Pergamon

Cement and Concrete Research 32 (2002) 1207–1213

CEMENT AND CONCRETE RESEARCH

Determination of the apparent activation energy of one concrete by calorimetric and mechanical means
Influence of a superplasticizer

E. Wirquin*, M. Broda, B. Duthoit

Laboratoire d'Artois Mécanique et Habitat, Université d'Artois, Technoparc Futura, Béthune 62400, France

Received 17 November 2001; accepted 11 February 2002

Abstract

An instrument has been developed to perform calorimetric tests on concrete in isothermal conditions using 0.11 × 0.22-m cylindrical samples. The purpose of this article is to determine the apparent activation energy of one concrete as a function of temperature (10, 20 and 40 °C) using this technique and to compare it with that obtained by a mechanical means in order to validate the hypothesis made in maturity measurements, according to which the apparent activation energy values are assumed to be equivalent. The two means give relatively similar results (with differences of the order of 3 kJ/mol). It also seems possible to use a single apparent activation energy value over the entire temperature range (10–40 °C). Lastly, the effect of a superplasticizer on the apparent activation energy is examined, and it appears that its role is relatively small in the case of the concretes studied here. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Maturity; Apparent activation energy; Isothermal calorimeter; Compressive strength; Superplasticizer

1. Introduction

In order to optimize concrete formwork removal, prestressing operations and the handling of prefabricated units, it is necessary to have reliable measurements of concrete strength. The most common method used for evaluating the strength of young concrete is to make sample cylinders that are cured in similar conditions to those of the structure, and to crush them in a laboratory in order to determine their compressive strength. Because of differences in volume, there is always a significant deviation between the temperature history within the structure and within the samples. This difference is all the more pronounced when the structure consists of thick elements (such as dams, foundations of large structures, etc.). As the hydration kinetics of concrete is strongly affected by temperature, major differences are obtained between the strength values measured on the samples and the real strength of the structure itself. Maturity measurements were developed to improve the forecast of young concrete strength. Using this technique, it is possible to calculate the degree of hydration at a given time using the temperature history within the structure [1]. With a given maturity, a concrete will have identical characteristics, irrespective of the conditions in which it has matured. Several definitions have been proposed and Arrhenius' experimental law has proved to be the most suitable. Applied to concrete, it introduces a parameter, the apparent activation energy, which is characteristic of the mix. It can be determined by either mechanical or calorimetric means.

Mechanical measurements are interesting in that they enable this parameter to be calculated from tests of the same type. However, this method is quite laborious owing to the frequent measurements that have to be taken. Calorimetric tests can be carried out in adiabatic or isothermal conditions. There are few adiabatic calorimeters and their complexity means that their use is limited to reference tests. Semi-adiabatic devices are simpler but it is difficult to take into account losses, and this leads to uncertain results. Another difficulty is due to the fact that the chemical reactions are thermally activated, and calorimetric processes deal with temperature, which changes in time. It is therefore preferable to work in isothermal conditions. Moreover, this type of approach has the advantage of fixing the temperature

---

* Corresponding author. Tel.: +33-321-63-71-45; fax: +33-321-61-17-80.

E-mail address: eric.wirquin@voila.fr (E. Wirquin).

0008-8846/02/$ – see front matter
PII: S0008-8846(02)00770-6

parameter on which the apparent activation energy is likely to depend. Following recent work in our laboratory [2], we developed an isothermal device for concrete based on specific fluxmeter instrumentation accepting 0.11 × 0.22-m cylindrical samples, which are much more representative and identical to those used in the mechanical tests.

After describing the experimental set-up and calorimetric and mechanical monitoring at three curing temperatures (10, 20 and 40 °C), the apparent activation energy values will be deduced by these two means for concrete with or without superplasticizer. The purpose of this work is, on one hand, to validate the hypothesis used in maturity measurements, which assumes that the apparent activation energy values determined by calorimetric and mechanical means are equal, and, on the other hand, to study the effect of a superplasticizer on the apparent activation energy.

2. Description of the isothermal calorimeter

2.1. Experimental device

The isothermal calorimeter for concrete (Fig. 1) consists essentially of:

- two heat exchangers which, when assembled, form an isothermal cylinder able to hold a sample measuring 0.11 × 0.22 m;
- two semiadiabatic bases made of polystyrene, each 60 mm thick;
- two pumps connected to a thermostat-controlled bath to maintain the liquid (water) at a constant temperature; and
- a data acquisition system composed of a multimeter and a computer.

2.2. Instrumentation

Instruments are fitted to monitor changes in heat fluxes and temperatures at various locations within the calorimeter. The fluxes are measured by means of "tangential gradient" sensors set on the surface of the exchangers [2,3]. The operating principle helps to limit perturbations in measurements and boundary conditions as much as possible. The total thickness of the fluxmeters is of the order of 0.3 mm. The time constant, RC, is of the order of 1 s. The very low thermal resistance produced by the sensors (close to 10^{-3} K/W/m^2) ensures a good heat sink on the material surface. The temperatures are measured by T-type thermocouples incorporated in the flux sensors and by a thermocouple placed in the core of the concrete. In this way, it is possible to check the quality of the isothermal conditions.

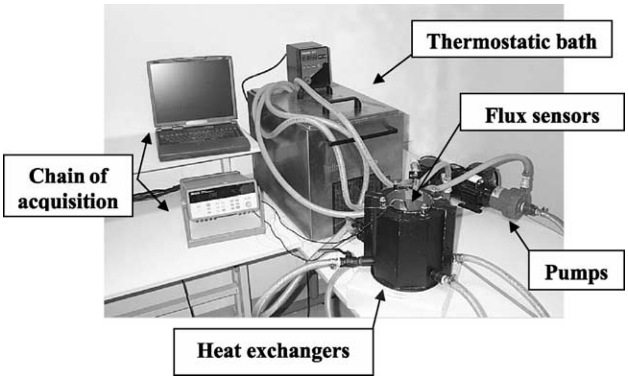

Fig. 1. General view of the experimental device.

2.3. Calibration of the device

Calibration is done in two stages:

- in situ calibration of the fluxmeters, and
- determination of a law governing losses from the device itself caused by the edges and proportional to the difference in temperature between the inside of the calorimeter and the outside atmosphere.

From these results, it is possible to calculate the total reaction flux Φ_{total} corresponding to the sum of the two fluxes measured on the heat exchangers faces, of the flux lost through the semiadiabatic bases and of the flux of edges losses (Eq. (1)):

$$\Phi_{\mathrm{total}} = \Phi_{\mathrm{measured}} + \Phi_{\mathrm{bases}} + \Phi_{\mathrm{edges}}. \quad (1)$$

The heat of hydration Q is obtained by integrating the total flux Φ_{total} with respect to time (Eq. (2)):

$$Q(t) = \int_0^t \Phi_{\mathrm{total}} \mathrm{d}t. \quad (2)$$

3. Concept of maturity—apparent activation energy

3.1. Definitions

3.1.1. Concept of maturity

The concept of maturity is used to express the degree of hydration of the concrete [4]. It integrates the coupled effects of temperature and time on the hydration kinetics of concrete. Saul [5] was one of the first to define this principle: "two concretes of the same composition with the same value of maturity will have the same strength, irrespective of the temperature history that led to this value of maturity."

The expression for maturity can be given by relation (3):

$$M(t,H(T)) = \int_0^t K(T(\tau))\mathrm{d}\tau \quad (3)$$

$M(t,H(T))$: maturity at instant t for a given temperature history $H(T)$; $K(T)$: kinetic constant at temperature T; $T(\tau)$: absolute temperature at instant τ, in Kelvin.

3.1.2. Definition of equivalent age

The concept of equivalent age was introduced later by Rastrup [6] and Mc Intosh [7]. It is defined in relation to a reference temperature T_{ref}, which is generally 20 °C. It is directly connected to the concept of maturity, giving it a better significance. The equivalent age t_{eq} corresponds to the time during which the concrete must be maintained at the reference temperature in order to obtain the same value of maturity as in the real conditions of curing (Eq. (4)):

$$M(t,H(T)) = \int_0^t K(T(\tau))\mathrm{d}\tau = \int_0^{t_{\text{eq}}} K(T_{\text{ref}})\mathrm{d}\tau = M(t_{\text{eq}},T_{\text{ref}}) = K(T_{\text{ref}})t_{\text{eq}} \tag{4}$$

$M(t_{\text{eq}},T_{\text{ref}})$: maturity at instant t for reference temperature T_{ref}; t_{eq}: equivalent age at reference temperature T_{ref}, generally 20 °C (293 K).

Hence (Eq. (5)):

$$t_{\text{eq}} = \int_0^t \frac{K(T(\tau))}{K(T_{\text{ref}})}\mathrm{d}\tau. \tag{5}$$

3.1.3. Introduction of Arrhenius' law

Several authors [8–10] have tried to find an expression for the kinetic constant $K(T)$ and Arrhenius' law has proved to be the one best suited to concrete (Eq. (6)):

$$K(T) = A\exp\left(-\frac{E_{\text{a}}}{RT}\right) \tag{6}$$

A: constant of proportionality, 1/s; R: perfect gas constant, 8.314 J/mol K; E_{a}: apparent activation energy of concrete, J/mol.

In this expression, E_{a} is the parameter relating the sensitivity of the hydration kinetics of concrete to a variation in temperature. In the case of concrete, the activation energy is referred to as "apparent" because cement hydration involves several simultaneous and coupled chemical reactions. Hence (Eq. (7)):

$$t_{\text{eq}} = \int_0^t \exp\left(-\frac{E_{\text{a}}}{R}\left(\frac{1}{T(\tau)} - \frac{1}{T_{\text{ref}}}\right)\right)d\tau. \tag{7}$$

3.2. Calculation of apparent activation energy

Two different thermal histories (T_1 and T_2) are needed to calculate the apparent activation energy E_{a}. This parameter can be determined by the method of "superposition" from the curves of released heat Q or compressive strength f_{c}. The purpose is to determine a single value of E_{a} over a given range. With this value, it is possible to superpose as well as possible two curves of evolution of Q or f_{c} as a function of the equivalent age (Fig. 2). The value of E_{a} that minimizes the difference between the various pairs of equivalent ages ($t_{\text{eq}1i}$, $t_{\text{eq}2i}$) over the given range is then sought.

The purpose of maturity measurements is to estimate the strength of the concrete at certain points in the structure. These points are where "target" strength values must be reached before, e.g., removing forms or prestressing the concrete. In general, these values are given by the design office. To cover the useful strength domain, a range of values $[f_{\text{c}_{\text{inf}}} - f_{\text{c}_{\text{sup}}}]$ is adopted, corresponding to the lowest of the "target" values reduced by 5 MPa and the highest increased by 5 MPa. Generally, $f_{\text{c}_{\text{sup}}}$ should not exceed 50% of the 28-day strength. In the present case, the concrete studied can be considered as building concrete with a relatively low final strength ($f_{\text{c}_{28}} = 32$ MPa). The study was therefore limited to 50% of the 7-day strength. The lower limit was fixed at 1 MPa, which corresponds to the threshold under which strength measurements have little meaning.

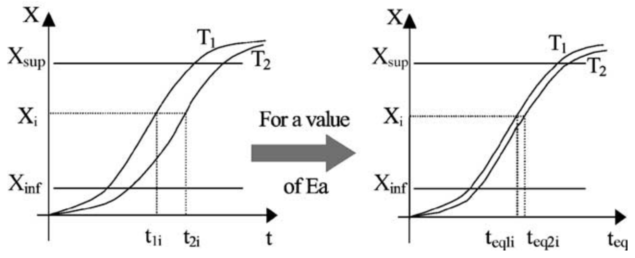

Fig. 2. Method of "superposition" (example).

With regard to the calorimetric means, the upper heat limit Q_{sup} is obtained by plotting the curve of heat of hydration Q as a function of strength f_{c} for the test at 20 °C. The value of Q_{sup} is thus deduced from the chosen value $f_{\text{c}_{\text{sup}}}$. The lower limit Q_{inf} was fixed at 10 J/g, which corresponds to a sufficiently significant value.

Regardless of the means chosen, the upper limit of the target range of heat or strength can be designated X_{sup} and the lower limit X_{inf}. The least error squares method (Eq. (8)) is then used to determine the apparent activation energy value E_{a} over the range $[X_{\text{inf}} - X_{\text{sup}}]$:

$$\min_{E_{\text{a}}}\left(\sum_{Xi\in[X_{\text{inf}}-X_{\text{sup}}]} |t_{\text{eq}1i} - t_{\text{eq}2i}|^2\right) \tag{8}$$

with:

$$t_{\text{eq}1i} - t_{\text{eq}2i} = \int_0^{t1i} \exp\left(-\frac{E_{\text{a}}}{R}\left(\frac{1}{T_1(\tau)} - \frac{1}{T_{\text{ref}}}\right)\right)\mathrm{d}\tau - \int_0^{t2i} \exp\left(-\frac{E_{\text{a}}}{R}\left(\frac{1}{T_2(\tau)} - \frac{1}{T_{\text{ref}}}\right)\right)\mathrm{d}\tau. \tag{9}$$

The times t_{1i} and t_{2I} correspond to the real curing ages for a same quantity of released heat Q_i or for a same strength f_{c_i} and $t_{\text{eq}1i}$ and $t_{\text{eq}2i}$ are the corresponding equivalent ages.

4. Mix design

The tests were carried out with ordinary Portland cement CEM I 42.5 R following the European standardization. The sand and gravels are siliceous aggregates.

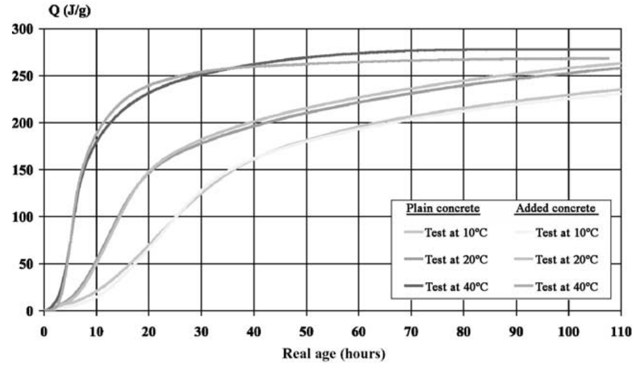

Fig. 3. Heat of hydration evolution.

The composition of the two concretes for 1 m^3 was:

Cement	300 kg
Water	171 kg
Sand 0/5	740 kg
Gravel 5/12	463 kg
Gravel 12/25	673 kg
Water/cement ratio	0.57

Workability measurements on the plain concrete have given an average slump of 60 mm. The superplasticizer, when used, is the Cimfluid 230 (0.8% of cement weight with no change in water content) and the slump was, in this case, 160 mm.

5. Measurement of the heat of hydration

The calorimetric tests were performed at three curing temperatures (10, 20 and 40 °C) using samples made from the concrete mix used for the mechanical tests. The evolution of the heat flux Φ_{total} as a function of age was measured for each curing temperature. The quality of the isothermal conditions was checked in each test by comparing the differences in temperature between the core and surfaces of the sample. The heat of hydration Q was obtained by integrating the total flux Φ_{total} (Fig. 3). It was verified that the temperature considerably accelerates the hydration reaction. In addition, it can be seen that the superplasticizer has no delaying effect on the hydration kinetics, as the curves are very close for both the concretes studied.

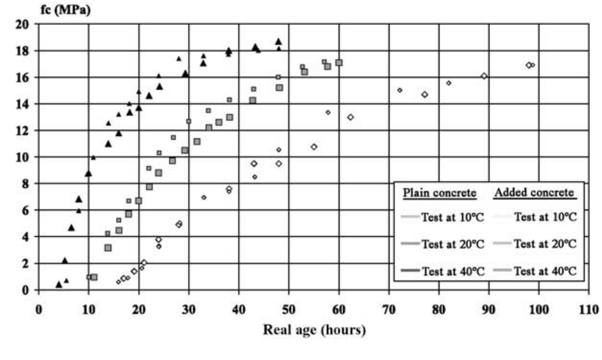

Fig. 4. Compressive strength evolution.

Table 1
Determination of apparent activation energy E_a for the plain concrete and for various pairs of temperatures over the range of heat of hydration (10–180 J/g)

Temperature ranges (°C)	10–20	20–40	10–40
E_a (kJ/mol)	36.1	39.7	38.4
Average deviation (h)	0.3	0.6	0.8

6. Mechanical tests

These are conventional compression tests on 0.11 × 0.22-m concrete samples identical to those used for the calorimetric tests. The samples are made and tested in accordance with French standards. About 14 regularly spaced breakings are realized for each curing temperature, in order to cover the target range of strength values and a 28-day contractual measurement. A recording of the temperature in the core of two distinct samples is made from the end of the mixing. The samples are cured in a temperature and climatic test chamber and are removed from the forms just before the compression test (even after 24 h). About 15 min elapse between the moment the samples are taken from the chamber and the moment they are crushed. The samples are coated with sulphur and the first measurements are made as quickly as it is technically possible. Two samples are tested at each breaking.

The experimental program provided for the same curing temperatures (10, 20 and 40 °C). The same influence of the temperature may be observed on the strength curves (Fig. 4). In addition, the effect of the superplasticizer is scarcely noticeable at 10 and 40 °C. However, there is a more notable difference at 20 °C between the concrete with or without superplasticizer, which can be put down to a difference between the measured temperature histories (of the order of 3 °C in favor of the added concrete). This experimental fluctuation will, however, be included in the equivalent age calculation (Eq. (9)) as it takes account of the thermal history of the samples.

7. Determination of the apparent activation energy

As explained in Section 3.2, the upper limit $f_{c_{sup}}$ of the range of strength was set at 50% of 7-day strength value,

Table 2
Determination of apparent activation energy E_a for the added concrete and for various pairs of temperatures over the range of heat of hydration (10–180 J/g)

Temperature ranges (°C)	10–20	20–40	10–40
E_a (kJ/mol)	38.2	39.9	39.3
Average deviation (h)	0.2	1	0.7

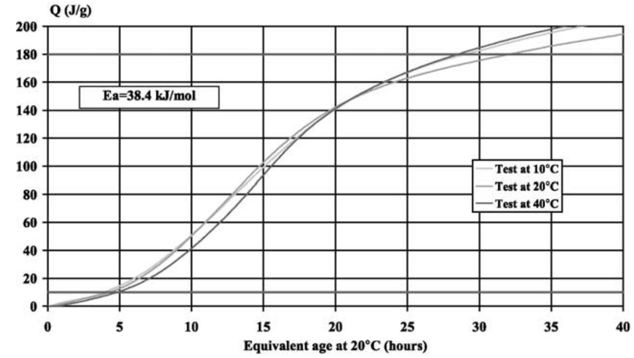

Fig. 5. Heat of hydration as a function of equivalent age at 20 °C for the plain concrete.

i.e., at 11 MPa. The lower limit was fixed at 1 MPa, corresponding to the threshold below which strength measurements have little meaning. The target range of strength thus corresponds to the interval (1–11 MPa).

The upper heat limit Q_{sup} is obtained by plotting the curve $Q=f(f_c)$ for the isothermal test at 20 °C. With a value of strength of 11 MPa, a value of 180 J/g is obtained for Q_{sup}. The lower limit Q_{inf} was fixed at 10 J/g, corresponding to a sufficiently significant value. The target range of heat of hydration thus corresponds to the interval (10–180 J/g).

7.1. By calorimetric means

Using the curves of evolution of Q (Fig. 3) and Eqs. (8) and (9), an apparent activation energy value is determined for each pair of temperatures (10–20 and 20–40 °C) over the range of heat of hydration (10–180 J/g). An apparent activation energy value is also calculated over the entire 10–40 °C temperature range (Tables 1 and 2).

The average deviation is obtained by calculating the mean of the equivalent age differences between the two curves (Eq. (9)).

According to these tables, it is possible to calculate a single apparent activation energy value over the entire 10–40 °C temperature range provided the variations in E_a as a function of temperature are relatively small in the case of the concretes studied. A variation of less than 3 kJ/mol with respect to this value is then tolerated.

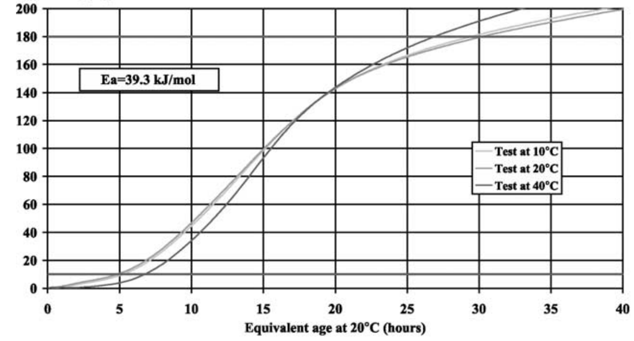

Fig. 6. Heat of hydration as a function of equivalent age at 20 °C for the added concrete.

Table 3
Determination of apparent activation energy E_a for the plain concrete and for various pairs of temperatures over the range of compressive strength (1–11 MPa)

Temperature ranges (°C)	10–20	20–40	10–40
E_a (kJ/mol)	34	36.4	35.6
Average deviation (h)	0.5	1.5	1.1

The evolution in the various heat curves as a function of their equivalent age at 20 °C can thus be plotted for this single value of E_a (38.4 kJ/mol for the plain concrete and 39.3 kJ/mol for the added concrete). The correct superposition of the heat curves is checked (Figs. 5 and 6). The average deviation between the envelope curves of each bundle of curves is less than 1 h and the choice of a single value for E_a therefore seems to be consistent.

7.2. By mechanical means

Using the curves of evolution of strength f_c (Fig. 4) and the same equations, it is possible to determine an apparent activation energy value for each pair of temperatures (10–20 and 20–40 °C) over the range of strength (1–11 MPa). An apparent activation energy value is also calculated over the entire 10–40 °C temperature range (Tables 3 and 4).

As previously, it is possible to calculate a single apparent activation energy value over the entire 10–40 °C temperature range. In this case, variations in E_a are less than 2 kJ/mol.

It is then possible to plot the evolution in the various strength curves as a function of their equivalent age at 20 °C for this single value of E_a (35.6 kJ/mol for the plain concrete and 37.5 kJ/mol for the added concrete). The correct superposition of the curves is also checked (Figs. 7 and 8). An average deviation of 1.6 h is obtained for the plain concrete and 0.8 h for the added concrete. In view of the rate at which these concretes strengthen, the deviations may be expressed in terms of average strength value scatter (0.6 MPa for the plain concrete and 0.4 MPa for the added concrete). These scatters are good compared with the normal order of magnitude (2 MPa) accepted on site.

Table 4
Determination of apparent activation energy E_a for the added concrete and for various pairs of temperatures over the range of compressive strength (1–11 MPa)

Temperature ranges (°C)	10–20	20–40	10–40
E_a (kJ/mol)	37.1	37.6	37.5
Average deviation (h)	0.8	0.8	0.6

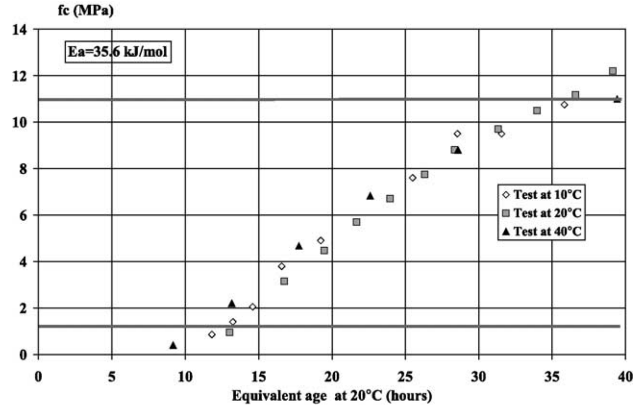

Fig. 7. Compressive strength as a function of equivalent age at 20 °C for the plain concrete.

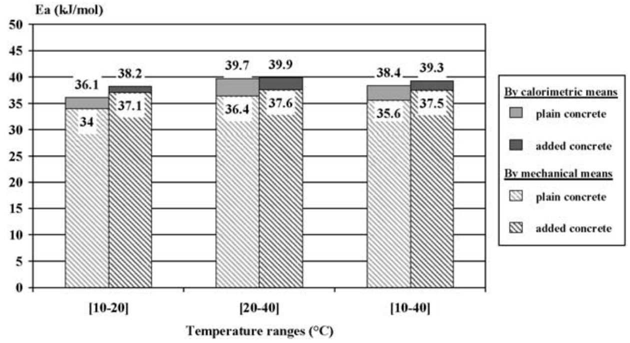

Fig. 9. Summary of the values of E_a.

7.3. Summary of results

Fig. 9 gives all the results obtained with the two means and both concretes.

First of all, the apparent activation energy values calculated by the two means over the various temperature ranges may be compared. The observed differences are close to 3 kJ/mol. These differences are satisfactory given the heterogeneity of the material and the complexity of the reactions involved. Indeed, the effect of this variation of ± 3 kJ/mol on the estimated strength is no more than 1 MPa, which is within the accepted margin of safety in maturity measurements. Either the calorimetric means or mechanical means may therefore be used to calculate the apparent activation energy. These results thus validate the hypothesis made in maturity measurements, which assumes that the apparent activation energy values determined by these two means are equal.

It may also be noted that, regardless of the means used, a single apparent activation energy value may be calculated over the entire 10–40 °C temperature range insofar as the variations in E_a as a function of temperature are relatively small for the concretes studied (less than 3 kJ/mol in relation to this single value).

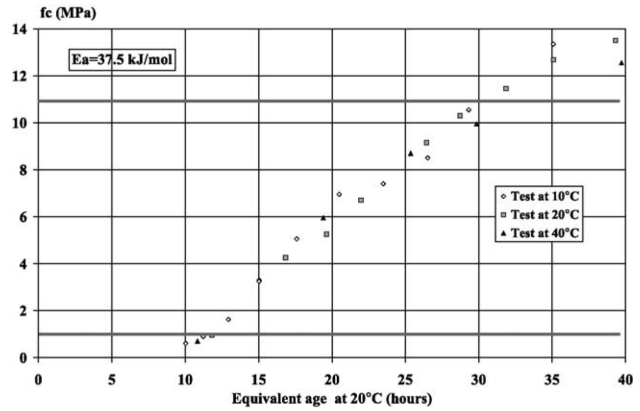

Fig. 8. Compressive strength as a function of equivalent age at 20 °C for the added concrete.

Furthermore, the effect of a superplasticizer on the apparent activation energy may also be studied. Regardless of the means used (calorimetric or mechanical), the effect of the superplasticizer on E_a is relatively small as the differences are no more than 3 kJ/mol. These results could nevertheless be expected in view of the heat of hydration and strength curves, insofar as the effect of the superplasticizer was not very pronounced.

8. Conclusion

The main purpose of this work was to compare the apparent activation energy values determined by calorimetric and mechanical means in order to validate the hypothesis used in maturity measurements, according to which they are equal. To do this, we used an isothermal calorimeter developed in our laboratory, based on fluxmeter instrumentation. With this device, it is possible to perform tests on cylindrical concrete samples measuring 0.11 × 0.22 m. On the basis of two isothermal tests, this calorimetric technique enables to determine directly the apparent activation energy. This article presents the results of calorimetric and mechanical monitoring obtained for concrete with or without superplasticizer and for three curing temperatures (10, 20 and 40 °C).

The apparent activation energy was determined by the method of "superposition" based on Arrhenius' law. It was calculated for two restricted temperature ranges (10–20 and 20–40 °C). In addition, it is possible to determine a single apparent activation energy over the entire 10–40 °C temperature range by accepting a variation of less than 3 kJ/mol.

Calorimetric and mechanical means give very similar apparent activation energy values as the observed differences are close to 3 kJ/mol. These differences are acceptable insofar as, once they are carried over to the strength curves, there is a maximum scatter of 1 MPa. This value is within the usual orders of magnitude tolerated on site (2 MPa). These results confirm the initial hypothesis and indicate that, for these concretes, the apparent activation energy determined by the method of "superposition" on the basis of the calorimetric results may legitimately be used to predict the strength of young concrete.

The other purpose of this work was to check the influence of a superplasticizer on the apparent activation energy. It appears that its effect on the hydration kinetics is minimal regardless of temperature. This is confirmed by the results of E_a, where, regardless of the means used, the differences are no more than 3 kJ/mol.

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 silica fume, limestone filler or blast furnace slag on the evolution of the apparent activation energy.

Acknowledgments

We particularly thank Mr. V. Waller (Centre Technique de Guerville, Italcementi Group) for his scientific and technical contribution.

References

[1] L. D'Aloïa, et. al., Projet National CALIBE, Résistance du béton dans l'ouvrage — La Maturométrie, 2001, pp. 1–62.

[2] H. Kada-Benameur, E. Wirquin, B. Duthoit, Determination of apparent activation energy of concrete by isothermal calorimetry, Cem. Concr. Res. 30 (2000) 301–305.

[3] D. Leclercq, P. Thery, Apparatus for simultaneous temperature and heat flow measurements under transient conditions, Rev. Sci. Instrum. 54 (1983) 374–380.

[4] P. Thery, B. Duthoit, New heat flow sensor for thermal non-destructive testing of wall sections in their natural environment, IMEKO TC7 International Symposium on AIMAC91 Japan, 1991, pp. 163–168.

[5] A.G.A. Saul, Principles underlying the steam curing of concrete at atmospheric pressure, Mag. Concr. Res. 2 (6) (1951) 127–140.

[6] E. Rastrup, Heat of hydration in concrete, Mag. Concr. Res. 6 (17) (1954) 79–92.

[7] J.D. Mc Intosh, Effect of low temperature curing on the compressive strength of concrete, Proceedings of the RILEM Symposium on Winter Concreting, Danish Institute for Building Research, Session B-II, Copenhagen, 1956, pp. 3–17.

[8] G.J. Verbeck, R.H. Helmuth, Structures and physical properties of cement paste. Proceedings of the 5th International Symposium on the Chemistry of Cement, Cement Association of Japan, Session III-1, Tokyo, 1968, 1969, pp. 1–32.

[9] P. Freiesleben Hansen, E.J. Pedersen, Maleinstrument til Kontrol af betons haerdning, Nord. Betong 1 (1977) 21–25.

[10] M. Regourd, E. Gauthier, Comportement des ciments soumis au durcissement accéléré, Annales de l'ITBTP Durcissement Accéléré des Bétons, Deuxième Partie, Les Paramètres à Connaître, vol. 387, 1980, pp. 83–96.