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Determination of the pozzolanic activity of fluid catalytic cracking residue. Thermogravimetric analysis studies on FC3R–lime pastes

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Abstract

Spent fluid catalytic cracking catalyst (FC3R) from a petrol refinery played a pozzolanic role in portland cement system as revealed by previous experimental data. In the present study, the pozzolanic activity of FC3R was investigated by means thermogravimetry (TG) of cured lime–FC3R pastes. The influence of pozzolan/lime ratio on the pozzolanic activity was investigated. Due to the chemical composition of FC3R is similar to metakaolin (MK), and knowing that MK has a high pozzolanic activity, the latter was used as a material of comparison in this study. The scope of the study is the determination of the pozzolanic activity of FC3R and the evaluation of amount and nature of pozzolanic products. The products obtained from the reaction between FC3R components (SiO_2/Al_2O_3) and calcium hydroxide (CH) have been characterized, finding that the main pozzolanic reaction product was similar to hydrated gehlenite (calcium aluminosilicate hydrate) CSH and CAH were also formed in the reaction. FC3R showed higher pozzolanic reactivity than metakaolin, for low-lime content pastes and early curing age. Thermogravimetry, Fourier transform infrared (FTIR) spectroscopy and scanning electron microscopy (SEM) became very useful techniques for evaluation of reactivity.

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Keywords: Hydration products; Metakaolin; Pozzolan; Spent fluid cracking catalyst; Thermal analysis

1. Introduction

Because of the incessant generation of solid waste materials, more and more new technologies are necessary to be developed to help us exploit them. In the cement and concrete industry, the use of waste materials is a widely practice whenever they maintain or, even better, add value to one or more of the goal properties of the final product.

One of the desired products is a pozzolanic material; it means that the material reacts with the calcium hydroxide (CH) produced in the hydration of the portland cement to generate calcium silicate hydrates (CSH), calcium aluminate hydrates (CAH) and/or calcium aluminosilicate hydrates (CASH). These hydrates are the principal components responsible of the increase of the mechanical strength in the cement paste.

In a petrol refinery, several types of waste materials are generated; one of them is a catalyst used in the cracking of naphtha in a fluidised bed process, the spent fluid catalytic cracking catalyst (FC3R). This catalyst is an inorganic aluminosilica material with a high specific surface area (zeolite type), a property that could be responsible for high pozzolanic activity. Escardino et al. [1] had studied the application of the FC3R as a substitute for kaolin in the industry of ceramic frits with very good results. A few recent studies of FC3R showed the excellent characteristics for improving compressive strength on portland cement pastes and mortars and concrete [2–4].

The aim of this work is, firstly, to compare the pozzolanic activity of the FC3R with respect to another artificial pozzolan, metakaolin (MK),which has a similar chemical composition and high pozzolanic activity, secondly, to establish the influence of the pozzolan/lime ratio on the pozzolanic activity, and finally, to determine the kind of calcium hydrates produced in the pozzolanic reaction towards lime.

2. Experimental

The petrol refinery which supplied the FC3R was BP OIL España (Castellón, Spain). With the aid of a laboratory ball

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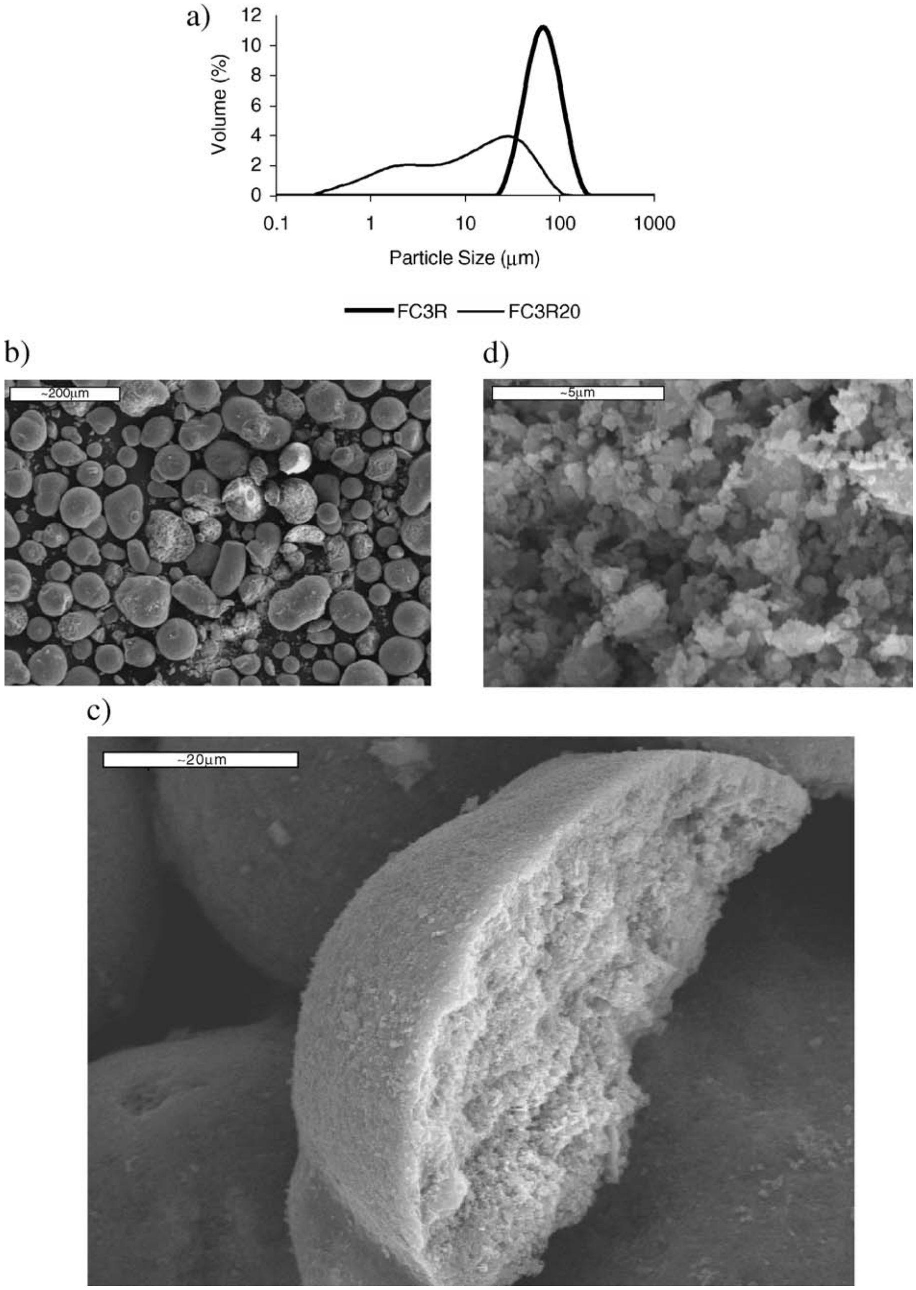

Fig. 1. (a) Particle size distribution for FC3R and FC3R after 20 min of grinding (FC3R20); (b) Scanning electron microphotographs (SEM) showing a general view of FC3R, (c) SEM of a detail of FC3R showing internal porous structure; (d) SEM of a ground FC3R20.

mill (Gabbrielli Mill-2), the reactivity of the catalyst was increased to the optimum particle size distribution, which was obtained after 20 min of grinding [2]. Fig. 1a shows the particle size distribution of the catalyst before and after grinding. In Fig. 1b–d, the particle morphologies of these materials are shown.

Table 1
Chemical composition (%)

Material	SiO_2	CaO	Al_2O_3	Fe_2O_3	MgO	Na_2O	K_2O	SO_3	LOI
FC3R [3]	48.2	< 0.01	46.0	0.95	< 0.01	0.50	< 0.01	0.04	1.50
MK [5]	52.1	0.07	41.0	4.32	0.19	0.26	0.63	–	0.6

In the preparation of the lime pastes, a general purpose laboratory reagent calcium hydroxide with a 96% purity (Riedel-deHaën) was used. The MK was a commercial product from Metastar. Chemical compositions for FC3R and MK are given in Table 1.

Table 2
Mix formulations

Pozzolan	Curing temperature (°C)	Water/ lime ratio	Pozzolan/ lime ratio	Curing time (days)
FCC20 MK	20	1	1:9, 3:7, 7:3 and 9:1	3, 7, 14 and 28

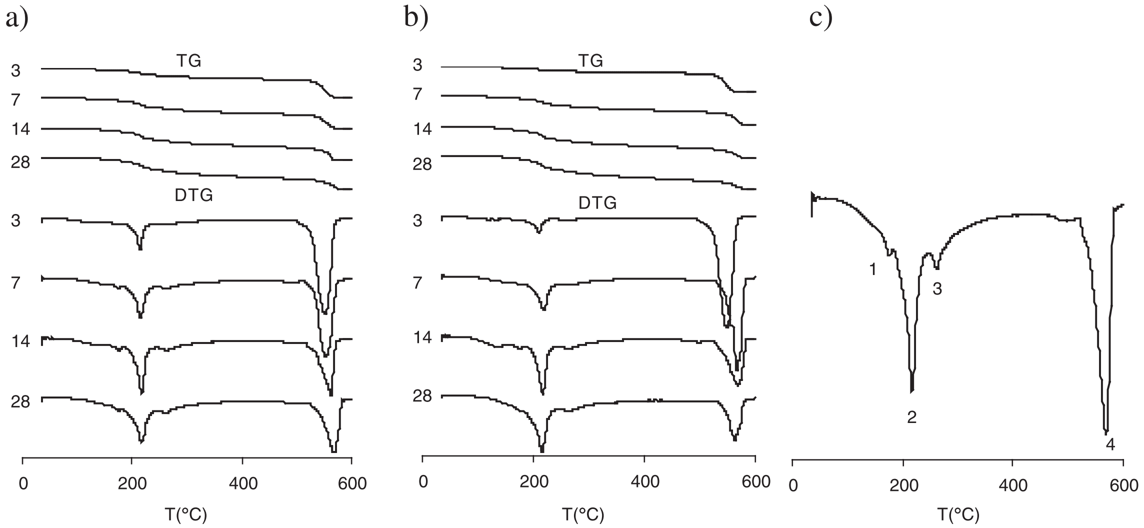

Fig. 2. TG and DTG curves for pozzolan/lime pastes. (a) FC3R, (b) MK. Pozzolan/lime ratio = 3:7. Curing time evolution (days). (c) Detail of a typical DTG curve.

The mix formulations prepared in this study are listed in Table 2. After mixing, the pastes were stored in sealed plastic bottles and then left in a curing room at 20 °C until the day of testing; then, they were pulverized by manual grinding in an agate mortar, the hydration was stopped with acetone and samples were dried at 60 °C for half an hour.

The spent catalyst (raw material and ground) and the products of hydration were observed by scanning electron microscopy (SEM) using a JEOL JSM-6300, equipped with energy-disperse X-ray for microanalysis.

Thermogravimetric analysis (TGA) was performed in a Mettler-Toledo TGA850, with a horizontal furnace. It has an ultramicrobalance with a resolution of 0.1 mg. Aluminium crucibles of 100 μl were used, having a lid with pinhole to obtain the self-generated atmosphere. The gas flow for the surrounding atmosphere was 75 ml/min of nitrogen. The heating rate was 10 °C/min in the 35–600 °C temperature range. The mass of the sample for thermogravimetric analysis was in the 40–45-mg range.

Fourier transform infrared (FTIR) spectrophotometric qualitative studies were performed in a Mattson Genesis II FTIR in the range of 400–4000 cm^{-1}.

3. Results and discussion

3.1. Thermal analysis studies in lime/pozzolan pastes

In Fig. 2a and b, the thermal analysis curves, thermogravimetric (TG) and its first derivate (DTG), for the FC3R–lime pastes and MK–lime pastes for 3–28 days of curing time are respectively represented. The selected pozzolan/lime ratio showed in Fig. 2 was 3:7, because this is the ratio where the lime consumption is better appreciated, since the pastes with lime-deficient ratios reach the 100% lime fixation before the 28 days of curing time. Four main zones can be identified [6], and additionally, a continuous and overlapped weight loss was observed over the 100–600 °C range. For a better zone appreciation, in Fig. 2c, a typical DTG curve is shown,

Table 3
Total weight loss (100–600 °C) and zone 4 weight loss (520–580 °C)

Pozzolan	Pozzolan/ lime ratio	Curing time (days)							
		3		7		14		28	
		Total weight loss (%)	Zone 4 (%)	Total weight loss (%)	Zone 4 (%)	Total weight loss (%)	Zone 4 (%)	Total weight loss (%)	Zone 4 (%)
FC3R	9:1	8.04	0.00	7.75	0.00	8.91	0.00	8.91	0.00
	7:3	13.28	1.10	15.14	0.21	18.68	0.00	18.08	0.00
	3:7	19.26	10.86	20.31	8.29	21.44	6.96	20.98	5.30
	1:9	21.79	17.83	21.52	16.14	21.99	14.28	21.94	14.26
MK	9:1	4.16	0.48	5.31	0.00	7.45	0.00	6.55	0.00
	7:3	9.00	3.05	10.49	0.91	19.18	0.00	16.54	0.00
	3:7	17.45	11.89	19.69	7.90	21.81	5.22	21.90	3.56
	1:9	21.14	18.04	21.63	15.45	23.10	13.94	22.51	13.58

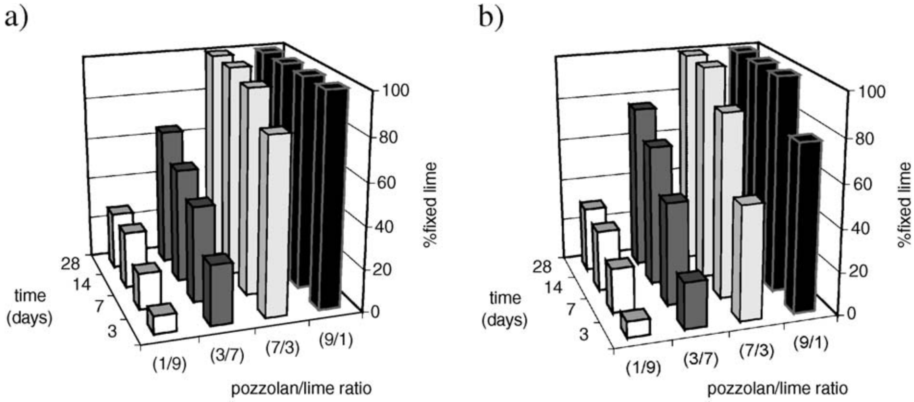

Fig. 3. Percent fixed lime. Influence of curing time (days) for all pozzolan/lime ratios studied. (a) FC3R, (b) MK.

since these curves are similar for both pozzolans. Zone 1 between 100 and 180 °C was attributed to the dehydration of CSH. Zone 2 includes from 180 to 240 °C, characterizing the decomposition of CASH and CAH (peak lying from 200 to 215 °C). The zone 3, ranging in 240–300 °C, must be an aluminate or aluminosilicate hydrate of different composition than the one observed in zone 2. Finally, the zone 4 (520–580°C) was attributed to the dehydroxylation of calcium hydroxide. As it can be appreciated, the main reaction products of both pozzolans are similar.

In Table 3, the total zone 4 weight losses are listed for all pozzolan/lime ratios. These last values were obtained by integration of the peaks on DTG curve, whereas total weight loss was evaluated by the difference in the sample weight between 100 and 600 °C.

Because one of the objectives of this work was to compare the pozzolanic activity of the FC3R with respect to the MK, the weight loss of the zone 4 was used to compute the % fixed lime as follows (Eq. 1):

$$\text{Fixed lime (\%)} = \frac{(\mathrm{CH})_0 - (\mathrm{CH})_\mathrm{P}}{(\mathrm{CH})_0} \times 100 \qquad (1)$$

where $(\mathrm{CH})_0$ is the initial amount of CH in the lime/pozzolan paste and $(\mathrm{CH})_\mathrm{P}$ is the amount of CH in the paste for a given age. Fig. 3 shows the evolution of % fixed lime with curing time for both pozzolans and for all the pozzolan/lime ratios. It can be noticed that the % fixed lime by FC3R is very similar to that observed in MK, being both very high, especially at high pozzolan/lime ratios. It seems that the optimal pozzolan/lime ratio is near the 1:1 ratio, since when the lime is deficient, it is consumed at very early ages (between 3 and 7 days for FC3R and between 7 and 14 days for MK), while when the lime is in excess, as with the pozzolan/lime ratio of 3:7 during 28 days of curing time, the lime is not yet totally consumed, and there is still reactive pozzolan, as evidenced by the continuous increase of fixed lime. On the other hand, the 1:9 pozzolan/lime ratio is probable because there is no reactive pozzolan, since at 14 days of curing time, there is no more increase in the % fixed lime. From these results, it is clear that FC3R is more reactive than MK, except for the 3:7 pozzolan/lime ratio in medium curing ages (14–28 days).

The total weight loss by itself does not give us an idea of the reactivity of the system, because it is affected by the dehydroxylation of CH. If we subtract this amount (zone 4) from the total weight loss, we can have a measurement of the total combined water content as calcium silicates, aluminates and aluminosilicates. There-

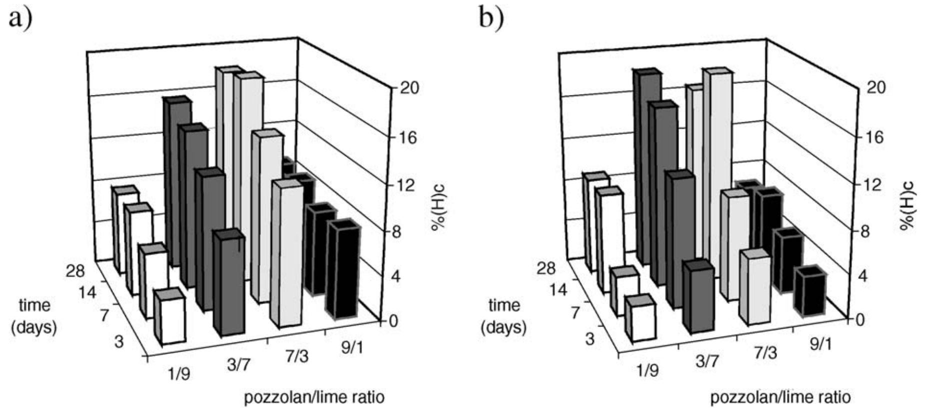

Fig. 4. Percent combined water in calcium hydrates. Influence of curing time (days) for all pozzolan/lime ratios studied. (a) FC3R, (b) MK.

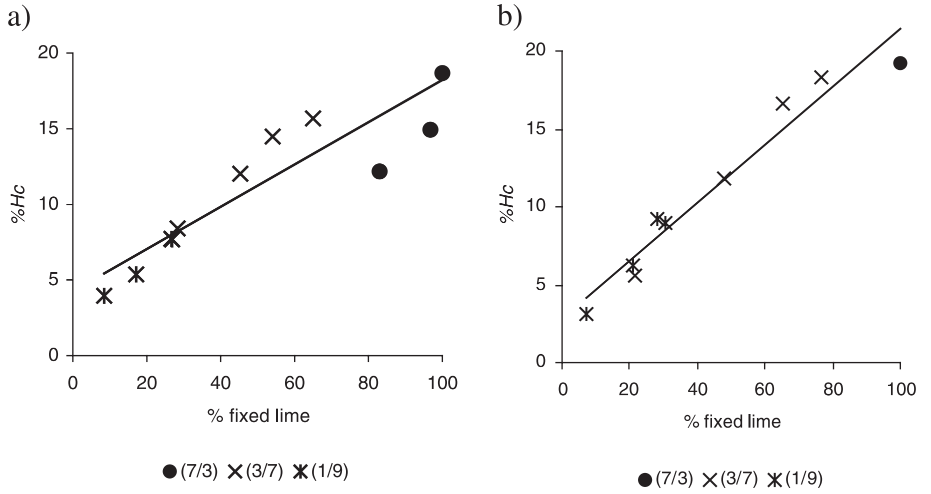

Fig. 5. Percent combined water in calcium hydrates as a function of percent fixed lime. (a) FC3R/lime pastes, (b) MK/lime pastes. Straight-line correlation (see Eqs. 3 and 4).

fore, the water incorporated in these hydrates can be calculated as follows (Eq. 2):

$$\%(H)_c = P_T - H \tag{2}$$

where P_T is the total weight loss percentage, H is the weight loss percentage of zone 4 corresponding to the dehydroxylation of calcium hydroxide (see Table 3) and $\%(H)_c$ is the water percentage incorporated to the pozzolanic reaction hydrates. In Fig. 4a and b, the $\%(H)_c$ is represented as a function of curing time for all pozzolan/lime ratios. It can be noticed that the $\%(H)_c$ is bigger in the FC3R pastes, except for the deficient pozzolan pastes with older curing times (14–28 days). This fact confirms firstly, the bigger reactivity of FC3R, and secondly, the possibility that for a given curing time and pozzolan/lime ratio, the pozzolanic reaction products of both pozzolans could be different.

In Fig. 5, the relationship between $\%(H)_c$ and % fixed lime is presented for both pozzolans. A linear correlation is also shown. For this mathematical fitting, only the experimental data until the first-in-time value of 100% fixed lime had been taken, because from this age forward, the variations on $\%(H)_c$ are attributed to transformations of some hydrate types to another with different water content [7]. Besides, the 9:1 pozzolan/lime ratio had been excluded, because at very early ages, the % fixed lime is already 100, therefore, the hydrate transformation surely took place. With those considerations, the following linear equations are obtained (Eqs. 3 and 4):

$$\text{FC3R paste} \quad \%(H)_c = 4.24 + 0.14 \times \%\ \text{Fixed lime}, \quad R = 0.92 \tag{3}$$

$$\text{MK paste} \quad \%(H)_c = 2.70 + 0.19 \times \%\ \text{Fixed lime}, \quad R=0.98 \tag{4}$$

These linear equations show a good agreement with the experimental data, indicating that when the % fixed lime is lower than 100, the $\%(H)_c$ is also a useful parameter to follow the pozzolanic reaction.

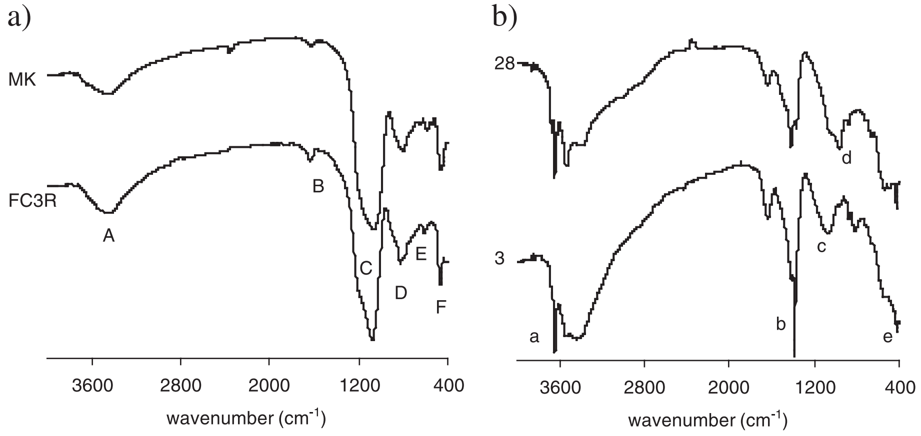

Fig. 6. FTIR spectra. (a) FC3R and MK, (b) FC3R/lime (3:7) pastes, evolution with curing time (days).

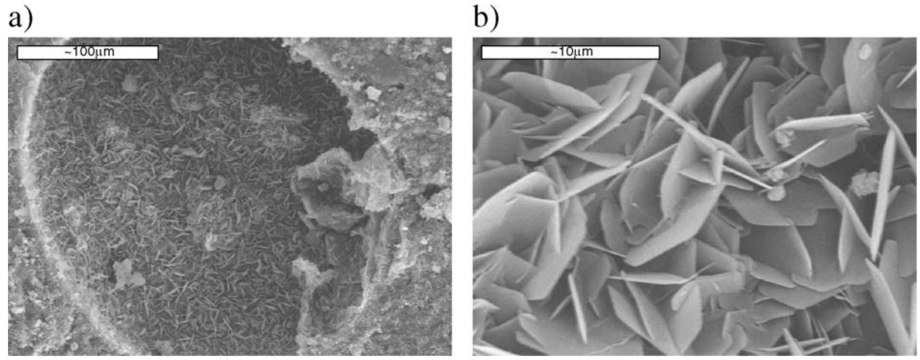

Fig. 7. Scanning electron microphotographs of typical hydration products of FC3R/CH (7:3) at 28 days of curing time.

3.2. FTIR studies

Qualitative FTIR studies had been made in order to follow the pozzolanic reaction. Firstly, the pozzolans were characterized by this technique, and their spectra are shown in Fig. 6a. It can be observed that their spectra is practically the same. The principal peaks are (A) 3000–3600 cm^{-1} for vibrations of valence –OH, (B) 1640 cm^{-1} for vibrations of deformation –OH, shoulder on the left side of C (1150 cm^{-1}) for amorphous silica polymerized and the minimum (1070 cm^{-1}) for vibrations of valence Si–O(Al)–O, (D) 800 cm^{-1} for the atomic group rings of three or more tetrahedrons of silica, being the band less intense as the silica becomes more amorphous, (E) 550 cm^{-1} for Si–OH bonds and finally, (F) 470 cm^{-1} for vibrations of deformation Si–O–Si [8,9].

In Fig. 6b, the FTIR spectra for FC3R/lime (3:7) pastes for 3 and 28 days of curing time is presented. The more relevant peaks are (a) 3640 cm^{-1} for the –OH of the calcium hydroxide, (b) 1366–1417 cm^{-1} for carbonates (from impurity of lime), (c) 1100 cm^{-1} for vibrations of valence Si–O(Al)–O, (d) 970 cm^{-1} for calcium silicate hydrates, and (e) 420 cm^{-1} for calcium aluminate and aluminosilicate hydrates [10]. It is noticed that the peak (a) decreases as a consequence of the pozzolanic reaction; this nevertheless shows a little diminution because of the high proportion of lime in the paste. One peak of the carbonates (b) decrease and the other increases, probably due to the fact that the former corresponds to calcium carbonate and the latter corresponds to a carboaluminate. The (c) peak, which belongs to the pozzolan, decreases, while the peak (d) of the CSH increases.

3.3. SEM studies

In Fig. 7, the products of hydration for the FC3R/CH system after 28 days of curing time are shown. The morphology of the hydrates has hexagonal platelets ranging in size from 5 to 10 µm. The quantitative analysis was carried out with the energy-dispersive X-ray adapted to the SEM for microanalysis. The results reveal that those crystals are hydrated gehlenite (calcium aluminosilicate hydrate) type (hydrogarnet) that had incorporated silicon to the microstructure. The elemental compositions of the hydrogarnet in the FC3R–lime pastes lie in the range $C_2A_{(0.40-0.96)}S_{(0.29-1.32)}H_{(3.12-10.21)}$ (similar crystals are reported in studies using MK [11,12]).

4. Conclusions

The main conclusions of this paper can be summarized as follows.

1. Thermal analysis reaction studies reveals that the pozzolanic reaction products between FC3R and lime are CSH, CAH and CASH of several compositions, being similar to the products yielded by MK towards lime.
2. From the percentage of fixed lime data, the optimal pozzolan/lime ratio is between 3:7 and 7:3 ratios, giving percentages of fixed lime between 60% and 95% at 28 days of curing time.
3. Both pozzolans exhibited very high percentages of fixed lime, showing for FC3R higher reactivity than MK for low lime content pastes.
4. The percentage of combined water [$\%(H)_c$] showed to be a useful parameter to follow the pozzolanic reaction, since it showed a good correlation with % fixed lime when the latter is lower than 100%.
5. The qualitative FTIR study is a useful technique to follow the advance of the reaction, especially the peaks belonging to CH and to CSH.
6. SEM reveals that the calcium hydrate products from FC3R–lime pastes showed a wide range of calcium silicates and aluminosilicates (hydrated gehlenite type) with a $C_2A_{(0.40-0.96)}S_{(0.29-1.32)}H_{(3.12-10.21)}$ composition range.

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