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THERMOGRAVIMETRY ON CALCINED MASS BASIS – HYDRATED CEMENT PHASES AND POZZOLANIC ACTIVITY QUANTITATIVE ANALYSIS

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When cement hydrated compositions are analyzed by usual initial mass basis TG curves to calculate mass losses, the higher is the amount of additive added or is the combined water content, the higher is the cement 'dilution' in the initial mass of the sample. In such cases, smaller mass changes in the different mass loss steps are obtained, due to the actual smaller content of cement in the initial mass compositions. To have a same mass basis of comparison, and to avoid erroneous results of initial components content there from, thermal analysis data and curves have to be transformed on cement calcined basis, i.e. on the basis of cement oxides mass present in the calcined samples or on the sample cement initial mass basis.

The paper shows and discusses the fundamentals of these bases of calculation, with examples on free and combined water analysis, on calcium sulfate hydration during false cement set and on quantitative evaluation and comparison of pozzolanic materials activity.

Keywords: *calcined mass basis, cement, false set, pozzolanic activity, TG/DTG*

Introduction

Thermal analysis techniques (DTA, TG and DTG) have been used to analyze hydrated cement pastes [1–5]. Through these techniques, mainly from TG and DTG data, usually combined water of the hydrated products can be quantified through the respective dehydration mass loss, which occurs during thermal analysis. One of the most important analytical parameters is the water released from calcium hydroxide dehydroxylation, from which the degree of cement hydration is usually evaluated [1]. These analyses are also used to evaluate cement based materials containing additives, including pozzolanic additives which activity is measured from the calcium hydroxide consumption that these materials present forming more similar hydrated products than those produced from the hydration of cement component substances [6–11].

Thermal analysis curves are plotted, by default, on sample initial mass basis (imb), which has been usually used to compare the main hydration phases in different products obtained using a same cement [11–16]. On imb basis, quantitative thermal analysis curve data of cement pastes with different hydration degrees and/or prepared with different water/solids ratio, can not be compared properly, because their initial compositions are not the same. The same applies when additives are used with cement, because the higher is the amount of added additive, the higher is the cement 'dilution' by the additive in the initial mass of the sample. To avoid this problem and to have a same composition basis of comparison with respect to the cement mass used in different compositions, all calculations of mass losses and thermal analysis data have to be obtained on a same composition basis, such as cement calcined mass basis (cmb), i.e. on the basis of the cement oxides mass present in the calcined sample at the end of the thermal analysis, and non on the basis of the initial mass of each sample, which have different composition [1, 5, 17–20]. As the ratio between the calcined mass of the cement oxides and the initial cement unhydrated mass is constant, the mass changes or the thermal analysis curves may be recalculated on the initial cement mass basis existent in the hydrated sample, to have an easier and more practical same basis of comparison, to analyze the TG/DTG data. The present paper contributes to

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the discussion of the fundamentals of this basis of calculation, with some examples on quantitative comparison of related differently composed hydrated cement products.

Experimental

Materials

The materials used in the applications are: demineralized water; Portland cement (PC) type II, code CPII-F32, manufactured by Lafarge, RJ, Brazil; commercial metakaolin (MK) manufactured by Metacaulim do Brasil, SP, Brazil. Metacaulim do Brasil, SP, Brazil, and a residual pozzolanic catalyzer (CE), discarded from a Fluidized Catalytic Cracking (FCC) unit of a Brazilian refinery.

Methods and instruments

TG and DTG were performed in a simultaneous TA Instruments TG-DTA equipment, model SDT 2960, with a 10°C min^{-1} constant heating rate, from 30 to 1000°C, in 100 mL min^{-1} nitrogen flow. Samples of about 10 mg were used in open platinum pans. Unless differently stated, all hydrated paste samples were initially dried at 35°C for 1 h in the equipment, before the constant heating rate step was initiated. All pastes were prepared with a water/total solids ratio=0.5.

Calculation methods

When no additives are added, the final calcined mass of these samples has the same oxide composition than that of the non-hydrated calcined cement [1] and Eq. (1) can be used to obtain the percentual mass loss of a step *i*, on calcined basis ($\Delta m_{\mathrm{i,\,cb}}$):

$$(\Delta m_{\mathrm{i,\,cb}})=100(\Delta m_{\mathrm{i,\,ib}})/R_{\mathrm{i,\,ib}} \qquad (1)$$

where $\Delta m_{\mathrm{i,\,ib}}$=original percentual mass loss of the step *i*, on initial sample mass basis and $R_{\mathrm{cem,\,ib}}$=percentual calcined mass of the original cement at 1000°C, obtained from its TG curve plotted on initial sample mass basis.

When an aggregate *k* is used to prepare a blend with cement before hydration, the final calcined mass of the sample at the end of the TG analysis (usually at 1000°C) is different than that of the non-hydrated calcined cement oxide composition. In this case, if *n* different aggregates are used to prepare the initial solid blend, the mass fraction of the original cement oxides present in the calcined blended sample ($f_{\mathrm{bcem,\,ib}}$) can be estimated by:

$$f_{\mathrm{bcem,\,ib}}=(R_{\mathrm{cem,\,ib}}M_{\mathrm{cem}})/(R_{\mathrm{cem,\,ib}}M_{\mathrm{cem}}+\Sigma(R_{\mathrm{agg\,k,\,ib}}M_{\mathrm{agg\,k}})\ (k=1\text{ to }n) \qquad (2)$$

where $R_{\mathrm{agg\,k,\,ib}}$=percentual calcined mass of the aggregate *k* at 1000°C, obtained from its TG curve, on initial sample mass basis; M_{cem}=cement mass used to prepare the blend and $M_{\mathrm{agg\,k}}$=aggregate *k* mass used to prepare the blend.

In these cases, to obtain the mass loss of a TG step of hydrated blended cement samples on a same cement calcined mass basis, Eq. (3) must be used:

$$(\Delta m_{\mathrm{i,\,ccb}})=100(\Delta m_{\mathrm{i,\,ibb}})/(R_{\mathrm{bcem,\,ib}}f_{\mathrm{bcem,\,ib}}) \qquad (3)$$

where $\Delta m_{\mathrm{i,\,ccb}}$=percentual mass loss of a step *i*, on cement calcined mass basis; $\Delta m_{\mathrm{i,\,ibb}}$=original percentual mass loss of the step *i*, on initial blend sample mass basis; $R_{\mathrm{bcem,\,ib}}$=percentual calcined mass of the blend sample at 1000°C, obtained from its TG curve, on its initial sample mass basis. As $R_{\mathrm{cem,\,ib}}$ is a constant, one may calculate the percentual mass loss of a step *i*, on blend initial cement mass basis ($\Delta m_{\mathrm{i,\,icb}}$) by Eq. (4), which is another easier and same composition basis of comparison.

$$(\Delta m_{\mathrm{i,\,icb}})=R_{\mathrm{cem,\,ib}}(\Delta m_{\mathrm{i,\,ccb}})/100 \qquad (4)$$

The above equations were used to obtain TG and DTG curves presented in this paper on the desired basis, applying the Universal Analysis software of the equipment to the original TG and DTG curves, plotted by default on sample initial mass basis.

It must be noted that when DTA or DSC curves on initial sample mass basis are used to study cement hydrated systems, these calculations on cement calcined basis or initial sample cement mass basis have also to be applied to respective curve signals to correctly compare, on a same basis, the thermal effects of dehydration and dehydroxylation peaks of samples with different initial compositions [7].

Results and discussion

Figures 1–3 show, respectively, TG and DTG curves of the unhydrated Portland cement sample and after being hydrated for 1 h on different calculation basis.

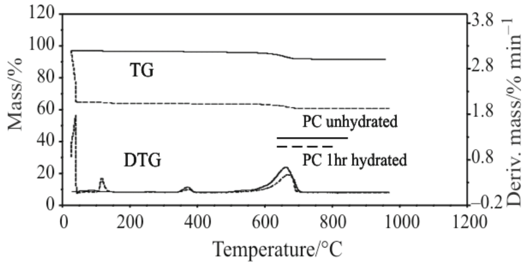

Fig. 1 TG and DTG curves of the unhydrated cement and after 1 h hydration paste on respective sample initial mass basis

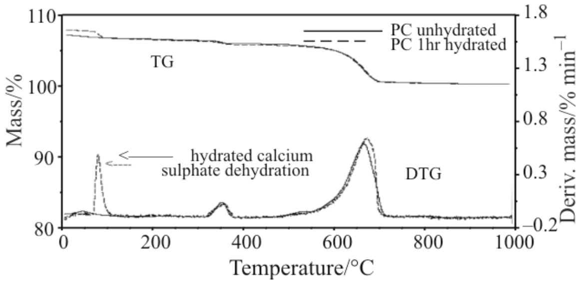

Fig. 2 TG and DTG curves of the unhydrated cement and after 1 h hydration paste on cement calcined mass basis

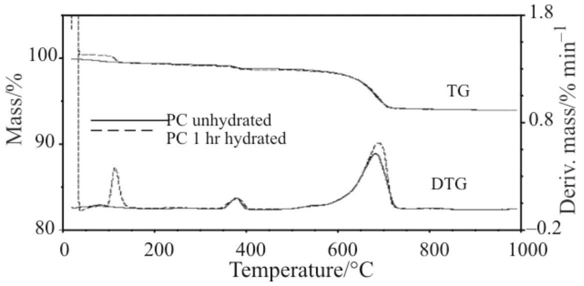

Fig. 3 TG and DTG curves of the unhydrated cement and after 1 h hydration paste, on initial cement mass basis

From Fig. 1 it can be seen that the unhydrated cement oxides represent 94.03% of its initial mass ($R_{\text{cem, ib}}$) and apparently, unhydrated cement has no calcium sulfate retardant, which is rehydrated after 1 h. As can be seen from Figs 2 and 3, the cement presents a false set, which is actually due to the rehydration of the anhydrous calcium sulfate in its composition, which was produced during clinker milling with gypsum [1]. Note that the free and combined water of a paste can be estimated from Fig. 1 on initial mass basis. However the correct comparison between the hydrated and unhydrated samples can only be done on a same basis as shown on Figs 2 and 3, respectively, on cement calcined basis or on initial cement mass basis in the paste.

Table 1 shows some mass loss data obtained from Figs 1 and 3 TG curves. From the water mass lost between 90 and 170°C of the PC 1 h hydrated sample data on initial cement mass basis, and considering dihydrated calcium sulfate stoichiometric decomposition, it can be estimated that before milling, in the original mixture composition the content of added gypsum was 4.20% of the PC unhydrated mass.

Figures 4 and 5 show TG, DTG curves of the cement paste and of the pastes with 10 and 20% cement substitution (PC10CE and PC20CE) by residual pozzolanic catalyzer after 28 days of hydration, respectively on initial mass basis of each sample and on cement calcined mass basis. These analyses were performed without the initial drying step at 35°C. From Fig. 5 the pozzolanic activity may be quantified from the decrease of the $Ca(OH)_2$ dehydroxylation mass losses, which were 6.276, 5.533 and 5.051% of respective calcined cement masses of PC, PC10CE and PC20CE samples. This indicates, on a same basis, that the higher is the cement substitution by CE, the lesser is the residual $Ca(OH)_2$ content in the partially substituted cement paste.

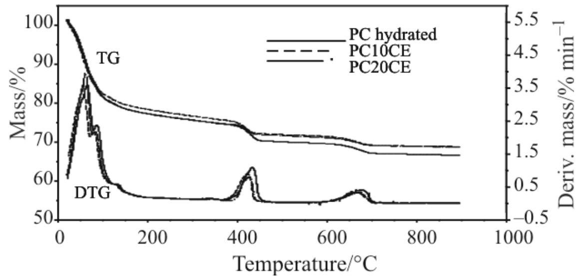

Fig. 4 TG, DTG curves of the cement paste and of the PC10CE and PC20CE pastes after 28 days of hydration

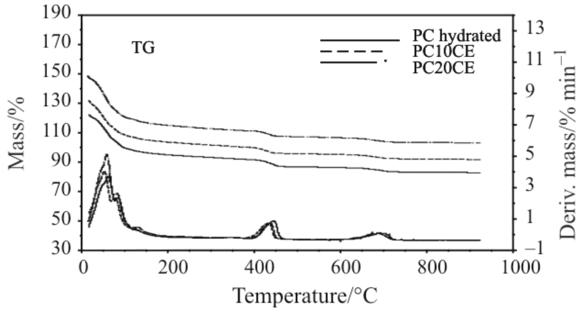

Fig. 5 TG, DTG curves of the cement paste and of the PC10CE and PC20CE pastes after 28 days of hydration on cement calcined mass basis

Table 1 Unhydrated (PC) and 1 h hydrated cement (PC 1 h) TG curves data

Basis	Sample	Mass loss during dehydration from 90 to 170°C/mass%	Mass loss during $Ca(OH)_2$ dehydroxylation/mass%	Percentual calcined mass at 1000°C/mass%
On initial sample	PC	0.1305	0.4262	94.03
mass basis (Fig.1)	PC 1 h	0.6067	0.2826	61.50
On initial cement	PC	0.1305	0.4262	94.03
mass basis (Fig. 3)	PC 1 h	0.8798	0.4326	94.03

(Estimation of $CaSO_4{\cdot}2H_2O$ content=0.8798/0.2093=4.20% of PC)

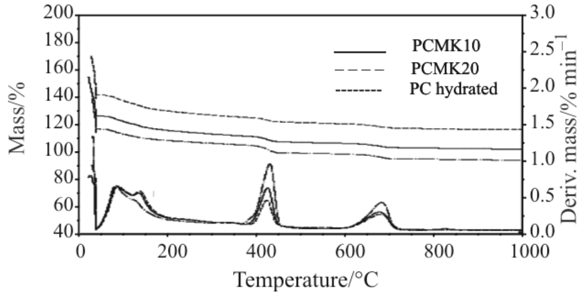

Fig. 6 TG, DTG curves of the cement paste and of the pastes with 10 and 20% cement substitution by metakaolin after 28 days of hydration on cement calcined mass basis

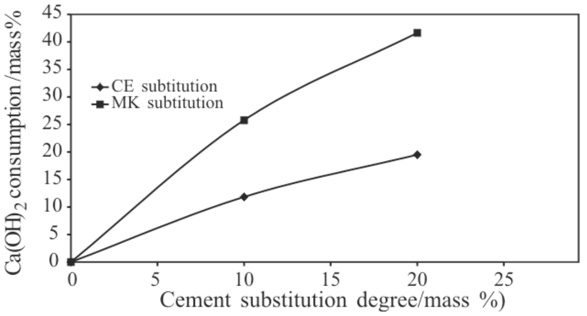

Fig. 7 Comparison of the pozzolanic activity of CE and MK in 28-day hydrated pastes, as a function of their cement substitution degree

Figure 6 shows TG and DTG curves of the PC cement paste and of the pastes with 10 and 20% cement substitution (PC10MK and PC20MK) by metakaolin, after 28 days of hydration, respectively on cement calcined mass basis. Note that in this case, the initial TG curve shape is different from the previous cases, because of the initial drying step performed to release and to quantify the uncombined water prior the combined ones. The calcium hydroxide (CH) dehydroxylation mass losses were 7.011, 5.204 and 4.091% of respective calcined cement masses of PC, PC10MK and PC20MK samples, showing that the reduction of mass loss due to CH dehydroxylation increases as the degree of cement substitution increases. This indicates that effectively increasing amounts of the CH produced with tobermorite during calcium silicates hydration were consumed by MK pozzolanic activity during the 28 days of hydration.

The comparison of the pozzolanic activity of the different materials CE and MK can be done from the relative decrease of the water released from calcium hydroxide dehydroxylation, with respect to that released in the case of the same time hydrated PC cement without any substitution. As shown in Fig. 7, obtained from Figs 5 and 6 data on cement calcined basis, for a same cement substitution degree, the calcium hydroxide consumption due to the pozzolanic activity of metakaolin (MK) is much higher than that of the CE catalyzer residue.

Conclusions

- Thermal analysis curve data of hydrated cement paste samples prepared from the same cement but with different initial compositions, must be transformed on a same composition mass basis to be properly compared for quantitative analysis.
- For this purpose, as applied in this paper to TG and DTG curves on respective sample initial mass basis, one of the options is to transform them on cement oxide calcined mass basis.
- From original unhydrated cement TG curve data, the ratio between calcined and initial cement mass can be used to transform cement calcined mass basis thermal analysis data on initial cement mass basis to have an easier comparison basis, when needed.
- On cement calcined basis or on initial cement mass basis, TG or DTG curves of cement pastes, mortars and concretes can be used for a more proper and correct comparative quantitative analysis of hydration parameters, such as the examples discussed in this paper.

Nomenclature

List of subscripts

i	mass loss step during thermal analysis (*i*=1 to *m*)
m	number of mass loss steps
cb	on calcined mass basis
ib	on initial mass basis
cem	cement
bcem	blended cement
agg k	aggregate *k*
n	number of aggregates used in the blend
ccb	on cement calcined mass basis
ibb	on initial blend sample mass basis
icb	on initial sample cement mass basis

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