1   **Evaluation of the pozzolanic activity of spent FCC catalyst/ fly ash mixtures in**

2   **Portland cement pastes**

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13   **Abstract**

14   High pozzolanic activity of the residue spent catalytic cracking catalyst (FCC) has been

15   reported by various authors in recent years. However, no report on the lime fixation of

16   this residue when dosed together with other pozzolan has been developed, such material

17   partially replacing Portland cement in the manufacture of hydraulic binders. One of the

18   possibilities is to mixture it with fly ash (FA). This joint replacement provides several

19   advantages in that: 1) Generation of FCC is low compared to other pozzolans including

20   fly ash (FA); 2) The FCC tends to react to short curing times, while the FA does at

21   longer times; 3) The FCC is demanding water, while the FA tends to improve the

22   fluidity of the binder. This paper studies on cement pastes by thermogravimetric

23   analysis of various mixed substitutions FCC:FA, varying the replacing percentage for

24   FCC in the 0-15% range and for FA in the 0-30% range. Evolution of pastes was

25   monitored by means of thermogravimetric analysis on pastes cured for 3-365 days.

Products of the pozzolanic reaction were identified by SEM, being some of them cubic crystals (C3AH6 and/or hydrogarnet). By TGA analysis it was observed that when the %FCC is increased in the system, the amount of the calcium aluminate hydrates (C-A-H) and calcium aluminosilicate hydrates (C-A-S-H) also increased. Negative values of fixed lime were obtained due to an acceleration of the hydration of OPC, since the FA particles acted as nucleation sites for the precipitation of hydrated compounds. Fixed rates up to 90% of hydrated lime with substitutions as high as 45% in Portland cement system at one year of curing were reached.

Keywords: Spent Fluid Catalytic Cracking Catalyst, Fly Ash, Pozzolanic Activity, Thermogravimetric Analysis, Cement Pastes.

1. Introduction

The effectivity of thermogravimetric analysis for the characterization of the reactivity of pozzolanic materials has been extensively used in the past [1, 2]. LP Esteves [2] studied by TGA / DTA techniques, the pozzolanic reaction in systems OPC-pozzolan (silica fume) developing an interesting model for this complex system of reactions. In this study, because the high reactivity of silica fume, accelerating effect on cement hydration was not evidenced. In our case, because the low reactivity of fly ashes, this effect has been evidenced at early curing times. In recent years it has been reported the use of spent catalytic cracking catalyst (FCC) as an excellent pozzolanic material, in the partially replacement of Portland cement for the manufacture of hydraulic binders [3-13]. These studies have demonstrated the high reactivity of the FCC, mainly by thermogravimetric analysis [6, 13] and compressive strength [3-5, 7, 9, 12]. On one hand, given the high reactivity of FCC, it has been reported that the optimum replacement of Portland cement by this material ranges about 15-20%. This is because with higher percentages of replacement, part of the catalyst acts as an inert material, for

1   having no calcium hydroxide, which it is generated by cement hydration, available for

2   the pozzolanic reaction [6]. On the other hand, the generation of spent catalyst is far

3   lower than that generated from other waste pozzolanic materials, such as Fly Ash (FA).

4   Several researchers have reported amounts of spent catalyst generated of around one

5   million tons per year [4, 7]; while the generation of fly ash is about 500 Mt/year [14].

6   The high reactivity of the catalyst implies a significant pozzolanic activity at short

7   curing times [15]; while the fly ash tends to react at longer times [16]. It has also been

8   reported that the catalyst is water demanding [12] while the fly ash reduces water

9   demand [17]. Zornoza et al. [18] have studied the phenomenon of corrosion in mortars

10   with substitutions of catalyst and fly ash, showing that substitutions as high as 45%

11   does not influence the risk of corrosion. Recently, Wilinska et al [19] studied fly ash-

12   cement systems, activating the system with spent FCC catalyst. The cement

13   replacements by pozzolans that they used were very high (80%). They assessed the

14   ternary system OPC:FCC:FA, demonstrating that the spent FCC catalyst accelerated the

15   early hydration of the system. With these considerations, the advantage of performing

16   mixed replacements of FCC:FA in hydraulic binders based on Portland cement is

17   evident. Therefore, the objective of this work is to study by means of thermogravimetric

18   analysis the pozzolanic activity of mixtures of FCC:FA that partially replace the

19   Portland cement.

20   **2. Experimental**

21   Ordinary Portland cement (OPC, CEM I-52.5-R) supplied by Cemex España (Buñol-

22   Valencia, Spain) was used for preparing the cement pastes in this study. Pozzolans used

23   to replace Portland cement were: FCC, supplied by BP OIL Spain (Castellón, Spain),

24   which prior to dosage was milled for 20 minutes in a laboratory mill (Gabbrielli Mill-2)

25   to increase its reactivity [3]; and FA class F (aluminosilicate) from the coal power plant

1   at Andorra-Teruel (Spain). Table 1 shows the chemical composition of cement and the

2   two pozzolans studied.

3

4   **Table 1** Chemical compositions and physical properties of OPC, FCC y FA (wt %).

Material	OPC	FCC	FA
SiO_2	19.56	48.21	40.92
Al_2O_3	5.29	46.03	24.72
Fe_2O_3	3.56	0.95	13.59
CaO	62.63	<0.01	9.83
MgO	2.1	<0.01	1.59
SO_3	3.6	0.04	1.59
K_2O	1.15	<0.01	1.43
Na_2O	0.09	0.49	0.34
LOI*	0.98	1.52	2.44
Relative density	3.05	2.42	2.44
Specific surface area (cm^2/g)	4000	11500	2841
Volume average diameter (μm)	15.01	19.95	25.40

5   *LOI: Loss on ignition

6

7   Figure 1 shows scanning electron microscopy micrographs of particles of FCC and FA.

8   In Figure 1a) the catalyst before being milled is shown, where its spherical shape and

9   their internal pore structure is seen. In Figure 1b) the morphology of the milled FCC

10   particles after the 20 minutes milling treatment is observed. Figures c) and d) show the

11   FA particle morphology where its sphericity has been highlighted. Figure 1d) shows a

12   cenosphere (hollow particle) as a result of high temperature combustion, showing

13   spheres inside (plerospheres).

a)   b)

c)   d)
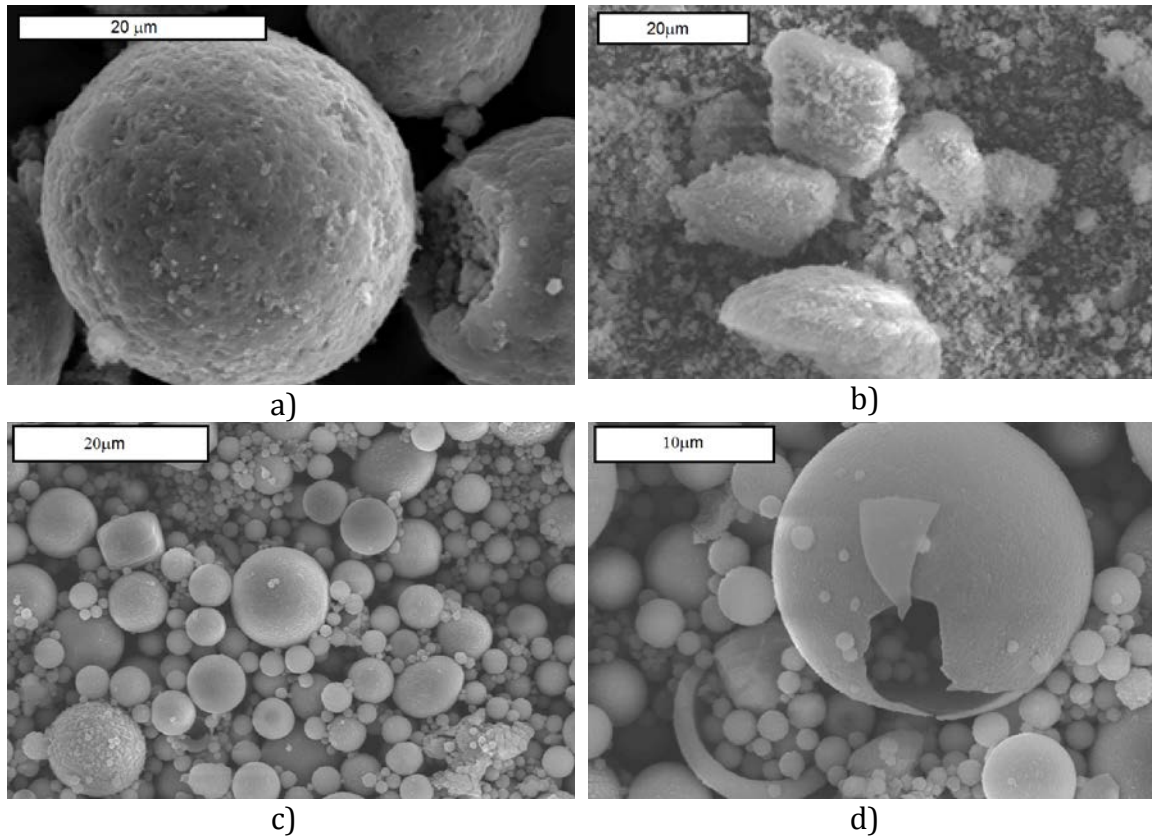
Fig. 1 Scanning electron micrographs of pozzolanic materials (SEM): a) Spherical particles of original FCC; b) Grounded FCC; c) FA general view, d) Detail of FA particles (cenospheres and plerospheres).

For this work 16 pastes were manufactured with different percentages of cement replacement by FCC and FA, which are shown in the ternary diagram of Figure 2. The maximum amount of OPC replacement was 15% and 30% by FCC and FA respectively. The test conditions for the pastes were: curing temperature = 20 °C, water/binder ratio = 0.40 and curing times = 3, 7, 14, 28, 90 and 365 days. The curing times tested were selected in order to study the pozzolanic activity of the FCC at short curing times and that of the FA at longer curing times. Immediately after mixing, the pastes were stored in sealed plastic containers and maintained at 20 °C until the test age. At this time, the samples were pulverized manually in an agate mortar, stopping the hydration with acetone. Finally the samples were dried at 60 ºC for half an hour.

1
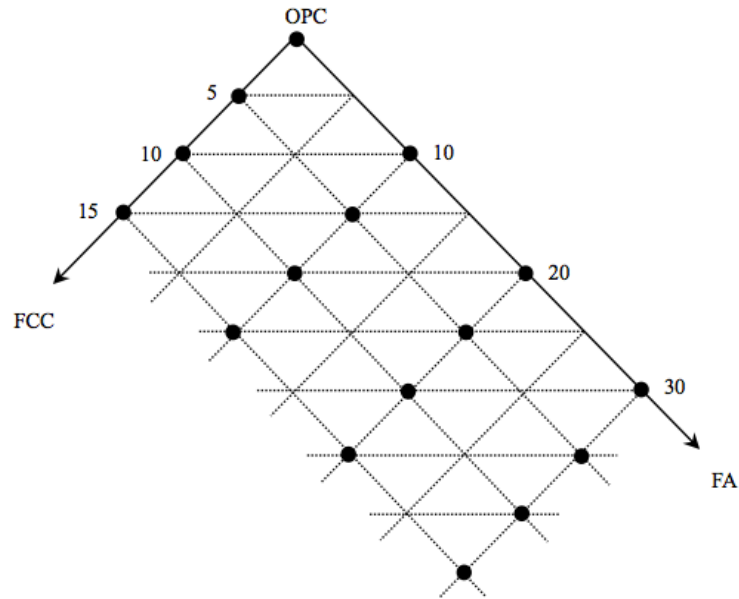
2   **Fig. 2** Detail of the ternary diagram of the different FCC:FA proportions studied (values

3   are given in percentage replacement of Porltland cement; small black circles depict the

4   selected mixtures).

5

6   Electron scanning microscopy micrographs were taken with a JEOL JSM-6300.

7   Mastersizer 2000 from Malvern Instruments was used in the determination of the

8   particle size distribution. The nitrogen adsorption isotherms were performed on a

9   Micromeritics ASAP2010 automated adsorption analyzer. Thermogravimetric analysis

10 (TGA) was performed in a Mettler-Toledo TGA850 module, with a horizontal furnace.

11 TGA is equipped with an ultramicro balance, having a resolution of 0.1 µg. The

12 sealable crucibles utilized were made of aluminum with 100 µL capacity having a

13 pinholed lid to obtain the water vapour self-generated atmosphere. Using this type of

14 crucible, the decomposition temperatures of hydrate products shift to higher

15 temperatures than those found using common alumina or platinum non-sealed crucibles.

1   This allows a better peak resolution when these peaks take place at similar temperature.

2   The gas flow for the surrounding atmosphere was 75 mL/min of nitrogen. The heating

3   rate was 10 ºC/min in the 35-600 ºC temperature range, and the mass of the samples

4   was maintained in the range of 40-45 mg.

5   **3. Results and discussion**

6   **3.1 Particle size distribution**

7   Figure 3 shows the particle size distributions for the FCC and the FA. To study the

8   effect of different proportions of pozzolans on the granulometry, the particle size

9   distributions were analyzed only for the pozzolan mixtures (regardless of the proportion

10   present on cement paste). Therefore, from 16 mix proportions that are shown in Figure

11   2, only 9 FCC:FA proportions were analyzed: 1:0, 1:1, 1:2, 1:3, 1:4, 1:6, 3:2, 3:4 and

12   0:1.
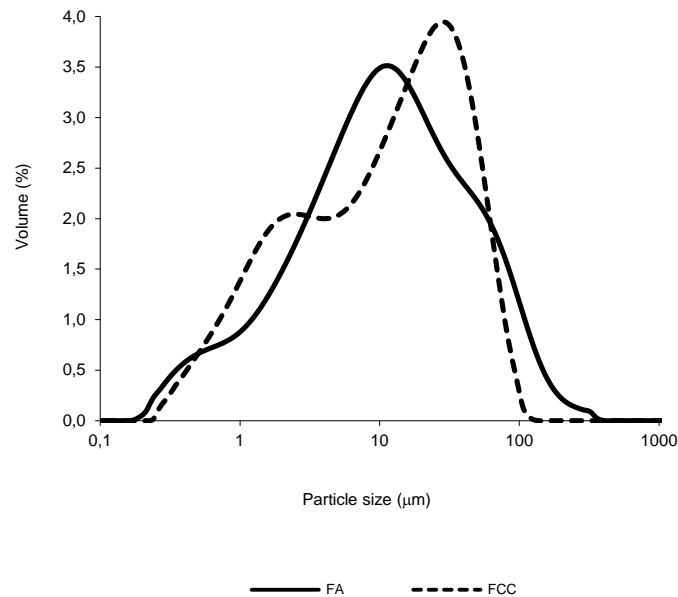
13   **Fig. 3** Particle size distributions for FCC and FA.

14

15   The values of the mean particle diameter (D [4,3]) are shown in Table 2 for the different

16   proportions. In general, an increase in the mean particle diameter was observed when

the FA proportion also increases, as expected, since FA has a mean particle diameter greater than the FCC (25.40 and 19.95 μm respectively). To facilitate the analysis of such data, in the same Table 2 are tabulated the volume percentages of the fractions within the following ranges: d (diameter)<10 μm, 10 μm≤d<45 μm, 45 μm≤d<100 μm, d≥100 μm. It is observed that the fraction including the particles with diameters less than 10 μm and the fraction 45 μm≤d<100 μm not show a definite trend. The other fractions do show a clear trend. The fraction comprising the diameters between 10 and 45 μm decreases with increasing the content of FA. And the fraction including diameters larger than 100 μm clearly increases by decreasing the FCC content.

Table 2 Mean particle diameters and percentages of volume fractions between the indicated diameters for the FCC:FA mix proportions studied.

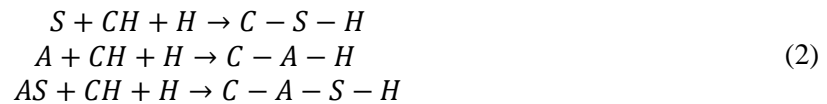| FCC:FA	D[4,3]μm	d<10μm	10μm≤d<45μm	45μm≤d<100μm	d≥100μm
1:0	19.95	44.50	42.74	12.42	0.35
3:2	21.90	43.07	41.91	13.65	1.36
1:1	21.85	43.09	41.95	13.60	1.35
3:4	22.07	43.82	41.22	13.06	1.88
1:2	24.92	43.47	40.20	13.13	3.21
1:3	24.36	43.39	40.14	12.68	3.79
1:4	24.49	43.80	39.83	12.77	3.60
1:6	25.97	43.68	39.32	12.70	4.30
0:1	25.40	45.80	37.20	12.34	4.67

It was carried out a linear correlation between the D [4,3] and the percentage of FCC present in the mix, the resulting equation was:

$$D[4,3](\mu m) = -0.06\% FCC + 25.88 \qquad (R = 0.93) \qquad (1)$$

1   where it can be appreciated that the correlation factor R is acceptable. In general, it can

2   be said that almost all mixes have similar granulometries; therefore the effect of the

3   fineness of the materials used will not have a determining influence regarding the

4   specific surface and the pozzolanic reactivity.

5   **3.2. Percentage of fixed lime**

6   When mixing a pozzolan containing silicates (S = SiO_2), aluminates (A = Al_2O_3), and /

7   or aluminosilicates (AS) with lime (CH = Ca $(OH)_2$) and water (H), the hydration

8   reactions that occur are:

$$
\begin{aligned}
S + CH + H &\to C - S - H \\
A + CH + H &\to C - A - H \\
AS + CH + H &\to C - A - S - H
\end{aligned}
\qquad (2)
$$

9

10   where C-S-H, C-A-H and C-A-S-H are calcium silicate hydrates, calcium aluminate

11   hydrates and calcium aluminosilicate hydrates respectively. The CH that the pozzolan

12   needs to react according to equation (2) is generated in the hydration reaction of OPC,

13   mainly from hydration of tricalcium silicate (C_3S) and dicalcium silicate (C_2S).

14   Therefore, the term "fixed lime" refers to the amount of CH that has reacted with the

15   pozzolan to generate hydration products.

16   Before performing the study by thermogravimetry, micrographs by scanning electron

17   microscopy (SEM) were taken in order to qualitatively analyze the hydration products

18   of the pozzolanic reactions, with spent catalyst and fly ash. To make these products be

19   more easy to detect, hydrated lime pastes (CH= hydrated lime) were prepared with a

20   ratio FCC:FA:CH (1:1:3). This proportion was decided given that Payá et al. [20]

21   reported lime fixations of 27 and 65 % for pastes with proportions FCC:CH (1:9) and

22   (3:7) respectively, cured at 28 days. With these percentages of fixed lime it can be

23   assume that would exist remaining hydrated lime for the slower pozzolanic reaction for

1   FA. Furthermore, to accelerate the pozzolanic reaction, the FCC:FA:CH paste was

2   cured at a temperature of 40 °C. It was decided to use a water / binder ratio of 0.80, to

3   have a paste with suitable fluidity to facilitate hydration and, additionally high porosity,

4   which allows easy identification of the pozzolanic reaction products. Figure 4 shows

5   micrographs obtained at 14 (Figures 4a and 4b) and 28 curing days (Figures 4c and 4d).

6   It can be appreciated in general terms of the 4 micrographs, typical hexagonal crystals

7   of hydrated gehlenite [20] (Strätlingite, $Ca_2Al_2SiO_7.8H_2O = C_2ASH_8$). Furthermore

8   some spherical particles of FA coated with hydration products are observed. In Figure

9   4a) a large hollow FA particle (cenosphere) is observed with plerospheres inside. A

10   smaller FA particle is also observed in the center of the micrograph. All these particles

11   show pozzolanic reaction products of the FA. These products are observed more clearly

12   in Figure 4b), where besides the hydrated gehlenite and a cenosphere, like cube particles

13   are observed that can be associated either to C_3AH_6 (that can be more readily formed at

14   high temperatures and with a high lime-alumina ratio) or to hydrogarnet ($C_3AS_3H_{2x}$)

15   [21]. This is also identified at 28 days of curing (Figure 4c), wherein a cenosphere with

16   these hydration products are observed. Finally, Figure 4d) shows clearly the pozzolanic

17   reaction on a FA particle, which is highly coated with hydration products.
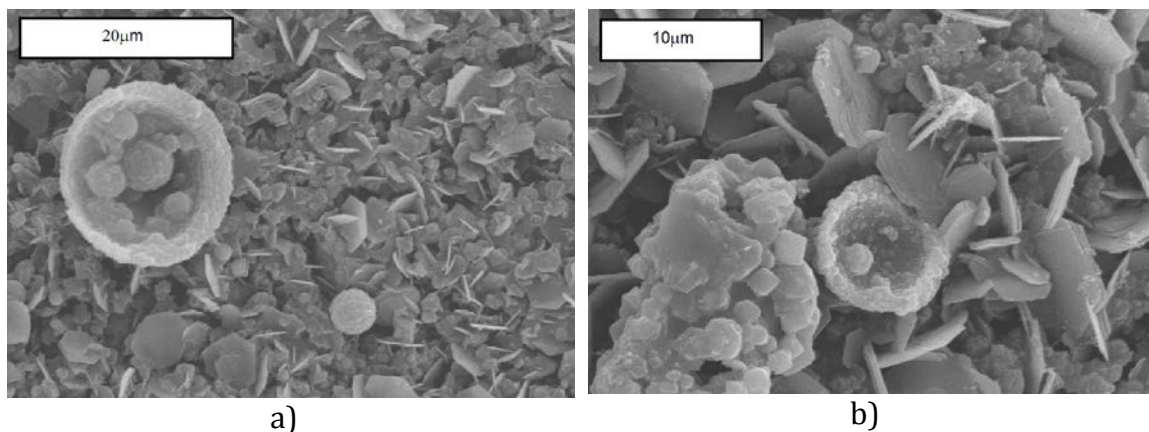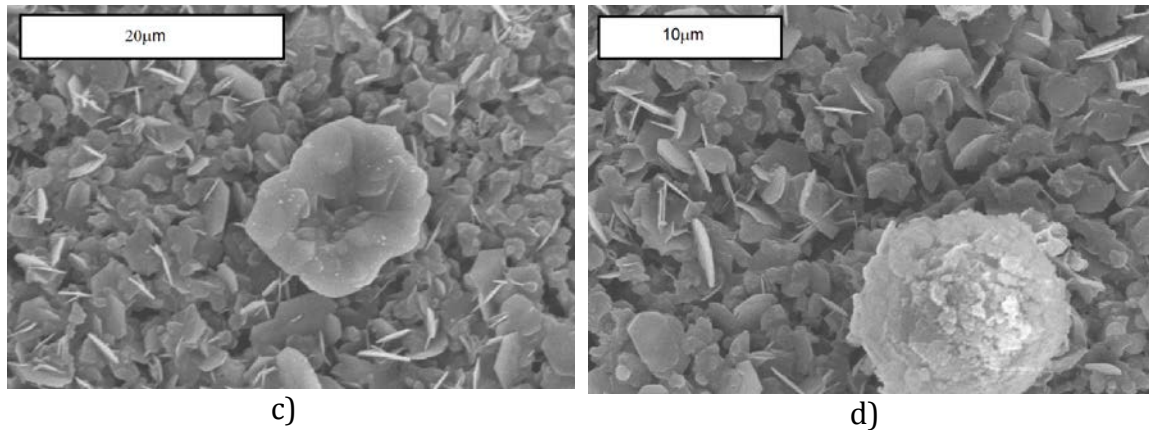
18

a)   b)

| c) | d) |

4

5   Once determined by SEM in hydrated lime pastes that the hydration products of the

6   pozzolanic reactions of both the FCC and the FA were generated, the study of

7   thermogravimetry in cement pastes was conducted to determine the percentages of fixed

8   lime. As an example, some differential TGA curves (DTG) of these pastes are shown in

9   Figure 5. In Figure 5a) there are shown the DTG curves of pastes with an age of 3 days

10 of curing, whereas in Figure 5b) are shown the corresponding ones after a year of curing

11 time. For comparison the following DTG curves were chosen: the control paste (without

12 pozzolan), the pastes containing only one pozzolan at maximum replacement (15 % for

13 FCC, 30 % for FA), and the paste with a content of each pozzolan (FCC:FA equal to

14 10:10, 20 % total replacement). The discussion of the area corresponding to the peak of

15 calcium hydroxide decomposition (hydrated lime, CH, 520-580 ºC) will be analyzed in

16 terms of percentage of fixed lime. Most notable in both curing times is the increase of

17 the peak corresponding to the dehydration of calcium aluminate hydrates and calcium

18 aluminosilicate hydrates (C-A-H and C-A-S-H) (peak in the range of 180-220 °C) with

1 increasing the amount of FCC in the paste. However, the presence of FA apparently not

2 seems to modify the types of hydrates obtained in the cement replaced pastes.

a)   b)
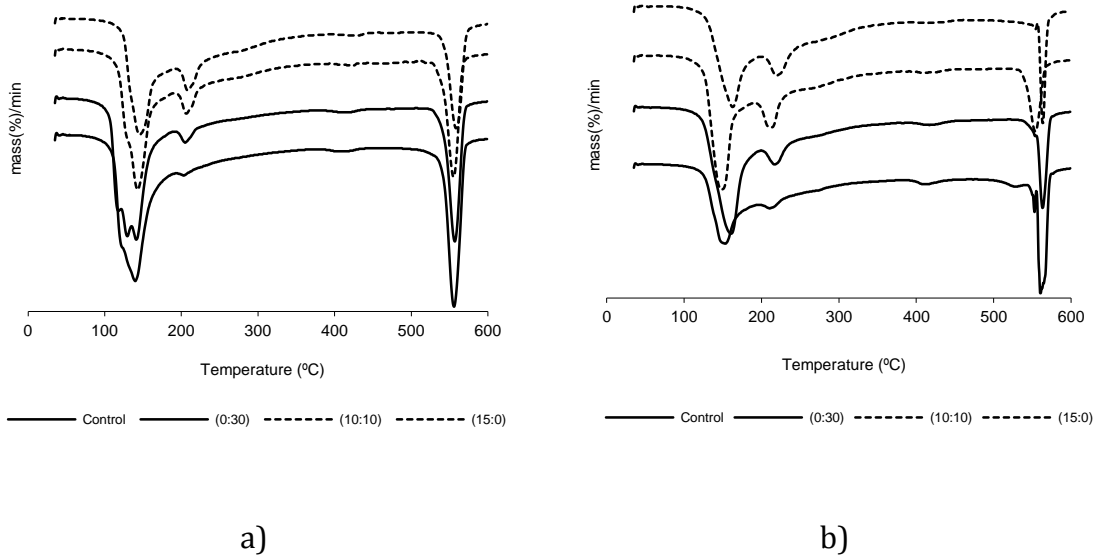
3 **Fig. 5** DTG curves for cement pastes with different replacements of FCC:FA (wt %). a)

4 3 days curing time; b) 365 days curing time.

5

6 Based on mass losses corresponding to the decomposition of calcium hydroxide,

7 percentages of fixed lime were calculated for each sample according to the following

8 equation [6]:

$$\%Fixed\ lime\ =\ \frac{\left[(CH)_c * C_\%\right] - (CH)_i}{\left[(CH)_c * C_\%\right]} * 100 \tag{3}$$

9 where $(CH)_c$ is the calcium hydroxide present in the control paste for a given curing

10 time, $(CH)_i$ is the amount of calcium hydroxide in the paste with the pozzolan/pozzolans

11 at the same curing time, and $C_\%$ is the proportion of cement present in the substituted

12 paste (e.g.: $C_\%$ is equal to 0.7 for 30% replacement percentage).

13 Table 3 shows the percentage values of fixed lime for all mixes studied as a function of

14 curing time (See supplementary material for the description of physical meaning of each

15 term of equation (3), and a calculation example).

1   It can be observed the following:

2   ✓ Negative values of fixed lime can be obtained when pozzolan particles

3   accelerated the hydration of OPC acting as nucleation sites (called particle

4   effect) for the precipitation of hydrated compounds. This produces that a great

5   amount of CH is present in the pozzolan-OPC system, relatively compared to

6   the control sample (plain OPC). For our study, these negative values were

7   obtained at short curing times, and for replacements of 0 and 5 % of Portland

8   cement by FCC, containing FA (it can be noticed that for the replacement of

9   FCC:FA (5:0) no negative values were obtained). This behaviour indicates the

10 contribution of the FA to the cement hydration reactions, as was reported by

11 Amahjour [16] (this behaviour was also reported when Metakaolin is used in a

12 OPC-pozzolan system, [6]). For pastes without FCC, the values are negative

13 until 28 days of curing time, and for pastes with 5 % FCC until 7 days. This

14 confirms the great difference in reactivity at short curing times of both

15 pozzolans.

16 ✓ The percentage values of fixed lime are positive for mixes with 10 and 15 % of

17 FCC, suggesting that the pozzolanic reaction at short curing times of the FCC

18 counteracts the effect of accelerating the cement hydration provoked by the FA.

19 ✓ In general, percentages of fixed lime increase when the curing times also

20 increase. Percentages of fixed lime are higher, as a higher percentage of FCC is

21 present in the paste.

22 ✓ The maximum percentage value of fixed lime tends to high replacement values

23 of FCC:FA and long curing ages. This indicates the contribution of both

24 pozzolans, the FCC at short curing times and the FA to longer times.

25

1

2 **Table 3** Percentages of fixed lime for cement pastes with replacements of FCC:FA.

FCC (%)	FA (%)	Curing time (days)					
		3	7	14	28	90	365
		Fixed lime (%)					
0	10	-9.32	-10.52	1.93	-2.41	3.19	15.90
	20	-15.59	-15.99	-8.78	-5.67	14.40	31.59
	30	-17.53	-20.57	-9.35	-6.43	15.46	28.49
5	0	7.40	4.04	16.69	5.13	11.85	15.82
	10	-1.80	-1.50	9.45	6.86	12.22	15.77
	20	-2.07	-7.21	3.14	7.69	21.87	32.45
	30	-11.69	-11.02	10.50	16.67	28.71	37.00
10	0	16.52	11.84	22.20	23.96	25.07	32.62
	10	13.90	10.83	20.27	18.22	27.31	37.43
	20	7.21	7.15	24.22	22.45	36.12	48.07
	30	9.95	5.11	27.88	39.03	43.09	59.21
15	0	27.68	20.10	31.47	38.28	41.34	53.91
	10	19.50	23.82	37.14	42.81	60.92	75.98
	20	21.85	24.85	44.87	47.76	55.02	73.10
	30	26.47	29.95	50.39	64.69	75.07	89.53

3

4 Values of reacted hydrated lime (R_{HL}) per gram of pozzolan for ages 28, 90 and 365

5 days were calculated according to the following equation [13]:

6

$$\Psi = \frac{R_{HL}}{g\ Pozzolan} = \frac{[(CH)_c * C_\%] - (CH)_i}{(1 - C_\%) * 100} \quad\quad (4)$$

1   These values are summarized in Table 4. It can be seen that higher $\boldsymbol{\Psi}$ values correspond

2   logically to systems without FA, because FCC is much more reactive.

3

4   **Table 4** Reacted hydrated lime (R_{HL}) per gram of pozzolan (Ψ, g/g), and grams of (R_{HL})

5   per 100 grams of hydrated paste.

FCC	FA	Curing time (days)					
		28	90	365	28	90	365
(%)	(%)	(R_{HL})/Pozzolan (Ψ, g/g)			(R_{HL})/100 g hydrated paste (g/g)		
5	0	0.11	0.23	0.32	0.55	1.18	1.62
	10	0.04	0.07	0.10	0.66	1.09	1.45
	20	0.03	0.07	0.10	0.66	1.71	2.63
	30	0.03	0.05	0.07	1.22	1.95	2.60
10	0	0.24	0.24	0.32	1.22	1.18	3.17
	10	0.08	0.11	0.16	1.23	1.71	3.23
	20	0.06	0.09	0.12	1.48	2.20	3.63
	30	0.07	0.07	0.10	2.31	2.36	3.83
15	0	0.24	0.24	0.33	1.22	1.22	4.95
	10	0.14	0.19	0.25	2.17	2.87	6.15
	20	0.10	0.11	0.15	2.50	2.67	5.13
	30	0.09	0.10	0.12	3.12	3.36	5.31

6

1   However, if the amount of R_{HL} per 100 grams of hydrated paste is calculated (Table 4),

2   the contribution of FA to fixing lime can be observed. For example, at 365 days of

3   curing time, the paste with 10 % FCC- 0 % FA has an amount of fixed lime of 3.17 g,

4   while for the paste with 10% FCC-30% FA that value is higher (3.83 g). The difference

5   between the two values considers the contribution of fly ash to the lime fixation. In the

6   paste with 15 % FCC-0 % FA, the value is 4.95 g, while for the paste with 15 % FCC-

7   10 % FA is 6.15 g.

8   In the Figure 6, evolutions of amount of R_{HL} per gram of pozzolan (Ψ, g/g) for several

9   mixes are depicted. For mixes containing 30 % of FA (Figure 6a) one can observe that

10   for sample for the highest percentage of FCC (15 %) the Ψ value is very high for early

11   age, however for the sample without FCC, a slow increasing with curing time is

12   observed (negative values for Ψ appeared for early curing times because the effect of

13   FA particles on the hydration of OPC). In Figure 6b, Ψ values for samples with 15 %

14   FCC, varying the percentage of FA are depicted. In this case, Ψ values increased

15   notably for samples with less amount of FA, due to the high reactivity of FCC.

16

a)   b)
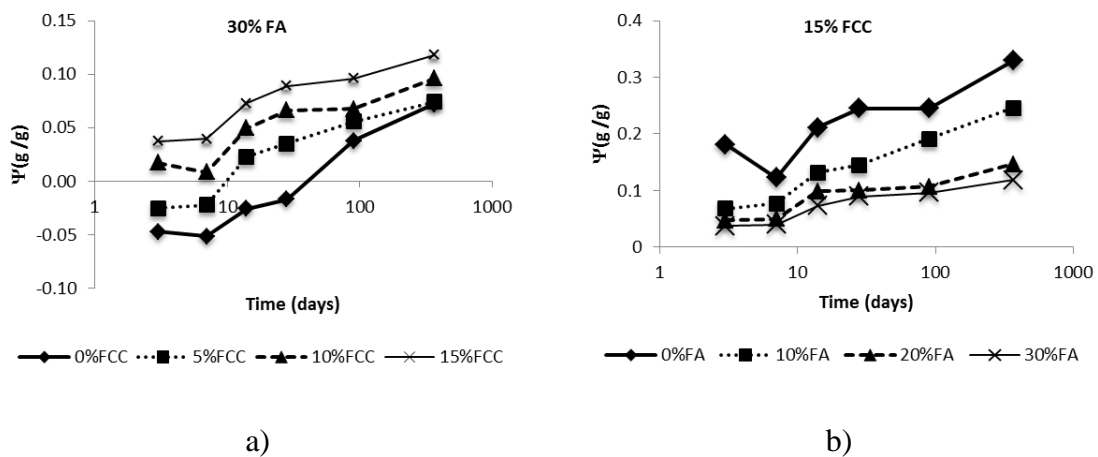
17   **Fig. 6** Evolution with curing time of grammes of reacted hydrated lime per gramme of

18   pozzolan (Ψ): a) 30 % of FA, variation of % FCC; b) 15 %of FCC, variation of % FA

1   **3.3. Combined water as hydration products**

2   There is a continuous mass loss throughout the temperature range of the

3   thermogravimetric analysis, which is associated with the water incorporated into the

4   hydration products present in the paste. Subtracting the water of portlandite

5   dehydroxylation to this total loss (peak in the range 520-580 ºC, see Figure 5), a

6   measure of the combined water of hydrates formed in the hydration reactions of cement

7   and pozzolanic reaction is obtained [22], that is:

8

$$\%(H)_c = P_T - H \tag{5}$$

9

10   where:

11   P_T: total mass loss of thermogravimetric analysis

12   H: water loss related to portlandite dehydroxylation

13    $\%(H)_c$: percentage of combined water into the hydration products.

14    $\%(H)_c$ was correlated with the percentage of replacement of each pozzolan, as well as

15   the joint contribution of both pozzolans. The correlation obtained was:

16

$$\% H_c = a + b \cdot \% FCC + c \cdot \% FA + d \cdot \% FCC \cdot \% FA \tag{6}$$

17

18   with an mean relative error calculated as:

$$e_{rm}(\%) = \frac{\sum_{i=1}^{n} \left(\frac{\left| \% H_{c,calculated} - \% H_{c,experimental} \right|}{\% H_{c,experimental}} \right)_i}{n} 100 \tag{7}$$

19

1   The parameters of the equations and mean relative errors obtained are tabulated in Table

2   5. It can be observed that the mean relative error is quite low (<3.51 %). As the term of

3   the coefficient d is affected by the product of the percentages of both pozzolans, three

4   decimal places were allowed for that parameter. Note that the parameter values d are

5   quite similar, except for the value on the seventh day, which is much higher, and for the

6   value at one year, which tends to be null. Regarding the influence of the FCC term

7   (parameter b), it can be observed that is the one that has the greatest effect on the

8      $\%(H)_c$. This can be stated because all values are positive, very similar (except for the

9   first value, at three days, which is negative; and for the value at one year, which is null).

10   The parameter values of % FA (parameter c) are negative or zero (in fact the only

11   positive value is at 90 days, but it is only noticeable with three significant digits),

12   therefore, compared to FCC, the influence of FA is null. Finally it can be concluded that

13   since the values of $\%(H)_c$ remain fairly constants, the correlation given by the control

14   (parameter a) is quite acceptable, being only slightly corrected by the percentage of

15   replacement of FCC.

16

17   **Table 5** Parameters for the $\%Hc$ correlations (equations 6 and 7).

Time (days)	a	b	c	d	e_{rm}
3	14.09	-0.01	-0.03	0.002	2.71
7	13.88	0.23	0.00	-0.007	3.51
14	14.70	0.09	-0.01	0.001	2.54
28	15.41	0.13	-0.02	0.002	1.53
90	14.92	0.19	0.00	0.003	1.51
365	17.26	0.00	-0.03	0.000	1.64

1   To study the effect of curing time, a single correlation with all data including a new

2   parameter that takes into account the curing time (t) was obtained. The equation

3   obtained was:

4

$$\% H_c = \alpha + \beta * \% FCC + \gamma * \% FA + \delta * \% FCC * \% FA + \tau * t = \\ 14.57 + 0.14 \cdot \% FCC + 0.00 \cdot \% FA - 0.005 \cdot \% FCC \cdot \% FA + 0.005 \cdot t \qquad (8)$$

5

6   This correlation has a mean relative error of 5.64 %. It is noted again that the FA (γ

7   term) does not affect the $\%(H)_c$; and that the mixed term and the term (δ) of the curing

8   time (τ) have a slight influence. Given the low values obtained for the coefficient δ, it

9   was decided to adjust equation 6, eliminating this coefficient. The parameter values for

10   these new correlations and their mean relative error are tabulated in Table 6. In general,

11   it can be seen how the trends discussed previously are similar in these new correlations.

12   The mean relative errors remain quite low, gaining in simplicity of the equations by

13   eliminating the term of the joint contribution.

14   **Table 6** Parameters for the *%Hc* correlations (equations 6 and 7) eliminating parameter

15   d.

Time (days)	a	b	c	e_{rm}
3	14.32	-0.03	-0.06	2.93
7	15.14	0.07	-0.05	4.64
14	14.92	0.08	-0.02	2.63
28	15.69	0.10	-0.04	1.75
90	15.28	0.13	-0.01	1.80
365	17.32	0.00	-0.03	1.75

1   Again, a single correlation was obtained including the curing time but eliminating the

2   term of the joint contribution (eliminating the fourth term, δ, of Equation 8) to obtain

3   the following expression:

4

$$\% H_c = 14.84 + 0.08 \cdot \% FCC - 0.02 \cdot \% FA + 0.005 \cdot t \tag{9}$$

5

6   This correlation has a mean relative error of 5.85 %, slightly higher than the correlation

7   of equation 7 (5.64 %), which is still very acceptable.

8

9   **4. Conclusions**

10   The main conclusions of this paper can be summarized as:

11   1. The increase in the proportion of FA in the FCC:FA mixture increases the

12   mean diameter slightly. A correlation for the D [4,3] and the % FCC was

13   obtained, with an acceptable correlation factor.

14   2. SEM reveals the products of the pozzolanic reaction, being those reported

15   for FCC pastes. Also FA particles with pozzolanic reaction products and

16   cubic crystals with possible assignment of C_3AH_6 and/or hydrogarnet were

17   observed.

18   3. By thermogravimetric analysis an increasing of the peak intensity of the C-

19   A-H and C-A-S-H when the% FCC is increased in the paste was observed.

20   The increasing of the FA proportion does not modify the hydrate types

21   obtained in cement pastes.

22   4. In pastes with FA or with low percentages of FCC, there is a notable

23   acceleration of hydration of Portland cement, leading to negative values of

24   fixed lime at early curing ages.

5. The maximum percentage of fixed lime is obtained with high replacements of FCC-FA and long curing times, indicating the contribution of both pozzolans, FCC at shorter times and FA to longer times.

6. A linear correlation for the percentage of combined water into hydration products as a function of the % FCC, % FA and curing time was obtained, with an acceptable error.

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4 **Supplemental Material**

5

6 This supplementary material describes the physical meaning of each term of equation

7 (3), and also a calculation example is given. For the calculation example, data from the

8 control paste (100% OPC) and from the paste with the following proportion OPC-FA-

9 FCC 55%-30%-15%, were used (both at 365 days of curing time).

10 By means of thermogravimetry, the percentage of water corresponding to the

11 dehydroxylation of $Ca(OH)_2$ is obtained from the peak observed in the range of 520-

12 580°C (see Figure 5).

13 For the control paste selected for the calculation example, this percentage was 2.62%.

14 Let us call it %H.

15 With this percentage (%H), the percentage of $Ca(OH)_2$ produced (portlandite) by the

16 hydration of cement in the control paste can be calculated. This percentage was defined

17 in the paper as *(CH)c*. The calculation is:

$$\%Ca(OH)_2 = (CH)_c = (\%H)\frac{\left(MW_{Ca(OH)_2}\right)}{\left(MW_{H_2O}\right)} = (2.62)\frac{74.082}{18.008} = 10.79\%$$

18 In the same way, for the paste with the pozzolans replacement, the %H obtained by

19 thermogravimetry was 0.15. With this percentage, the percentage of $Ca(OH)_2$ present in

20 this paste can be calculated. This percentage corresponds to the portlandite produced by

21 the hydration of cement present and that was not consumed by the pozzolans at this

22 curing age. This was defined as *(CH)i* in the paper. The calculation is:

$$\%Ca(OH)_2 = (CH)_i = (\%H)\frac{\left(MW_{Ca(OH)_2}\right)}{\left(MW_{H_2O}\right)} = (0.15)\frac{74.082}{18.008} = 0.62\%$$

1   The amount of Ca(OH)$_2$ which have reacted with the pozzolans should be calculated

2   taking into account the lower amount (respect to the control paste) in cement present in

3   the paste due to the cement replacement by the pozzolans. The cement content that was

4   defined in the paper as $C_\%$ can be calculated from the dosage of the paste. For this

5   example, the proportion of cement is calculated as (fraction):

$$C_\% = \frac{100 - \%FCC - \%FA}{100} = \frac{100 - 15 - 30}{100} = 0.55$$

6   The percentage of Ca(OH)$_2$ that must be generated in the paste with the pozzolans

7   replacement, if the pozzolans had not reacted (acting as inert) is calculated as:

$$(CH)_c \cdot C_\% = (10.79)(0.55) = 5.94\%$$

8   To this percentage of Ca(OH)$_2$ that generates the Portland cement hydration, we

9   subtract the percentage of Ca(OH)$_2$ actually present in the pozzolan paste (*(CH)i*), then

10   we obtain the calcium hydroxide consumed by the pozzolans due to pozzolanic reaction,

11   this is:

$$[(CH)_c \cdot C_\%] - (CH)_i = 5.94\% - 0.62\% = 5.32\%$$

12   Finally, to obtain this data related to Ca(OH)$_2$ that should be in the pozzolans containing

13   paste, if pozzolans had not reacted, and multiplying by 100 to have it in percentage, the

14   expression given in the paper as equation (3) is obtained. This was defined as

15   percentage of Fixed lime:

$$\%Fixed\ lime = \frac{[(CH)_c \cdot C_\%] - (CH)_i}{[(CH)_c \cdot C_\%]} 100 = \frac{5.32\%}{5.94\%} 100 = 89.53\%$$

16   This value was reported in Table 3 in the paper in the curing time indicated in this

17   example.

18

19

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