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Accelerated carbonation of cement pastes partially substituted with fluid catalytic cracking catalyst residue (FC3R)

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ABSTRACT

Accelerated carbonation tests have been carried out on Portland cement pastes and pastes partially substituted with a spent fluid catalytic cracking catalyst (FC3R) to investigate possible differences between the composition of FC3R/cement and plain cement matrices. Cement/FC3R pastes have been tested by thermogravimetry and X-ray diffraction analyses. This study has revealed that the incorporation of FC3R on pastes produces a significant reduction of the alkaline reserve and an increase in the quantity of cementing products such as hydrated calcium silicoaluminates. The carbonation of cement/FC3R pastes leads to the total consumption of the porlandite of the paste. Further carbonation will produce the capture of the calcium contained in the cementitious phases, yielding calcium carbonate and silica and alumina gel. The main product of the carbonation process is calcite, but vaterite has also been detected in the carbonated pastes. No major differences were observed between the composition of FC3R/cement and plain cement pastes after the carbonation that could add additional risk to carbonation processes of FC3R-containing binders.

1. Introduction

There is a general consensus that the majority of concrete deterioration processes are connected to corrosion of steel reinforcement bars due to carbonation or chloride-induced depassivation. Concrete carbonation is a complicated physicochemical process. The process includes the diffusion of CO_2 in the gaseous phase into the concrete pores, its dissolution in the aqueous film of these pores, the dissolution of solid $Ca(OH)_2$ in the water of the pores, the diffusion of dissolved $Ca(OH)_2$ in the pore water and its reaction with the dissolved CO_2 (Eq. (1)), and the reaction of CO_2 with CSH (Eq. (2)) and with the yet unhydrated C_3S and C_2S [1]. Carbonation does not only affect CSH phases but also CAH phases [2] (Eq. (3)). When CO_2 penetrates into the hardened concrete, it reacts with portlandite in the presence of moisture forming $CaCO_3$. All three modifications of $CaCO_3$ (vaterite, calcite and aragonite) have been reported in the literature on carbonation, with aragonite being least common. CSH gel, when carbonated, first forms vaterite which then transforms either partly or fully to the more stable calcite [3]. A similar reaction has been observed in the carbonation of CAH gel [4].

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O \qquad (1)$$

$$CSH + CO_2 \rightarrow SiO_2 \cdot xH_2O + CaCO_3 \qquad (2)$$

$$CAH + CO_2 \rightarrow Al(OH)_3 + CaCO_3 \qquad (3)$$

Thaulow et al. [5] proposed that, as carbonation proceeds, the reduction in the pH shifts the form of the carbonation from a microscopic precipitation of carbonate (which densifies the paste) to a form which is dominated by growth of discrete calcite crystals in a matrix of silica gel. The strength of the resulting microstructure is extremely dependent on the moisture content of the concrete. This effect could be further aggravated by the presence of competing demands for calcium hydroxide, either from pozzolanic activity, leaching or sulphate attack.

Suryavanshi and Swamy [6] observed that the formation of well-crystallized and amorphous calcite in concrete subjected to long-term carbonation is related to the flux of atmospheric CO_2 through the concrete cover. Well-crystallized calcite forms in concrete with a high CO_2 flux while amorphous calcite forms in concrete with a restricted CO_2 flux.

The affected properties after carbonation are [7]: (i) mass, which can either increase or decrease depending on the balance between water lost and CO_2 gained in the carbonation reaction; (ii) non-evaporable water, as the bound water is liberated; (iii) porosity, as pores are filled up by expansive $CaCO_3$ products or vacated by lost water; (iv) strength, according to final compactness, which is closely related to porosity; (v) shrinkage,

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depending on soluble carbonatable products such as $Ca(OH)_2$, and on relative humidity; and (vi) pH, with a reduction of hydroxyl ions in the pore solution leading to more neutral values.

Wee [8] studied the influence of curing time in order to prevent major carbonation in concretes with pulverized fuel ash and ground granulated blast furnace slag. This work showed the relationship between pores having a radius above 45 nm and the resistance to carbonation of concrete. In addition, the presence of mineral admixtures did not greatly affect the carbonation resistance as much as other parameters, such as the water/binder (w/b) ratio or curing time.

Sanjuán et al. [9] compared natural and accelerated conditions for carbonation tests. Their results showed that accelerated testing changed the ranking of concrete resistance with respect to carbonation and therefore, the comparison should be made among concrete with the same additions. They also find that the carbonation rate depends on the square root of time, which is useful in comparing concretes.

Zeolitic catalysts, such as FC3R, are commonly used in the petrochemical industry and account for one fifth of the overall catalyst production in the world. The lifetime of these catalysts is very short and the deactivated catalyst must be replaced by a new active catalyst. Thus, significant quantities of fluid catalytic cracking catalyst residue (FC3R) are produced (up to 400,000 tons/year), causing waste disposal problems. Fluid catalytic cracking catalyst residue (FC3R) is mainly composed of silicoaluminates and some previous works have demonstrated its potential use as a construction material due to its pozzolanic activity [10–12]. It is necessary to study how the pozzolanic products (i.e. CASH, gehlenite type) of FC3R can be affected by carbonation attack. Other researchers have studied the carbonation process of CSH and CAH, but little is known about the carbonation of CASH phases.

The aim of this work is to study the influence of carbonation on the hydration and pozzolanic products of cement/FC3R pastes since it is necessary to know the behaviour of this by-product before it is included in commercial cement composition. This means knowing which pozzolanic products are affected by carbonation and which products are obtained through this process.

2. Experimental

2.1. Materials and sample preparation

CEM I 52.5 R Portland cement was used for pastes preparation. Four pastes have been prepared using various dosages of FC3R (0%, 20%, 35%, 50% by weight of cement). A water/binder ratio (w/b) of 0.8 has been used for all pastes. The source of the FC3R was the BP-Oil España, S.A refinery in Castellón, Spain. The chemical composition of FC3R is shown in Table 1. The FC3R was ground using a laboratory ball mill for 20 min in order to activate its pozzolanic activity [10].

Pastes were stored in a 100% relative humidity (RH) environment after setting, and samples of each paste were taken after a curing period of 9 and 28 days. Then, these pastes were introduced into a carbonation chamber with a 100% CO_2 atmosphere at 65 ± 5% RH for one month in order to ensure the complete carbonation of samples. After that, an additional sample was taken.

Table 1
Chemical composition of FC3R [12].

Parameter	FC3R (%)
LOI	1.50
SiO_2	48.2
Al_2O_3	46.0
Fe_2O_3	0.95
Na_2O	0.50
SO_3	0.04

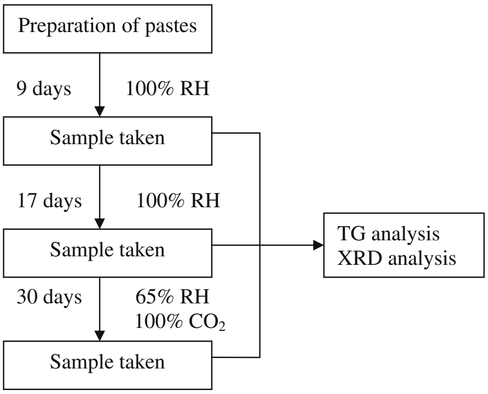

Fig. 1. Scheme of the experimental procedure.

Samples taken from the pastes were pulverized using an agate mortar. They were then sieved using a 80 μm sieve, and only the sieved portion was used in analysis. Non-combined water was eliminated from the samples by several washes with acetone. The samples were studied by thermogravimetric analysis and X-ray diffraction analysis. In Fig. 1 it is shown a scheme of the experimental procedure.

2.2. Thermogravimetric analysis

Thermogravimetric analysis was performed in a Mettler–Toledo TGA850, with a horizontal furnace. Two different tests were made. The first method consisted of using 100 μl aluminium crucibles, having a lid with a pinhole to obtain the self-generated atmosphere. Using this type of crucible, the decomposition temperatures of hydrated products shift to higher temperatures than those found using common crucibles, because of the higher partial pressure of water. The gas flow rate for the surrounding atmosphere was 75 ml/min of nitrogen. The heating rate was 10° C/min over the 35–600° C temperature range. This method was employed to analyze hydrated phases of pastes and portlandite. The second method consisted of using alumina crucibles of 80 μl, having a lid with a hole. The gas flow rate for the surrounding atmosphere was 75 ml/min of dry air. The heating rate was 20° C/min over the 35–1000° C temperature range. This method was used to evaluate thermogravimetric losses in the high temperature range, where decomposition of calcium carbonate takes place. The sample size was approximately 30 mg.

2.3. X-Ray Diffraction Analysis

X-ray analyses were made with a PW1710 diffractometer. Diffraction angles (2θ) were those obtained by using $K_{\alpha 1}$ of a copper cathode (0.154056 nm). Scanning was made in the 5°–60° angle range.

3. Results and discussion

3.1. Thermogravimetric analyses of pastes

Fig. 2 shows thermograms (DTG curves) obtained after the short curing period (9 days). It can be observed several decomposition processes in the thermogram. These reactions and others that appear in the following figures are summarized in Table 2. Dehydration of cementitious phases (CSH, CASH and CAH) takes place in

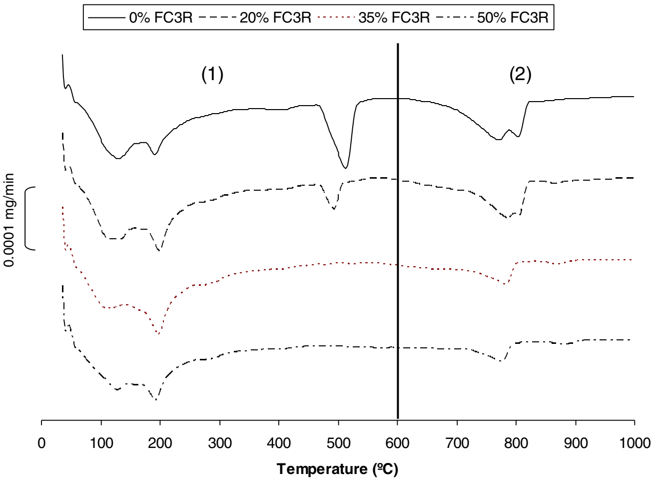

Fig. 2. DTG curve of cement/FC3R pastes after 9 days of curing time. (1) Heating rate of 10° C/min; nitrogen atmosphere; sealed pin-holed aluminium crucible. (2) Heating rate of 20° C/min; dry air atmosphere; alumina crucible with a hole.

the 100 °C–300 °C temperature range. There are two main peaks within this temperature range. The first occurs at a local minimum at 125 °C, and corresponds to the dehydration of CSH. The second minimum occurs at 190 °C and it is due to the dehydration of gehelenite type CAH [13]. This behaviour of the thermograms is very similar in all the pastes, independently of the percentage of FC3R substitution. Nevertheless, it can be observed that the presence of FC3R offers two new peaks. One of them appears at 180 °C, and is associated with the dehydration of a CASH phase. The other one has its minimum at 140 °C and is associated with the decomposition of ettringite [13]. As would be expected, the higher the substitution of FC3R, the higher the losses associated with aluminate phases.

There are minor differences in the thermograms below 300° C, however, over the rest of the temperature range the differences are more significant. First of all, portlandite decomposition takes place at about 500° C, and its intensity decreases when 20% of FC3R is added to the paste. For larger substitutions of FC3R, this peak does not appear. The reason for this is the high pozzolanic activity that FC3R exhibits, even for very short curing periods. At 9 days, 70% of the portlandite released by cement hydration has reacted in the 20% substituted paste.

Table 2
Summary of the decomposition reactions observed in the thermograms.

Temperature (°C)	Reaction
125	$3CaO \cdot 2SiO_2 \cdot 3H_2O \rightarrow 3CaO \cdot 2SiO_2 + 3H_2O$
140	$3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O \rightarrow 3CaO \cdot Al_2O_3 \cdot 3CaSO_4 + 32H_2O$
180–190	$2CaO \cdot Al_2O_3 \cdot SiO_2 \cdot 8H_2O \rightarrow 2CaO \cdot Al_2O_3 \cdot SiO_2 + 8H_2O$
210	$4CaO \cdot Al_2O_3 \cdot 13H_2O \rightarrow 4CaO \cdot Al_2O_3 + 13H_2O$
500–550	$Ca(OH)_2 \rightarrow CaO + H_2O$
770–870	$CaCO_3 \rightarrow CaO + CO_2$

Table 3
Weight losses of cement/FC3R pastes after 9 days of curing time.

FC3R	Losses (%)			
	Total	$Ca(OH)_2$	$CaCO_3$	CSH–CAH–CASH
0	21.24	2.51	5.25	13.48
20	20.52	0.78	4.81	14.93
35	18.61	0	3.56	15.05
50	15.71	0	2.81	12.90

There are significant differences in the high temperature range of the thermograms. Within this range, the decomposition of calcium carbonate can be observed. At 9 days, in all cement pastes, FC3R substituted or not, we note a peak at 770 °C, corresponding to calcium carbonate [14]. The intensity of this peak decreases when the amount of FC3R is increased in the paste. In addition, we observe an additional peak at 805 °C in pastes with 0% and 20% FC3R substitution. This peak is not observed in pastes with 35% and 50% of FC3R. Finally, there is an additional low intensity peak at 870 °C, whose intensity increases when the quantity of FC3R is increased. All these peaks are associated with the decomposition of carbonates. The peak that appears at 870 °C is, in fact, a carboaluminate that is produced by the reaction between the carbonate included in the cement and the aluminate of FC3R. It is thought that the carbonate and carboaluminate that have appeared at the end of this curing period were not produced by a carbonation of the pastes because of the short curing time and because the samples were not in contact with the atmosphere until they were taken for analyses.

Weight losses obtained in the analyses made after the 9 days of curing period are presented in Table 3. The quantity of portlandite in the pastes decreases when the substitution of FC3R is increased because the amount of cement has been reduced by pozzolanic reaction with FC3R. The weight loss of carbonates is directly related to the amount of cement in the paste, so it is possible that these carbonates were included in the cement. Finally, the weight loss associated with dehydration of cementitious phases increases with a 20% substitution of FC3R, but then decreases when further substitution is made. This is due to the low quantity of cement in the pastes with a 35% or a 50% FC3R substitution: there is not enough portlandite to react with FC3R due to lack of cement.

Fig. 3 shows thermograms of pastes after 28 days of curing time. For this curing period, most of the FC3R in the paste has reacted in case enough portlandite is present. In addition, the hydration of the cement is almost complete, so the microstructure of the paste is well developed. Over the low temperature range the results are very similar to those presented in Fig. 2. Over the medium temperature range, where decomposition of portlandite takes place, we observe a significant reduction in the portlandite peak when 20% of the cement is substituted by FC3R, as it was noted for the 9 day period. In this case, 20% of the FC3R has consumed 95% of the portlandite released by cement hydration. Further substitution of cement by FC3R exhausts all the portlandite released by cement. In the high temperature range, the peak of the decomposition of calcium carbonate appears again. When increasing the quantity of FC3R in the paste, a slight shift of the minimum of peak towards lower temperatures is observed, from 790 °C to 765 °C. In addition to this effect, the intensity of this peak is reduced.

Table 4 shows weight losses obtained for pastes after 28 days of curing time. The trends of these data are same that those observed in Table 3. In addition, we observe an increase in weight loss associated with the dehydration of cementitious phases, because, in this case, the curing time is longer.

Fig. 4 shows the thermograms of pastes after an accelerated carbonation, which was performed after a curing period of 28 days. In these thermograms, there is only one peak in the low temperature range at 125–135 °C. This peak is associated with the dehydration of CSH. Additionally, there is a very low intensity peak at 200 °C that is due to the dehydration of CAH. It is evident that the process of carbonation has mainly destroyed the CASH phase, as a consequence of the reaction of CO_2 with the calcium contained in this phase. In addition, as would be expected, the peak corresponding to the decompositon of portlandite has disappeared because all the portlandite has reacted with CO_2 in the carbonation process. Fi-

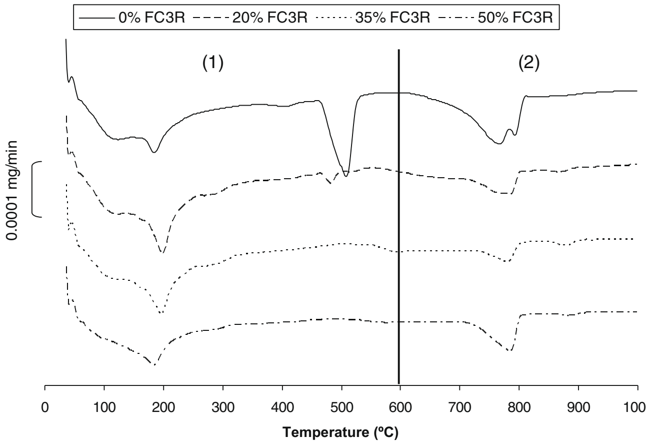

Fig. 3. DTG curve of cement/FC3R pastes after 28 days of curing time. (1) Heating rate of 10° C/min; nitrogen atmosphere; sealed pin-holed aluminium crucible. (2) Heating rate of 20° C/min; dry air atmosphere; alumina crucible with a hole.

Table 4
Weight losses of cement/FC3R pastes after 28 days of curing time.

FC3R	Losses (%)			
	Total	$Ca(OH)_2$	$CaCO_3$	CSH–CAH–CASH
0	24.57	3.33	6.59	14.65
20	23.58	0.22	4.93	18.43
35	20.65	0	3.96	16.69
50	17.28	0	3.17	12.95

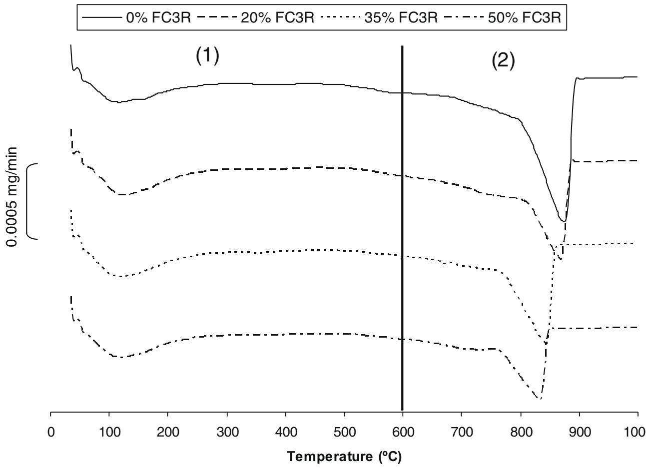

Fig. 4. DTG curve of cement/FC3R pastes after carbonation. (1) Heating rate of 10° C/min; nitrogen atmosphere; sealed pin-holed aluminium crucible. (2) Heating rate of 20° C/min; dry air atmosphere; alumina crucible with a hole.

Table 5
Weight losses of cement/FC3R pastes after the carbonation process.

FC3R	Losses (%)			
	Total	$Ca(OH)_2$	$CaCO_3$	SH–AH
0	36.94	0	24.37	12.57
20	33.82	0	19.13	14.69
35	29.42	0	16.05	13.37
50	23.84	0	11.92	11.92

Table 6
Weight losses of the decomposition of calcium carbonate compared with its source: before carbonation, portlandite and cementitious phases.

FC3R (%)	Losses of calcium carbonate associated with (%)			
	Before CO_2	$Ca(OH)_2$	CSH–CAH	After CO_2 (total)
0	6.59	8.14	9.64	24.37
20	4.93	0.54	13.66	19.13
35	3.96	0	12.09	16.05
50	3.17	0	8.75	11.92

nally, there is a large peak with a minimum at 830–870 °C that is associated with the decomposition of calcium carbonate. The intensity of this peak decreases when substitution of cement by FC3R is increased.

Weight losses of pastes after the accelerated carbonation process are presented in Table 5. There are no losses due to decomposition of portlandite since it has been consumed by CO_2 and the pozzolanic reaction of the FC3R. The quantity of calcium carbonate decreases when the substitution of cement by FC3R is increased. Additionally, the weight loss associated with the decomposition of calcium carbonate is directly related to the amount of cement, which is the only source of calcium in the pastes. Because of this, the samples were totally carbonated after the carbonation process, including the cementitious phases. The last column of this table presents weight losses of silica and alumina gel because it is assumed that all the calcium contained in the CSH and CAH phases has reacted with CO_2 to yield calcium carbonate.

Table 6 shows weight losses of the decomposition of calcium carbonate when compared with its source (calcium carbonate can be formed from calcium contained in portlandite or CASH-CSH). This table points out that when carbonation is very aggressive, as it is in this case, the CO_2 not only reacts with portlandite, but also with cementitious phases when there is no more portlandite to react with.

3.2. X-ray diffraction of the carbonation products

Figs. 5 and 6 show those diffractograms corresponding to cement pastes with 0% and 20% substitution, respectively, after curing 28 days and before the carbonation process. Both figures show the presence of calcium carboaluminate, porlandite and calcite as main crystalline products. The difference between them is in the amount of portlandite. The figure corresponding to the paste with 20% FC3R substitution presents the lower intensity portlandite peaks due to their consumption by FC3R pozzolanic reaction. The presence of calcite in the raw materials is demonstrated by these diffractograms as well as the presence of calcium carboaluminate. The cal-

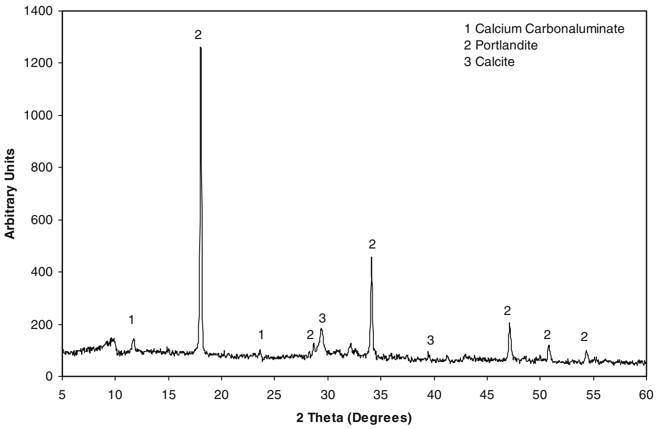

Fig. 5. Diffractogram of cement paste without FC3R after 28 days of curing time.

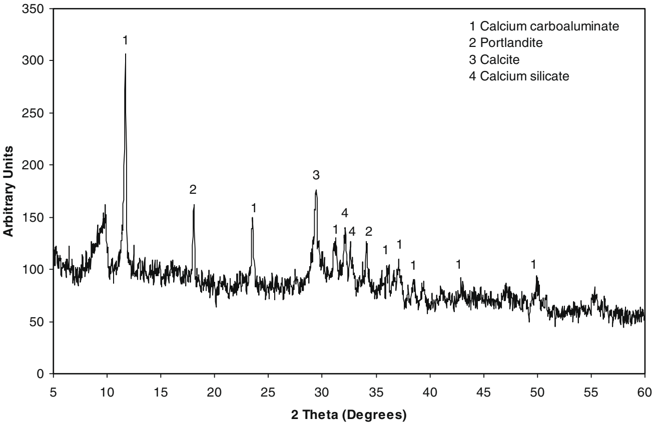

Fig. 6. Diffractogram of cement paste with 20% of FC3R after 28 days of curing time.

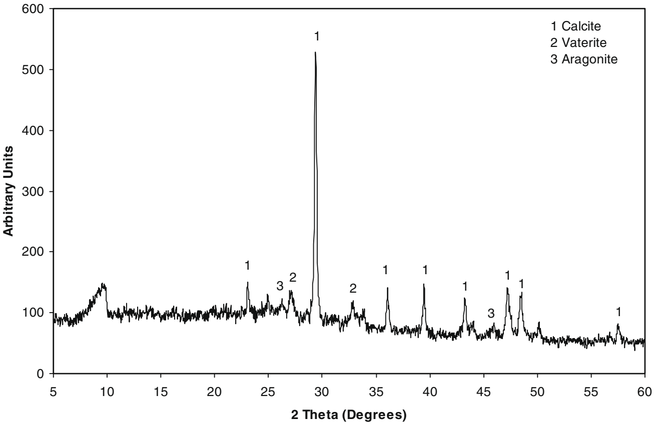

Fig. 7. Diffractogram of cement paste without FC3R after carbonation.

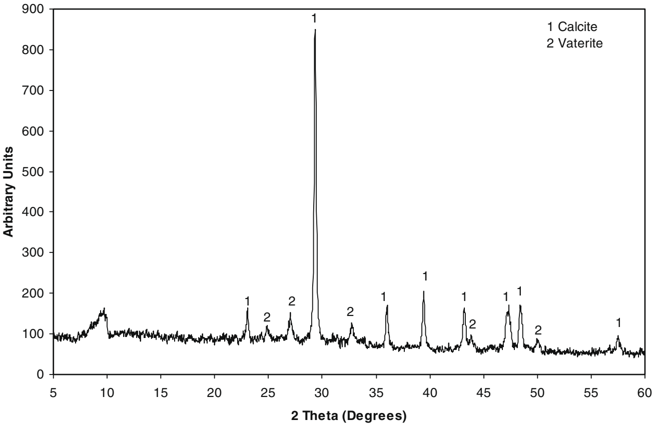

Fig. 8. Diffractogram of cement paste with 20% of FC3R after carbonation.

cium carboaluminate is produced by the reaction between aluminate and calcium carbonate.

Figs. 7 and 8 show the diffractograms corresponding to cement pastes with a substitution of 0% and 20%, respectively, after a curing time of 28 days and once the carbonation process has been completed. In these diffractograms we observe that calcium carbonate is mainly produced as calcite, but there are also peaks corresponding to vaterite in both figures. In Fig. 7 low intensity peaks of aragonite are apparent. No other peaks may be identified because portlandite is not present, since it has been consumed by the carbonation process and silica and alumina gel are not crystalline products.

4. Conclusions

In this study, it has been found that 20% substitution of cement by FC3R can yield additional cementing products due to the pozzolanic reaction of FC3R with the portlandite released by cement hydration. Nevertheless, further substitution of cement exhausts all of the portlandite. We detect the presence of calcium carboaluminate in the pastes (before carbonation) as a reaction product between calcium carbonate included in the raw materials and the aluminate compounds from the cement and the FC3R. Furthermore, the carbonation of cement/FC3R pastes leads to the total consumption of the porlandite in the paste. Further carbonation results in the capture of the calcium contained in the cementitious phases, yielding calcium carbonate and silica and alumina gel. The main product of the carbonation process is calcite, but vaterite has also been detected in the carbonated pastes. Therefore, the presence of FC3R adds CASH phases to a common plain cement matrix and reduces the amount of portlandite (this should be taken into account for applications with steel reinforcements). As a result, a lower amount of calcium carbonate is produced as a consequence of carbonation, but no major differences can be observed with respect to a carbonated plain cement matrix. These facts show that the carbonation of FC3R/cement matrices produces compounds similar to those produced in a plain cement paste, so no additional risk is added when FC3R is used when carbonation attack is expected, apart from the reduction in the alkaline reserve.

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