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The use of thermal analysis in assessing the effect of temperature on a cement paste

Lucia Alarcon-Ruiz[a,*], Gerard Platret[b], Etienne Massieu[b], Alain Ehrlacher[a]

[a] *Laboratoire d'Analyse des Matériaux et Identification, Institut Navier, 6 et 8 Av. Blaise Pascal-Cité Descartes-Champs sur marne, 77455 Marne la vallée CEDEX 2, France*

[b] *PCM, Laboratoire Central des Ponts et Chaussées, 58 boulevard Lefébvre 75732 Paris cedex 15, France*

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Abstract

Upon heating, the cement paste undergoes a continuous sequence of more or less irreversible decomposition reactions. This paper reports studies on a cement paste fired to various temperature regimes up to 800 °C in steps of 100 °C for a constant period of 24 h. This work has been carried out using thermal analysis technique to study the effect of temperature in the mineralogical composition of cement hydration products. The thermal decomposition of the cement paste is analysed with the thermogravimetric analysis (TGA) and the derivative thermogravimetric analysis (DTG) curves. Such techniques can be used to determine fire conditions and the consequent deterioration expected in the cement paste. Therefore, the aim of this work is to have a better knowledge of the reactions that take place in a cement paste during a fire and thus to be able to determine the temperature history of concrete after a fire exposure. The results show that even if the dehydroxylation reaction is reversible, the portlandite formed during the cooling has an onset temperature of decomposition lower than the original portlandite and can thus be considered as a tracer for determining the temperature history of concrete after a fire exposure.

Keywords: Thermal analysis; Cement; C-S-H; Portlandite; Fire

1. Introduction

Thermoanalytical techniques, including differential thermal analysis and derivative thermogravimetry, have all been used successfully [1–3], over the years, for determining the temperature history of concrete after fire exposure.

The concrete is mainly composed of cement paste and aggregates. Harmathy [4] explains that the investigations with thermoanalytical techniques make use of the fact that, upon heating, the cement paste undergoes a continuous sequence of more or less irreversible decomposition reactions. Therefore, once heated piece of the specimen will behave for some time as a stable material up to the temperature of heating. The author has demonstrated the use of the differential thermogravimetric technique for gauging the temperature to which concrete could have been exposed during an accidental fire [4]. Raina et al. [5] and Handoo et al. [6] have also reported the application of DTA/TGA technique for assessing fire-damaged concretes. Recently, Handoo et al. [7] have shown that the decrease in portlandite content with increase in temperatures can be used for assessing the condition of building elements subjected to accidental fires.

As the cement paste is the component of the concrete that makes all these investigations possible and as the presence of aggregates tends to mask certain features of the thermogravimetric curves [4], the present work analyses the thermal effects on a cement paste by studying the thermogravimetric analysis (TGA) and the derivative thermogravimetric (DTG) curves.

2. Theoretical considerations

Hydrated cement paste is composed of four major compounds: tricalcium silicate (C_3S), dicalcium silicate (C_2S),

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* Corresponding author. Tel.: +33-1-64-15-37-01; fax: +33-1-64-15-37-41.

E-mail address: alarcon@lami.enpc.fr (L. Alarcon-Ruiz).

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tricalcium aluminate (C_3A) and tetracalcium aluminoferrite (C_4AF). The most important products of the hydration reactions are the calcium silicate hydrate (C-S-H) and the portlandite, also called calcium hydroxyde, (CH) [8].

Different authors have described the reactions that occur with an increase of temperature in cement paste and concrete:

- 30–105 °C: the evaporable water and a part of the bound water escapes. It is generally considered that the evaporable water is completely eliminated at 120 °C [9]
- 110–170 °C: the decomposition of gypsum (with a double endothermal reaction) [9,10], the decomposition of ettringite [11] and the loss of water from part of the carboaluminate hydrates [13] take place
- 180–300 °C: the loss of bound water from the decomposition of the C-S-H and carboaluminate hydrates undergoes [9,12,14]
- 450–550 °C: dehydroxylation of the portlandite (calcium hydroxyde) [9,10]
- 700–900 °C: decarbonation of calcium carbonate [9,15]

To analyse the thermal effects in the cement paste, we have studied the DTG and the TGA. The DTG curves have marked inflexion points and plateaus, features that are not present in the TGA curves. Therefore, DTG curve better marks all different processes than its precursor, TGA. A change in TGA slope is reflected as a marked peak in DTG [16].

3. Experimental procedure

The cement used for this study was taken from Gaurain in Belgium. The chemical analysis of the CEM II/B indicating the presence of main constituent oxides and the main components of the cement are given in Table 1. Some of the cement paste physical characteristics are listed in Table 2.

The samples to be investigated were originally for other studies [17–19]. The cement paste was made with a water/cement ratio of 0.33. The cement paste cylinders (diameter of 3 cm and height of 8 cm) were stored for at least 28 days under water at a temperature of 22 ± 2 °C while waiting to proceed to the heat treatment.

The water-cured cylinders were heated in a PROLABO Volca MC 25 furnace at a heating rate of 100 ± 10 °C every 90 min up to various temperature regimes for a constant period of 24 h. The samples were then left in the furnace until they cool to ambient temperature and were stored afterwards in a dessicator.

Table1
Oxide constituents and main components (%) of the cement

Oxide constituents (%)									
CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	SO_3	TiO_2	K_2O	Na_2O	P_2O_5
59.00	19.45	4.80	1.75	3.10	2.95	0.30	0.70	0.19	0.23

Main components			
Clinker	Slag	Calcareaus	Gypsum
73	14	13	3.5

Table 2
Physical characteristics of cement

Blaine's (m^2/kg)	Density (g/cm^3)	Compressive strength (MPa)			
		1 day	2 days	7 days	28 days
351.5	3.02	10.0	21.5	37.0	48.5

The test samples were cut from the inner core of these cylinders. The amount of material to be subjected to TGA was crushed and ground until a grain size of 80 μm is obtained. The apparatus used in the thermogravimetric studies was a NETZSCH STA 409. The temperature of the furnace was programmed to rise at constant heating rate of 5 °C/min up to 1150 °C. The tests were performed under an air flow of 80 ml/min. The amount of material used for the tests was weight with a balance of ± 0.1 mg of accuracy and was ranging between 220 and 226 mg.

4. Results and discussion

The results of the thermogravimetric tests obtained at a rate temperature of 5 °C/min are summarized in Fig. 1.

The reference specimen corresponds to an unfired sample of cement paste. It can be observed that the curve of the reference specimen shows three rapid weight loss. The first weight loss, located between 100 and 200 °C, is the result of dehydration reactions of several hydrates (C-S-H, carboaluminates, ettringite, etc.). This loss of water is mainly due to the dehydration of the C-S-H. Consequently, we will include the different hydrates under the annotation C-S-H.

The second major weight loss, observed at 450–500 °C, corresponds to the dehydroxylation of portlandite, another hydration product.

The third loss of weight appears at 750 °C and corresponds to the decarbonation of calcium carbonate coming from the clinker and the filler.

Let us consider the behaviour of the heat-treated samples. Fig. 1 shows that the second weight loss, corresponding to the dehydroxylation reaction, remains even for samples fired beyond 500 °C. If we consider that, for a previous heat treatment beyond 600 °C during 24 h, the dehydroxylation reaction is completed in the sample, then it can be deduced that this reaction is reversible. Nevertheless, it is of notice that the beginning of the weight loss seems to shift towards lower temperatures when the temperature of the previous heat treatment exceeds 500 °C.

Moreover, considering the decarbonation reaction, the results show that the samples fired to temperatures above 600 °C do not present the third weight loss. Thus, it can be deduced that this reaction is irreversible.

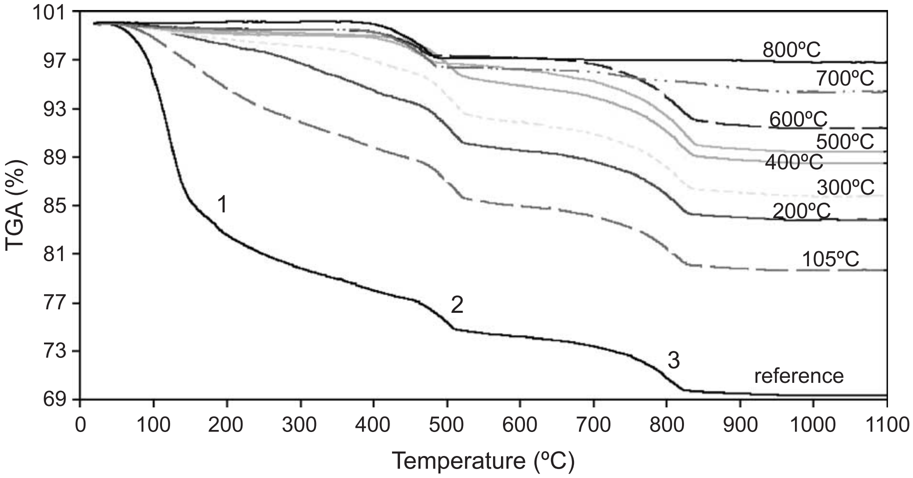

Fig. 1. TGA curves of cement paste fired to various temperature regimes.

The weight loss for each sample in the three different reactions are summarized in the Table 3.

These values are reported in the Fig. 2. We can observe the evolution of each reaction according to the previous heat treatment.

The dehydration reaction of the hydrates decreases gradually and can be considered as an irreversible reaction. Therefore, the dehydration reaction can be used as an indicator to determine the temperature history of concrete after a fire exposure.

The dehydroxylation and decarbonation reactions are correlated. We can observe that for the samples fired up to 700 and 800 °C, the increase of portlandite is correlated to the decrease of the decarbonation reaction. This is mainly due to the recrystallization of the portlandite during the cooling in the furnace after the heat treatment. These reactions are studied more carefully with the DTG results.

The DTG curves are represented in Fig. 3. By analysing the different peaks, it is possible to obtain several parameters as the temperature at different decomposition degrees and the mass loss in each process.

A simple view to the DTG curve of reference shows that the DTG better marks all different process than the TGA. We can observe a smaller peak in the lap of the dehydratation of C-S-H peak at 170 °C. The peak probably corresponds to the monocarboaluminates' decomposition. This reaction is very difficult to see in the TGA curves as it is just a slightly change of slope.

A comparison between the curve of reference to the curves representing heat-treated cement paste samples reveals that, as expected, above the temperature of previous heating, the various curves are close to the thermogravimetric curve of the reference specimen. The peak of the dehydration of the C-S-H reaction decreases with the increase of the previous heat treatment and disappears for a heat treatment superior to 300 °C. These results are in agreement with Refs. [9,14].

We can observe that the peak of decarbonation of calcium carbonate disappears completely for a heat treatment of 800 °C as expected [9]. This reaction can therefore be used as a marker for determining the temperature history of concrete exposed to a fire regime.

The second peak corresponding to the dehydroxylation of portlandite does not disappear completely even for previous heat treatment of 800 °C. This is due to a recrystallization of the amorphous part of portlandite [20] after the heat treatment during the cooling in the furnace. This shows the importance to make the tests very quickly after a fire. Harmathy [4] wrote that the maximum temperatures attained at various locations in a concrete construction during a fire exposure can be determined if the samples of the concrete can be procured within 1 or 2 days of the fire. A better study of the portlandite dehydroxylation is done in Fig. 4.

In Fig. 4, we have reported the onset temperature of the peak for the dehydroxylation reaction. One can observe three main ranges for the onset temperature. For a tem-

Table 3
Loss of weight (%)

Reaction	Ref.	100 °C	200 °C	300 °C	400 °C	500 °C	600 °C	700 °C	800 °C
(1)	79.83	54.09	41.82	20.13	10.68	12.16	8.22	11.21	0.00
(2)	9.05	25.51	28.25	44.61	37.91	26.56	27.59	57.01	88.76
(3)	11.12	20.41	29.92	35.25	51.41	61.28	64.19	31.78	11.24

Reaction (1): dehydration reactions mainly due to the loss of water from C-S-H. Reaction (2): dehydroxylation of porlandite. Reaction (3): decarbonation of calcium carbonate.

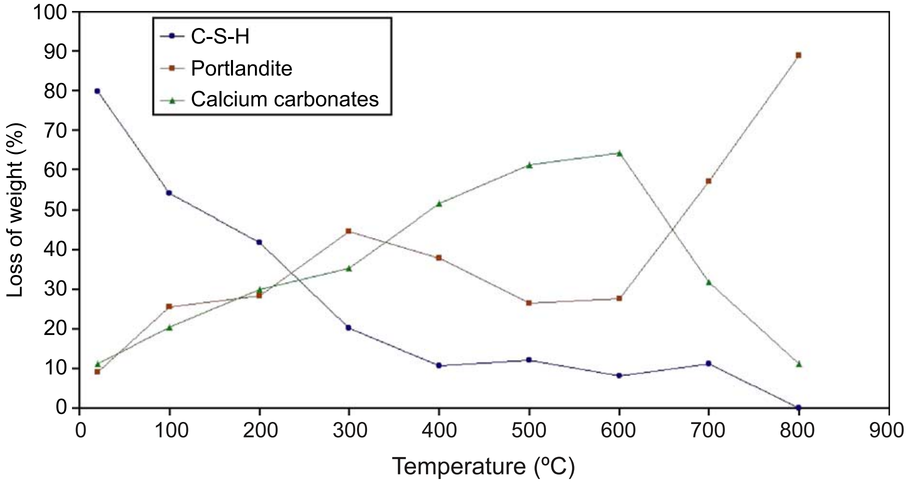

Fig. 2. Loss of weight (%) for the dehydration reaction (C-S-H), the dehydroxylation reaction (portlandite) and the decarbonation reaction (calcium carbonates) versus previous temperature treatment.

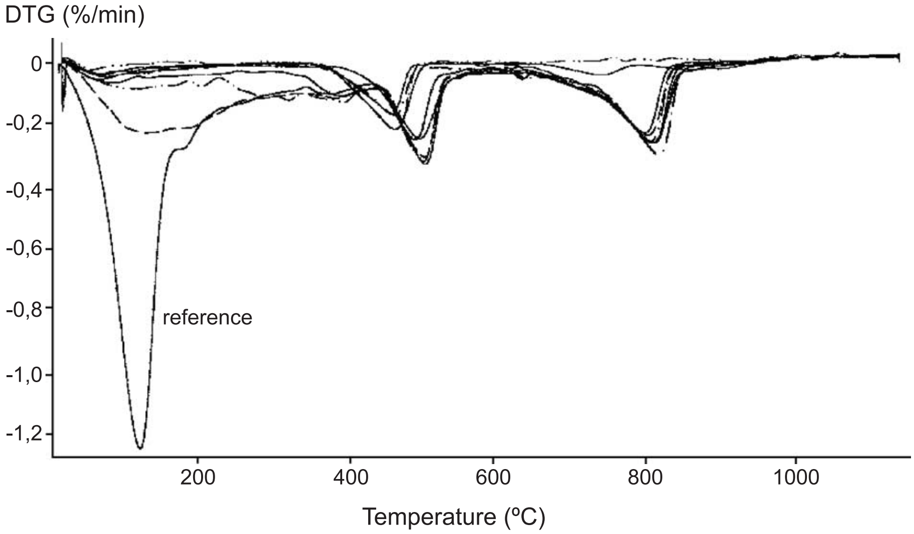

Fig. 3. DTG curves of cement paste fired to various temperature regimes.

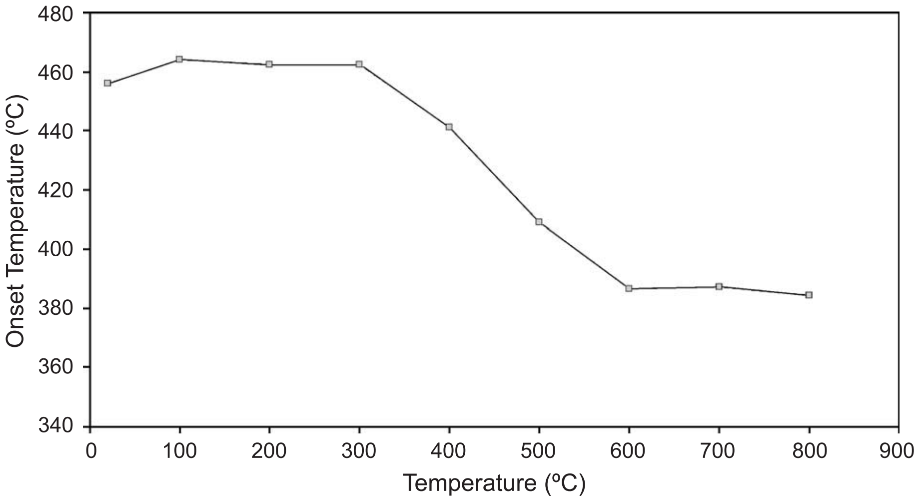

Fig. 4. Onset temperature of the peak for the dehydroxylation reaction versus previous temperature treatment.

perature treatment below 400 °C, the onset temperature is almost constant and close to 460 °C. If we consider now the previous thermal treatment above 600 °C, we can observe that the onset temperature range is also almost constant but the values are close to 386 °C. Finally, the samples fired up to 400 or 500 °C have an onset temperature value intermediary. This means that the recrystallized portlandite is not as thermically stable as the portlandite of origin and can be identified by the onset temperature of the peak.

The onset temperature of the portlandite dehydroxylation reaction peak can be used as a marker for determining the temperature history of concrete after a fire exposure.

5. Conclusion

In this paper, a cement paste fired to various temperature regimes up to 800 °C has been studied using thermal analysis technique. The investigations with thermal analysis make use of the fact that during the heating, the cement paste undergoes a continuous sequence of more or less irreversible decomposition reaction. The cement paste is therefore the component of the concrete which makes these investigations possible.

The accomplishments and conclusions of the study are summarized below:

- The TGA curves have shown that the dehydration and the decarbonation reactions are irreversible in the cement paste and can be used as tracers for determining the temperature history of concrete after a fire exposure.
- The dehydroxylation reaction of the portlandite is reversible. This hydration product seems to rehydrate rapidly after a heat treatment.
- The derivative thermogravimetric curves give the onset temperature of the reactions. The onset temperature of the dehydroxylation reaction decreases (from 460 to 386 °C) for a previous heat treatment above 500 °C.

In prospect, other studies about the onset temperature of the peak of the dehydroxylation reaction in addition to the portlandite content in the cement paste must be done.

Furthermore, concrete is a mixture mainly composed of cement paste and aggregates. The presence of aggregates tends to mask certain features of the thermogravimetric curves but does not affect significantly the accuracy of the conclusions [4]. Nevertheless, further investigations must be done in order to take into account the decomposition and degradation of aggregates.

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