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Kinetic modelling of the thermal decomposition of ettringite into metaettringite

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Abstract

Despite recent insights into thermal stability of ettringite and structural changes during decomposition, a lack of knowledge on nucleation and growth mechanisms of metaettringite remained. Therefore, a better understanding of the kinetic modelling of this heterogeneous reaction was proposed. Thanks to an experimental approach allowing to check the validity of kinetic assumptions (rate-determining step, expression of the rate as $d\alpha/dt = k\,f(\alpha)$...), a good agreement was found between the calculated and experimental α vs. t and $d\alpha/dt$ vs. t kinetic curves. The reaction area of the region in which the rate-limiting step occurs was also elucidated. Finally, we demonstrated that the rate-limiting step of the growth process follows an Arrhenius law in non-isothermal conditions.

Keywords: Ettringite; Metaettringite; Thermal decomposition; Kinetic modelling

1. Introduction

Ettringite, $Ca_6[Al(OH)_6]_2(SO_4)_3 \cdot 26\ H_2O$, is a common hydrated phase of Portland cement. The structure of this hydrous calcium-alumina-sulfate mineral is well-known [1]. Ettringite contains globally 32 H_2O molecules (hydroxyls, channel waters and bonding waters occupying various sites) per six calcium ions. Even if the thermal decomposition of ettringite has been the subject of several studies, the nucleation-growth mechanism and reaction kinetics of this transformation remains poorly understood [2]. Nevertheless, recent works reported interesting data concerning the thermal stability of ettringite [3] and the evolution of structural changes during thermal decomposition [4,5]. It was proved that ettringite could be thermally unstable for temperature lower than 120 °C, depending on the water pressure (Fig. 1). During the dehydration process, the removal of hydroxyls and water molecules from the structure occurs [5]. Ettringite decomposes to a product containing 10–13 H_2O molecules per formula unit (Fig. 2). The structure of this partially dehydroxylated product, called metaettringite, was examined [4]. It was found that the columnar structure of metaettringite was similar to ettringite (cylindrical shape of grain), but with closer packing of columns in the *a* direction. These authors precisely characterized the decomposition product, and rigorously described the reaction in terms of both temperature and water vapour partial pressures. Due to these reliable data, the kinetic modelling of ettringite decomposition becomes possible.

The elucidation of the mechanisms of a reaction from thermogravimetric data is not a well-resolved problem. Several authors have been using different mathematical methods (well known functions as Jander's equation, Ginstling and Brounstein's equation, Johnson-Mehl-Avrami's equation, etc.) in order to determine the mechanism that governs a given reaction [6]. Therefore, the studied phenomenon can appear to be another example of the moving boundary problem where mathematical methods can be applied to describe the rate of conversion. But, the shortcomings of these mathematical methods usually used for the analysis of the kinetics of solid-state reactions were perfectly put in evidence by Galwey [7]. Consequently, the

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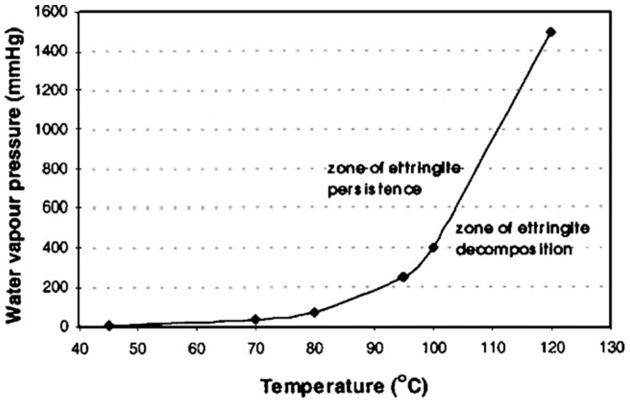

Fig. 1. Stability diagram of ettringite, showing the equilibrium water pressure of the decomposition versus temperature from Zhou et al. [3].

approach proposed consists in establishing a relation between the experimental thermogravimetric measurement and the degree of conversion thanks to theoretical assumptions corresponding to a specific nucleation-growth process: characterictics of the nucleation process (instantaneous or not), nature and location of the growth rate-limiting step (diffusion or interface reaction). In this sense, several models corresponding to various transformation mechanisms were evaluated [7]. Then the best fit between one of these models and the experimental data allows to determine the kinetic model of the involved transformation.

2. Experimental procedures

The examined reaction is the thermal decomposition of ettringite as shown in the thermogram in Fig. 3. The experiments were conducted with a thermobalance (Setaram, ATG-DSC 111) under dynamic argon environment. The mass of sample was 15 mg. The temperature and the partial water vapour pressure represented key variables of the decomposition process. Although the water vapour pressure was not rigorously controlled, a very low water vapour pressure was maintained during the transformation, owing to the programmation temperature applied (a 50 °C isothermal condition or a 0.5 °C min^{-1} heating rate), the dynamic argon environment and the low mass of sample introduced. The complete decomposition of ettringite at 50 °C was achieved for a 20 h experiment duration necessary to obtain the final thermogravimetry plateau (Fig. 3). Thanks to data from Zhou et al. shown in Fig. 2, we know that the duration of the transformation can reach several days as a function of the decomposition temperature for a water vapour pressure fixed at 6 mm Hg. This observation confirms that the water vapour pressure, not directly controlled and monitored, was very low and remained under 6 mm Hg.

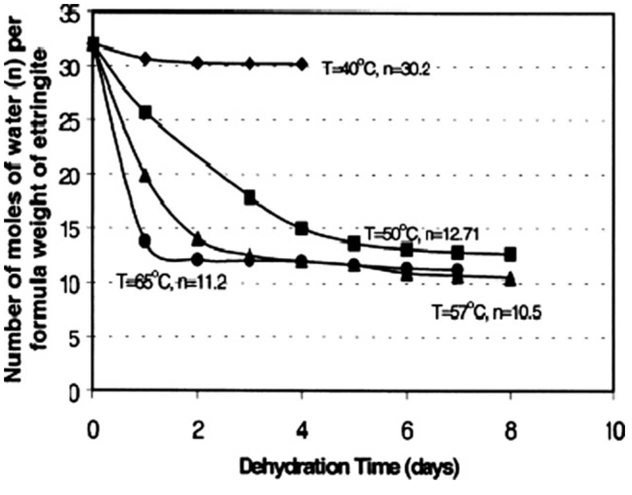

Fig. 2. Static dehydration curves for ettringite as a function of time and temperature on isobar at $P_{H_2O}=6$ mm Hg from Zhou et al. [4].

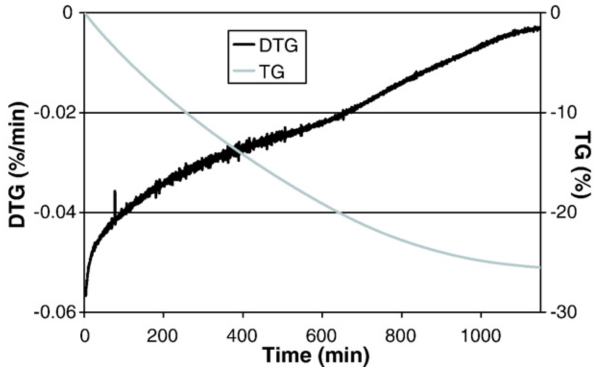

Fig. 3. Weight loss and rate of weight loss versus time of ettringite decomposition in isothermal condition ($T=50$ °C in argon environment).

To control more easily the water content of ettringite before the thermal decomposition, ettringite was stored in a drying oven at 35 °C. These storage conditions allow ettringite to loose two of its maximum 32 H_2O molecules (water contents specified per six calcium ions is noted “n”). The loss of zeolitic water (“zeolitic” because the transformation is reversible) was always performed to maintain the water content per formula unit at 30 H_2O ($n=30$) at the beginning of each experiment.

Finally, the degree of conversion of the reaction $\alpha(t)$ was simply expressed by means of the mass loss at time t, and the mass loss when the transformation was considered as finished. The thermogravimetry curves were converted into the kinetic curves $\alpha(t)$ using Eq. (1). It was observed that the water content of the initial ettringite can change owing to the zeolitic behavior of a part of water. As a result, the final mass loss ($\Delta m{\cdot}f$) which was indicated by a thermogravimetry plateau, varied between 25% and 25.2%.

Eq. (1): Expression of the degree of conversion by means of the mass loss at time t (noted $\Delta m(t)$), and the mass loss when the transformation is considered as finished (noted $\Delta m{\cdot}f$)

$$\alpha(t) = \frac{\Delta m(t)}{\Delta m{\cdot}f} \qquad (1)$$

3. Theoretical approach of the kinetic modelling

In numerous kinetic studies on solid-state reactions [7,8], in isothermal or non-isothermal conditions, the reaction rate is given by Eq. (2) in which A is called the preexponential factor, E_a is the activation energy and $f(\alpha)$ is an analytical function.

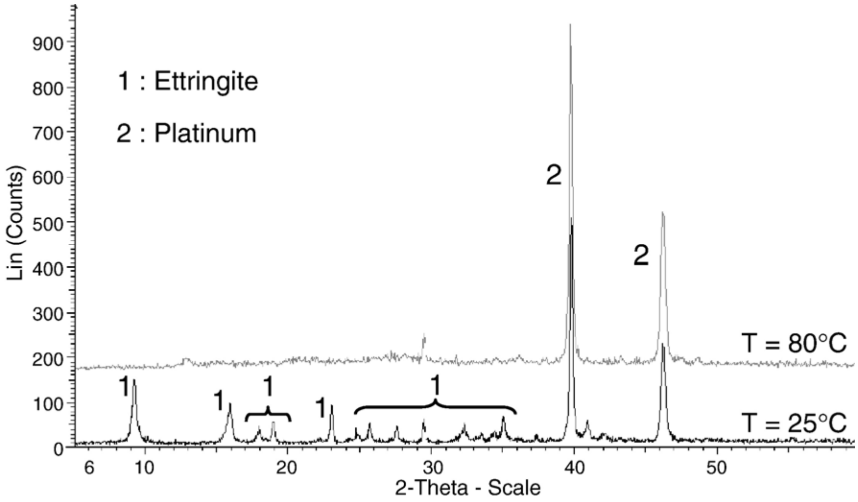

Fig. 4. In situ decomposition of ettringite monitored by HTXRD under helium environment. The first diffractogram was recorded at a constant temperature of 25 °C (before the decomposition), and the second diffractogram was recorded at a constant temperature of 80 °C (after the decomposition). The presence of platinum corresponds to the sample carrier.

Eq. (2): Rate of reaction expressed by means of an Arrhenius law and a $f(\alpha)$ function

$$\frac{d\alpha}{dt} = A\exp\left(\frac{-E_a}{RT}\right) \times f(\alpha) \tag{2}$$

Several $f(\alpha)$ functions can be used, depending on the shape of the grains and the step controlling the growth process. The most commonly used functions are detailed in [7]. However Eq. (2) is only valid in a few cases: the nucleation process (respectively the growth process) is instantaneous, which means that the model describes only the growth process (respectively the nucleation process). Typically, Eq. (2) is not valid when nucleation and growth processes are in competition. Moreover, Eq. (2) implies that the rate is controlled by a step following the Arrhenius law, which is not always the case (for example, when an adsorption step is involved, following the Langmuir isotherm). For these reasons, we prefer a more general expression of the rate, given by Eq. (3) [9,10], in which ϕ is a rate per unit area (mol s^{-1} m^{-2}) and depends on the nature of the rate-determining step (interface step or diffusion), it is independent on time in isothermal and isobaric conditions. $E(t)$ (m^2 mol^{-1}) corresponds to the extent of the reaction zone where the rate-limiting step occurs. The constant γ is defined as the areic frequency of nucleation (*i.e.* a number of nuclei m^{-2} s^{-1}), some nucleation and growth process being described elsewhere [11]. Moreover, in Eq. (3) α is the conversion degree, t is the time in s, T is the temperature and P is the partial pressure. Eq. (3) is interesting since it only assumes the existence of a rate-limiting step for the growth, but no additional assumption is made concerning the nature nor the localization of this step.

Eq. (3): Rate of reaction expressed by means of E and ϕ functions.

$$\frac{d\alpha}{dt} = \Phi(T,P)\ E(t,\Phi,\gamma) \tag{3}$$

The validity of Eq. (3) can be verified experimentally, as shown later (Section 5). Moreover, this approach was successfully used in the kinetic modelling of many heterogeneous reactions such as the decomposition of $CaCO_3$ [12], the reduction of U_3O_8 into UO_2 [13,14], the dehydroxylation of kaolinite [15] or the decomposition of $CeOHCO_3$ [16].

4. Investigation of the thermal decomposition

Before the kinetic modelling, it was essential to precisely characterize the investigated reaction, in order to prove that the ettringite decomposition occurs with the formation of a new solid phase. Thus, two ways are possible: to characterize the decomposition product (and to prove that it is a new solid phase), or to calculate the variance of the system (and if the system is divariant, it means that there is only one solid phase which is non-stoechiometric and so the approach described previously is not valid). In the thermogram shown in Fig. 3, we notice that the investigated transformation of the ettringite induced a weight loss of 25% which corresponds to a final

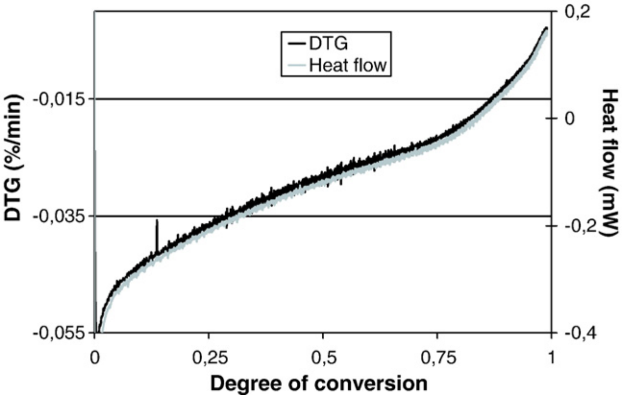

Fig. 5. Rate of weight loss and heat flow versus time of ettringite decomposition in isothermal condition (T=50 °C in argon environment).

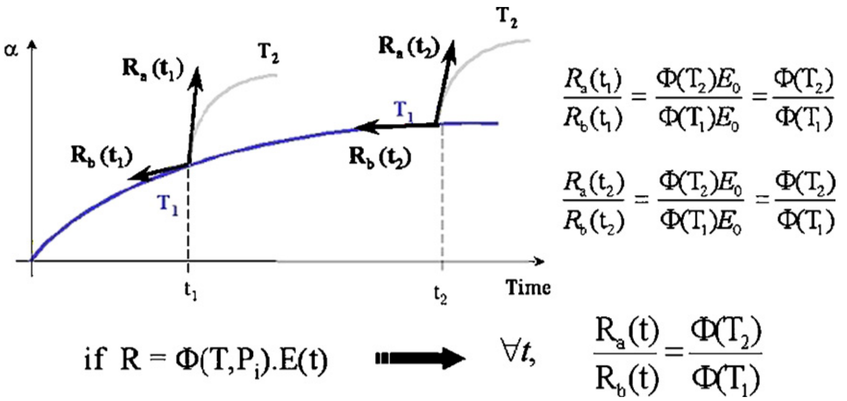

Fig. 6. Principle of the experimental procedure based on sudden changes of temperature to demonstrate the validity of Eq. (3).

weight loss of water of about 17.5 mol per mol of ettringite. As the initial water content of ettringite is close to 30 mol/mol ettringite (noted $n=30$), we find a degradation product which contains between 12 and 13 water per mol of decomposition product. The dehydration enthalpy found is equal to 850 ± 10 kJ mol^{-1} which is perfectly coherent with bibliographic data [17]. In situ dehydratation of ettringite was performed thanks to high temperature X-ray diffraction (or HTXRD with a BRUKER D8 Advance diffractometer) under helium environment (8 L h^{-1}) and using Cu-Kα radiation ($\lambda K\alpha=1.5406$ Å). HTXRD experiments showed that the decomposition product obtained is amorphous (Fig. 4). All these results concerning the decomposition product of ettringite are perfectly coherent with the metaettringite characterization data from Zhou et al. [3,4]. So, we can say that the examined transformation of ettringite gives rise to a new solid phase (called metaettringite) containing 12–13 H_2O per formula unit:

$$\text{ettringite}(n=30) = \text{metaettringite}(n=13) + 17H_2O$$

5. Experimental validation of Eq. (3) : "ϕE test"

The considered approach is based on the existence of a rate-limiting step for the growth process. A growth mechanism is generally composed of several elementary steps involving reaction intermediates (adsorbed species, point defects). One of these steps can be assumed to be rate-determining, which implies that the system is in a steady-state. This validation of the steady state assumption was conducted by showing that the reaction rates obtained by two different experimental methods remained strictly proportional during the whole reaction. We have used simultaneous thermogravimetry and calorimetry and we succeeded to demonstrate that a scale factor can be found to superimpose the rate of weight loss (DTG) and the heat flow signal (Fig. 5). As a result the steady state assumption is verified.

Then we must also demonstrate the validity of Eq. (3). This is possible owing to sudden changes in temperature (or partial pressures) during the transformation [9,10,14–16]. Indeed, a first experiment was performed in fixed temperature conditions (noted T_1). At time t_1, the temperature was suddenly changed from T_1 to T_2. In a second experiment, the same change (from T_1 to T_2) was conducted at time t_2, different from t_1. Let us consider the ratio of the rates before (noted Rb) and after (noted Ra) the sudden change. If Eq. (3) can be applied, it is easy to see that the ratios of the rates before and after the sudden change at t_1 and t_2 must be equal (since the $E(t)$ function is eliminated in the ratios). This procedure is featured in Fig. 6. This experimental method was performed for the transformation of ettringite with a sudden change of $T_1=50$ °C to $T_2=60$ °C, at t_1 corresponding to $\alpha=0.3$ and t_2 corresponding to $\alpha=0.55$ (Fig. 7). The ratio of the rates before and after this sudden

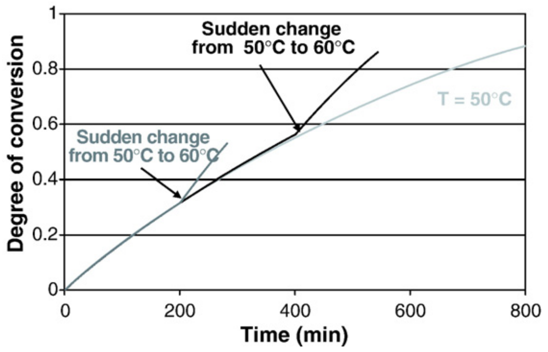

Fig. 7. Decomposition of ettringite (in argon environment) with sudden changes from 50 °C to 60 °C to validate Eq. (3) (existence of rate limiting step).

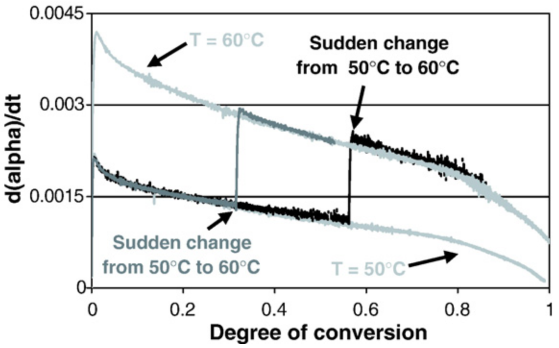

Fig. 8. Decomposition of ettringite (in argon environment) with sudden changes from 50 °C to 60 °C to validate Eq. (4) (the E function only depends on α).

change of temperature is 1.93 ± 0.01 for $\alpha = 0.3$ and 1.91 ± 0.01 for $\alpha = 0.55$. Consequently Eq. (3) can be applied to investigate the decomposition of ettringite into metaettringite.

6. Determination of *E*(*t*)

The function $E(t)$ represents the extent of the reaction zone where the rate-limiting step occurs. It depends on several factors: the initial geometry and size of the ettringite grains, the nature of the process which is involved (instantaneous nucleation or growth, competition between both processes), the nature of the region in which the rate-limiting step of the growth process occurs (interfacial step or diffusion step), and finally the direction of the development of the metaettringite (internal or external development).

The nature of the process is the key to determine the complexity of the E function. A complex case appears when nucleation and growth are competitive processes. On the contrary, if nucleation or growth occur with a supposed infinite rate, the modelling is easier [9,10]. In this last case, one process is instantaneous and $E(t)$ is fully determined by means of the fractional conversion, independently to the way chosen to reach this value of α [11]. In others words, if the physico-chemical stresses (temperature and water vapour pressure) are fixed, the degree of conversion fully determines the rate of reaction and the E function can be written as $E(\alpha)$. The experimental method used to verify this point consisted at first beginning with an isothermal experiment at 50 °C and performing a sudden change of temperature from 50 °C to 60 °C. Then, the curve $\mathrm{d}\alpha/\mathrm{d}t$ vs. α obtained after the sudden change is compared to a curve obtained from an isothermal transformation at 60 °C. Results are illustrated in Fig. 8. The curves are superimposed after the temperature change, which means that the E function is fully determined by the degree of conversion. Therefore, we can say that either the nucleation or the growth process is instantaneous during the decomposition of ettringite into metaettringite.

To determine the E function, experiments were performed in isothermal condition. As we proved that nucleation (or growth) is instantaneous, the rate of reaction can be expressed by Eq. (4) (in which k may depend on temperature and partial pressure of gases, thus k is a constant in isobaric and isothermal conditions).

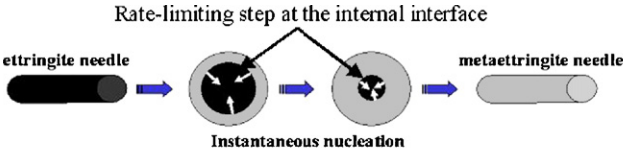

Fig. 10. Description of the different theoretical assumptions corresponding to the E function $E(\alpha) = (1-\alpha)^{1/2}$.

Eq. (4): Rate of reaction in isothermal and isobaric conditions (k is a constant)

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = k f(\alpha) \tag{4}$$

The principle is then to plot $\mathrm{d}\alpha/\mathrm{d}t$ vs. $f(\alpha)$ using the classical $f(\alpha)$ functions [7] in order to check if one of them could fit the experimental curves. If it is the case, the curve $\mathrm{d}\alpha/\mathrm{d}t$ vs. $f(\alpha)$ obtained must be linear. Even if a bias is observed for α lower than 0.1, the best function found is $f(\alpha) = (1-\alpha)^{1/2}$ (Fig. 9). This bias can be explained owing to the non-isothermal and non-isobaric conditions at the very beginning of the decomposition reaction (since it is not realistic to consider the increase of temperature up to 50 °C as instantaneous), or the fact that the nucleation process may not be instantaneous during this short period, a distribution of grain size or a shape not perfectly cylindrical for all grains. This geometrical model corresponds to the following theoretical assumptions (all the factors defining the E function are featured in Fig. 10):

- ➢ a cylindrical shape of the grains (it is well-known that ettringite particles are needle-shaped [1]),
- ➢ the nucleation of metaettringite is instantaneous (i.e. entire surfaces of ettringite are very rapidly covered with a thin layer of metaettringite),
- ➢ the metaettringite grows inward the starting grains,
- ➢ the rate-limiting step of growth is located at the internal interface (between ettringite and metaettringite).

7. Variations of the ϕ function with temperature

Concerning the determination of the ϕ function, the first stage consisted in verifying if the Arrhenius law could be

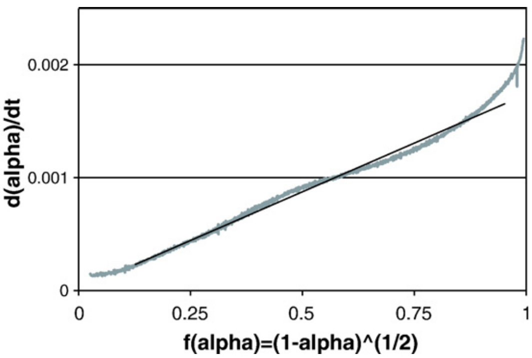

Fig. 9. Theoretical model ($E(\alpha) = (1-\alpha)^{1/2}$) fitting more accurately the experimental date to validate the expression of the reaction rate.

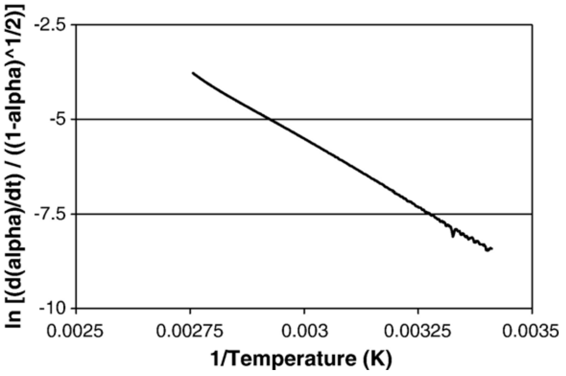

Fig. 11. Verification of the validity of the Arrhenius law (thermogravimetric measurement in argon environment at 0.5 °C min^{-1}).

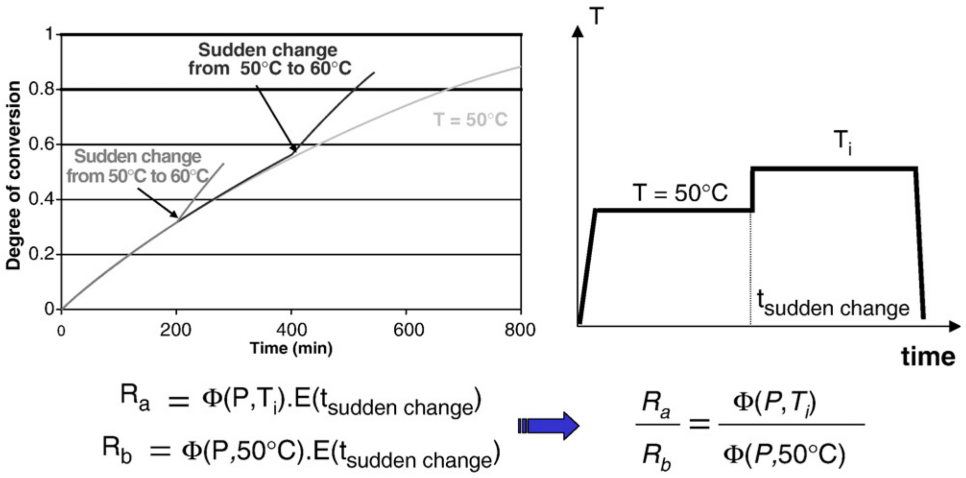

Fig. 12. Principle of the experimental procedure based on the sudden changes of temperature to determine the variations of ϕ function with temperature.

applied to the investigated decomposition. If the Arrhenius law is valid, then the reaction rate can be expressed by Eq. (5) and the curve $\ln(f(\alpha))$ vs. $1/T$ must be linear (Eq. (6)).

Eq. (5): Rate of reaction if the ϕ function follows an Arrhenius law

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = A\exp\left(\frac{-E_\mathrm{a}}{RT}\right) \times (1-\alpha)^{\frac{1}{2}} \tag{5}$$

Eq. (6): Expression which must be valid if we apply an Arrhenius law

$$\ln\left(\frac{\frac{\mathrm{d}\alpha}{\mathrm{d}t}}{(1-\alpha)^{\frac{1}{2}}}\right) = \ln(A) - \frac{E_\mathrm{a}}{RT} \tag{6}$$

An experiment in non-isothermal condition was performed with a temperature programmation of 0.5 °C min^{-1}. Between 20 °C and 140 °C, we doubtlessly notice that the curve $\ln(f(\alpha))$ vs. $1/T$ is linear (Fig. 11). Therefore, we can conclude that the decomposition of ettringite into metaettringite follows an Arrhenius law, between 20 °C and 140 °C. The variations of $\phi(T)$ have been obtained experimentally in the temperature range 55–70 °C, using again temperature jumps. In that case, temperature changes from T_0 (50 °C) to different values of T have been performed at a given fractional conversion (α=0.55), the ratio of the rates being then equal to $\phi(T)/\phi(T_0)$ (see Fig. 12). The variations of ϕ with temperature T are given in Fig. 13, the experimental data were fitted using an Arrhenius law, according to Eq. (7) (continuous line in Fig. 13).

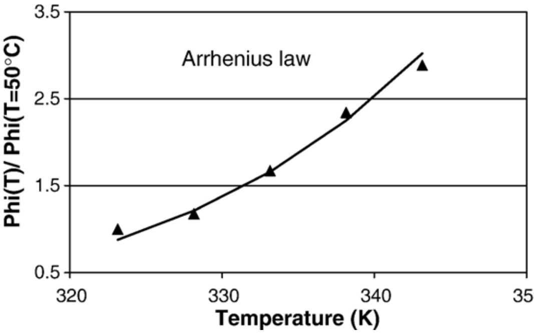

Fig. 13. Experimental variations of $\phi(T)$ and validation of the Arrhenius law in a restricted temperature range.

Eq. (7): Expression using an Arrhenius law in order to fit the experimental data (Fig. 13)

$$\frac{\phi(T)}{\phi(T_0)} = \frac{\exp\left(-\frac{E_\mathrm{a}}{RT}\right)}{\exp\left(-\frac{E_\mathrm{a}}{RT_0}\right)} \tag{7}$$

The agreement between Eq. (7) and the experimental data is correct, which confirms that an Arrhenius law is a good approximation for the ϕ function. The apparent activation energy can be calculated thanks to Eq. (6) with a temperature programmation of 0.5 °C min^{-1}. The apparent activation energy is estimated to 59 kJ mol^{-1}. Then, theoretical curves $\alpha(t)$ and $\mathrm{d}\alpha/\mathrm{d}t\cdot(t)$ can be calculated, and compared to the experimental ones. Fig. 14 shows a good agreement between these curves.

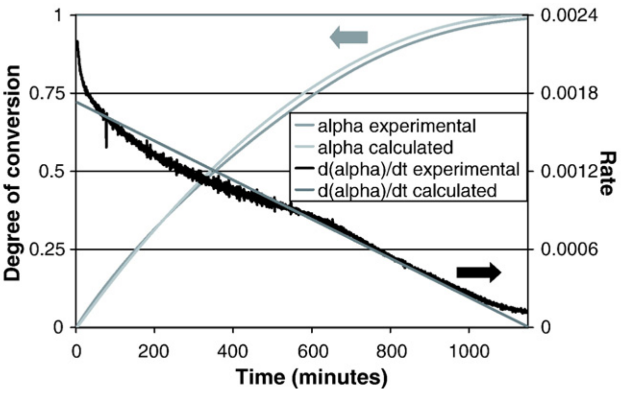

Fig. 14. Comparison between experimental and calculated kinetic curves for the isothermal decomposition of ettringite into metaettringite (T=50 °C in argon environment).

8. Conclusions

To complete recent insights into thermal stability and decomposition mechanisms, this paper proposed a kinetic modelling of the decomposition of ettringite into metaettringite, leading to an expression of the reaction rate which allows to fit satisfactorily the experimental curves $d\alpha/dt$ vs. α. The transformation of ettringite needles occurs by instantaneous nucleation of metaettringite. The growth of metaettringite appears to be internal and the rate-limiting step of growth is located at the internal interface (between the two solid phases). Concerning the effect of temperature on the rate, we proved that the decomposition of ettringite followed an Arrhenius law.

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