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KINETIC ANALYSIS OF THE CALCIUM HYDROXIDE FORMED IN THE HYDRATION OF PURE C_3S AND WITH THE ADDITION OF $Ca(NO_3)_2$

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Abstract

By using a simultaneous thermogravimetry (TG) and differential thermal analyzer (DTA), the hydration processes of the pure C_3S and with the addition of $Ca(NO_3)_2$ was followed. The peak temperature was determined and kinetic analysis on one of the hydration products, calcium hydroxide, was performed. Results show that the use of $Ca(NO_3)_2$ increased the activation energy value of calcium hydroxide formed which is one aspect of the accelerating properties of $Ca(NO_3)_2$ while there is no sign of hydration for the addition of sucrose which proved its retarding property. It was also shown that the activation energy increased when the hydrated pastes aged.

Keywords: $Ca(OH)_2$ determined as extent of hydration process, hydration of C_3S, hydration of C_3S with $Ca(NO_3)_2$ adducts, thermogravimetry

Introduction

In the Portland cements and most other special kinds of cements, C_3S is the main component of the clinker. The hydration properties of C_3S will determine most hydration characteristics of the cements. Therefore, it is very important to understand the hydration process of C_3S. According to reports, [1–12] the hydration process of C_3S can be expressed as:

$$2C_3S+6H \rightarrow C_3S_2H_3+3CH$$

where CH is the calcium hydroxide and $C_3S_2H_3$ is the product that contributes to the strength and is related to the hydration properties. The composition of

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[*] Cement chemists note: $C=CaO$, $H=H_2O$ and $S=SiO_2$.

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$C_3S_2H_3$ is changed during the hydration process and is therefore normally represented as $C_xS_yH_z$ with variable x, y and z [3]. It is also found that these values of x, y and z will vary with the aging of the hydrated paste. Such a series of hydration products is often referred to as the C–S–H gel without specifying the exact composition.

Because there is about 20% (weight) of calcium hydroxide formed in the hydrated cement pastes, the hydration process is often followed by determining the amount of calcium hydroxide formed. Various methods have been used which include, quantitative X-ray diffraction (XRD), chemical extraction, weight loss at two different temperatures (normal values are 300 and 500°C), TG, differential scanning calorimeter (DSC) and DTA, etc. Among these methods, TG, DSC and DTA are the most commonly used. In this study a simultaneous TG–DTA unit was used.

Experimental

Materials and sample preparation

The pure C_3S sample was purchased from the Portland Cement Association with a Blaine surface area of 3500±100 cm^2/g. The purity was confirmed by XRD. Analytical grade $Ca(NO_3)_2$ and sucrose from the Fisher company were used.

The hydration of C_3S was performed by using distilled water with a solid-water ratio of 0.4. The percentage of $Ca(NO_3)_2$ and sucrose added was 2% by weight against C_3S. In order to correspond with normal testing procedures on cement paste, the paste prepared here was stirred for ten minutes and stored in a loosely sealed plastic jar at room temperature (20±1°C). At different ages, 3, 7, 14, 28 days and 12 weeks, a sample of the paste was ground with alcohol, dried in a vacuum oven at 60°C, ground with alcohol for a second time, dried in the vacuum oven followed by grinding with acetone and finally dried in the vacuum oven for 30 minutes. The powder then was sieved using sieve #200 (75 micrometer) and stored in a desiccator.

A further hydration of the C_3S was carried out in order to determine the complete hydration condition. This was performed at a water to solid ratio of 15:1. The mixture was stirred for two days and filtered by using a quantitative filter paper. The residue was washed with alcohol and acetone twice. It was then dried in the vacuum oven at 60°C for 30 minutes and then sieved using sieve #200 (75 micrometer) and finally stored in a desiccator.

Apparatus

A TA SDT 2960 Simultaneous TG-DTA unit was used for collecting TG and DTA signals. The samples were run in a flowing atmosphere of nitrogen (50 ml/min) with sample sizes of 55±1 mg. Calcined alumina was used as the reference material. Heating rates were 3, 5, 8, 10 and 12 deg·min^{-1}. The analysis of data was performed by using the software provided by TA Instruments Inc.. Other graphic treatment of data was performed by using Cricket software on a Macintosh computer. The kinetic treatment of data was performed by using the Kaleidagraph software on a Macintosh computer.

Results and discussion

It should be noted that, a retarder such as sucrose when added to a C_3S paste shows no sign of any hydration over 12 weeks. The following results deal with the kinetic analysis of calcium hydroxide formed in the hydration process for pure C_3S and with the addition of $Ca(NO_3)_2$. Figure 1 shows the typical TG–DTA curve for the hydrated paste. Quantitative analysis of such data gives the amount of calcium hydroxide and the extent of hydration for the pure C_3S and with the addition of $Ca(NO_3)_2$. In this paper, a detailed analysis of the TG–DTA curves is performed and the kinetic analysis results based on such data are shown. The discussion will initially deal with the changing trend of the peak temperature and then this is followed by an evaluation of the kinetic aspects of the subject.

Peak temperature

From the TG–DTA data, the weight loss from TG analysis, peak area from DTA analysis and the peak temperatures were obtained. Due to the large number of experiments performed, only the peak temperatures for the hydrated pure C_3S pastes at the age of 7 days are listed in Table 1 as an example. It can be seen that under the same heating rate, the peak temperature determined from the DTA method are higher than the corresponding temperature determined by the TG method. This is due to the thermal lag of the DTA signal which causes a thermal delay.

Figures 2a–2d show the changing trend of peak temperatures against hydration age for the hydrated pastes from C_3S and C_3S–$Ca(NO_3)_2$ at different heating rate determined by TG and DTA methods. From the figures, it can be seen that as the hydrated paste ages, the peak temperatures increases. Such temperature increase is slowed down as the hydrated paste ages [12].

The peak temperatures plotted against the heating rates at different hydration ages are shown in Figures 3a–3d. In these plots, the corresponding peak temperatures determined for the fully hydrated C_3S pastes are also shown. It can be seen that the peak temperature increases when the heating rate increases, which can also be seen from data in Table 1. As the hydration paste ages, the peak temperature reaches that of the fully hydrated C_3S paste.

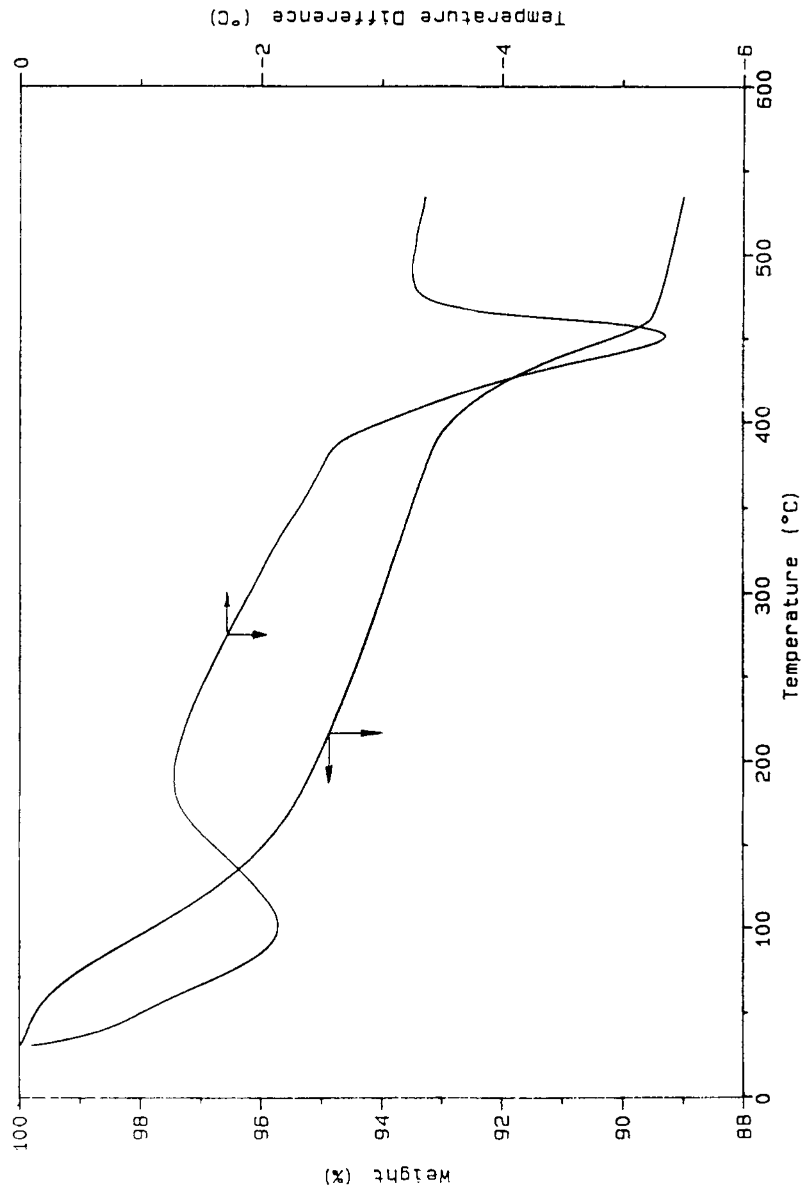

Fig. 1 TG-DTA curves for the hydrated C_3S paste at the age of 4 weeks under a heating rate of 10 $deg.min^{-1}$

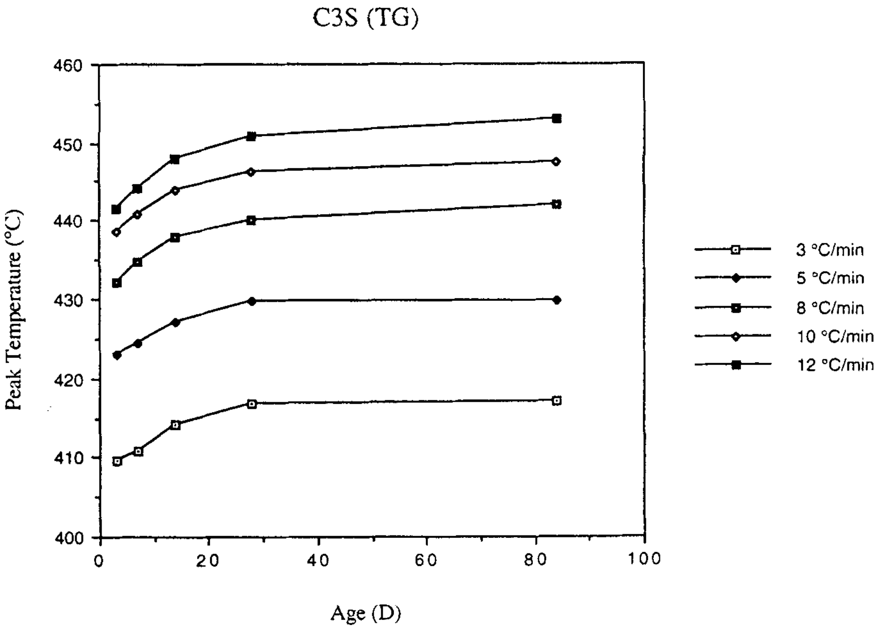

Fig. 2 Peak temperature *vs.* hydration age plots for C_3S and $C_3S–Ca(NO_3)_2$ samples at different heating rates determined by TG and DTA. **a**. C_3S (TG)

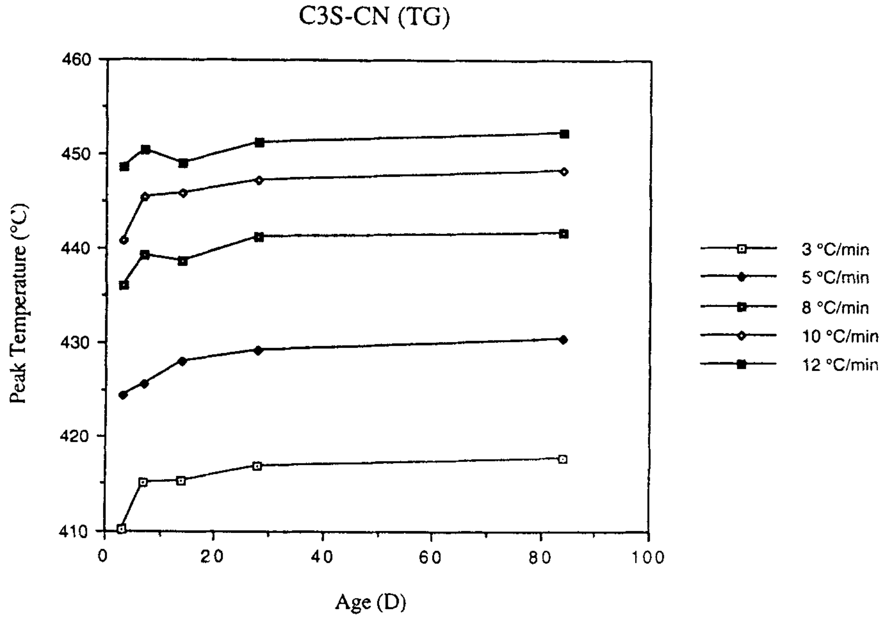

Fig. 2 Peak temperature *vs.* hydration age plots for C_3S and $C_3S–Ca(NO_3)_2$ samples at different heating rates determined by TG and DTA. **b**. $C_3S– Ca(NO_3)_2$ (TG)

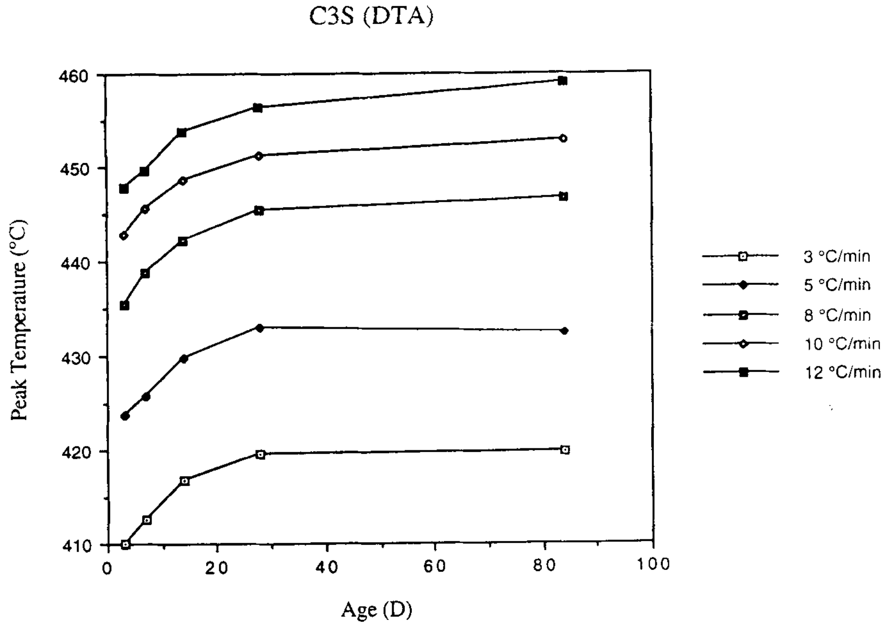

Fig. 2 Peak temperature *vs.* hydration age plots for C_3S and C_3S–$Ca(NO_3)_2$ samples at different heating rates determined by TG and DTA. **c.** C_3S (DTA)

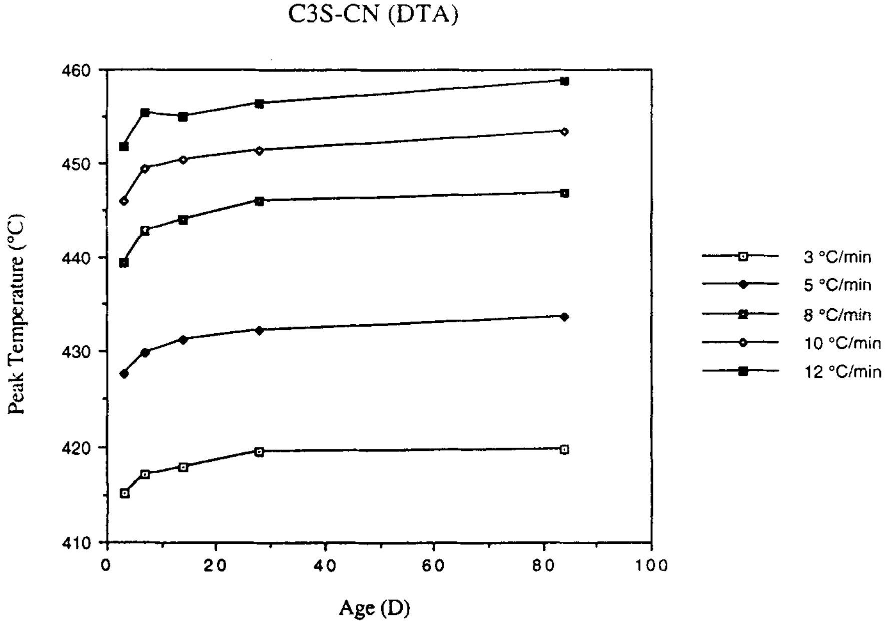

Fig. 2 Peak temperature *vs.* hydration age plots for C_3S and C_3S–$Ca(NO_3)_2$ samples at different heating rates determined by TG and DTA. **d.** C_3S–$Ca(NO_3)_2$ (DTA)

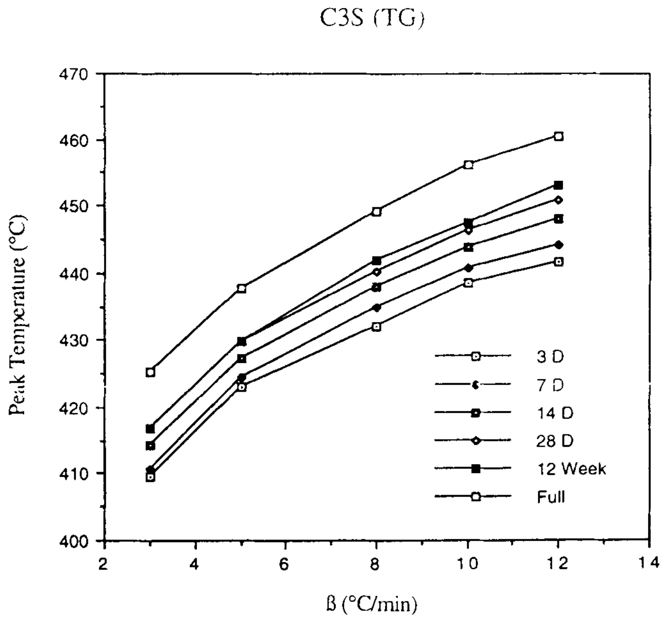

Fig. 3 Peak temperature *vs.* heating rate plots for C_3S and C_3S–$Ca(NO_3)_2$ samples at different hydration age determined by TG and DTA. **a**. C_3S (TG)

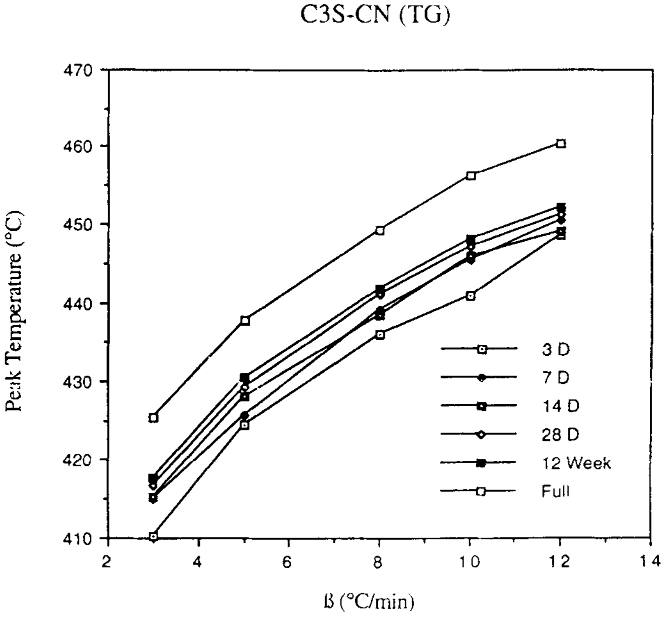

Fig. 3 Peak temperature *vs.* heating rate plots for C_3S and C_3S–$Ca(NO_3)_2$ samples at different hydration age determined by TG and DTA. **b**. C_3S– $Ca(NO_3)_2$ (TG)

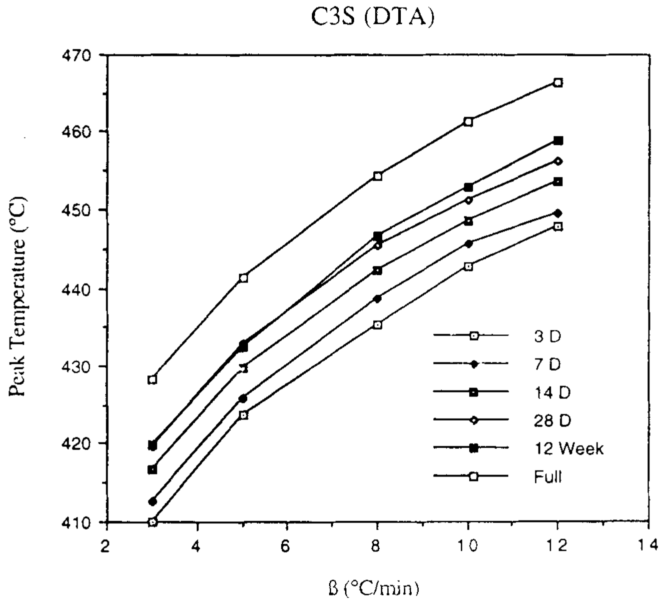

Fig. 3 Peak temperature *vs.* heating rate plots for C_3S and $C_3S-Ca(NO_3)_2$ samples at different hydration age determined by TG and DTA. **c.** C_3S (DTA)

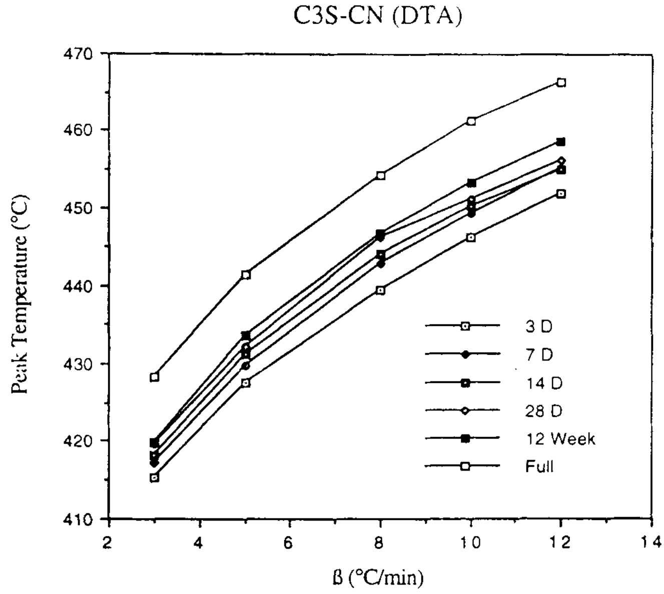

Fig. 3 Peak temperature *vs.* heating rate plots for C_3S and $C_3S-Ca(NO_3)_2$ samples at different hydration age determined by TG and DTA. **d.** $C_3S-Ca(NO_3)_2$ (DTA)

Table 1 Peak temperatures of hydrated C_3S paste at the age of 7 days

Heating rate/deg·min^{-1}	TG/°C	DTA/°C
3	410.69	412.63
5	424.41	425.85
8	434.82	438.70
10	440.77	445.63
12	444.22	449.53

Kinetic analysis results

The activation energy can be calculated by many methods [13], but the dehydration of calcium hydroxide in this study was affected by the dehydration of C–S–H gel which caused the slope in Fig. 1. Therefore, the dehydration of calcium hydroxide can not be considered as a simple reaction and the most suitable method to determine its activation energy value is the Kissinger method [14] which uses the following equation:

$$\ln\frac{\beta}{T_m^2} = C - \frac{E}{RT_m}$$

in which β is the heating rate (deg·min^{-1}), T_m here represents the peak temperature (in Kelvin), R is the gas constant, C is a constant and E is the activation energy (kJ/mol). By using this equation, the calculated results are listed in Table 2. Figures 4a–4b show the changing patterns of the calculated activation energies.

Table 2 Activation energy values (kJ/mol) from the kinetic analysis result

		3D	7D	14D	28D	84D
C_3S	TG	139.68	146.40	154.68	158.32	159.04
	DTA	135.84	140.81	144.84	146.66	146.85
C_3S–$Ca(NO_3)_2$	TG	141.84	147.68	156.31	158.66	160.80
	DTA	138.40	140.37	144.15	145.42	148.21

From Table 2 and Figs 4a–4b, it can be seen that the activation energy values increased as the hydrated pastes aged. This is mainly due to the increase of the crystallinity of calcium hydroxide as the hydrated paste ages. Ben Dor and Perez [12] however believe that it might be due to the increase of bonding strength of calcium hydroxide and unhydrated paste. The calculated activation energy values from TG and DTA methods for fully hydrated C_3S paste are 165.86 kJ/mol and 154.64 kJ/mol respectively, which are higher than the values listed in Table 2.

When the activation energy values for the calcium hydroxide formed from the pure C_3S are compared with those from C_3S–$Ca(NO_3)_2$, it can be found that the addition of $Ca(NO_3)_2$ to C_3S increased the activation energy values. By relating this to the larger amount of calcium hydroxide formed and the above discussion, this can be explained as being due to the accelerating properties of $Ca(NO_3)_2$.

It can also be seen that the activation energy values calculated from DTA curves are different from those of TG curves (in the case, smaller activation energy values are obtained from DTA curves). In the Ref. [14] the equation is only deduced for the data obtained from DTA curves, but the thermal lag, which will affect the temperature determined, will cause the misdetermination of the peak temperature as discussed above in the discussion on peak temperature. It was shown theoretically in another report [15] however that the use of TG curves can provide the activation energy value with more accuracy. The above results can also serve as an experimental proof of such a prediction.

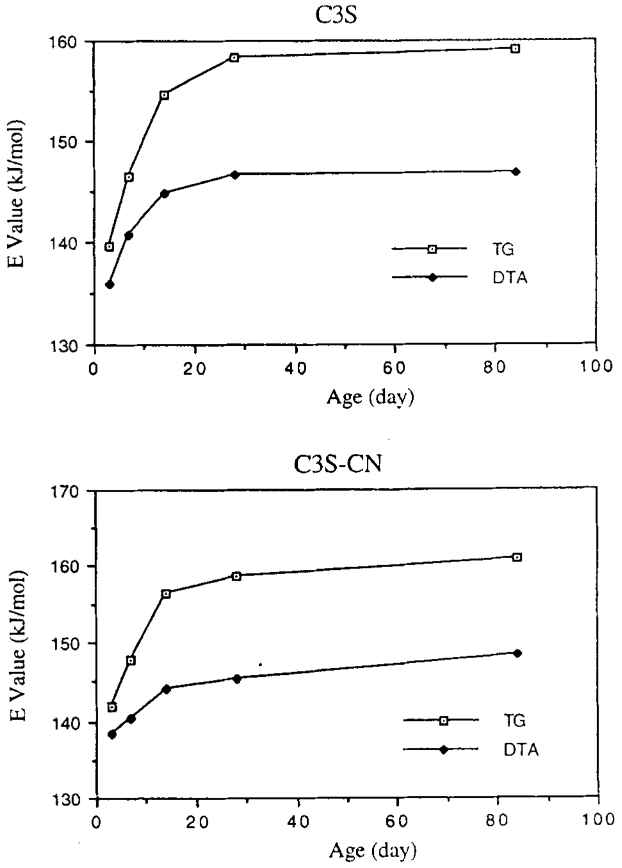

Fig. 4 Plots of kinetic analysis results. a. C_3S (TG); b. C_3S–$Ca(NO_3)_2$

The above discussion shows the advantage of using the Kissinger method to calculate the activation energy value by a process which does not require a knowledge of the reaction mechanism. At the same time, it shows the advantage of using TG curves to obtain the peak temperature which can further be used in calculating the activation energy value.

Conclusions

It is shown that the use of a simultaneous TG–DTA station can obtain more accurate value of the amount of calcium hydroxide formed (from DTA signal) and the activation energy value from the TG curves. The combination of TG and DTA can reduce the error in quantitatively following the hydration process of C_3S and it is a combination which is recommended to be used in studies on the hydration of cement.

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Zusammenfassung — Unter Einsatz eines simultanen TG-DTA-Gerätes wurde die Hydratation von reinem C_3S und unter Zusatz von $Ca(NO_3)_2$ verfolgt. Die Peaktemperatur wurde ermittelt und eine kinetische Analyse an einem der Hydratationsprodukte – Calciumhydroxid – durchgeführt. Die Resultate zeigen, daß der Einsatz von $Ca(NO_3)_2$ den Wert der Aktivierungsenergie des gebildeten Calciumhydroxides erhöht, was einer der Aspekte der beschleunigenden Eigenschaften von $Ca(NO_3)_2$ ist, während es für eine Hydratation bei der Addition von Saccharose keine Anzeichen gibt, was eine verzögernde Eigenschaft beweist. Ein Ansteigen der Aktivierungsenergien beim Altern der hydratisierten Massen konnte nachgewiesen werden.