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STUDY BY THERMOGRAVIMETRY OF THE EVOLUTION OF ETTRINGITE PHASE DURING TYPE II PORTLAND CEMENT HYDRATION

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Abstract

Thermogravimetry (TG) and derivative thermogravimetry (DTG) have been used by the authors as very effective tools to study hydration steps of cements used for solidification/stabilization of tanning wastes. The present paper presents a method which was applied to separate the peaks shown by DTG curves of type II Portland cement pastes, analyzed at different times during the first 4 weeks of setting. Through a specific software a more detailed study of the evolution of the cement hydration may be done, which allows the measurement of the amount of hydrated water present in tobermorite gel as well as in ettringite, which are the main phases formed from the original components of the cement. The number of moles of water present in the ettringite phase calculated by the method is in very good agreement with the values found in the literature, validating the method to calculate the same parameter in tobermorite gel. In the latter case the water content decreases significantly during the first day of hydration, then remains at a constant value over the rest of the analyzed period.

Keywords: ettringite, hydration, Portland cement, thermogravimetry

Introduction

Thermogravimetry (TG) and derivative thermogravimetry (DTG) are effective tools to follow the different stages of cement hydration as well as to quantify the different phases, as shown in previous papers of the authors based on solidification/stabilization of tanning waste and related subjects [1–4]. In this paper a method to separate overlapped DTG peaks is presented, which allows, as other deconvolution methods do [5], a greater precision than conventional procedures to quantify the main substances and to better understand the hydration process.

The method was applied to the hydration of type II Portland cement, to quantify the moles of water present in two main substances formed during the hydration pro-

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cess, which are the tobermorite gel and the ettringite phase. The former is the main contributor to the strength of cured Portland cement, and the latter has been implicated as a principal phase responsible for metal ion immobilization in S/S [6–9].

Materials and methods

The cement used in this work is produced in Brazil by Lafarge Company. It is designated as type II Portland cement code CP II F 32. Besides Portland clinker, it contains calcium sulfates and calcium carbonates [10, 11].

The pastes were prepared with water, using water/cement mass ratio of 0.5 and were analyzed after different hydration periods (1, 4 and 24 h; 1 and 4 weeks). In this work they are designated as MA cement pastes.

Thermal analyses were realized, after a drying stage of the sample at 28°C, in a Seiko Instruments Model Exstar TG/DTA, from ambient temperatures up to 1000°C with a heating rate of 10°C min^{-1}, using 100 mL min^{-1} of air as purge gas.

Using the PeakFit$^{\text{TM}}$ software, SPSS Inc, the overlapped peak separation is applied to the original DTG curve data given by the equipment. A set of separated peaks is achieved, and a new DTG curve which represents the sum of the separated peaks is drawn. The software compares the new curve with the original curves and a correlation factor is given to evaluate the effectiveness of the peak separation. The software allows one to choose the mathematical function which best fits with each new peak in order to have the best correlation factor. A set of separated peaks is produced, and in the present case, for practically all the main identified phase peaks the best fit was obtained by using the EMG (exponentially modified Gaussian) function, which is capable of modeling tailings [12]. However the best fit for calcium carbonate peaks was given by the HVL (Haarhoff–Van der Linde) function. The respective area under each peak is then calculated, and it represents the total mass loss in a defined temperature range.

The content of each phase was calculated on the initial cement mass basis as follows:

$$Q_{\mathrm{j}}=100\frac{A_{\mathrm{j}}}{WL_{\mathrm{j}}}\frac{M_{\mathrm{i}}}{M_{0}}F \tag{E-1}$$

where Q_{j} – mass percent of a phase j in the paste after hydration on initial cement mass basis; A_{j} – area of the separated peak of the DTG curve due to the respective gas released during the decomposition or dehydration of the phase j during analysis, from dried paste; WL_{j} – theoretical percent mass loss during the decomposition or dehydration reaction of phase j, on initial cement mass basis; M_{i} – mass of the dried sample; M_{o} – original mass of the sample, before drying; F – correction factor to calculate on initial cement mass basis; F=1.5 (1 part of cement/0.5 parts of water).

The values of WL_{j} are shown below for each phase:

- Ettringite (j=1)

$$3CaO\cdot Al_2O_3\cdot 3CaSO_4\cdot 31H_2O \rightarrow 3CaO\cdot Al_2O_3\cdot 3CaSO_4 + 31H_2O \tag{R-1}$$

WL=45.14%

- Dihydrated calcium sulfate (*j*=2)

$$CaSO_4{\cdot}2H_2O \rightarrow CaSO_4+2H_2O \tag{R-2}$$

WL=20.93%

- Calcium hydroxide (*j*=3)

$$Ca(OH)_2 \rightarrow CaO+H_2O \tag{R-3}$$

WL=24.32%

- Calcium carbonate (*j*=4)

$$CaCO_3 \rightarrow CaO+CO_2 \tag{R-4}$$

WL=44.00%

- Tobermorite (*j*=5)

The WL_j factor for tobermorite gel is not constant, and depends on the hydration time of each paste as will be discussed in the next item.

Tobermorite and ettringite phases

Tobermorite ($3CaO{\cdot}2SiO_2{\cdot}xH_2O$) is formed during hydration of the calcium silicate phases, which are C_3S ($3CaO{\cdot}SiO_2$) and C_2S ($2CaO{\cdot}SiO_2$) [13]. In the equations that follow, the following common cement chemistry abbreviations are used: C=CaO; S=SiO_2; A=Al_2O_3. The amount of water evolved by the hydrated phase (xH_2O) may vary due to a possible gel form of this substance. Using the present method the amount of water in the gel can be measured after different hydration periods. The tobermorite gel formation reaction can be described as follows:

$$2C_3S+nH_2O \rightarrow C_3S_2{\cdot}(H_2O)_{n-3}+3Ca(OH)_2 \tag{R-5}$$

where

$$\frac{n-3}{3}=\frac{X}{Y} \tag{E-2}$$

X and Y are, respectively, the number of moles of water released by the CSH-gel and by the $Ca(OH)_2$ during the thermal analysis. The stoichiometry of CSH formation from C_2S is slightly different, but C_3S is present in much larger amounts than C_2S. Furthermore, C_3S reacts faster than C_2S and contributes much more to CSH formation in the first 4 weeks of hydration.

To calculate the amount of water present in the ettringite phase, its general formation reaction must be analyzed:

$$C_3A+3CaSO_4{\cdot}2H_2O+nH_2O \rightarrow C_3A{\cdot}3CaSO_4{\cdot}(n+6)H_2O \tag{R-6}$$

where

$$\frac{6}{n+6}=\frac{Z}{W} \tag{E-3}$$

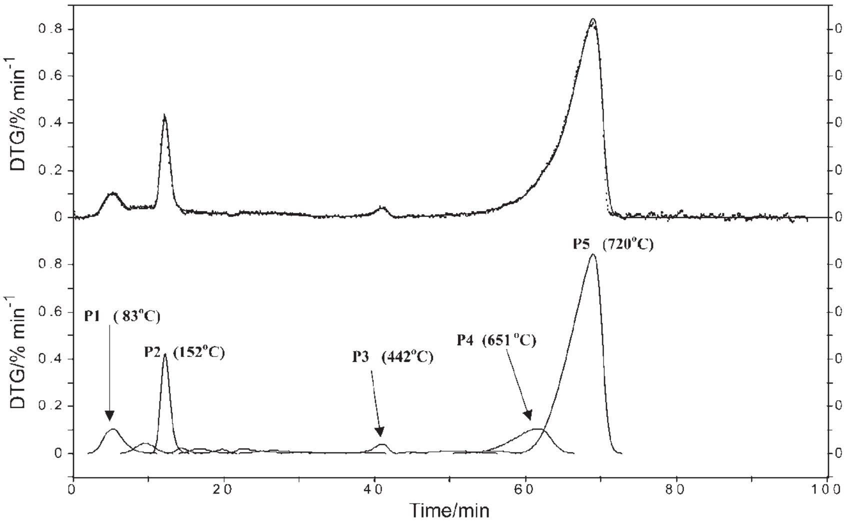

Fig. 1 Peak separation of the DTG analysis of MA cement paste hydrated for 1 h

Z and *W* are, respectively, the number of moles of water evolved from the maximum amount of gypsum ($CaSO_4 \cdot 2H_2O$) and from ettringite, which are in turn obtained from the 1 h and 4 weeks paste analysis.

Results and discussion

To illustrate the overlapped peak separation and its quantification method, Figs 1 and 2 show, respectively, characteristic plots for cement MA hydrated pastes after 1 hour (MA1H) and 1 week (MA1W). The latter case plot is similar to that obtained for the paste hydrated for 4 weeks. Because gypsum is absent after 16 h of reaction, these periods were chosen to show the two main stages of hydration. On those plots each peak is due to the mass loss from decomposition of the respective substance, as shown in Table 1.

Table 1 Correlation of each decomposition peak to its respective substance

Peak	MA1H	MA1W
P1	tobermorite	tobermorite
P2	gypsum	ettringite
P3	calcium hydroxide	calcium hydroxide
P4	poorly crystallized calcium carbonate	poorly crystallized calcium carbonate
P5	crystallized calcium carbonate	crystallized calcium carbonate

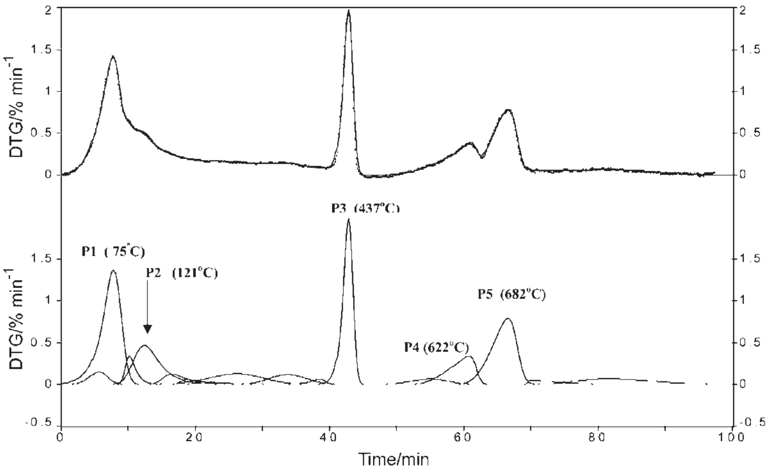

Fig. 2 Peak separation of the DTG analysis of MA cement paste hydrated for 1 week

Figure 3 shows the evolution of the content of each phase in the MA hydrated pastes over time up through 28 days. These values were calculated on the basis of the original cement mass according to Eq. (E-1). Some characteristics can be observed:

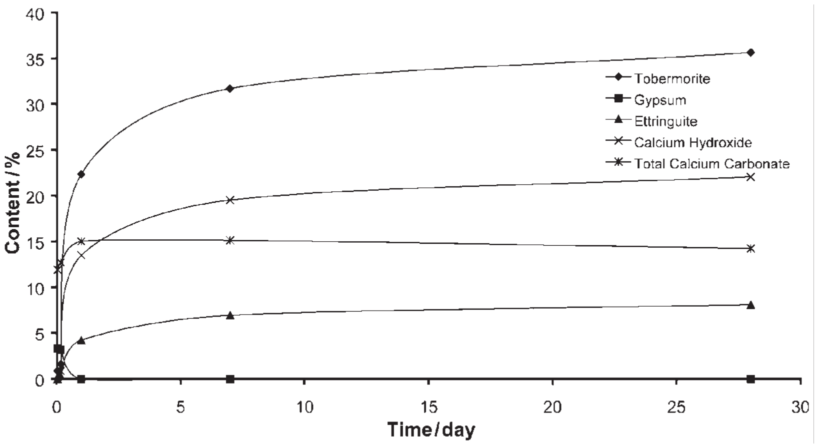

Fig. 3 Evolution of the content of hydrated phases on original cement mass basis

Tobermorite and calcium hydroxide

As was shown in reaction R-5, the amount of calcium hydroxide depends strictly on the formation of the tobermorite gel phase during cement hydration. This expected behavior seems to be the reason why tobermorite and calcium hydroxide content curves have the same shape, even after 4 weeks of hydration. It is also seen that after 1 week of hydration the reaction rate is lower in both cases.

Gypsum

As discussed above, gypsum is no longer present in hydrated cement pastes after 16 h. No more products are found in MA pastes at 1 day of hydration.

Ettringite

Ettringite formation is still not well understood, and some authors argue about the correct formation mechanism of this substance. The respective content curve indicates that this reaction may be occurring with formation of other intermediary products. It can be observed that after 4 weeks of hydration the amount of ettringite is larger than that after 1 week of hydration, when, apparently, there was no more gypsum to react with the calcium aluminates. Presumably sulfate is being partitioned into phases other than ettringite, but is nevertheless eventually available for ettringite formation.

Calcium carbonates

The total amount of calcium carbonates (non-crystallized and crystallized) of 1-day to 4-week pastes is slightly higher than in the younger pastes. There is no organic matter present in these pastes to release CO_2 on burnout, or any other known source of CO_2, which could result in carbonation of $Ca(OH)_2$, thus increasing the $CaCO_3$ content. We assume that there is a minor amount of carbonation due to inadvertant air exposure during storage.

Figure 4 shows the amount of water present on the CSH-gel phase as a function of hydration time, which was calculated according to reaction (R-5) and Eq. (E-2). It can be noticed that at early hydration periods the gel is holding much more water. As hydration proceeds the gel liberates the water tending to a constant value of 4 mol for this cement.

As discussed in reaction R-6 and in Eq. (E-3), the number of moles of water present in a mole of ettringite may be calculated using the method developed in this work. The maximum amount of gypsum occurs at 1 h of hydration, because cement clinker may contain some hemi-hydrated calcium sulfate, which is rapidly converted to gypsum. And the maximum amount of ettringite occurs at 4 weeks, where the

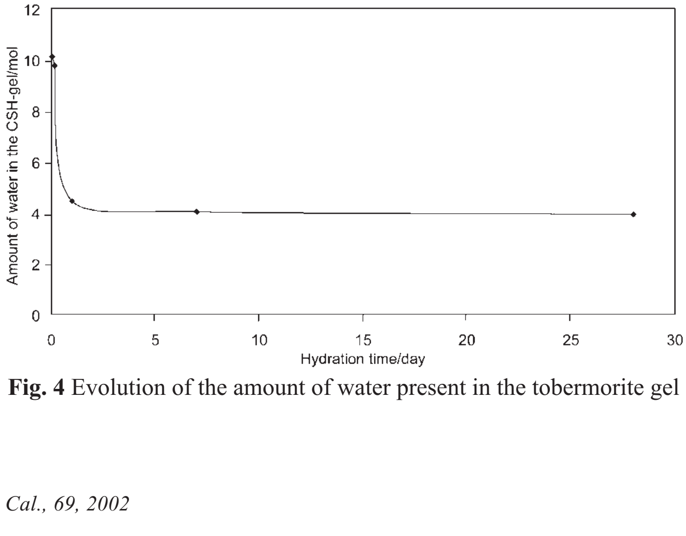

Fig. 4 Evolution of the amount of water present in the tobermorite gel

hydration process is practically stabilized. The values for *Z* and *W* were 0.004592 and 0.024334, respectively. Thus the calculated value of (n+6) was 31.14 which is an intermediate value between 32 or 31 which are given in literature as being the number of moles of hydration water of the ettringite.

The deconvolution method is very reliable, since the number of moles of water present in the ettringite phase calculated in this work is very close to that presented in the literature [13, 14]. In view of this fact, the method can be expected to work well when applied to calculation of the water present in the tobermorite gel, which shows that the higher is the hydration time, the lower is the amount of water present. This water reduction can be seen already to begin in the first 24 h of hydration.

Conclusions

The method which was used to separate overlapped derivative thermogravimetry peaks allows higher precision in the quantification of each main phase present in hydrated cement pastes and consequently the hydration process of the calcium silicate and aluminate present in the cement clinker can be better understood.

The decrease of the combined water in the tobermorite phase during the first day confirms that this is one of the first phases to be formed, which in the subsequent cement hydration stages supplies the water needed for the hydration of the other components present in the cement clinker.

This method allows the quantification of the amount of combined water present in the ettringite phase formed during calcium aluminate hydration, which is very close to the values found in literature.

By using the deconvolution method the many cement hydration phases are better detailed than by conventional TG and DTG. Some new peaks are observed, identification of which will require complementary study.

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