# Use of high resolution thermogravimetric analysis (HRTG) technique in spent FCC catalyst - Portland cement pastes

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**Abstract**

Thermogravimetric analysis (TG) is one of the most common instrumental techniques used for the characterization of pastes, mortars and concretes based on both calcium hydroxide or Portland cement. Important information about pozzolanic materials can be assessed concerning to calcium hydroxide consumption and the formation of new hydrated products. Nevertheless, in some cases, problems associated to the overlapped decomposition processes for hydrates difficult the analysis of obtained data. In this paper the use of high resolution thermogravimetric analysis (HRTG), a powerful technique that allows separating decomposition processes in analysis of hydrated binders, was performed for spent FCC catalyst -Portland cement pastes. These pastes were monitored for 1, 4, 8 hours and 1, 2, 3, 7 and 28 curing days. In order to study the influence of the pozzolanic material (spent FCC catalyst), Portland cement replacements of 5, 15 and 30 % by mass were carried out. The presence of spent FCC catalyst in blended pastes modified the amount and the nature of the formed hydrates, mainly ettringite and stratlingite.

**Keywords:** high resolution thermogravimetric analysis, Portland cement, spent FCC, pozzolan.

**1. Introduction**

Thermogravimetric analysis is an instrumental technique that relates mass change and temperature. In this technique, parameters such as mass loss, time and temperature are continuously monitored [1]. For mortars or pastes based on Portland cement, the decomposition/dehydration associated to mass loss of hydrated products can be measured [2]. Several papers reported the use of thermogravimetric analysis (TG) to assess the formation of hydrates in Portland cement pastes [3-5].

For thermogravimetric analysis, some parameters may be selected in order to carry out the test according to the required conditions: a rapid test or a slow test can be performed. For both conditions, the heating rate parameter is very important. When a rapid heating rate is carried out, short testing time is required and the main disadvantage is a poor separation (low resolution in the derivative thermogravimetric curve, DTG) of different dehydration processes. On the other hand, when a slow heating rate is used, and consequently large testing time is spent, a better separation of peaks in DTG curve related to the mass loss processes could be yielded. Nevertheless, even an increased testing time do not guarantee a complete separation of dehydration processes.

In order to solve this problem, high resolution thermogravimetric analysis (HRTG) should be carried out. HRTG is based on a dynamic process that controls the heating rate, proportioning an "quasi" isothermal condition during the reaction proceeds (decomposition, dehydration,...), fact that does not affect the nature of reaction. In the same way, HRTG can be considered a short testing time experiment and can also be used as an useful tool for some topics in thermal analysis such as: overlapped reactions, decomposition process poorly resolved when the signal between peaks in DTG curve does not return to baseline, noticeable shoulders appeared in the DTG curve for the decomposition process, complex reactions, separation of volatile substances in plastic and elastomers and also for water evaporation in hydrated compounds.

For HRTG technique, when the mass loss rate (W) is lower than the lowest predefined mass loss threshold (Wmin), the heating rate (Vint) is increased progressively until to the maximum heating rate (Vmax). The factor of increasing the heating rate may be also predefined. Hence, the testing time is reduced in this part of experiment. On the other hand, when the mass loss rate (W) is higher than the

highest mass loss threshold (Wmax), the heating rate (Vint) is reduced progressively until the minimum heating rate (Vmin). On this way, the obtained peaks on the thermogravimetric DTG curves are narrower and the overlapping of peaks decreases. In these conditions, the temperature range decomposition is reduced if compared to conventional TG experiment. Figure 1 shows a schematic representation of high resolution thermogravimetric method.
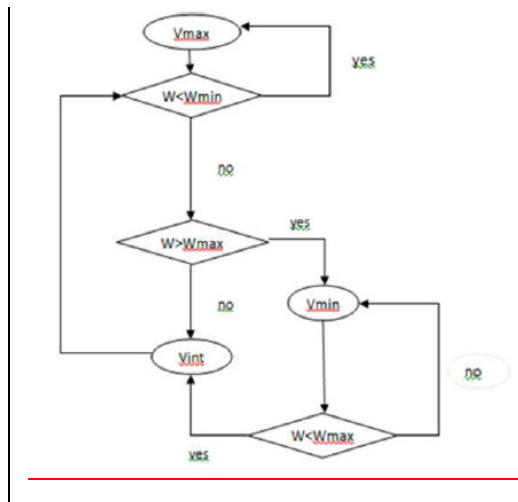


Figure 1. Schematic representation of high resolution thermogravimetric method (HRTG).

The use of HRTG have commonly been applied in the decomposition of minerals (hydrotalcite, organoclays, peisleyite, montmorillonite), polymers and oil shales [6-13]. In the field of civil construction, only few studies have been reported using HRTG technique [14-18]. Payá et al. [14] applied this technique in the study of dehydration of gypsum, yielding the total separation of the two decomposition processes for $CaSO_4.2H_2O$. The use of HRTG was performed by Tobón et al. [18] in order to assess the effect of $SiO_2$ nanoparticles blended in Portland cement pastes in the range 100-300 ºC, related to the dehydration of calcium silicate hydrate (C-S-H gel), C-A-S-H and C-A-H. For HRTG, the hydrated phases were successfully separated in the DTG curve.

The aim of this paper is to assess the behavior of spent FCC catalyst-Portland cement pastes using HRTG. Spent FCC catalyst is an aluminosilicate waste material from petrochemical industry with high pozzolanic reactivity, even for the first curing ages [19-23]. The hydration products formed due the pozzolanic reaction of FCC as well the Portland cement products formed during its hydration are well known and have been characterized by means conventional thermogravimetric techniques [24-30]. The main

hydration products formed are C-S-H gel, ettringite (AFt), calcium aluminate and silicoaluminate hydrates (C-A-H and C-A-S-H).

## 2. Experimental

### 2.1. Materials

Spanish Portland cement type I 52.5R supplied by Cemex (Buñol, Spain) and fluid catalytic cracking catalyst residue (FCC) supplied by BP OIL (Grao de Castellón, Spain) were used for the production of FCC blended pastes. Chemical compositions of these materials, determined by X ray fluorescence (Philips MAGIC PRO, PW2400 model), are shown in Table 1.

|  | $SiO_2$ | $Al_2O_3$ | $Fe_2O_3$ | CaO | MgO | $SO_3$ | $K_2O$ | $Na_2O$ | LOI | Other |
|---|---|---|---|---|---|---|---|---|---|---|
| FCC | 47.76 | 49.26 | 0.60 | 0.11 | 0.17 | 0.02 | 0.02 | 0.31 | 0.51 | 1.24 |
| CEM | 17.42 | 4.30 | 3.30 | 66.17 | 1.45 | 3.33 | 1.21 | 0.46 | 2.35 | 0.01 |

Table 1. Chemical composition of Portland cement and spent FCC catalyst.

Fluid catalytic cracking catalyst residue was dry milled during 20 minutes before its use, obtaining a powder material with mean particle size of 19.73 μm and d(0.1) of 1.34 μm, d(0.5) of 12.15 μm and d(0.9) of 49.89 μm [19]. This process improves the pozzolanic reactivity of FCC due the reduction on the particle size. To assess the hydration products formed during Portland cement hydration and the effect of FCC on the hydrates, different replacing percentages (5, 15 and 30 % of FCC) were tested using a water/binder ratio of 0.5 (being the binder as the sum of Portland cement and FCC). HRTG tests were performed for 1, 4, 8, 24, 48 hours and 3, 7 and 28 curing days.

### 2.2. Experimental procedure

Fresh paste samples were prepared and put into cylindrical plastic containers with hermetic closing to avoid carbonation and then, they were stored at room temperature with RH ~ 100 % until the testing age. To stop the hydration process of pastes, paste samples were milled in an agate mortar with acetone. The milled sample was filtered and dried off during one hour at 60 ºC. Finally, powder sample was sieved on 80 μm sieve. Powdered and dried samples were stored into a desiccator before to thermogravimetric experiments.

A TGA 850 Mettler-Toledo thermobalance, that allows the measurement of thermogravimetric curve and differential thermal analysis curve simultaneously, was used. The software used for this application is MaxRes from Mettler-Toledo and consist basically in the choice of selected main parameters. For this work the following values have been selected:

- maximum heating rate (Vmax, 10 ºC.min$^{-1}$);

- minimum heating rate (Vmin, 0.5 ºC.min$^{-1}$);

- maximum mass loss threshold (Wmax, 3 μg.s$^{-1}$);

- minimum mass loss threshold (Wmin, 1 μg.s$^{-1}$).

The increase or decrease of heating rate between Vmax and Vmin was changed using factor = 2, this means that for changing the heating rate, the previous value was divided or multiplied by 2.

The selected temperature range was 35-250 ºC and a 75 mL.min$^{-1}$ of nitrogen gas flow was used. Sealed 100 μL aluminum crucibles with a pin-holed lid were used for these experiments. For all experiments, the initial mass sample into the crucible was 40 ± 2 mg.

## 3. Results and discussion

The conventional TG experiment let to obtain the mass loss (typically in percentage, %) with the testing time (t) using a constant heating rate: in this case, the % *vs.* t curve is exactly equal to the % *vs.* temperature curve. Assessing a Portland cement paste using the conventional method between 35-600 ºC with a heating rate of 10 ºC.min$^{-1}$, a DTG curve similar to the represented in Figure 2 should be obtained.
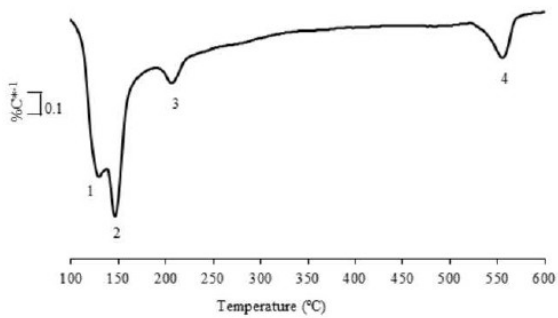
Figure 2. Typical DTG curve for Portland cement paste cured at 28 curing days.

In Figure 2, four main peaks can be noted. Peak 1 overlapped with peak 2 (100-180 ºC) belong to the dehydration of C-S-H gel and AFt. Peak 3, located in the range 180-240 ºC, correspond to the dehydration of C-A-H and C-A-S-H. Finally, the dehydroxilation of portlandite can be observed in the range of 500-550 ºC (see peak 4).

As it can be observed, the conventional thermogravimetric analysis is not able to separate the dehydration of C-S-H gel and AFt. Hence, authors propose the use of HRTG method in order to separate the different dehydration processes that occur in the Portland cement paste or in blended pastes. Figure 3 shows a comparative analysis of a conventional thermogravimetric analysis and a high resolution thermogravimetric analysis for a sample containing 15 % of FCC after 28 days of curing.
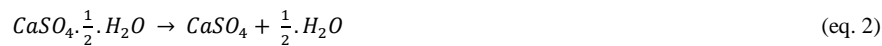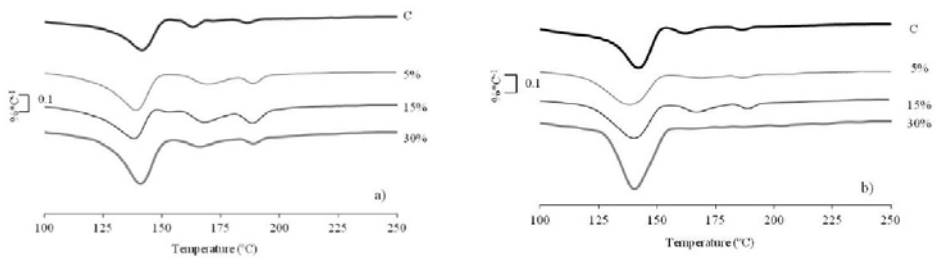


(a)

(b)
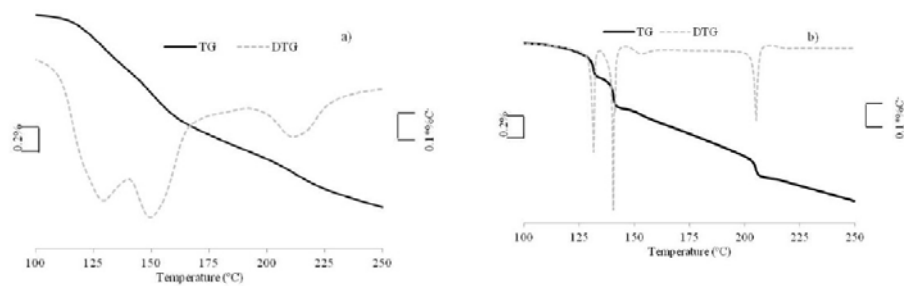
Figure 3. TG and DTG curves for 15 % FCC blend after 28 days of curing: a) conventional thermogravimetric method; b) high resolution thermogravimetric method.

For the conventional TG curve, a continuous mass loss observed from 100 to 250 °C, and three different peaks (129, 149 and 214 °C) are observed in the DTG curve. It is important to notice that the peak broadness is very important: e.g. for the third peak the beginning of the dehydration is at ca. 194 °C and finishes at ca. 227 °C, that is 33 °C of peak broadness. Thus, the two first peaks (in the 100-175 °C range) belong to the dehydration of C-S-H and AFt. Nevertheless, for this temperature range, the use of HRTG method allows separating mass loss processes in two clearly differentiated steps, with peaks at 128 °C and 140 °C. And additionally, the peaks are sharper: e.g. for the third peak, the dehydration process begins at 200 °C and finishes at 207 °C, that is only 7 °C of peak broadness.

The DTG curves for control (C) paste and FCC blended pastes (5, 15 and 30 %) cured at 1 and 4 hours and obtained under HRTG conditions are depicted in Figure 4. For all pastes, there is a peak in the range 136-143 °C that can be attributed to the decomposition of AFt phase (ettringite), which is one of the first hydrates formed during Portland cement hydration. In this case, because the low mass loss obtained (1-2 %) a broad peak appeared: this behavior is attributed to the fact that the mass loss rate is low and then the heating rate was not reduced to Vmin. Besides it, two others peaks are also detected (163 °C and 186 °C) and they can be attributed to the presence of calcium sulfate dihydrate ($CaSO_4.2H_2O$) in the Portland cement. This compound is added to Portland clinker for controlling the setting time, and is rapidly dissolved in the first hours of hydration. The reaction between dissolved calcium sulfate and tricalcium aluminate ($C_3A$) yields ettringite (AFt phase). So, the dehydration of calcium sulfate dihydrate is observed in two steps according to the following equations:

$$CaSO_4.2H_2O \rightarrow CaSO_4.\frac{1}{2}.H_2O + \frac{3}{2}.H_2O \qquad \text{(eq. 1)}$$

$$CaSO_4.\frac{1}{2}.H_2O \rightarrow CaSO_4 + \frac{1}{2}.H_2O \qquad \text{(eq. 2)}$$

Figure 4. DTG curves from HRTG experiment for pastes cured at 1 and 4 hours.

In Figure 5, the DTG curves from HRTG experiments for all pastes at 8, 24 and 48 hours of curing are depicted. For pastes cured for 8 hours, only the peak corresponding to the dehydration of AFt phase can be noted. At this curing age, no evidence of the presence of calcium sulfate dihydrate was observed, meaning that most of this compound reacted towards $C_3A$ for form AFt phase. Probably, C-S-H gel is already formed after 8 hours of hydration, however the amount would be very low and the mass loss rate produced, when heating, was under Wmin. The peak related to the decomposition of AFt is also observed for all pastes cured at 24 and 48 hours, and it appeared in the range 137-142 ºC.
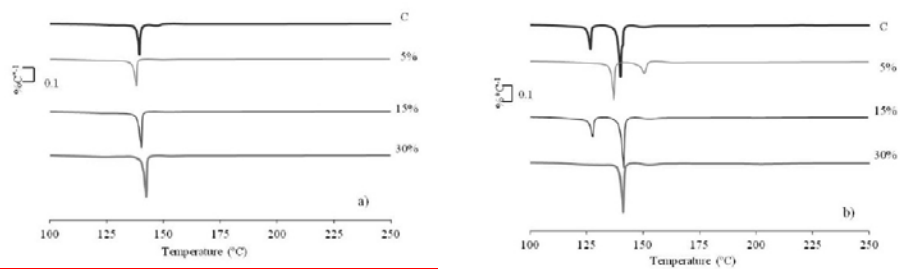


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Figure 5. DTG curves from HRTG experiments for pastes cured at 8, 24 and 48 hours.

For control paste, an additional peak appears at 126 ºC for sample cured at 24 hours which is assigned to the dehydration of C-S-H gel. After 48 hour of curing, in the control paste a third peak centered at 150 ºC was observed, which was attributed to the dehydration of C-S-H gel formed with different Si/Ca ratio.

For paste with 5 % of FCC, the peak at 150 ºC is also observed for 24 and 48 hours. Nevertheless, when the percentage of FCC is increased to 15 %, the peak located at 150 ºC is not detected. For pastes with 30 % of FCC, none of these peaks are detected for 8 and 24 hours. A peak at 124 ºC is observed only for paste cured at 48 hours. In this curing period, 8-48 hours, the identification of different hydrates is different depending on the replacing FCC percentage: this behavior could be due to the low amount of the hydrates which has an important effect on the changing of the heating rate. Additionally, the presence of FCC particles could promote the acceleration of the hydration of Portland cement grains and also the pozzolanic reaction take place, influencing in different way depending on the amount of the pozzolan.

Figure 6 shows the DTG curves from HRTG experiments for all pastes cured at 3, 7 and 28 curing days. For these curing ages, control paste present the peaks related to AFt (136-138 ºC) and the peak at lower temperature (120-122 ºC) associated to the dehydration of C-S-H gel. Peaks related to the dehydration of calcium aluminate and calcium silicoaluminate hydrates were not observed.

For pastes with 5 % of FCC, the peak centered at ca. 120 ºC was observed for 3 and 7 days of curing, however, after 28 curing days this peak is displaced for higher temperatures and is overlapped with the corresponding to the AFt decomposition.

For pastes with 15 % of FCC, after 7 curing days the presence of a new peak centered at 206 ºC is observed, that can be attributed to dehydration of C-A-S-H. In fact, the main product due to the pozzolanic reaction of FCC is stratlingite, that is a C-A-S-H compound [6].

For paste with 30 % of FCC, different peaks are identified depending on the curing time. After 3 curing days, peaks associated to Aft and C-S-H can be observed. After 7 curing days, a peak centered at 126 ºC corresponding to the C-S-H gel and a broadband at 140-150 ºC (Aft and C-S-H overlapped) were observed. Finally, for 28 curing days, the peaks corresponding to C-S-H gel and C-A-S-H can be noted, moreover a broadband centered at 140-150 ºC. In this paste, an increasing in the peak attributed to C-A-S-H (200 ºC) is larger than those found for 15 % FCC sample, and the amount of Aft for 30 % FCC paste was lower than those found for 15 % FCC paste.
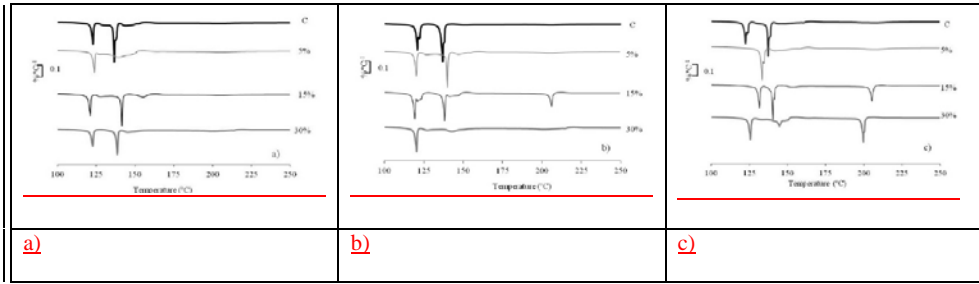
Figure 6. DTG curves from HRTG experiments for pastes cured at 3, 7 and 28 days.

Total mass loss values in the range 35-250 ℃ are shown in Table 2. These values were calculated for calcined mass basis, that is, the percentage of mass loss was the ratio between the mass loss measured and the corresponding mass remaining after calcination (Because the mass loss for anhydrous cement and FCC were negligible in the selected temperature range analysis, no corrections were made in this sense). In the first 4 hours of test, all FCC blended pastes presented a total mass loss higher than control paste.  It is due the presence of aluminates in the FCC that reacts to form ettringite. For the longest curing time (28 days), FCC blended pastes presented similar mass loss than control paste, despite the lower amount of Portland cement: that is related to the enhanced formation of C-S-H gel and C-A-S-H compounds due to the pozzolanic reaction. This fact confirms that pozzolanic reaction compensate the dilution effect (less Portland cement when increasing the percentage of replacement) in terms of the amount of formed hydrates.

**Table 2. Total mass loss values in the range 35-250 °C.**

|  | C | 5% | 15% | 30% |
|---|---|---|---|---|
| 1h | 1.3542 | 1.3892 | 1.8647 | 2.4570 |
| 4h | 1.9752 | 1.8625 | 2.7903 | 3.2199 |
| 8h | 3.7431 | 4.0524 | 4.8303 | 5.5659 |
| 24h | 7.3153 | 6.4809 | 7.7798 | 7.2405 |
| 48h | 8.6695 | 7.556 | 8.0897 | 8.4593 |
| 3d | 9.0747 | 9.1727 | 9.2465 | 8.7749 |
| 7d | 10.2859 | 10.5004 | 10.9287 | 10.4392 |
| 28d | 10.2845 | 9.7885 | 10.4963 | 11.2533 |

**Con formato:** Sangría: Primera línea: 1,25 cm

## 4. Conclusions

High resolution thermogravimetric (HRTG) technique is able to separate all the thermal dehydration processes in Portland cement pastes and also for spent FCC blended pastes in the 35-250 ºC temperature range. The addition of spent FCC catalyst produced different hydration products when compared to the control paste due the chemical composition of this pozzolanic material: an aluminosilicate material. On this way, the use of spent FCC increased the amount of ettringite formed during the Portland cement hydration and some new hydrated phases can also be identified such as stratlingite (C-A-S-H). Since the first hours of test, the mass loss of spent FCC blended pastes are similar to control paste, demonstrating that pozzolanic reaction compensate the dilution effect (less Portland cement present in FCC containing pastes).

## 5. Acknowledgments

## 6. References

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