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Determining the "apparent" activation energy of concrete E_a—numerical simulations of the heat of hydration of cement

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Abstract

The "apparent activation energy" of concrete—E_a—is usually determined by means of mechanical or calorimetric tests. This parameter, which characterises the sensitivity of concrete hydration processes to temperature, is required for estimating the compressive strength of concrete at early age by the "method of equivalent age." The major aim of this paper is to show how numerical simulations of released heat under adiabatic conditions could be an alternative to experiments for determining E_a. The simulation model—the CHAL program—which is developed here, is based on the kinetic model of Avrami–Erofeev. The coupling by temperature between the different chemical reactions of the main anhydrous components of cement is taken into account by using the Arrhenius' law. The model leads to a better understanding of the polymineral characteristic of cement as regards heat of hydration and E_a determination. The "apparent" nature of E_a and its dependence on hydration degree can be underlined. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Calorimetry; Hydration; Kinetics; Cement; Modeling

1. Introduction

1.1. The "method of equivalent age"

The method of equivalent age is currently used for concrete strength estimation at early ages [1,2]. It enables the combined effects of time and temperature on compressive strength development to be accounted for. It is based on the Arrhenius' law (Eq. (1)), which has shown itself to be the most accurate for describing the kinetic influence of temperature on many chemical and physical processes.

$$K(T) = A\exp\left(-\frac{E_a}{RT}\right) \tag{1}$$

T: absolute temperature (K); $K(T)$: rate constant; A: proportionality constant; E_a: "apparent" activation energy of concrete (J/mol); R: gas constant (8.314 J/mol K).

The rate of hydration is then expressed as follows (Eq. (2)):

$$\frac{d\alpha}{dt} = g(\alpha)K(T) \tag{2}$$

α: degree of hydration; $g(\alpha)$: function of the hydration degree; $K(T)$: rate constant.

A satisfactory estimate of the compressive strength of concrete is directly related to a correct determination of the "apparent" activation energy of concrete, E_a. This is the unique parameter, which characterises the concrete mixture and which can be found in the Arrhenius' law. It must be stressed that the Arrhenius' law allows the influence of temperature on a simple chemical reaction kinetic to be described. Its application to the case of cement hydration is an approximation because the hydration of the different anhydrous components of cement involves several interdependent chemical reactions. This is the reason why the activation energy is called "apparent."

1.2. The "apparent activation energy" and its determination

The use of a constant E_a value depending only on the type of cement was suggested by Bresson [3]. Several recent

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studies led to the conclusion that it may not be satisfactory to consider only the type of cement. E_a characterises the whole concrete mixture including, of course, the type of cement, but also the water to cement ratio w/c, admixtures, mineral additives, etc. Moreover, E_a cannot be considered as a constant that is independent of the age of curing, i.e., from the degree of hydration [2,4,5]. Some dependence on temperature has also been suggested and underlined on the basis of experimental results [6,7]. This dependence is much debatable from the thermodynamic point of view [8], but can be explained by the "apparent" feature of E_a.

Mechanical and, more recently, calorimetric approaches under isothermal or variable conditions have been proposed for the experimental determination of E_a [1,9,10]. The heat of hydration is assumed to be proportional to the quantity of hydrated products and thus to the hydration degree of cement. Both mechanical and calorimetric tests can be performed to follow changes in early hydration rate. However, the general new trend, which consists in determining E_a by performing calorimetric tests, has raised a number of queries with regard to the nature of the correlation between strength and hydration heat, especially under variable temperature conditions and at early age [11]. Considering the polymineral characteristic of the binder, certain parameters can affect strength and released heat in different ways. For example, the hydration of C_3A is highly exothermic, although its contribution to strength is very low. Concerning only parameters influencing concrete strength development, the experimental results are full of inconsistencies. However, several main points are summarised in a technical report of the RILEM [12]. Nevertheless, according to recent experimental results, relative strength, relative hydration heat and hydration degree are well correlated, at least during the first stages of hydration when the microstructural effects are negligible [13]. Hence, determining E_a from calorimetric tests and mechanical ones should lead to similar results at early age.

This leads to the conclusion that heat of hydration and strength must only be considered as closely correlated macroscopic responses on the basis of experimental results. Such a correlation between degrees of hydration defined from these two variables would be very difficult to explain by physical assumption.

In addition, a number of numerical models based on calorimetric measurements have been proposed in order to describe the changes in the reaction rate of C_3S, or even that of cement.

Most of them take into account the mineral composition [13], and some of them the presence of mineral additives too [14]. Others consider the binder as a whole [15]. They make it possible to estimate the rate of hydration through the prediction of the released heat by assuming proportionality between released heat and quantity of hydrated products. Other more complex types of numerical model have also been developed recently. Some of them involve C_3S hydration [16]. The effects of the development of the microstructure on the rate of hydration are explicitly taken into account, as in the model proposed by Van Breugel [7]. Finally, other iterative hydration models such as "Digital, Image-Based" [17] do not consider directly time as a variable. This model encompasses the mechanisms of dissolution–diffusion–nucleation and enables several properties of the hydrated material such as porosity and permeability to be predicted on the basis of the theory of percolation.

As far as they are based on a relevant and exhaustive description of hydration processes, all these simulation models lead to the attractive prospect of predicting the behaviour of cementitious materials by reducing tests to be performed.

2. Research significance

The major aim of this paper is to show how numerical simulations of released heat under adiabatic conditions could be an alternative to complex test procedures for determining E_a. The numerical model we propose is based on the mineral composition of cement. The effects of the microstructural changes in the cement paste, i.e., fineness of cement, particle size distribution and w/c, are not taken into account. Only the couplings by temperature between the different hydration reactions of the main phases of cement—silicates and aluminates—are considered. This is the reason why, in the present stage of development, the simulation model (the CHAL program) cannot really replace the experimental approaches. However, it does lead to a better understanding of the influence of the mineral composition of cement on the released heat and on the E_a determination. The "apparent" nature of E_a, in the case of cement hydration, can be underlined.

3. The new simulation model: the CHAL program

3.1. The idea behind the model

First of all, as already indicated, the activation energy is called "apparent" in the case of cement hydration. The idea is then to consider the polymineral nature of cement and to separate out the different rates of hydration. It is assumed that each phase of the cement hydrates as a "simple" chemical reaction does. The Arrhenius' law is applicable to each of them and distinct values of activation energy E_{a_i} should be adopted. Secondly, the heat of hydration is chosen as an indicator of hydration rate. The rate of hydration of the cement is obtained from the individual rates of each phase. Finally, the "apparent" activation of concrete can be calculated from the simulated changes in heat rate for different initial temperatures under adiabatic conditions.

3.2. Principal assumption

"Independent fractional rates" are assumed rather than "equal fractional rates." A number of researchers agree with the fact that hydration of cement proceeds through a mechanism lying somewhere between these two extremes. The latter is probably verified after 24 h of hydration [18] and, for this reason, the former was adopted in our framework of early age. According to this assumption, the rates of hydration of the different phases are distinct and independent of the mineral composition of cement.

For each phase, the relative heat of hydration is assumed to be proportional to the quantity of hydrated products (Eq. (3)):

$$\alpha_i(t) = \frac{m_i(t)}{m_i^0} = \frac{Q_i(t)}{Q_i^{\max}} \tag{3}$$

$\alpha_i(t)$: degree of hydration of phase i at time t; m_i^0, $m_i(t)$: initial mass of phase i, hydrated mass of phase i at time t; $Q_i(t)$, $Q_i^{\max}$: heat of hydration of phase i at time t, released heat of phase i at complete hydration.

The released heat and the degree of hydration of cement are then obtained from the individual values of each phase (Eq. (4)):

$$\begin{cases} Q_c(t) = \sum_i p_i Q_i(t) \\ \alpha_c(t) = \sum_i p_i \alpha_i(t) \end{cases} \tag{4}$$

$Q_c(t)$, $\alpha_c(t)$: heat of hydration and degree of hydration of cement at time t; $p_i = m_i^0/m_c$: mass proportion of phase i in cement.

3.3. Temperature coupling

The different phases of cement are assumed to hydrate at different rates independent of the composition of the cement. The only coupling taken into account is that due to temperature, which is modelled by the Arrhenius' law. Under adiabatic conditions, all the heat released during a particular time interval contributes to the temperature rise of the whole mixture characterised by its specific heat C and its cement content.

3.4. Data required for the simulations

3.4.1. Cement

The mineral composition of cement including the sulphate content is required, based on Bogue's formula for example (Table 1).

Table 1
Bogue's composition of cements

	CEMI (%)	PMES (%)
C_3S	47.66	53.63
C_2S	24.89	21.83
C_3A	9.52	3.04
C_4AF	7.14	12.31
SO_3	3.55	2.86

3.4.2. The determination of materials data

The data characterising the hydration and, more particularly, the kinetics of each phase of cement are required. These include:

- activation energy Eq. (1),
- quantity of released heat at complete hydration $Q_i^{\max}$,
- reference curve of heat rate $(\mathrm{d}Q_i/\mathrm{d}t)_{T_{\mathrm{ref}}}(Q_i)$ at the reference temperature 20 °C.

The rate of hydration of each phase at temperature T is obtained from the Arrhenius' law. The released heat is regarded as being equivalent to degree of hydration to the extent that the temperature at early ages has no significant influence on the final heat of hydration [19]. For this reason, the degree of hydration was replaced by the heat of hydration in the following equation:

$$\left(\frac{\mathrm{d}Q_i}{\mathrm{d}t}\right)_T (Q_i) = \left(\frac{\mathrm{d}Q_i}{\mathrm{d}t}\right)_{T_{\mathrm{ref}}} (Q_i) \exp\left(-\frac{E_{\mathrm{a}_i}}{R}\left(\frac{1}{T} - \frac{1}{T_{\mathrm{ref}}}\right)\right) \tag{5}$$

T: actual test temperature; $(\mathrm{d}Q_i/\mathrm{d}t)_T$: heat rate of phase i at the temperature T.

Published values of the final heat of hydration are adopted for each phase [20]. Activation energies and reference curves were obtained by fitting a kinetic model from Eqs. (5) and (6) and after discretisation.

$$\frac{\mathrm{d}Q_c}{\mathrm{d}t} = \sum_i p_i \frac{\mathrm{d}Q_i}{\mathrm{d}t} \tag{6}$$

$\mathrm{d}Q_c/\mathrm{d}t$: heat rate of cement.

3.5. Fitting the kinetic model

The first attempt was to use data from the literature. The results of the simulations were not satisfactory because the description of the kinetics (segments) was too unrefined [13]. Moreover, the data from experimental results obtained on pure phases under isothermal conditions and the kinetic model of Kolmogorov–Erokeev did not lead to consistent simulations under adiabatic conditions [21]. Accordingly, a different approach was adopted here. The slightly different model of Avrami–Erofeev and used by Banfill in the case of "ciment fondus" was adopted [22] and the parameters were fitted to experimental results under semiadiabatic conditions [10] (Eq. (7)).

$$\begin{cases} \alpha_i(t) = 1 - \exp(-(K_i t)^{n_i}) \\ \frac{\mathrm{d}\alpha_i}{\mathrm{d}t}(t) = n_i K_i^{n_i} t^{n_i - 1} \exp(-(K_i t)^{n_i}) \\ \frac{\mathrm{d}\alpha_i}{\mathrm{d}t}(\alpha^i) = n_i K_i (1 - \alpha_i)(-\ln(1 - \alpha_i))^{1 - \frac{1}{n_i}} \end{cases} \tag{7}$$

n_i, K_i: parameters characteristic of the kinetics of phase i.

This model allows a correct description of the calorimetric results obtained under semiadiabatic conditions in a previous experimental program [19]. Experiments were carried out on concrete formulated with two different cements. The initial temperatures of fresh concrete were 10, 20 and 28 °C. The least squares method was not used to fit the kinetic model on experimental results because mathematical solutions were not satisfactory from a physical point of view. Hence, the parameters were fitted by eye to experimental curves of heat rate at the initial temperature of 20 °C. The fitted parameters are then used for calculating heat rates at the two other initial temperatures of 10 and 28 °C. The good correlation between experimental results and calculations validates the fitted parameters. The fitting process was subjected to a set of constraints:

(1) Only the C_3S and C_3A phases were used for the simulations. They are the most important phases as far as heat of hydration at early age is concerned.

(2) The C_3A hydration is described by two distinct reactions:

- ettringite formation in presence of sulphate,
- conversion of the ettringite formed into monosulfoaluminate when the sulphate is exhausted.

The second reaction is assumed to start when the first one is 0.9 complete (α_0=0.9).

(3) The heat rate peak corresponding to the formation of ettringite is assumed to precede the peak of the C_3S hydration.

(4) E_{a_i} is liable to take a value in the range from 20 to 70 kJ/mol.

(5) K_i is positive.

(6) n_i is an integer and corresponds to the sum of two other integers characteristic of growth and nucleation of hydrated products. Each of them can take the values 1, 2 or 3 depending on the dimension of the mechanism involved. Hence, n_i can take a value between 2 and 6. In practice, one is restricted to the values of 2 and 3, or even 4.

A supplementary constraint was proposed:

(7) The sulphate content is assumed to be optimal. All the ettringite formed is converted into monosulfoaluminate when the sulphate is exhausted. This assumption is made because there are various possible sources for the sulphate: gypsum, hemihydrate and anhydrite. Moreover, the actual quantity of sulphate combined during the C_3S hydration is not accurately known.

Fitting by eye could lead to several satisfactory solutions. For this reason, two series of parameters were fitted to the experimental results. The second one is remarkable because of greater differences between the individual values of activation energies E_{a_i} (Table 2). The results of the fit show similar trends for the two series of parameters. They are shown in Fig. 1 for Set 1 and two different cements: CPA-CEMI 52.5 and CPA-CEMI 52.5 PM ES CP2 Gaurain CCB (Calcia), referred to as "CEMI" and "PMES" [23]. The fitting is satisfactory as far as the description of the main and the secondary peaks of heat rate are concerned. It is less satisfactory for the PMES, i.e., in the case of a low C_3A content binder.

Table 2
Sets 1 and 2 of fitted parameters of the kinetic model

	C_3S		C_3A→ettringite		Ettringite→ monosulfoaluminate	
	Set 1	Set 2	Set 1	Set 2	Set 1	Set 2
$K_i(1/t^{ni})$	$5.4^{E}-3$	$5.5^{E}-3$	$4.7^{E}-4$	$4.7^{E}-4$	$4.8^{E}-3$	$3.5^{E}-3$
n_i	2	2	3	3	2	2
q^i_{max} [a](J/g C_3S or C_3A)	502	502	1420	1402	1300	1300
$E_a{}^i/R$ (1/K)	4000	4000	4700	5200	3000	3500

[a] These values are taken from the literature [20].

4. Simulations

4.1. The calculation procedure (adiabatic conditions)

The steps for obtaining the heat rate are summarised in the following panel: Δt: a sufficiently small time interval and an initial low value of α_i:$\alpha_i{}^0$ are chosen. Let us consider time t_k, the quantity of released heat at t_k is calculated using the following equation:

$$Q_c(t_k) = Q_c(t_{k-1}) + \left(\frac{dQ_c}{dt}(t_{k-1})\right)\Delta t$$

Each value of $Q_i(t_k)$ with:

$$Q_i(t_k) = Q_i(t_{k-1}) + \left(\frac{dQ_i}{dt}(t_{k-1})\right)\Delta t$$

...and the corresponding reaction completion values are calculated:

$$\begin{cases} \alpha_i(t_k) = \frac{Q_i(t_k)}{Q_i^{max}} \\ \alpha_c(t_k) = \sum_i p_i \alpha_i(t_k) \end{cases}$$

The temperature is obtained using the following equation:

$$T_k = \frac{Q_c(t_k)}{C/m_c} + T_0$$

where T_0 is the initial temperature of the concrete mixture and C is the specific heat of concrete.

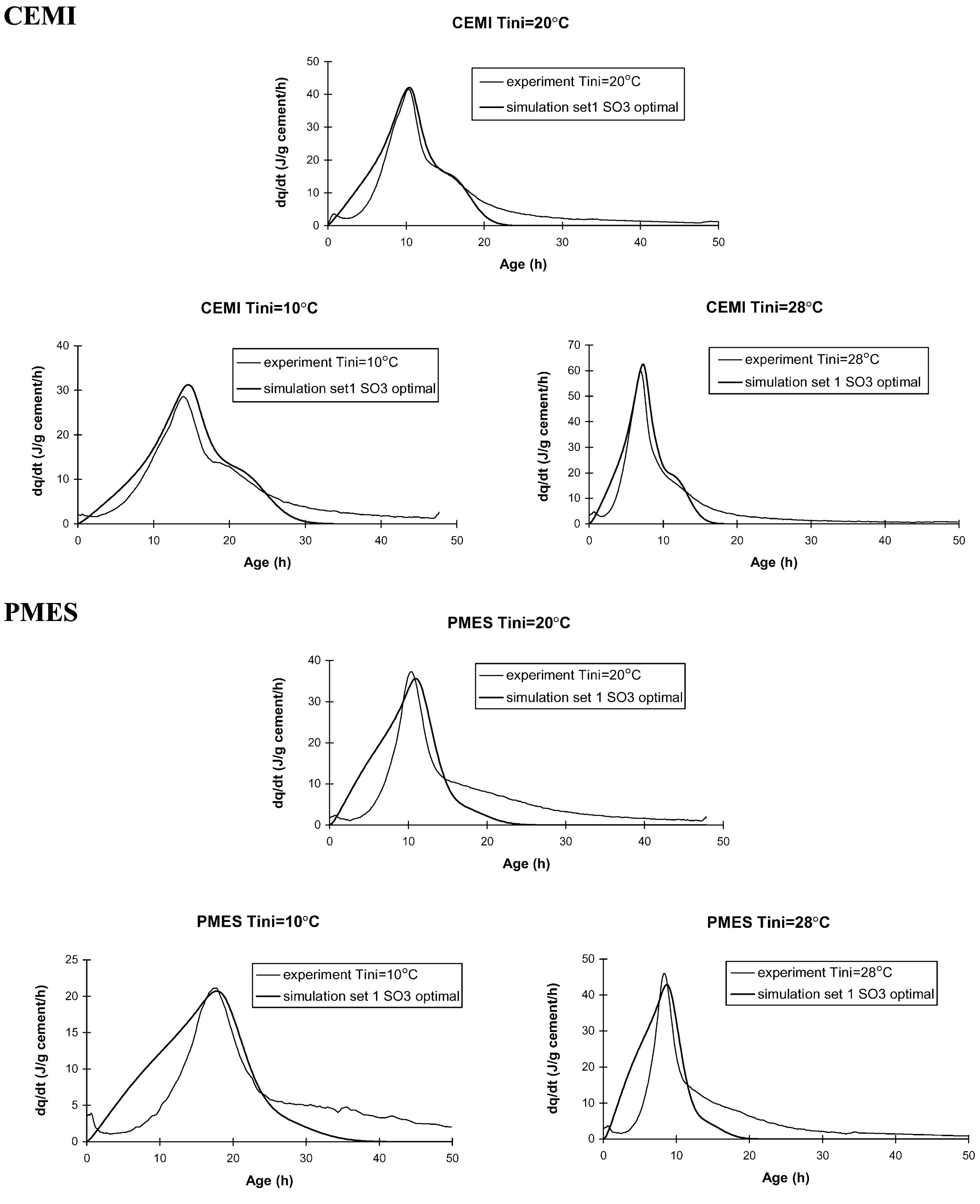

Fig. 1. Results of fitting: Set 1 of kinetic parameters.

From the reference curves of heat rate, we obtain:

$$\left(\frac{\mathrm{d}Q_i}{\mathrm{d}t}(t_k)\right) = \left(\frac{\mathrm{d}Q_i}{\mathrm{d}t}(Q_{i,k})\right)_{T_k} = \left(\frac{\mathrm{d}Q_i}{\mathrm{d}t}(Q_{i,k})\right)_{T_{\mathrm{ref}}} \exp\left(-\frac{E_{\mathrm{a}_i}}{R}\left(\frac{1}{T_k}-\frac{1}{T_{\mathrm{ref}}}\right)\right)$$

with $Q_i(t_k)$=$Q_{i,k}$ and finally:

$$\left(\frac{\mathrm{d}Q_\mathrm{c}}{\mathrm{d}t}(t_k)\right) = \sum_i p_i\left(\frac{\mathrm{d}Q_i}{\mathrm{d}t}(t_k)\right)$$

Next step: t_{k+1}.

Table 3
Details of the first simulations

	Objective 1	Objective 2
Set of parameters	1	1
α_0	0.5 ; 0.7 ; 0.9	0.9
Cement composition	CEMI : $C_3S = 47.66\%$ $C_3A = 9.52\%$	CEMI :
SO_3/C_3A*	1 (optimal)	1 ; 2 ; 3
T_{ini} (°C)	20	20

*Sulphate to C_3A molar ratio.

1. Optimal (complete conversion of ettringite into monosulfoaluminate),
2. intermediate value: both ettringite and monosulfoaluminate remain,
3. only ettringite remains.

4.2. Initial simulations

Heat rates were first simulated on the basis of the CEMI composition and Set 1 of fitted parameters to emphasise the roles of both sulphate content and degree of coupling between the two reactions involved in C_3A hydration.

Apparent activation energy was then calculated for pure phases C_3S and C_3A on the basis of simulated heat rates curves to underline the influence of both temperature and degree of coupling.

4.2.1. Heat rate

The first simulations of heat rate under adiabatic conditions are done with Set 1 of the fitted parameters. The CEMI composition is used and the specific heat of the concrete mixture is assumed to be 2.4 J/cm^3 °C. The cement content 400 kg/m^3 concrete.

The two main objectives of these simulations are:

1. to clarify the influence of α_0 on heat rate. That is to say the influence of the coupling degree of the two reactions involved in the C_3A hydration. (α_0 represents the advancement degree value of the first reaction for which the second one is starting.)
2. to clarify the influence of the sulphate content on heat rate.

The different simulations are detailed in Table 3. The results of the first simulations are shown in Fig. 2a for Objective 1 and Fig. 2b for Objective 2.

Objective 1: The chosen values of α_0 are close to 1, which theoretically corresponds to the time when the sulphate is exhausted. It can be expected that because of the small sulphate content and its dispersal in the cement paste, it will be exhausted locally at an earlier stage. The main observation is the earlier start of the second reaction when α_0 is low, resulting in a single main peak of heat rate instead of two. The two reactions tend to become synchronised (Fig. 2a).

Objective 2: The higher the molar ratio SO_3/C_3A, the less important is the second reaction relative to the C_3A hydration (conversion of ettringite into monosulfoaluminate). The secondary heat rate peak becomes less and less marked and vanishes when the molar ratio reaches a value of 3. There is no second reaction and only ettringite remains. Moreover, the main heat rate peak becomes significantly higher and narrower. All the C_3A is concerned by the first reaction of ettringite formation (Fig. 2b).

4.2.2. Activation energy

The activation energy is calculated "instantaneously" from the of heat rate results (Eq. (8)):

$$E_a(Q_0) = -\frac{R}{\frac{1}{T_1}-\frac{1}{T_2}}\ln\frac{\left(\frac{dQ}{dt}\right)_1(Q_0)}{\left(\frac{dQ}{dt}\right)_2(Q_0)} \tag{8}$$

The change in E_a is given in relation to the global degree of hydration defined as:

$$\alpha_c{}^*(t) = \frac{Q_c(t)}{Q_c^{\max}} \tag{9}$$

This definition (Eq. (9)) is not exactly correct if it is assumed that the different phases hydrate according to "independent fractional rates." However, the values of the extent of hydration given by this expression are close to

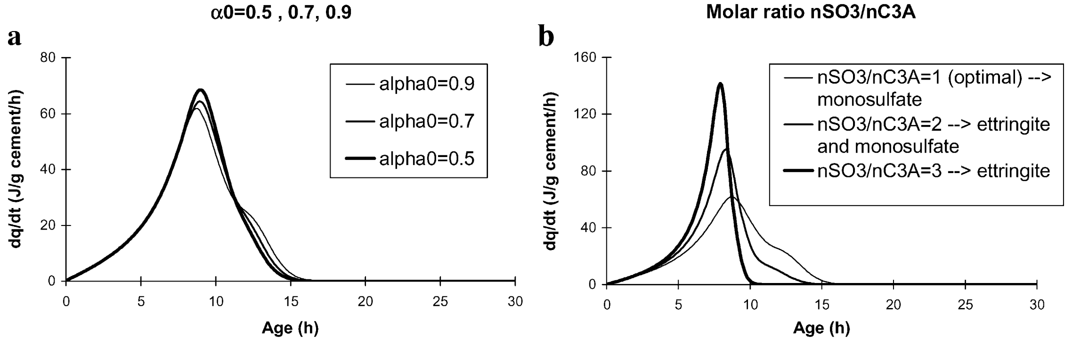

Fig. 2. First results of simulations: influence of α_0 and nSO_3/nC_3A on heat flow.

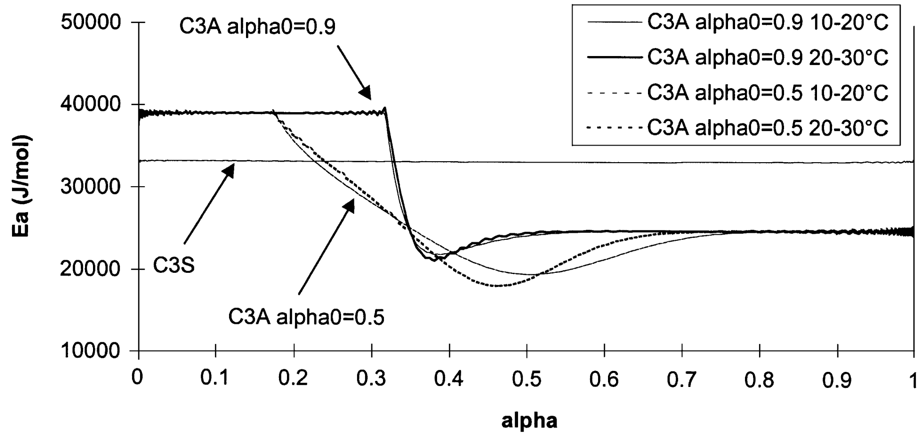

Fig. 3. First results of simulations: calculation of E_a for pure phases.

those given by the degree of hydration of each phase (Eq. (10)) and is more convenient to use.

$$\alpha_c(t) = \sum_i p_i \alpha_i(t) = \sum_i p_i \frac{Q_i(t)}{Q_i^{\max}} \tag{10}$$

The first calculations of activation energy were done for pure C_3S and C_3A phases with an optimal sulphate content. In the case of pure C_3S, a constant value of E_a is obtained, which is of course the input data of the C_3S hydration. The case of pure C_3A is more interesting because of the two successive reactions and their degree of coupling. In the short term, the value of E_a characteristic of the first reaction of C_3A hydration—ettringite formation—is obtained. In the long term, the one characteristic of the second reaction—conversion of ettringite—is obtained. Between these two

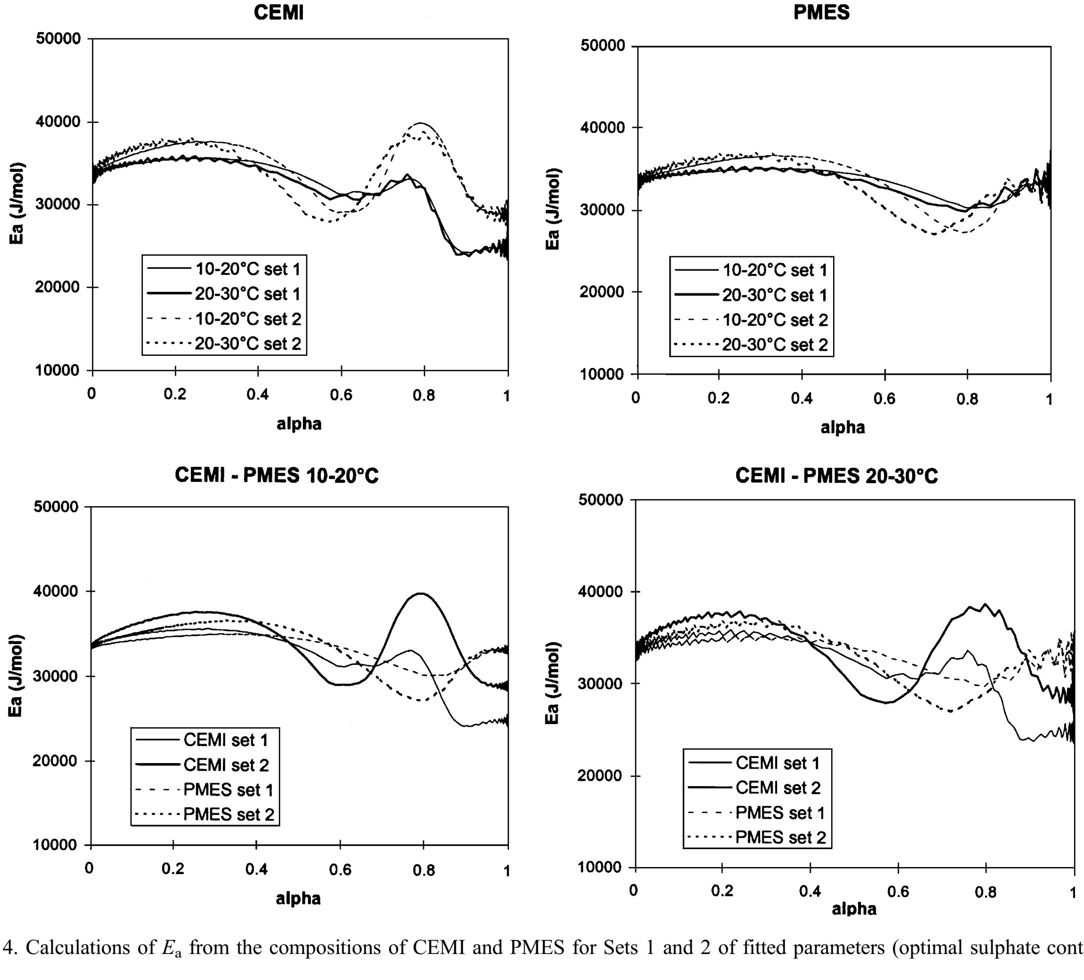

Fig. 4. Calculations of E_a from the compositions of CEMI and PMES for Sets 1 and 2 of fitted parameters (optimal sulphate content).

domains, there is a transition period during which the variations in activation energy depend on temperature and degree of coupling. The higher the temperature or the greater the degree of coupling (i.e., the lower the value of α_0), the more extensive the transition period and the greater the variations in E_a (cf. Fig. 3).

The main conclusion is that the coupling of reactions in opposite stages (growing and slowing down) lead to substantial variations in apparent activation energy. Moreover, the influence of temperature on the calculated E_a values becomes more complex.

4.3. Simulations on the basis of actual cement compositions

4.3.1. Activation energy

In this case, the compositions of CEMI and PMES and their actual sulphate content are used. In the case of CEMI, the sulphate content is close to optimal, whereas in the case of PMES, there is no potential conversion of ettringite. Both Sets 1 and 2 of the fitted parameters were chosen for calculating the apparent activation energy. E_a can systematically be regarded as constant at early age, i.e., in a more or less extensive domain of early hydration. This domain is less remarkable for Set 2 of the fitted parameters, when the differences between activation energies of phases are greater. Over this region, the variations in apparent activation energy are considerable. These variations are the greatest when a reaction of ettringite conversion takes place (CEMI), and when the differences between individual activation energies are more important (Set 2). Moreover, in this case, the influence of temperature is more noticeable (Fig. 4). According to the literature, the influence of temperature on E_a is debatable from the thermodynamic point of view (cf. Section 1.2). However, this dependence was underlined after experimental data analyses [19] and can be explained by the "apparent" feature of E_a in the case of cement hydration.

4.3.2. Comparison with experimental results

Comparing simulations with experimental results is a tricky and uncertain process because of the different meanings placed upon the degree of hydration. For the experimental results, the hydration degree is defined according to Eq. (9), whereas the simulations do not take into account

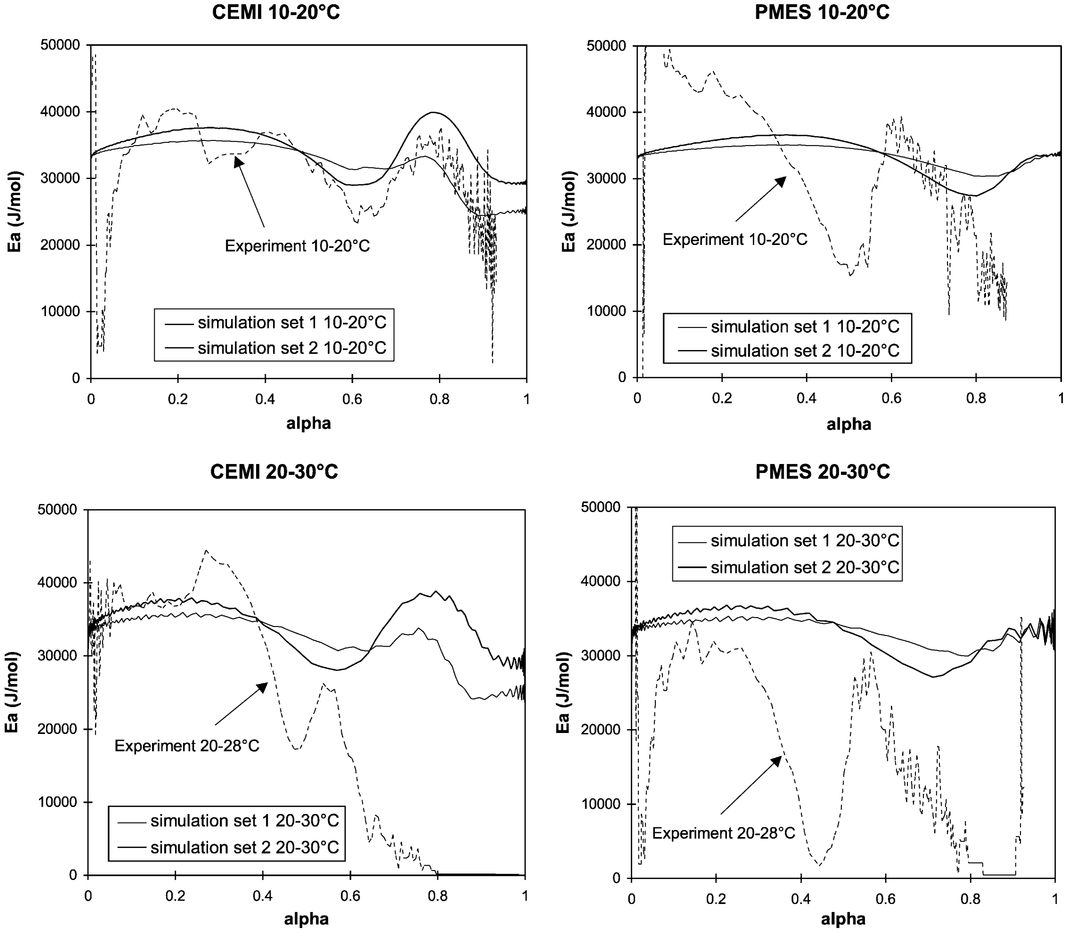

Fig. 5. Comparison of simulations with experimental results of E_a for CEMI and PMES.

both the C_2S and the C_4AF contributions to the hydration degree. To compare experiments and simulations, the simulated hydration degrees were divided by their final values (advancement degree). This implies that the contributions of C_2S and C_4AF to the hydration degree are assumed to be regularly distributed in time. However, what is interesting to

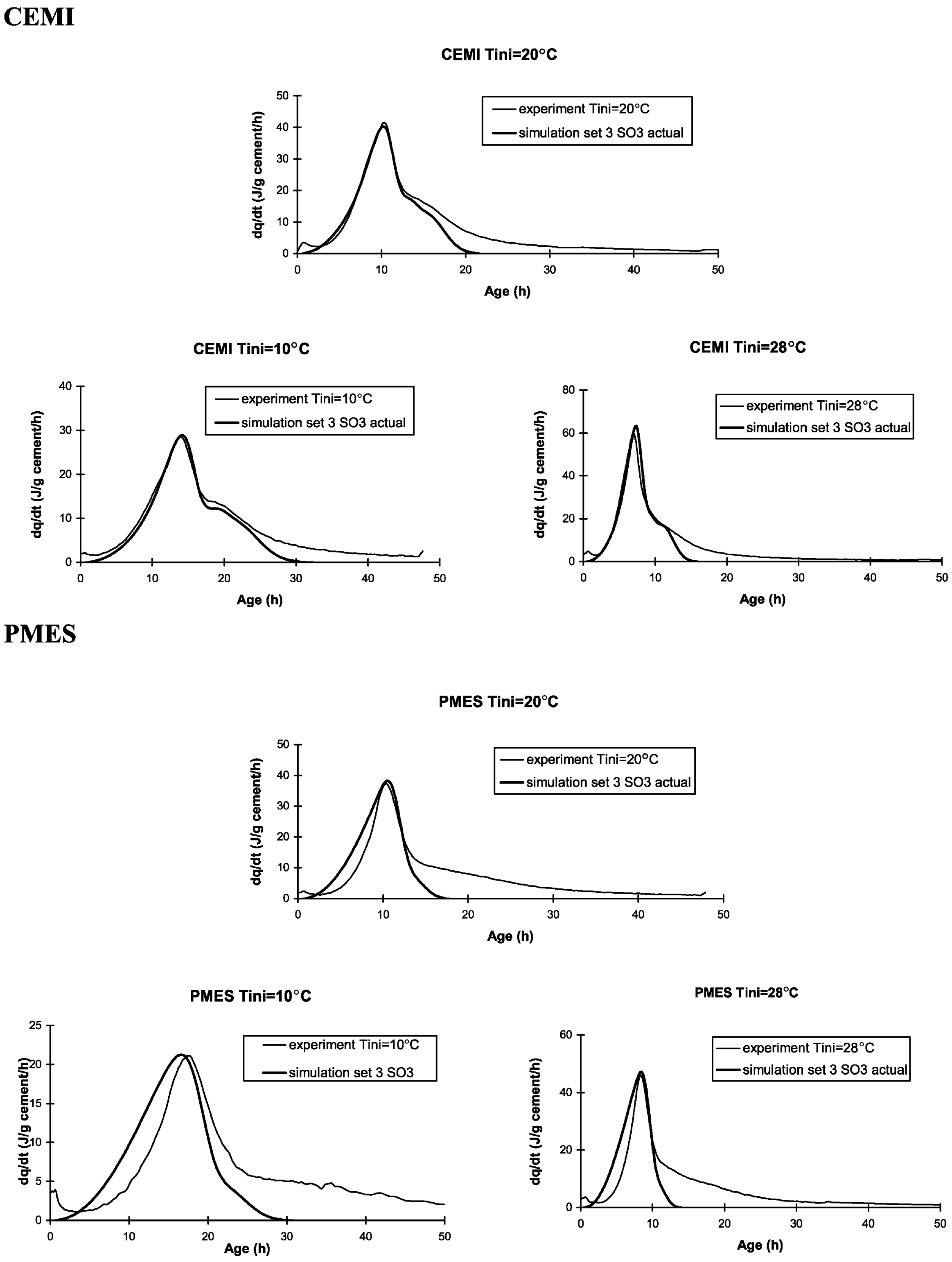

Fig. 6. Results of fitting: Set 3 of kinetic parameters (another framework of constraints).

Table 4
Set 3 of fitted parameters of the kinetic model (another framework of constraints)

	C_3S	C_3A→ettringite	Ettringite→ monosulfoaluminate
	Set 3	Set 3	Set 3
$K_i(1/t^{n_i})$	$6^{E}-4$	$1^{E}-4$	$3.1^{E}-3$
n_i	3	3	2
q^i_{max} *(J/g C_3S or C_3A)	502	1420	1300
$E_a{}^i/R$ (1/K)	4000	4800	4100

bear in mind is that in the case of CEMI, the same variations in E_a can be encountered in experimental results and in simulations (Fig. 5). This is particularly true for low and moderate initial temperatures. It can be assumed that for high temperatures, the microstructural effects become more significant at middle and later ages. This is why differences between simulations and experimental results could appear during these periods. On experimental curves, E_a drops drastically down to 0 due to microstructural effects. The E_a values are lower because they characterise diffusion phenomena, which become predominant at later ages. Moreover, the higher the temperature, the earlier the transition from reaction control to diffusion one. In the case of PMES, the simulations did not lead to great variations in E_a, as did the experimental results. This could be explained by the fact that the C_4AF (12.31%) is not taken into account here, and by a different reactivity of the C_3A phase due to a different morphology.

4.4. A different set of constraints in the simulations

It seems reasonable to assume that all the C_3S and C_3A constituents should not be taken into account. Not all the quantities react at early age owing to the particle size distribution and the change from reaction to diffusion control, which become predominant at middle age. In this different framework of constraints, it is assumed that only 70% of C_3S and 90% of C_3A are involved in early hydration. The value of 70% is in good agreement with experimental observations [24]. The value of 90% is higher because of the two successive hydration reactions. The interpretation of the heat rate peaks is not always consistent in the literature, particularly under adiabatic conditions,

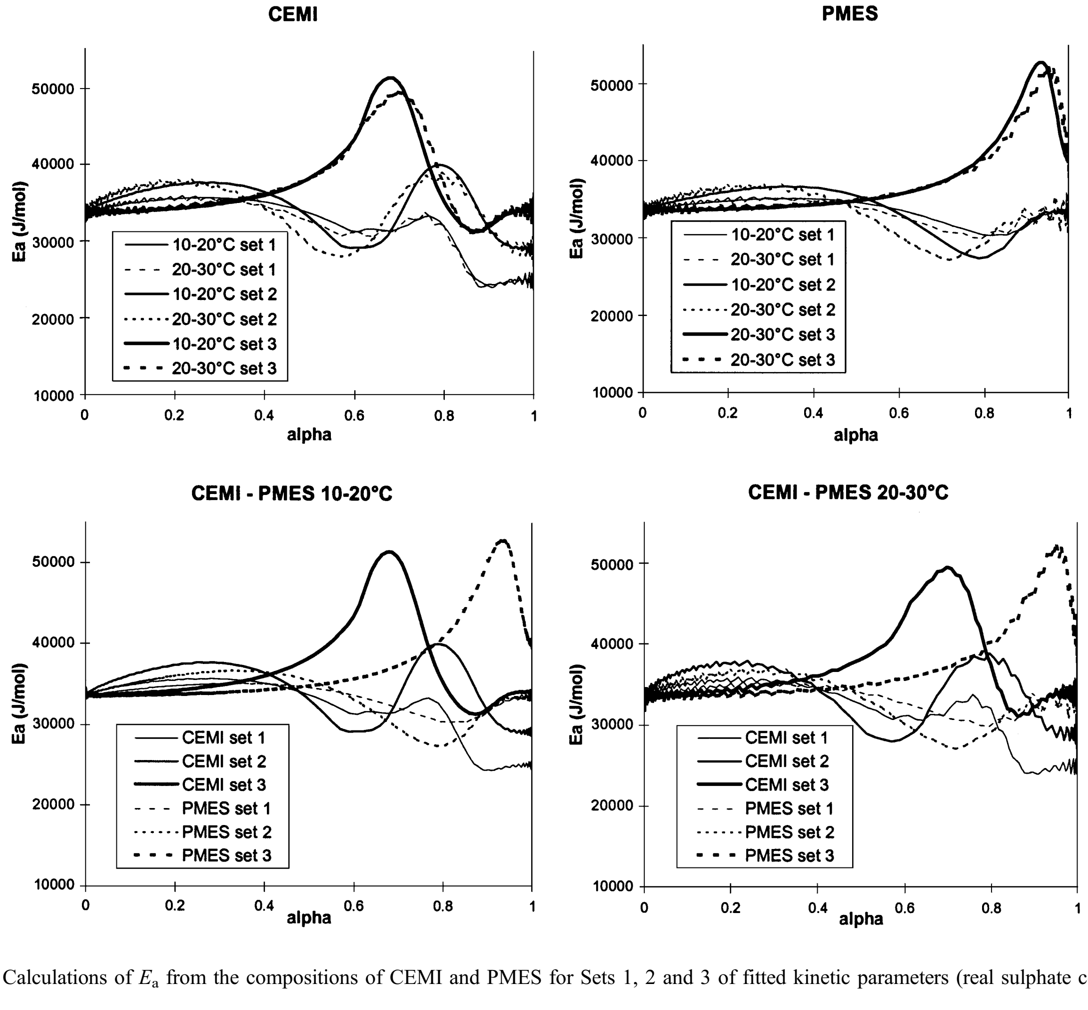

Fig. 7. Calculations of E_a from the compositions of CEMI and PMES for Sets 1, 2 and 3 of fitted kinetic parameters (real sulphate content).

which is why the framework of constraints was slightly modified and a new set of kinetic parameters fitted.

1. The first peak of C_3A hydration (formation of ettringite) closely follows the C_3S hydration peak.
2. The second reaction of C_3A (conversion of ettringite into monosulfoaluminate) is assumed to start when the first one is 0.4 complete. The two reactions are synchronised at a higher degree.
3. The sulphate content is the real one.

The results of fitting can be considered as more satisfactory in both cases—CEMI and PMES—as far as the description of the initial phase and the main peak are concerned (Fig. 6). The Set 3 of fitted parameters is indicated in Table 4.

The calculations of activation energy were performed for CEMI and PMES. The results are shown in Fig. 7 (Sets 1, 2 and 3). The activation energy is almost constant and equal to that of C_3S at early age. The E_a curve reaches a very definite plateau prior to fairly wide variations. It must be pointed out that different constraints on fitting could induce various differences in the results of simulations. Supplementary knowledge about kinetic and chemical mechanisms under adiabatic conditions is needed for incorporation in the model. Nevertheless, the main conclusion is that the "apparent" nature of E_a is confirmed.

5. Conclusion

5.1. Main conclusions of the simulations

The main conclusions are the following.

(1) The E_a curves show a plateau at early age. The hydration region in which E_a can be regarded as constant corresponds to the phase during which the hydration of C_3S and C_3A (first reaction) are almost synchronised.

(2) Assuming that the contributions of C_2S and C_4AF to the heat of hydration are regularly distributed in time, it can be asserted that E_a is constant up to a degree of hydration of 30–50%. This conclusion is in good agreement with experimental results [4,10].

(3) The smaller the difference in activation energy of C_3S and C_3A (first reaction), the more marked is the plateau of E_a at early age.

(4) The influence of temperature on the level of the plateau is not significant, but its influence on the extent of

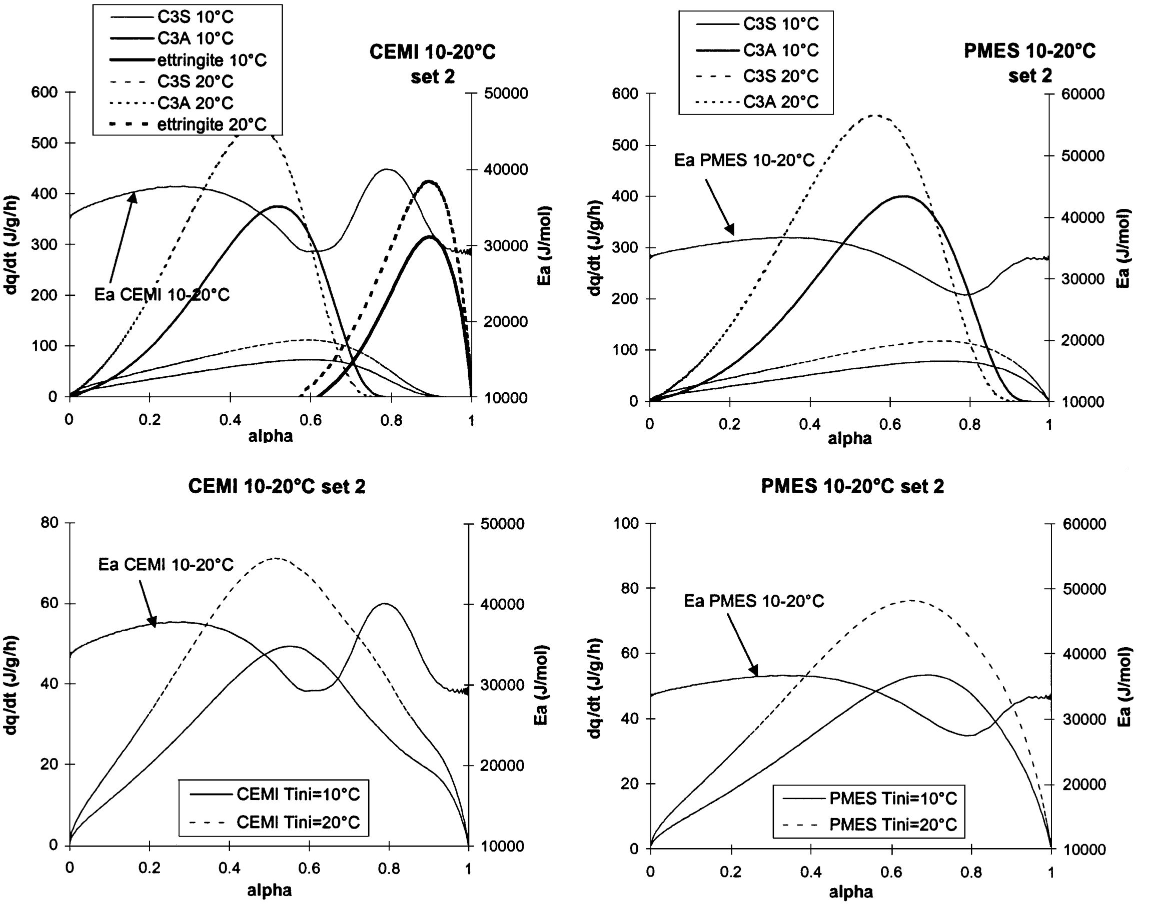

Fig. 8. Parallel evolution of E_a and heat flow for CEMI and PMES (real sulphate content) and Set 2 of fitted kinetic parameters.

the plateau is hard to clarify because of the lack of accuracy in defining the degree of hydration (not all the phases and no microstructural effect are taken into account).

(5) The E_a variations at middle and later ages are of the same magnitude as in the experimental results. These variations are due to the coupling of chemical reactions in opposite stages (growing and slowing down) (Fig. 8). They depend on the C_3A/C_3S ratio: the higher this ratio, the greater the variations. This last point is not consistent with experimental results in the case of PMES (low C_3A content) and can be attributed to the fact that neither microstructural effects nor C_4AF are taken into account in the model. Moreover, the coupling of chemical reactions can be modified by the nature of the sulphate source (alkali, gypsum, etc.).

(6) Finally, the variations in E_a are wider at all ages when the differences between individual activation energies are greater. The influence of temperature also becomes more significant.

5.2. The limitations of simulations

Although simulations are more attractive than experiments, they are not usually used for determining E_a. Several assumptions underlie the modeling process and therefore place limits on the simulations. Especially the main assumption: hydration of phases proceeds of independent fractional rates.

It must be pointed out that this assumption cannot be verified during the whole hydration.

The approach adopted here is more complex, and implies describing the individual degrees of hydration of each phase instead of a global value. Data on the kinetics of each phase are required. Coupling should be taken into account implicitly. Accurate modeling is directly related to a correct understanding of the mechanisms of hydration. The case of C_3A hydration is the most tricky, including the fact that minor constituents like MgO, alkali and the nature of the sulphate source are not considered in the model. Only coupling due to temperature is taken into account and, although this is of primary importance, the microstructural effects and the transition from reaction to diffusion control should also have been modeled. Accordingly, this modeling is only a first approach to the problem. It can be asserted that the results of simulations are not relevant at later ages.

The simulation program CHAL, which was developed as part of this study, does in fact emphasise the "apparent" nature and the influence of the polymineral characteristic of cement. Its originality consists in the coupling by temperature of the chemical reactions characterised by independent rates of reaction. This is of prime importance under adiabatic conditions, which more closely resemble actual conditions on construction sites than isothermal ones. It must be emphasised that several experimental results were already obtained in the framework of the French National Project CALIBE [25]. They enable to clarify the relationship between heat of hydration and strength development under different temperatures. Hence, the calorimetric approach can be used to determine the "apparent" activation of concrete E_a, with the purpose of concrete strength estimation at early age.

The modeling should be improved in order to develop this type of tools. The influence of *w/c*, cement fineness and particle size distribution, in close conjunction with microstructural effects, should be taken into account.

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