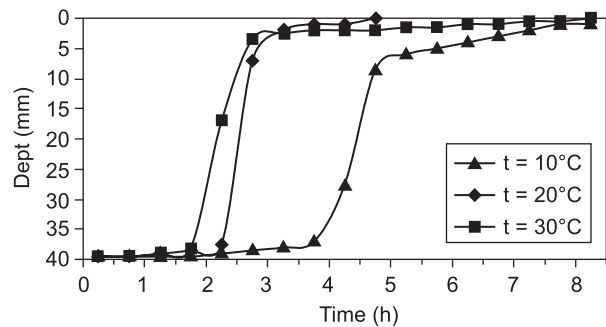Figure 5. Course of setting process of CEM I under different temperatures.

Figure 6. Course of setting process of CEM II (containing 25 wt.% BFS and 5 wt.% limestone) under different temperatures.
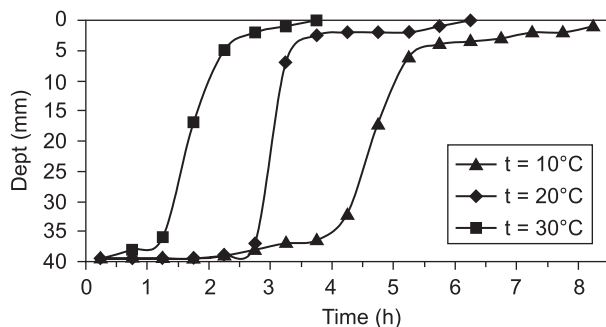

Figure 7. Course of setting process of CEM III /A (containing 55 wt. % BFS and 5 wt. % limestone) under different temperatures.

Hydration heat and apparent activation energy of different cements

Determination of hydration heat by calorimeter TAM at 20°C

The values of heat evolved within different period decreases with the replacement ratio of BFS and with decreasing temperatures. The important finding here is the rate at which hydration heat of different cement samples progresses with temperature. By exploring the values reported in Table 5, it is clear that CEM I and CEM II with dominant clinker content are more sensitive to the curing temperatures at early period, while CEM III develops faster hydration heat at later period. The progress in hydration course determines the rate of compressive strength development. These findings are in agreements with the values of index of temperature strength development.

Determination of apparent activation energy by conduction calorimeter ZIAC

The kinetics parameters were investigated by exploring the main peaks of calorimeter curves obtained at different temperatures for each cement samples.

To determine the apparent activation energy of different cement samples, we express the dependence of time corresponding to the hydration peak on temperatures at which hydration occurs. The peak of hydration heat denotes the maximal rate of conversion at given time. Then the temperature dependence of time position can be expressed for a special case of isothermal processes according to Equation (2) This equation, stimulant Arrhenius one was successfully applied by [18,19] to calculate the activation energy of the induction period for glass crystallization.

$$\tau_m = A \exp\left(\frac{E}{RT}\right) \qquad (2)$$

where is the time corresponding to the peak of hydration curves, A is the constant of proportionality, R is the perfect gas constant, 8.314 J/molK; and E_a is the apparent activation energy.

By simple linearisation, one obtains Equation (3) from Equation (2)

$$\ln \tau_m = \ln A + \frac{E}{R}\frac{1}{T} \qquad (3)$$

known in general form as $y = a + b \cdot x$, where $y = \ln \tau_m$, a $= \ln A$, $x = 1/T$, $b = E/R$.

The dependence relation $\ln \tau_m = f(1/T)$ is a straight line that the value of slope $b=E/R$ was used to the apparent activation energy.

Apparent activation energy of CEM I 42.5 R

The flow of hydration heat of CEM I 42.5 under different temperatures from 10°C to 50°C are depicted in Figure 8. At the first glance, it is clear that the intensity of the main peaks and the duration of hydration courses depend on temperatures. At the lower temperatures, the curves of hydration have reduced intensity with extension form over the time. With increasing temperatures, the intensity of hydration peaks increases and becomes sharper and the hydration is ended within short time. As it can be remarked, not only intensity and shape of calorimetric curves depend on temperatures, but also the time position of the peak is dependent on temperatures.
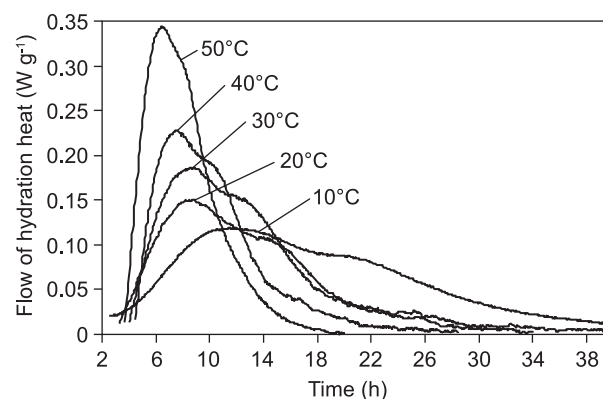

Figure 8. The influence of temperature upon the flow of hydration heat of CEM I.

Table 5. Heat of hydration and rate of heat evolution of cement samples at different periods.

Cement sample	Heat evolved within different periods (J/g)				
	1 day	2 days	Rate of heat evolution per day (%)	7 days	Rate of heat evolution per day (%)
CEM I	130.3	195.3	50	297.0	10.4
CEM II	116.8	176.2	51	283.7	12.2
CEM III	78.1	103.4	32.4	224.9	23.50

Table 6. Main parameters needed to calculated apparent activation energy of cement sample CEM I.

Temperature (°C)	10	20	30	40	50
Time/h	11.67	8.61	8.56	7.50	6.39
T/ K	283.15	293.15	303.15	313.15	323.15
1/T	0.003532	0.003411	0.003299	0.003193	0.003095
Ln τm	2.457476	2.15384	2.147394	2.015721	1.855389

Although the calorimetric curves could have one or two peaks more, the time position of the highest intensity is considered in these studies.

The apparent activation energy E_a = 10. 24 ±0.36 kJ kmol^{-1}. The correlation coefficient of 92.34 % indicates a relative good fit with the chosen model.
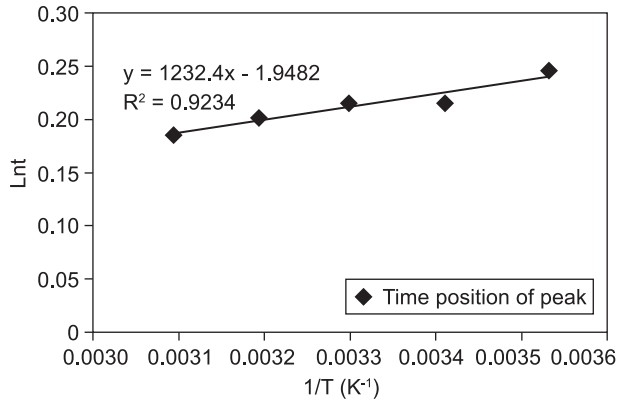

Figure 9. Relation between $ln\,\tau_m$ and $1/T$.

Apparent activation energy of CEM II / B-S 42.5 N

The hydration behaviours of CEM II under different temperatures reported in Figure 10 differ from those of CEM I in intensity, but have the same characteristics. The intensity and the shape of curves depend on temperatures, as well as time position of the main peak and the end of hydration.
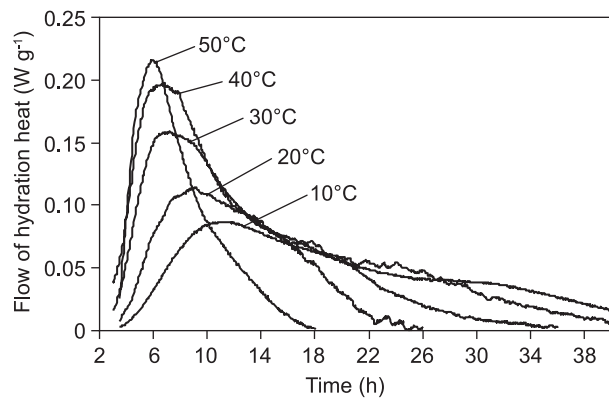

Figure 10. The influence of temperature upon the flow of hydration heat of CEM II.

The apparent activation energy E_a = 11. 95 ±0.97 kJ kmol^{-1}. The linear dependence between $ln\tau_m$ and $1/T$ presents a good correlation and the apparent activation energy is higher than that of CEM I.

The curves of the flow of hydration heat of CEM III are more extended over the time. The influence of temperature upon the time position of the main peak is more pronounced than with the two first samples. The intensities of hydration peaks are reduced, but are influenced also by temperature. The shape of curves is less uniform due to the complexity of the heterogeneous hydration of blended cements.
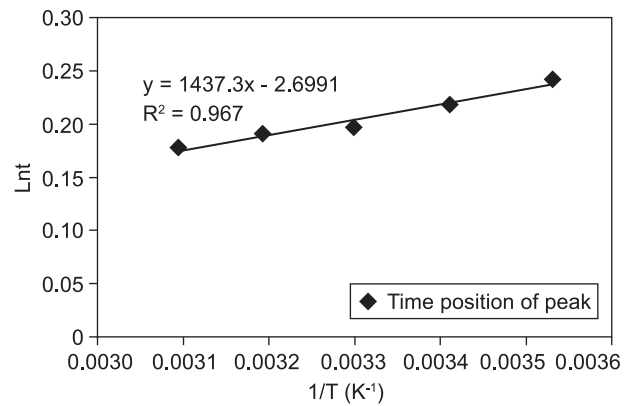

Figure 11. The relation between $ln\,\tau_m$ and $1/T$.

The apparent activation energy E_a = 17. 33 ±0.60 kJ kmol^{-1}. The correlation coefficient is the best approaching the 100 %; also the value of apparent activation energy is the highest.
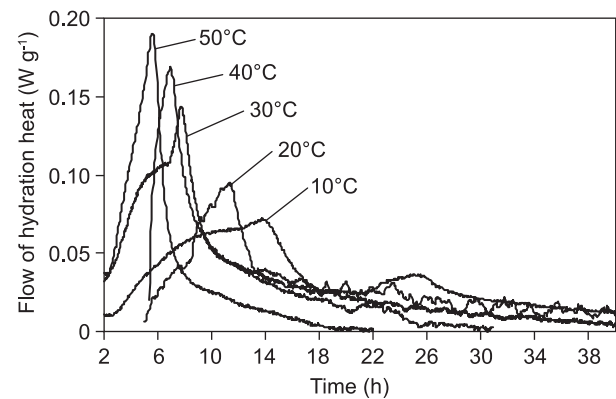

Figure 12. The influence of temperature upon the flow of hydration heat of CEM III.

Table 7. Main parameters needed to calculated apparent activation energy of cement sample CEM II.

Temperature (°C)	10	20	30	40	50
Time (h)	11.23	8.89	7.17	6.78	5.89
Temperature (K)	283.15	293.15	303.15	313.15	323.15
1/T	0.003532	0.003411	0.003299	0.003193	0.003095
ln τm	2.418643	2.185612	1.97024	1.91448	1.773852

Table 8. Main parameters needed to calculated apparent activation energy of cement sample CEM III.

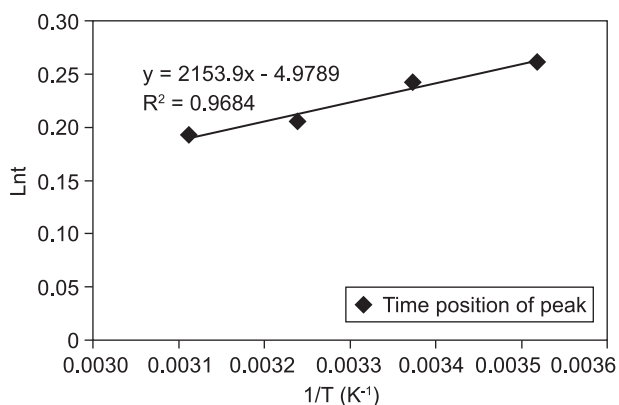| Temperature (°C)	10	20	30	40	50
Time (h)	13.67	11.28	7.78	6.89	5.615
Temperature (K)	283.15	293.15	303.15	313.15	323.15
1/T	0.003532	0.003411	0.003299	0.003193	0.003095
ln τm	2.615712	2.423553	2.052142	1.93073	1.725499

Figure 13. Relation between $ln\ \tau_m$ and $1/T$.

It can be seen that the apparent activation energy increases with increasing BFS replacement ratio in cement.

CONCLUSION

The mechanical and physical properties of three kinds of cements were investigated under different practical temperatures. All parameters were found temperature dependent, but the sensitivity of this dependence depends on kinds of cements and curing period. A new criterion "index of temperature strength development" was introduced to evaluate the value of compressive strength at any temperature within a curing period. The rate of hydration heat and mechanical properties of CEM I are accelerated by temperature at early curing period of 1 to 2 days, those of CEM II at middle period of 2 to 7 days and those of CEM III at later period of 7 to 28 days. The apparent activation energy was found dependent on the replacement ratio of BFS. The higher value of apparent activation energy indicates that the reaction is more sensitive to temperatures. From the experimental results of this investigation, it can be recommended to use blended cements under increasing temperatures, while pure cements should be applied under lower temperatures.

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