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NON-ISOTHERMAL THERMOKINETIC OF CEMENT HARDENING

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Abstract

Thermokinetic analysis of cements hydration under nonisothermal conditions was performed. The influence of the application moment, intensity and duration of heat effect on the velocity and completeness of the character of hydration was estimated.

Keywords: cement, coherence principle, kinetics

Introduction

The hardening of cements and other binders is a heterogeneous process of phase and structural transformations in non-equilibrium disperse systems. The complexity of studying and directing the hardening process in order to predict required properties is increased by a great number of external factors, of which temperature is most essential. Temperature range is –50...+80°C. Depending on the moment, the level, the intensity and the duration of temperature application, the characteristics of composition, structure and properties of cement stone and concrete were changing within a wide range [1].

In chemistry and technology of cement and concrete the data on heat evolution (one of the fundamental phenomena accompanying the hardening) were used to study and regulate the processes. The knowledge of applying characteristics and mathematical models of thermokinetics was accumulated and main periods of initial stages of hydration in expert systems and in informational technologies were selected [2]. All that can testify to high scientific and practical importance of the research in heat evolution and of establishing the regularities in its characteristics effected by temperature (under the influence of temperature).

To study heat evolution in hardening of binders various methods of calorimetry are used according to the aims of research-solution, adiabatic and isothermal. They all do not provide concrete results due to non-isothermality of cements and concretes. Earlier [3] we suggested an original methodological ap-

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proach based on physico-chemical apparatus of thermokinetics to obtain the data on nonisothermal heat evolution of cement for any temperature regimes. What is of importance is quantitative information on indicators of velocity and completeness of hydration. Thermokinetic approach determines the border between formal and conceptual kinetic apparatus for identification and interpretation of measurements results. To examine heat evolution thermokinetics dependencies and their processing on four levels are to be obtained [4]. The first level provides dynamic correction of results, the second-formation of differential $-dQ/dt=f(t)$ and integral $-Q=f(t)$ dependencies. The third allows to select characteristic periods of hydration – induction, accelerated and slowed-up. On the fourth level long-term prediction of the heat evolution is made.

The methodics envisages carrying out the experiment in an isothermal calorimeter within the borders 5–10°C. In the given work thermokinetics of hydration of the main clinker mineral – C_3S and the varieties of Portland cements – fast hardening and plastified – was examined. Water–solid relation is 0.5, temperature interval 20–80°C.

The results of determining complete heat evolution during binders hydration are shown in Fig. 1. Temperature rise intensifies reactions, deepens hydration

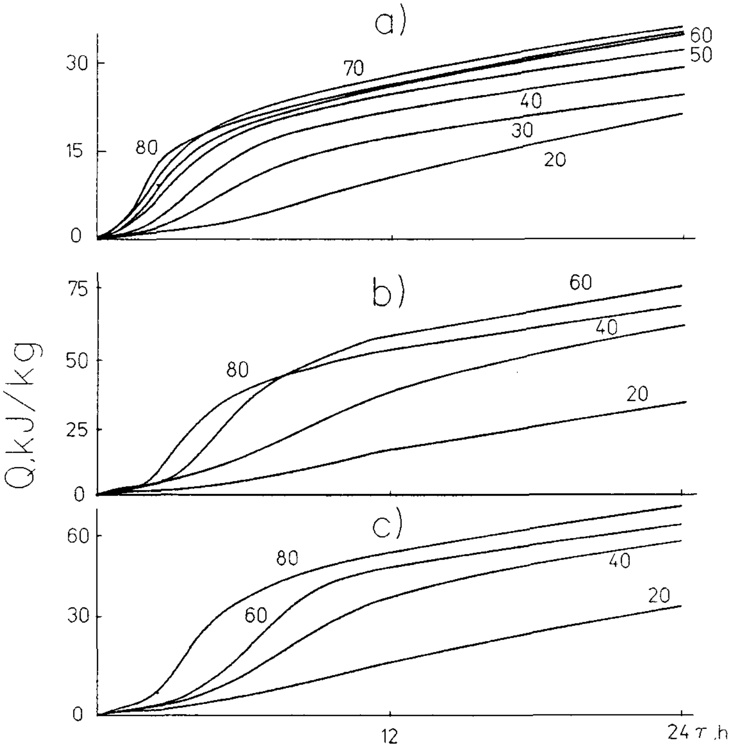

Fig. 1 Heat evolution at the hardening of $3CaOSiO_2$ (a) fast hardening (b) and plastified (c) Portland cements

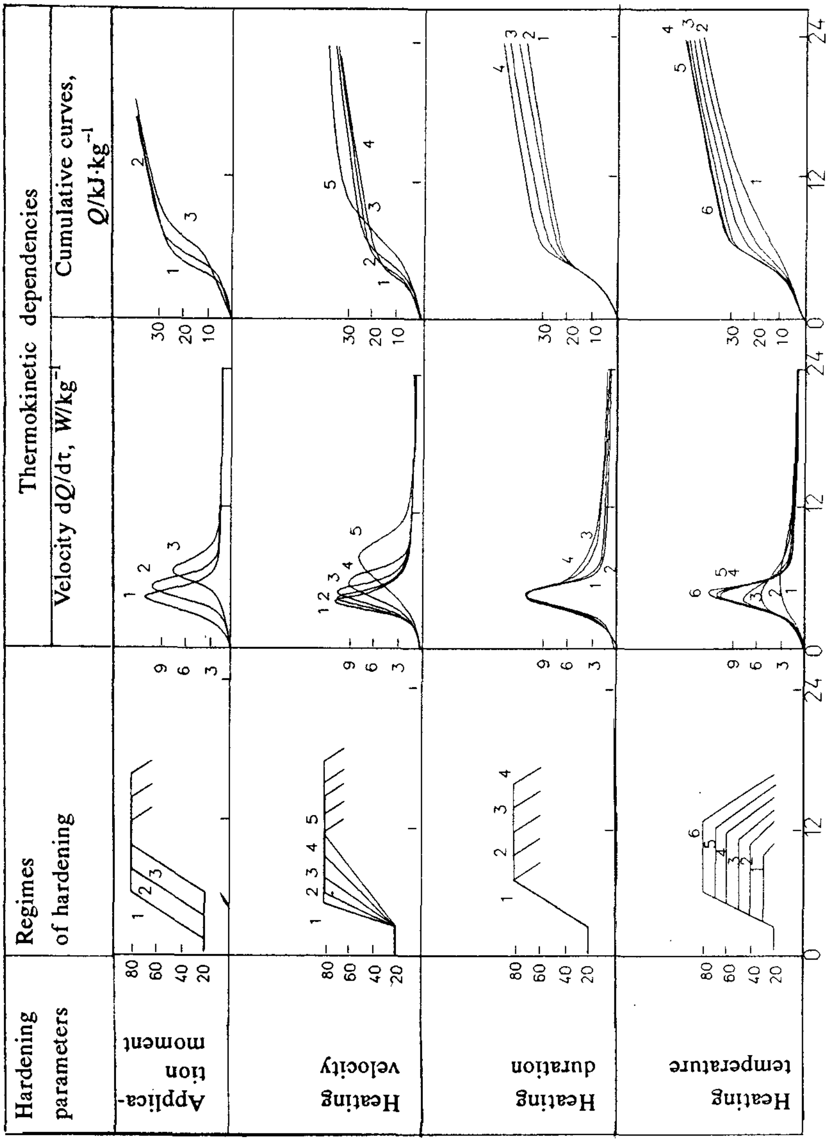

Fig. 2 Non-isothermal heat evolution at the hardening of $3CaOSiO_2$

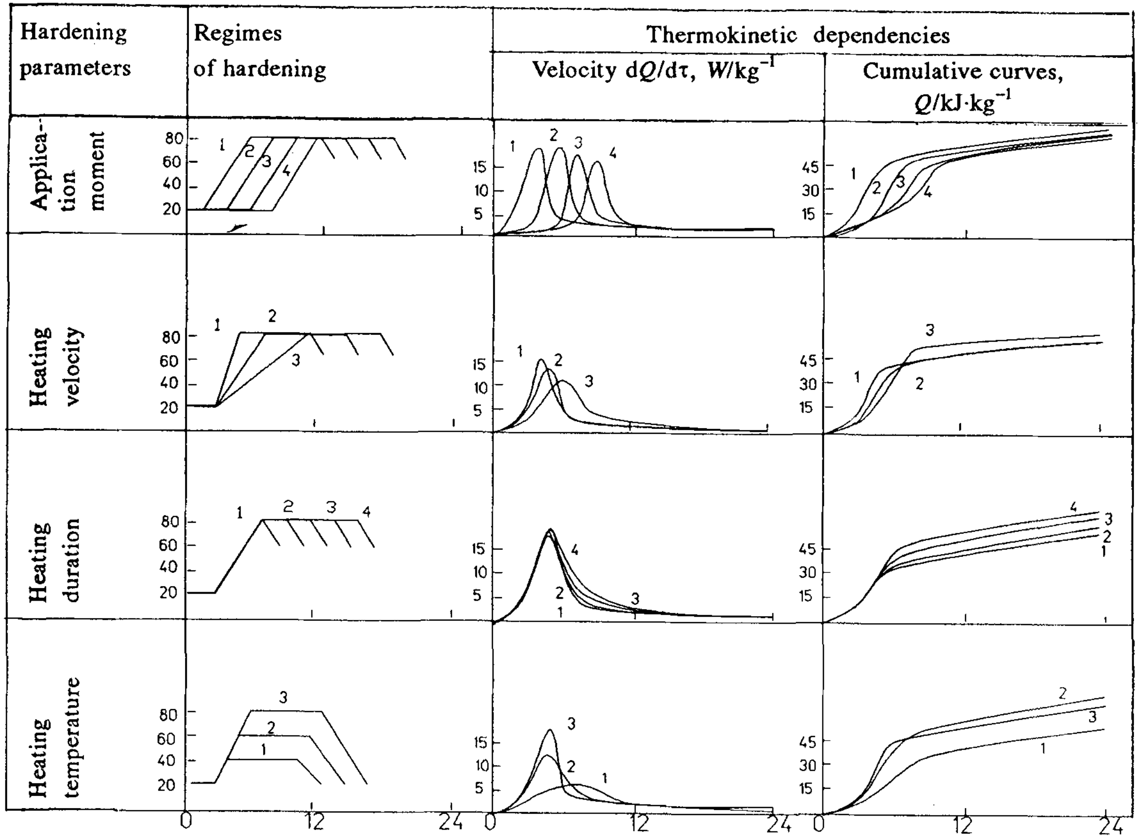

Fig. 3 Non-isothermal heat evolution at the hardening of fast hardening Portland cement

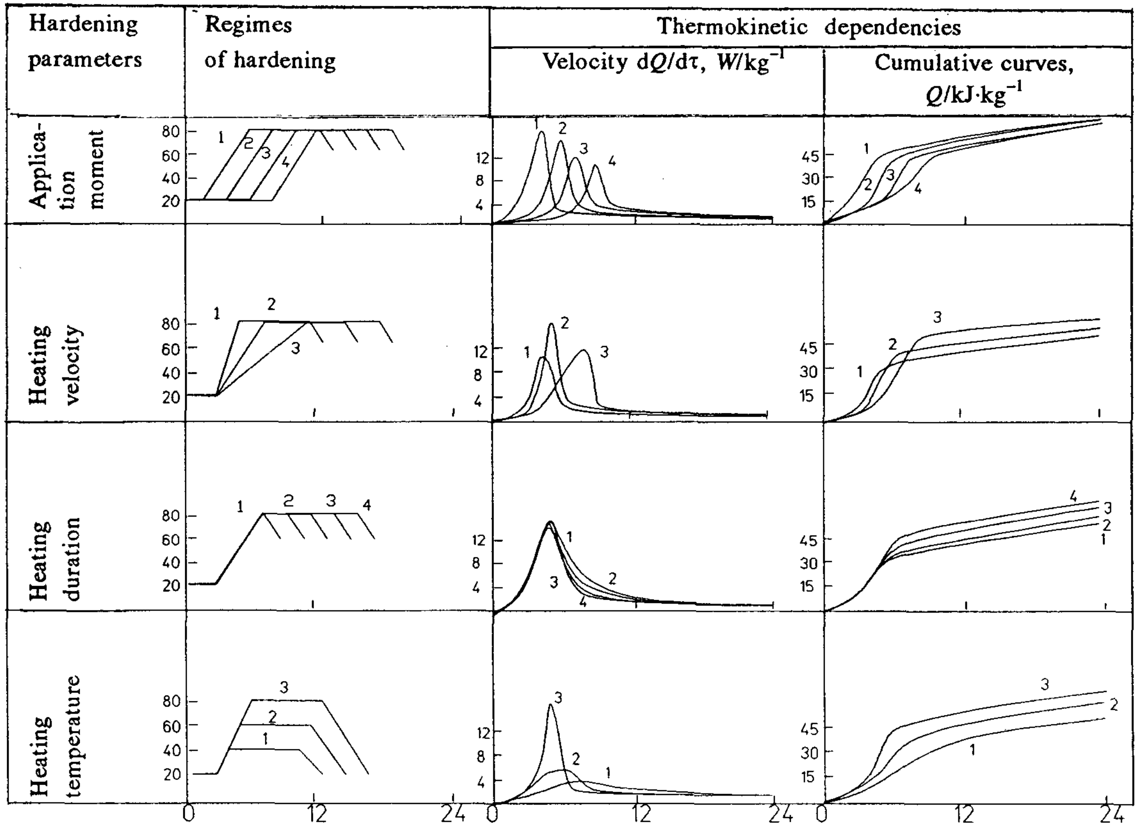

Fig. 4 Non-isothermal heat evolution at the hardening of plastified Portland cement

up to a certain limit. At $3CaOSiO_2$ hardening a low-governed growth of heat evolution up to 60°C is observed (Fig. 1a). At 80°C, as well as in the case of fast hardening cement (Fig. 1b) the lowering of this indicator due to the formation on the binder grains of hydrate shells hindering reactions is observed. At the hardening of plastified Portland cement (Fig. 1c) with addition of technical lignosulphonates the initial hydration is essentially slowered due to the adsorption of surfactants on the grains of cement and new hydrate formations. But later the completeness of heat evolution is not decreased.

The processing of the isothermal calorimetry data was carried out according to the accepted methodics while taking into account the most important parameters of temperature effect, used under the conditions of the thermal processing of concrete. These are, as mentioned above, the moment of application, velocity, duration and temperature of heating (Figs 2–4). Thermal treatment was performed after 2, 4 and 6 h. The intensity of heating varied from 10 to 30 deg/h. The duration of heating (isothermal exposure) changed from 0 to 8 h, temperature interval – from 20 to 80°C.

The analysis of the obtained data testifies to the substantial impact of the studied parameters on thermokinetic indicators of velocity and hydration completeness.

The later the thermal treatment of hardening mixture, the lower is the intensity of heat evolution. The value of dQ/dt is especially lowered at the hydration of $3CaOSiO_2$ and plastified Portland cement. The main maximum of the velocity of heat evolution for all the binders is shifted to the right on the axis of time proportional to the moment of treatment. It can be ascribed to the specific character of elementary stages of hardening – adsorption, dissolving, formation, crystallization, etc. What is really important, is that certain lowering of the cumulative heat evolution at the hydration beginning is replaced by levelling the values of cumulative heat evolution already after 10–12 h, judging by the dependencies $Q=f(t)$.

The change in heating velocity also causes time shift for the maximum of thermal effect. It is quite explicable. However in the case of hydration of plastified Portland cement the initial reactions are blocked due to the adsorption of surfactant molecules. The value of exoeffect at the heating velocity 10 deg/h is minimal.

It's hard to interpret the effect of heating duration. Within the analysed interval of hardening – up to 24 h the completeness of the observed reactions cannot probably change essentially.

In non-isothermal thermokinetics the limit of heating temperature plays the most appreciable part. The absolute value of the heat evolution maximum grows proportional to the treatment temperature. Its time for cements shifts to the left on the axis of abscissas and doesn't practically change at hydration of $3CaOSiO_2$. The change in the degree of hydration is analogous to isothermal conditions.

The data on thermokinetic analysis are basis for constructing imitation models of cement hardening. Interconnection of parameters of these models and models of changing of concrete strength is established. The obtained results concerning the kinetics of non-isothermal heat evolution at the cement hardening and the growth of concrete strength constitute computer data bases on the informational technology of concrete motivation and selecting optimal regimes for hardening during thermal and non-thermal treatment of concrete. They justify the principle of coherence of hardening parameters to kinetic characteristics of cement [1].

Conclusion

With the help of the developed physico-chemical apparatus of non-isothermal kinetics the impact of parameters of temperature treatment on the indicators of velocity of heat evolution at cement hydration was studied.

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Zusammenfassung — Es wurde eine thermokinetische Analyse der Zementhydratation unter nichtisothermen Bedingungen durchgeführt. Dabei wurde der Einfluß von Anwendungszeitpunkt, Intensität und Länge des Wärmeeffektes auf die Geschwindigkeit und die Vollständigkeit der Art der Hydratation abgeschätzt.