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Determination of apparent activation energy of concrete by isothermal calorimetry

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Abstract

In recent works at our laboratory, instrumentations have been developed to carry out calorimetric tests on concrete in isothermal conditions, which give much information. The objective of this article is, on the basis of this technique, to study the validity of the Arrhenius law and to determine the evolution of apparent activation energy of the concrete. This parameter is necessary for the calculation of the maturity of the concrete. Measurements of hydration heat have been carried out for various conditions of isothermal curing and have allowed us to study the evolution of apparent activation energy according to the degree of hydration. Generally, activation energy is constant for a degree of hydration ranging between 5 and 50%. On the other hand, we have observed that this parameter varied with the temperature, which limits the use of this technique to thin elements.

Keywords: Apparent energy activation; Isothermal calorimeter; Fluxmeter; Concrete; Degree of hydration; Temperature

1. Introduction

A few examples of industrial concerns related to the behavior of the concrete at a young age are removing the formwork to optimize its use on building sites and prestressing as quickly as possible. These concerns often amount to a single question: at what time will characteristic strength be reached?

Thus, the concept of maturity has been introduced. This notion allows us to determine the state of concrete curing at a given time. It integrates the coupled effects of temperature and time on the kinetics of concrete curing. The evolution of physical magnitudes such as mechanical strength or released heat can be connected to the maturity of the concrete. For a given maturity, a concrete has identical characteristics whatever the conditions under which it has matured. Several definitions have been proposed and the experimental Arrhenius law has appeared to be the most adequate. It is based on the law of acceleration of the simple chemical reactions and makes it possible to describe the coupled effects of temperature and time on the hydration kinetics of the concrete. It introduces a parameter, called activation energy, which characterizes the mix. In the case of concrete, this activation energy is considered as "apparent" because the hydration of cement implies several simultaneous and coupled chemical reactions.

The determination of apparent activation energy is carried out either by mechanical or calorimetric methods. The measurement by mechanical method is interesting insofar as it makes it possible to calculate this value from tests of similar nature. However, the mechanical strength, unlike the heat of hydration, does not reflect a purely chemical mechanism and cannot, therefore, fully abide by the Arrhenius law. On the other hand, this method is too complex because of the important number of measurements.

The calorimetric method can be carried out in isothermal conditions or in adiabatic conditions. The isothermal test presents the advantage of fixing the temperature parameter on which the apparent activation energy is likely to depend. In recent work at our laboratory [1], an instrumentation was developed to carry out tests on concrete in isothermal conditions and is particularly informative. This innovative measurement technique is based on fluxmetric measures using specific sensors.

The objective of this work is to present, on the basis of this technique, the first measurement results of the apparent activation energy of a concrete according to the degree of hydration. This study has been carried out within a range of temperature from 10 to 40°C.

2. Theoretical aspect

The coupled effects of temperature and time on the curing kinetics of concrete have largely been studied for many

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years [2–4]. The term “maturity” was introduced to reflect the state of the concrete curing at a given time. The expression of maturity is given by the relation shown in Eq. (1):

$$M[t,H(T)] = \int_0^t K[T(\tau)]d\tau \tag{1}$$

where $M[t,H(T)]$ is maturity at the moment t for a history of temperature given $H(T)$; and $K(T)$ is the kinetics constant at the temperature $T(\tau)$ is the absolute temperature at the moment τ.

Several authors [3,5,6] have tried to describe the expression of the kinetics constant and it appeared that the experimental Arrhenius law was the most adequate in the case of concrete [see Eq. (2)]:

$$K(T) = A\exp\left(-\frac{Ea}{RT}\right) \tag{2}$$

where A is the constant of proportionality; R is the perfect gas constant, 8.314 J/mol • K; and Ea is the apparent activation energy.

The introduction of a new parameter, the apparent activation energy, makes it possible to approach also, as well as possible, the reality of the cement hydration. It is apparent in the case of concrete because the cement hydration implies several coupled and simultaneous chemical reactions. The sensitivity of the rate of hydration to the temperature varies from one cement to another [7]. This rate of hydration can be correlated to the degree of hydration.

The degree of hydration can be defined in several ways. It can be calculated from the evolution of either mechanical properties or physical properties such as heat of hydration, as seen in Eq. (3):

$$\alpha(t) = \frac{X(t)}{X(\infty)} \tag{3}$$

where $X(t)$ and $X(\infty)$, respectively, represent the value of the physical or mechanical property at the moment t and at an infinite time.

The rate of hydration can thus be expressed, for two temperatures of isothermal curing $T1$ and $T2$, as shown in Eq. (4):

$$\begin{aligned}\left(\frac{d\alpha_1}{dt}\right)_{T1} &= K(T_1)f(\alpha)\\ \left(\frac{d\alpha_2}{dt}\right)_{T2} &= K(T_2)f(\alpha)\end{aligned} \tag{4}$$

With $f(\alpha)$ being function depending on the degree of hydration.

For the same degree of hydration $\alpha = \alpha_1(t_1) = \alpha_2(t_2)$ and by introducing the Arrhenius’ law [Eq. (2)], one obtains [see Eq. (5)]:

$$\left(\frac{d\alpha_1}{dt}\right)_{T1} = \left(\frac{d\alpha_2}{dt}\right)_{T2}\frac{K(T_1)}{K(T_2)} = \exp\frac{Ea}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \tag{5}$$

The knowledge of this ratio of affinity for two curing temperatures makes it possible to determine the apparent activation energy associated with the concrete for each degree of hydration [see Eq. (6)].

$$Ea(\alpha) = R\left[\frac{T_1 \cdot T_2}{T_1 - T_2}\ln\left(\frac{\frac{d\alpha_1}{dt}}{\frac{d\alpha_2}{dt}}\right)\right] \tag{6}$$

3. The experimental device

The hydration of a concrete is a thermoactive reaction. The temperature of the medium strongly influences the kinetics of reaction. The traditional adiabatic or semiadiabatic calorimeters consequently are not adapted to the principle of measurement. The size of the sample is also a parameter that influences the studied reaction. The examination of such measurements is very delicate and implies corrections. Important uncertainties remain related to the results. The isothermal calorimeter here finds application. The temperature of the reaction is imposed and constitutes a perfectly controlled study parameter.

The developed isothermal calorimeter is based on measures of heat flux using specific sensors. This technique has been based on the experiment of the fluxmetric instrumentation and associated treatments, largely developed in the Laboratoire d’Artois Mécanique et Habitat for several years.

The developed device is represented on Fig. 1. The sample is a prism of square base of $0.09 \times 0.09 \times 0.16$ m^3. The fresh material is laid out in a carry-sample made up of four plane exchangers that form the lateral sides of the device. The two insulating bases consist of polystyrene plates of 0.05-m thickness. The exchangers are connected to a thermostatic bath and the circulation of the water is ensured by two pumps.

The flux sensors are integrated into the surface of the exchanging plates. The developed specific sensors are “tangential gradient” type [8,9]. Their principle of operation makes it possible to limit the disturbance of measurement and the boundary conditions. The thickness of the fluxmetric layer is lower than 10^{-4} m and the total thickness of the sensor is about $3 \cdot 10^{-4}$ m. The “RC” time constant is about 1 s. The very low thermal resistance generated by the sensors (of around $10^{-3}\ K \cdot \mathrm{m}^2 \cdot W^{-1}$) guarantees a good condition of heat sink on the material surface. The quality of the isothermal conditions is checked by thermocouples of K type included in the flux sensors and one included in the middle of the concrete. The temperatures of the internal and external faces of the two polystyrene bases are measured to enable the estimation of escapes.

The total flux of the reaction is estimated according to the calibration. It results from the sum of the four fluxes measured on the side faces of the device, the flux loss by the semiadiabatic bases, and the flux estimated at the level of the edges [see Eq. (7)].

$$\Phi_{\mathrm{total}} = \Phi_{\mathrm{measured}} + \Phi_{\mathrm{bases}} + \Phi_{\mathrm{edges}} \tag{7}$$

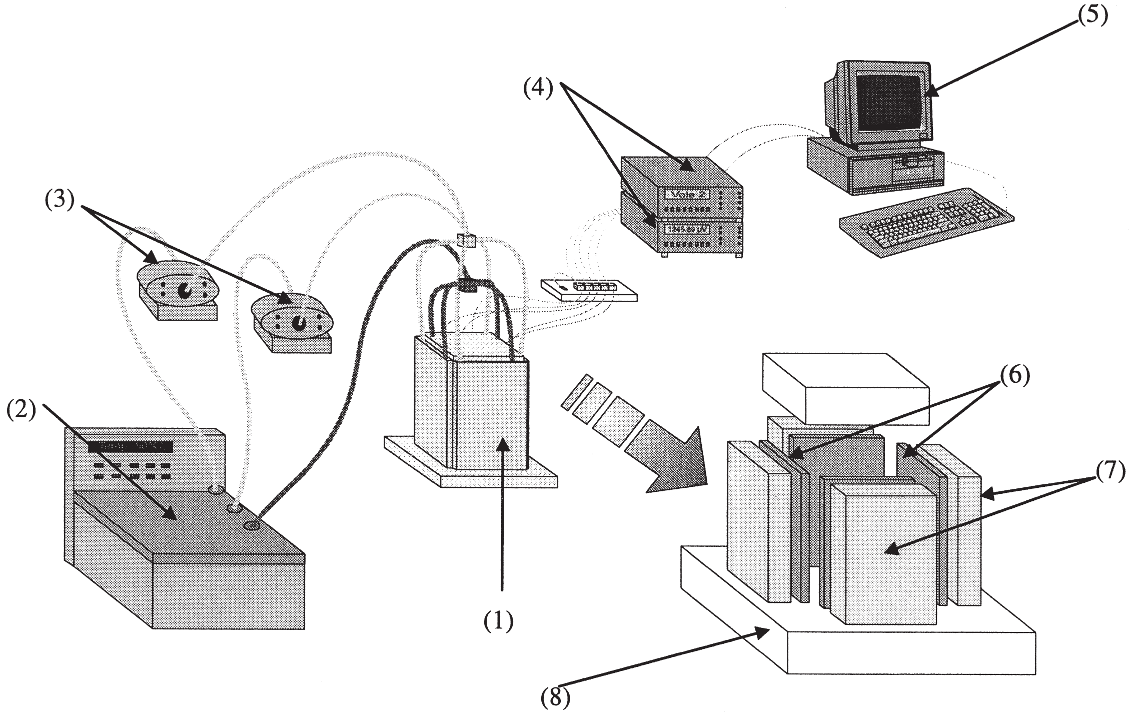

Fig. 1. Isothermal calorimeter [(1) Carry-sample; (2) thermostatic bath; (3) pumps; (4) multimeter and scanner; (5) computer; (6) flux sensors; (7) plane exchangers; (8) polystyrene plates.]

Let us recall that in this relation, the last two components are dependent on the difference of the temperatures that exists between material in evolution and the ambient conditions. From the total flux, the quantity of hydration heat released at one moment t is obtained by integration [see Eq. (8)]:

$$Q(t) = \int_{t_0}^{t} \Phi dt \tag{8}$$

4. Composition of the concrete

The tests have been carried out with ordinary Portland cement CEM I 42.5 R following the European standardization. The aggregates used are siliceous sands and limestone aggregates. The composition of the concrete for 1 m^3 is as follows: cement, 350 kg; water content, 199 kg; sand 0/1, 443 kg; sand 1/2, 177 kg; sand 2/4, 177 kg; aggregates 4/7, 301 kg; aggregates 7/14, 674 kg; water/cement ratio, 0.56.

5. Experimental results

The hydration of cement components is a complex phenomenon dependent on many factors and its modeling constitutes a problem that is difficult to solve [10]. However, from the practical point of view, it seems that the determination of a global degree of hydration for all the reactions is sufficiently significant in the case of concrete. This is why many authors, including Byfors [11], have chosen this way and shown that one can, in a first phenomenological approach, obtain a good picture of the quantity of formed hydrates. We have therefore chosen to characterize the hydration kinetics by the measurement of the quantity of released heat.

The experimental program is composed of four temperatures of curing: 10, 20, 30, and 40°C. For each temperature of curing, the evolutions of the heat flux according to time are recorded (Fig. 2).

For practically all the tests, the heat flux evolves according to three stages. The sharp instantaneous peak (seen on the curve at 10°C) excluded, at the beginning, the released heat is weak (latent period). It is followed by the period of acceleration that indicates the formation of new hydrates. Finally, the period of deceleration results from the diffusion

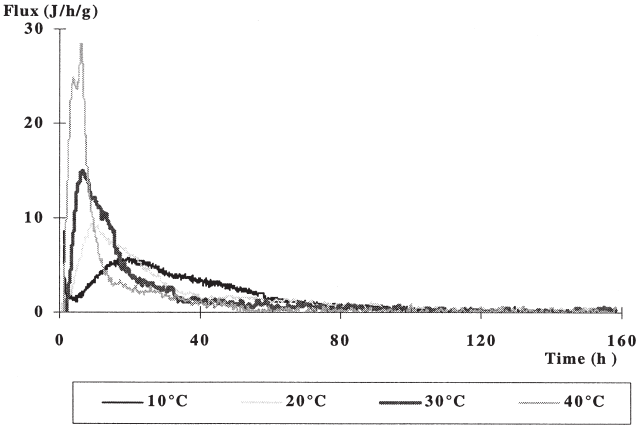

Fig. 2. The heat flux evolution.

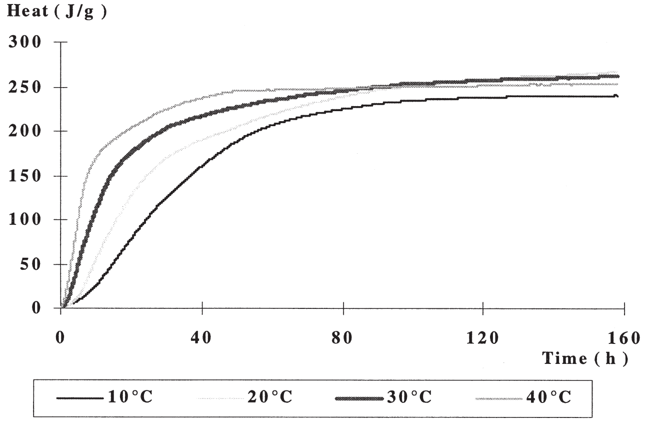

Fig. 3. The heat of hydration evolution.

of water and the ions through the layers of hydrates, which become increasingly thick. The quantity of heat is obtained by integration of the flux (Fig. 3).

We notice that the temperature considerably accelerates the reactions of hydration. One finds the traditional reduction of the heat of hydration, at a relatively advanced age, when the temperature rises. The fast initial hydration caused by a high temperature leads to the formation of a layer coating of hydrated product around the cement grains that then delays the continuation of the hydration.

Another manner of representing the quantity of formed hydrates is to introduce the concept of degree of hydration. Within the framework of our study, it is defined from Eq. (9):

$$\alpha = \frac{\text{released heat quantity at } t}{\text{released heat quantity at } = \infty} \tag{9}$$

The quantity of released final heat at $t = \infty$ is considered equal to the asymptotic value of the curves $Q(t)$. In practice, it is obtained by plotting the curve $Q = f(1/t)$ and the required asymptotic value $Q(\infty)$ is obtained by regression to X-axis $1/t = 0$. Fig. 4 represents the degree of hydration according to time for the various temperatures of curing.

From these curves and Eq. (6), we have studied the variations of the apparent activation energy and the degree of hydration according to the temperature. Energy is determined for a given degree of hydration and within a range of selected temperature. The obtained results are represented in Fig. 5.

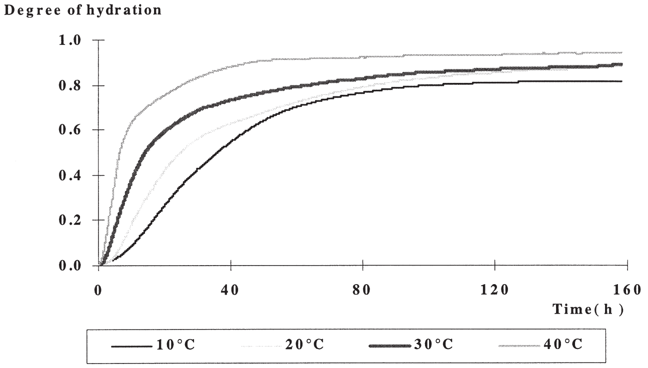

Fig. 4. Degree of hydration evolution.

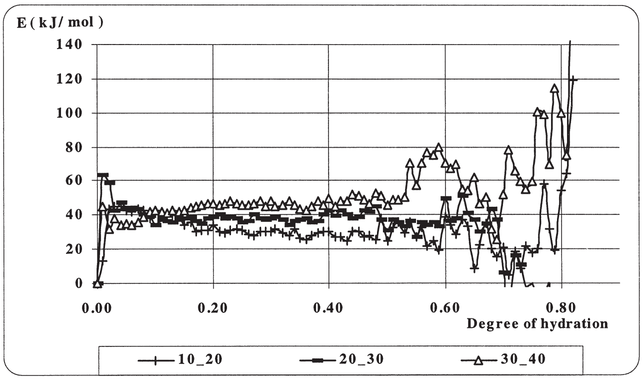

Fig. 5. Evolution of apparent activation energy for different ranges of temperature.

We have deduced the evolution from the apparent activation energy on the ranges of temperature from 10 to 20, 20 to 30, and 30 to 40°C. It is noticed that generally, it remains appreciably constant between $\alpha = 0.1$ and $\alpha = 0.5$.

The variations at a very young age ($\alpha < 0.05$) can be explained by the fact that the reaction is more directed by a mode of diffusion. Moreover, in the long term ($\alpha > 0.5$), one passes from a mode controlled by chemical reactions to a mode controlled by the diffusion of water through the layers of hydrates. The sensitivity to the temperature of these periods is different and the Arrhenius law cannot be applied in those cases.

Table 1 shows the values of the apparent activation energy obtained in the stabilized parts. One observes that the apparent activation energy varies with the temperature. In principal, this variation is not illogical insofar as the Arrhenius relation had been established for simple reactions only. This energy represents then a constant having a chemical significance. In the case of the reaction of cement hydration, it concerns a macroscopic apparent activation energy, which translates no chemical law at the microscopic level [12].

6. Conclusions

The thermal aspects of the hydration kinetics of concrete have been studied by techniques of isothermal calorimetry based on fluxmetric measures. From a formulation of concrete, we have shown the influence of temperature on the degree of hydration. The Arrhenius law seems to suitably describe the influence of temperature on the rate of the cement hydration reactions, although this material is com-

Table 1
Values of the apparent activation energy obtained in the stabilized parts ($0.05 < \alpha < 0.5$)

Ranges of temperature (°C)	10–20	20–30	30–40
Apparent activation energy (KJ/mol)	32.0	38.3	45.7

posed of several various elements. It introduces a parameter, the apparent activation energy, which makes it possible to describe this coupled effect.

The calorimetric technique that we have developed enables us, from two isothermal tests, to determine the apparent activation energy according to the degree of hydration. It was calculated on three ranges of temperature (10–20, 20–30, and 30–40°C). It remains more or less constant for all the tests at a degree of hydration ranging between $\alpha = 0.05$ and $\alpha = 0.5$. Outside this period, the apparent activation energy varies considerably. Indeed, the hydration kinetics is no longer controlled by a chemical reaction but rather by a process of diffusion through hydrated layers. The Arrhenius law does not apply in that case. It cannot completely depict the complexity of the cement hydration reactions.

We have also checked that the apparent activation energy varied with the temperature. For the studied concrete formulation, it seems difficult to determine a single activation energy for all the ranges of temperature. One is entitled, however, to calculate an average on more reduced ranges of temperature and tolerate a variation of about 5 kJ/mol. It is the case ,for example for thin elements, where the rise in temperature is about 15°C.

In a research program to come, it would be interesting to complete these works by the study of symptomatic concrete usually used in the building industry and in civil engineering works. The objective is to examine the influence of products such as superplasticizers or additions on the evolution of the apparent activation energy.

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