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Evaluation of the pozzolanic activity of fluid catalytic cracking catalyst residue (FC3R). Thermogravimetric analysis studies on FC3R-Portland cement pastes

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Abstract

Spent fluid catalytic cracking catalyst (FC3R) from a petrol refinery has shown a great pozzolanic activity in lime pastes as have been demonstrated in previous studies. Based on these results, the pozzolanic activity of the FC3R in Portland cement pastes has been investigated. This evaluation has been carried out by means of thermogravimetry (TG) of cured FC3R-Portland cement pastes. The influence of water/binder ratio and the replacement percentage of FC3R on the pozzolanic reaction were investigated. Due to the chemical composition of FC3R that is similar to metakaolin (MK), and knowing that MK has a high pozzolanic activity, the latter was used as a material of comparison in the study of the water/binder ratio influence. The scope of this study is the determination of pozzolanic activity of FC3R when incorporated to Portland cement, and the evaluation on amount and nature of pozzolanic products. FC3R has shown a similar reactivity to MK, yielding similar pozzolanic products: CSH, CAH and CASH. The optimum replacing percentage in Portland cement pastes was in the 15–20% range.

Keywords: Metakaolin; Pozzolan; Spent fluid cracking catalyst; Thermal analysis; Waste management

1. Introduction

The continuous increase in the generation of waste materials outlines a challenge to the investigators to propose solutions to its reuse. More and more, it is a habitual practice to incorporate these materials to hydraulic binders as a solution to their final confinement, besides that, in many occasions, the incorporation results in improvements of the properties of the resulting material, as much in mechanical resistance as in durability. Pozzolanic materials are an ideal example of waste materials that contribute to the improvement of the binder properties, given their capacity to react with the calcium hydroxide (CH) generated by the cement hydration, to produce similar hydrates to those of the hydrated cement responsible for the development of the mechanical resistances, besides that contribute to the densification of the matrix binder, sealing pores and reducing the attack of external agents.

The FC3R is a waste material generated in petrol refinery from fluidised bed process, which is an inorganic alumino-silica material with a high specific surface area (107 m^2/g), that has more influence to obtain the high pozzolanic activity that the catalyst has shown in lime pastes, as one of its properties [1]. Lately, studies with FC3R focused to show the contribution to the gain of mechanical resistance in mortars and concretes have been carried out [2–9], varying the replacement percentage; however, some studies have not investigated the influence of the water/binder ratio and others have not reported values of lime fixation.

The aim of this work was to determine the pozzolanic activity of the FC3R in Portland cement systems, investigating the water/binder influence and comparing their reactivity with respect to other artificial pozzolan, metakaolin (MK), which has a similar chemical composition and high pozzolanic activity. Also, to establish the influence of the replacement percentage of the catalyst waste in

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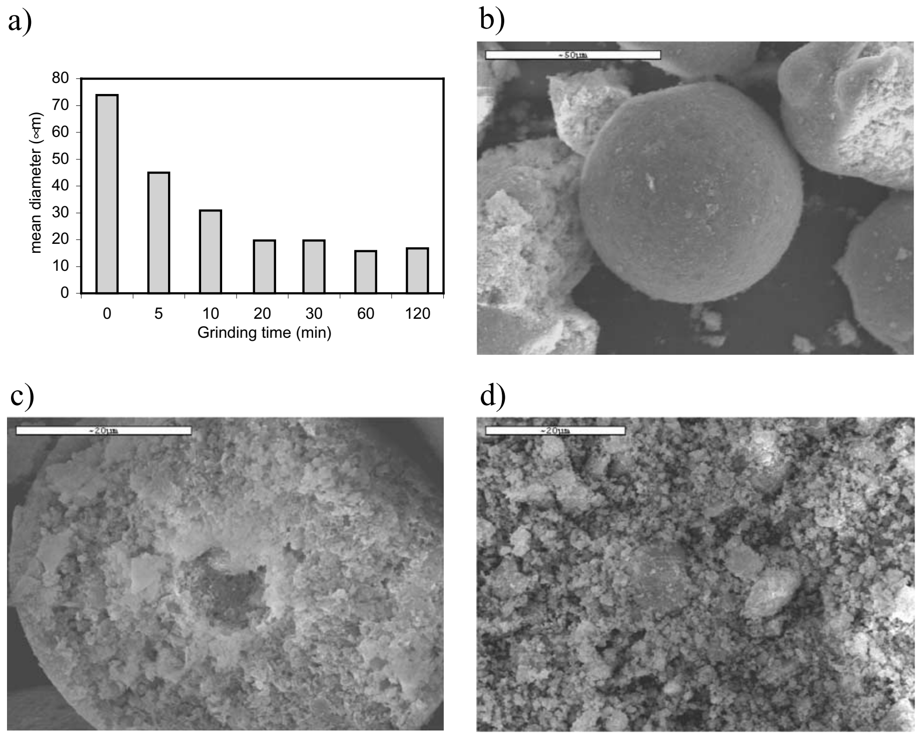

Fig. 1. (a) Mean diameter particle for FC3R samples after several grinding times; (b) scanning electron microphotographs (SEM) showing a spherical particle of FC3R; (c) SEM of a detail of FC3R showing internal porous structure; (d) SEM of a ground FC3R20.

such reactivity, and the nature of the pozzolanic reaction products.

2. Experimental

FC3R was supplied by BP OIL España (Castellón, Spain), which was grounded with a laboratory ball-mill (Gabbrielli Mill-2) during 20 min to increase their reactivity to the optimum, just as it has been established in previous works [1,2]. Fig. 1a shows the mean particle diameter of the catalyst after several grinding times. It can be noticed that, in the first 20 min of grinding, the mean particle diameter is reduced drastically, while the subsequent grinding practically does not affect the particle diameter. Fig. 1b shows a typical spherical FC3R particle, where particles with an irregular shape can also be appreciated as consequence of their use in the cracking process. Fig. 1c shows the highly porous internal structure of a FC3R particle. Finally, Fig. 1d shows the aspect that the catalyst has after 20 min of grinding (FC3R20).

In the preparation of cement pastes, ordinary Portland cement (CEM I-52.5-R) supplied by Valenciana de Cementos de Buñol (Valencia, Spain) was used. The MK was a commercial product from Metastar. Chemical compositions for the cement, FC3R and MK are given in Table 1.

The mix formulations prepared in this study are listed in Table 2. In all mixes, grounded FC3R was used (20 min grinding). As can be appreciated, a superplasticizer was used to obtain pastes with similar fluency. For the water/binder ratio influence study, pastes with MK were used to compare with the behaviour of the catalyst. On the other hand, in the study of the influence of the replacement percentage, MK was not used and the superplasticizer level for the 20% replacement was raised due to the high requirement of water by the catalyst. 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 catalysts (raw material and ground) were observed by scanning electron microscopy (SEM) using a JEOL JSM-6300.

Thermogravimetric analysis (TGA) were performed in a Mettler-Toledo TGA850, with a horizontal furnace. It is equipped with an ultramicrobalance, which has a resolution of 0.1 µg. Aluminium crucibles with 100 µl capacity having a sealable lid with pin hole to obtain water vapor self-generated atmosphere were used. Using this type of crucible, the decomposition temperatures of hydrate products

Table 1
Chemical composition (%)

Material	SiO_2	CaO	Al_2O_3	Fe_2O_3	MgO	Na_2O	K_2O	SO_3	LOI
Cement	19.9	63.69	5.4	3.62	2.14	0.10	1.17	3.66	2.0
FC3R [3]	48.2	< 0.01	46.0	0.95	< 0.01	0.50	< 0.01	0.04	1.5
MK [10]	52.1	0.07	41.0	4.32	0.19	0.26	0.63	–	0.6

Table 2
Mix formulations

Paste	Curing temperature (°C)	Water/binder ratio	% Super-plasticizer	% Substitution	Curing time (days)
		0.25	2.00 (3.00)[a]		
		0.30	1.50 (2.50)[a]	0	
Control		0.35	1.00 (2.00)[a]	5	3, 7, 14, 28 and 90
FCC20	20	0.40	0.50 (1.50)[a]	10	
MK[b]		0.45	0.25 (1.00)[a]	15	
		0.50	0.00 (0.50)[a]	20[a]	
		0.55	0.00 (0.30)[a]		

[a] Superplasticizer level for pastes with 20% of substitution.
[b] Only for 15% of substitution.

shift to higher temperatures than those found using common aluminium or platinum crucibles. 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, and the sample mass was in the 40–45 mg range.

3. Results and discussion

3.1. Water/binder ratio influence studies

In Fig. 2, the derivative thermogravimetric curves (DTG) for the control, FC3R and MK cement pastes, for some of the water/binder ratios are represented. The selected curing time was 3 days. Four main peaks can be observed. Peak 1 overlapped with peak 2 (100–180 °C) belonging to the dehydration of calcium silicate hydrates (CSH) and ettringite (Af_T), Peak 3 (180–240 °C) corresponding to the dehydration of calcium aluminate and aluminosilicate hydrates (CAH and CASH) of different composition and, finally, Peak 4 (520–580 °C) due to the dehydroxilation of portlandite (CH). With respect to Peaks 1 and 2, they are less overlapped in the pozzolan containing pastes than in the control paste, due to the pozzolans' contribution to a higher ettringite production, because pozzolans are an extra source of aluminates, in addition to the lower CSH production since there is 15% less cement due to replacement and that the pozzolanic reaction produces mainly CAH and CASH. Moreover, the presence of pozzolan particles contributed to accelerate the hydration of cement particles, yielding more hydrated products. Peak 3 is hardly perceptible in the control paste, while in the pozzolan pastes, it is strongly appreciable. The decomposition of hydrates at those temperatures, CAH and CASH, take place for both pozzolan containing pastes, suggesting the similarity of pozzolanic products in FC3R and MK. Peak 3 becomes more important as the water/binder ratio increases. This can be attributed to two factors, on one hand, to the higher lime availability and, on the other hand, to the higher accessibility of the reagents, since more liquid phase exist. Finally, the peak attributed to the portlandite [4] decreases as the water/binder ratio diminishes. It is attributed to that when having less liquid phase, the transport of ions to form new hydrate products is obstructed, being this effect more marked for the pozzolan pastes than for the control paste, as it is expected due to the pozzolanic behaviour of the additions.

In Table 3, Peak 4 weight losses for the three types of pastes (control, FC3R and MK) are listed. These values were obtained by integration of the peaks on DTG curve. For control pastes, a continuous increase of the weight loss with curing time is obtained, according of the hydration of anhydrous calcium silicates in Portland cement composition. Moreover, the portlandite produced increases in the water/binder ratio due to hydration process, which is

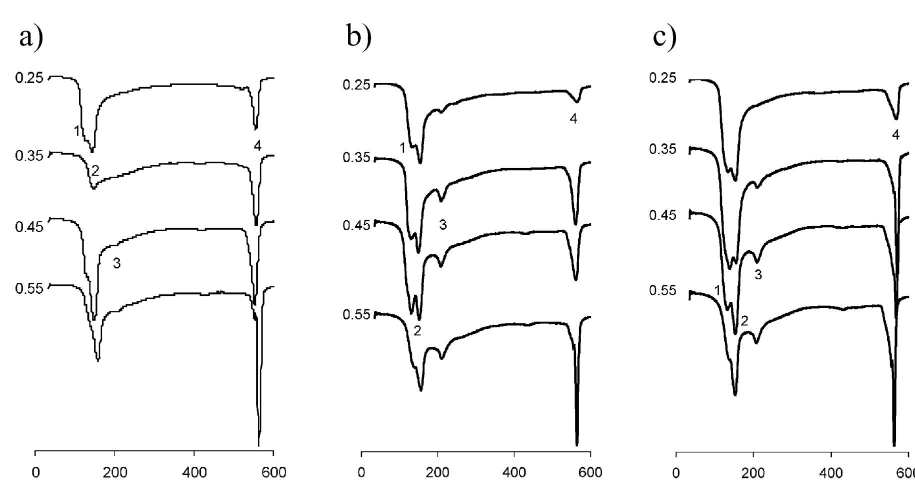

Fig. 2. DTG curves for the indicated water/binder ratios for pastes: (a) control (only cement), (b) 15% FC3R and (c) 15% MK. Three days of curing time.

Table 3
Weight losses in %, 520–580 °C range temperature in studied pastes (control and 15% pozzolan replacing pastes)

Pozzolan	w/b	Curing time (days)				
		3	7	14	28	90
Control	0.25	1.15	1.25	1.45	1.57	1.58
FC3R		0.36	0.32	0.30	0.32	0.18
MK		0.74	0.69	0.63	0.47	0.30
Control	0.30	1.53	1.40	1.77	1.82	2.12
FC3R		0.73	0.86	0.83	0.78	0.67
MK		1.30	1.12	0.90	0.85	0.78
Control	0.35	1.82	1.95	2.26	2.33	2.39
FC3R		1.50	1.25	1.15	1.10	1.00
MK		1.47	1.35	1.20	1.14	1.02
Control	0.40	1.98	2.03	2.11	2.12	2.46
FC3R		1.10	1.10	1.09	1.10	1.06
MK		1.57	1.67	1.50	1.11	1.10
Control	0.45	2.29	2.91	2.93	2.94	2.94
FC3R		1.49	1.85	1.48	1.54	1.28
MK		1.57	1.67	1.53	1.42	1.14
Control	0.50	2.47	3.12	2.72	2.90	2.81
FC3R		1.83	1.80	1.79	1.54	1.27
MK		2.29	1.55	1.59	1.45	1.09
Control	0.55	2.77	2.83	3.16	3.20	3.07
FC3R		1.84	1.73	1.72	1.65	1.39
MK		2.10	1.72	1.64	1.53	1.08

favoured by increasing the liquid media. Weight losses in FC3R and MK pastes were lower than those found in control pastes, due to the lower proportion of cement in those pastes and, of course, the pozzolanic reaction. Thus, the pozzolanic fixation of portlandite produced, in general, a decrease of weight losses in Peak 4 with the curing time of the pastes, and the portlandite content in pozzolan pastes at 90 days is notably lower than portlandite content at 3 days.

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

$$\text{Fixed Lime }(\%) = \frac{[CH_C{*}C_{\%}] - CH_P}{[CH_C{*}C_{\%}]}100 \qquad (1)$$

where CH_C is the amount of CH in the control paste for a given curing time, CH_P is the amount of CH in the pozzolan paste at the same age and $C_{\%}$ is the proportion of cement in the paste, in this case is 0.85. Fig. 3 shows the evolution of the fixed lime with curing time and water/binder ratio for both pozzolans. In general, it is observed for both pozzolans that the fixed lime increases with curing time, reaching a maximum in the range of 50–60% for all water/binder with exception of the lowest water/binder ratio (0.25) where the FC3R and MK pastes yielded more than 86% and 77%, respectively. For FC3R pastes, fixed lime values are positive and, in general, for 3 days of curing time, become higher than those found in MK pastes, indicating the high reactivity of the catalyst from the first days of curing time, while the MK begins to be active at longer times, such as it has been observed in lime pastes [1]. Thus, for 0.25 water/binder ratio, FC3R fixed more than 60% of the available portlandite, whereas MK was able to combine less than 30% of CH.

The erratic initial behaviour (more appreciable for MK, Fig. 3b, negative values) can be indicative that the pozzolans are activating the cement hydration process, causing that a higher quantity of calcium hydroxide be generated, registering an apparent smaller lime fixation. Finally, although both pozzolans have a similar reactivity, the FC3R is more reactive, from the pozzolanic point of view, when the water/binder ratio is lower than 0.45 in the whole time interval, while MK behaviour is better for higher water/binder ratios (0.45–055) and curing times in the range of 7–90 days. This fact could be explained due to the higher water demand of MK than FC3R.

3.2. Replacement percentage influence studies

Fig. 4 showed the DTG curves for the FC3R/cement pastes in all the replacement percentages studied, for 0.25, 0.40 and 0.55 water/binder ratios, being selected for the discussion, the highest, the lowest and the intermediate ratios, at 3 days of curing time. This curing time was selected because when the process of lime fixation is not so advanced, the changing events are more appreciable. It has to be noticed that the DTG curves are comparable within the same graph, but are only qualitatively comparable among different graphs, because the *y*-axis (not showed) is not the same.

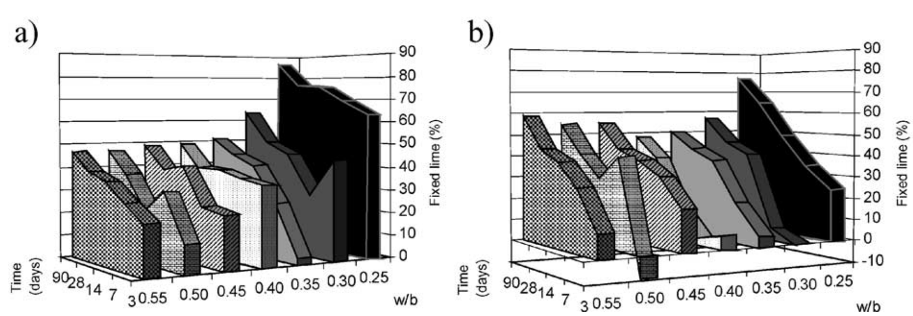

Fig. 3. Percentage of fixed lime evolution with curing time for cement pastes with 15% of cement replacement by pozzolan. Influence of water/binder ratio: (a) FC3R and (b) MK.

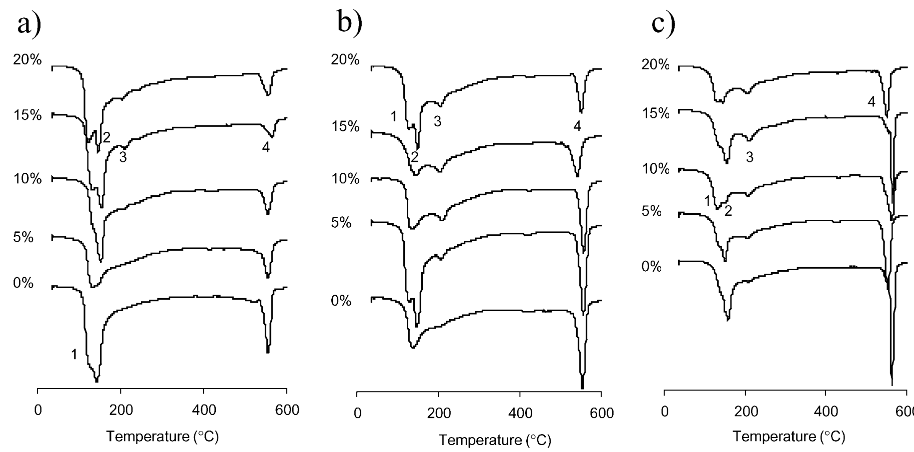

Fig. 4. DTG curves for the indicated replacement percentages of FC3R on cement pastes at 3 days of curing time. Water/binder ratios: (a) 0.25, (b) 0.40 and (c) 0.55.

With respect to the replacement percentage influence, it is clearly seen that, for a given water/binder ratio, the amount of hydration products (CSH, CAH CASH and AF_T) increases as the replacement percentage increases, being better separated Peaks 1 and 2, due to the higher generation of these products. Obviously, Peak 4 decreases as the replacement percentage increases, since, on one hand, the FC3R are acting as a pozzolan, consuming more lime, and on the other hand, there are less lime due to the cement replacement. This last fact is taking into account in the calculation of the percentage of fixed lime (see Eq. (1)), since the $C_{\%}$ term makes possible the comparison between pastes with different cement contents.

In Table 4, the weight losses for Peak 4, for all the different replacement percentages, and the water/binder ratios studied are tabulated. The values of the 0% and 15% replacement percentages were omitted, since they are already tabulated in Table 3. In general, for lowest replacing percentage pastes (5%), the CH content evolution from 28 to 90 days is not very important, suggesting that an important fraction of the pozzolan has been reacted at 28 days of curing time. On the other hand, for 20% replaced FC3R pastes, a noticeable decrease in CH content was observed for the same curing time period. Thus, the pozzolanic reactivity of FC3R is important at early ages, although the proportion of the pozzolan is high, very important pozzolanic progress is observed for long-term curing time.

In Fig. 5, the percentage of fixed lime as a function of the FC3R replacement and water/binder ratios for 3, 14 and 90 days of curing time is showed. For 3 days curing time and lowest replaced FC3R pastes (5%), some negative values for fixed lime were observed. This fact confirms the contribution to the acceleration of cement hydration pointed out in the previous section. Fixed lime values showed a strong relationship to percentage replacement. Thus, in general, 20% replaced pastes presented highest values due to higher proportion of FC3R and lower cement content, that is more active pozzolan and less available portlandite. Likewise, this fact is more accentuated when the water/binder ratio diminishes, since less lime is generated (see Fig. 4), being the paste richer in catalyst. When the % FC3R content rises, the % fixed lime increases. However, the % fixed lime of the 15% FC3R content paste is bigger than the 20% replacement for the two lowest water/binder ratios in the whole curing time range, this effect being slightly smaller at early curing ages for the remaining ratios. This observation suggests that,

Table 4
Weight losses in %, 520–580 °C range temperature for FC3R pastes containing different levels of replaced cement

% Replacement of FC3R	w/b	Curing time (days)				
		3	7	14	28	90
5	0.25	0.73	0.98	1.02	1.91	0.94
10		0.65	0.71	0.75	0.84	0.76
20		0.58	0.57	0.44	0.45	0.34
5	0.30	0.92	1.48	1.33	1.21	1.29
10		0.79	0.84	1.08	1.01	0.99
20		0.81	0.76	0.82	0.75	0.54
5	0.35	1.60	1.49	1.55	1.76	1.74
10		1.26	1.46	1.37	1.41	1.32
20		1.15	1.09	1.03	1.00	0.62
5	0.40	2.08	1.75	1.85	2.13	1.96
10		1.53	1.73	1.48	1.47	1.46
20		0.95	1.03	0.83	1.03	0.63
5	0.45	2.38	2.11	2.07	2.39	2.26
10		1.71	1.97	1.70	1.76	1.56
20		1.15	1.37	0.99	1.12	0.84
5	0.50	2.23	2.19	2.36	2.32	2.29
10		1.86	2.12	1.89	1.91	1.96
20		1.28	1.15	1.19	1.07	0.85
5	0.55	2.37	2.41	2.57	2.53	2.52
10		1.85	2.17	2.09	1.01	1.96
20		1.55	1.54	1.52	1.24	0.88

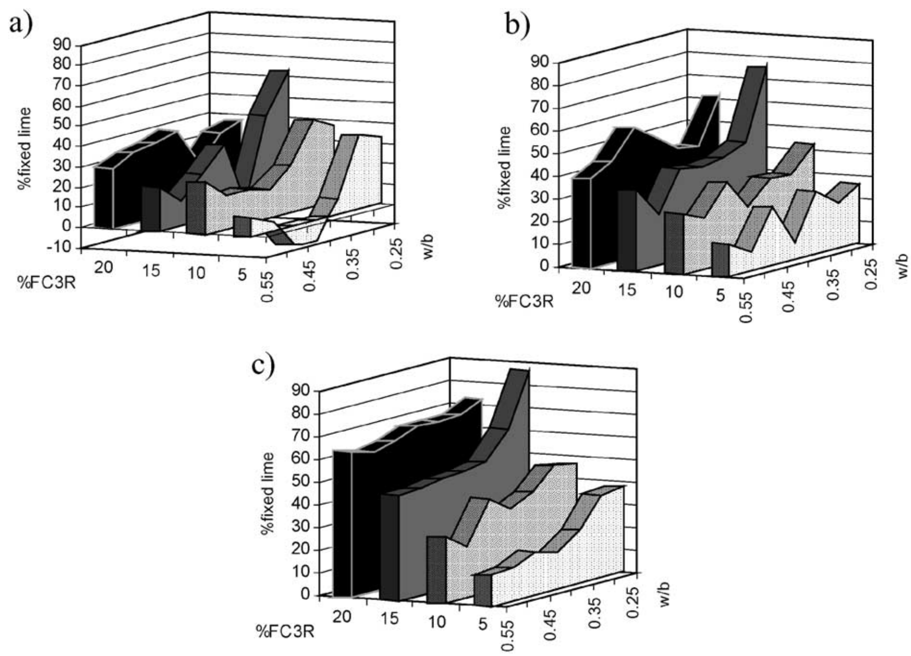

Fig. 5. Influence of FC3R replacement percentage and water/binder ratios on % fixed lime. Curing times: (a) 3, (b) 14 and (c) 90 days.

although the 20% replacement seems better at early ages, a portion of FC3R is behaving as inert, probably due to the deficiency of lime, being less marked for higher water/binder ratios, since the lime accessibility is increased due to the paste porosity. The highest % fixed lime values are obtained when the water/binder ratio decreases for a given curing time, as it was pointed out in the previous section, remembering that, in this situation, the catalyst content is in a bigger proportion, and therefore fixes the deficient lime content more easily.

4. Conclusions

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

From the water/binder ratio studies, we can point out that:

1. Thermal analysis studies reveal that the lime content decreases as the water/binder ratio diminishes, this effect being more marked for the FC3R and MK pastes than the control paste due to their pozzolanic activity, and because accessibility of reagents is lower since the paste has less liquid phase.
2. The presence of CAH and CASH in the pastes with pozzolan are more marked than in the control paste, the concentration being higher as the water/binder ratio increases.
3. The % fixed lime increases as the water/binder ratio diminishes, this tendency being more marked for the FC3R pastes than MK ones.
4. The erratic initial behaviour on the values of fixed lime indicates that the pozzolans are acting as accelerators of the cement hydration, generating more lime than is expected.
5. Both pozzolans have a similar reactivity, being lightly higher for FC3R at early ages than MK, which is little more reactive for longer curing ages.

From the replacement percentage study, we can conclude that:

1. Thermal analysis reaction studies reveal that content of hydration products (CSH, CAH, CASH and Af_T) increases as the % replacement increases, and the lime content diminishes.
2. The % fixed lime increases as the curing time is older for a given % replacement and a water/binder ratio, with some exceptions made for the 5% replacement at early ages, when the cement hydration is accelerated by the catalyst.
3. As the replacement percentage rises, the % fixed lime increases, being the optimum % replacement in the 15–20% range.

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