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Physical, chemical and mechanical properties of fluid catalytic cracking catalyst residue (FC3R) blended cements

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Abstract

The use of fluid catalytic cracking catalyst residue (FC3R) as a cement replacement material has been studied. Four FC3R-blended cements were prepared by the replacement of Portland cement by FC3R in the 6–20% range by mass. Chemical, physical and mechanical properties of the FC3R-blended cements were compared to those of ordinary Portland cement (OPC). Chemical and mechanical tests suggested important pozzolanic activity of FC3R-replacing material. An increase in the compressive strength of the FC3R-blended cements was observed, yielding equal or greater compressive strength than mortars prepared with OPC.

Keywords: Characterization; Pozzolan; Blended cement; Spent fluid cracking catalyst

1. Introduction

A large number of natural and artificial pozzolanic materials have been studied and used for manufacturing several types of blended cements: trass, Santorin earth and other volcanic deposits [1], pulverized fly ashes [2] and, more recently, silica fume [3]. New industrial wastes and by-products with pozzolanic properties are being tested in cement mixtures, e.g. sewage sludge ashes [4], red mud [5] and fluid catalytic cracking catalyst residue (FC3R) [6–8].

Payá et al. [7] demonstrated the high reactivity of FC3R in cement mixtures when the pozzolanic material was previously ground. Pacewska et al. [8] observed the pozzolanic activity of spent fluid catalytic cracking catalyst by several techniques, particularly infrared spectroscopy and thermal analysis.

In order to study the reactivity of FC3R towards cement, a systematic study of some FC3R-blended cements has been carried out. In this paper, some physical, chemical and mechanical properties of FC3R-blended cements are summarized and discussed.

2. Experimental

Spent fluid catalytic cracking catalyst (FC3R) was obtained from BP OIL España S.A. petrol refinery (Castellón, Spain). This material was ground using a laboratory ball-mill. The ground sample presented the following granulometric parameters (wet sieving): 2% retained on 80-μm sieve, 25% retained on 40-μm sieve and 50% retained on 20-μm sieve. The cement for preparing FC3R-blended cements was an ASTM type I Spanish commercial cement (ordinary Portland cement, OPC). Chemical compositions for FC3R and OPC are summarized in Table 1. Mortars

Table 1
Chemical compositions for FC3R and OPC

Parameter (%)	FC3R	OPC
SiO_2	48.2	20.21
CaO	< 0.01	62.87
Al_2O_3	46.0	4.94
Fe_2O_3	0.95	2.85
MgO	< 0.01	1.05
Na_2O	0.50	0.10
K_2O	< 0.01	0.95
SO_3	0.04	3.37
TiO_2	1.65	0.23
Chloride	0.004	0.018
LOI	1.50	2.34
IR	11.11	1.98

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Table 2
Selected chemical parameters for FC3R-blended cements

Cement	FC3R (%)	LOI (%)	SO_3 (%)	IR (%)	Cl^- (%)
A	0	2.34 ± 0.08	3.37 ± 0.11	1.98 ± 0.06	0.0176 ± 0.0007
B	6	2.46 ± 0.08	3.22 ± 0.02	2.0 ± 0.2	0.0167 ± 0.0007
C	10	2.40 ± 0.11	3.03 ± 0.06	2.7 ± 0.4	0.0167 ± 0.0007
D	15	2.40 ± 0.03	2.88 ± 0.11	2.9 ± 0.3	0.0160 ± 0.0007
E	20	2.46 ± 0.2	2.77 ± 0.04	3.19 ± 0.17	0.0167 ± 0.0007

were prepared using a siliceous sand conforming to EN 196-1 [9]. The water used for preparing pastes and mortars had the following chemical parameters: 93 mg/l chloride, 480 mg/l calcium and magnesium (expressed as $CaCO_3$), 298 mg/l SO_4^{2-}, 939 μS/cm in electrical conductivity and pH 7.88. Water/blended cement ratio in prepared mortars was 0.5.

Five cements were studied. Cement A was the commercial cement without FC3R, whereas B, C, D and E cements contained 6%, 10% 15% and 20% by mass of ground FC3R, respectively. These cements (A–E) were chemically characterized, and loss on ignition (LOI) [10], insoluble residue (IR) [10], sulphur trioxide [10], chloride content [11] and pozzolanicity [12] were determined according to EN European standards. The preparation of mortars, setting time determination, constancy of volume and mechanical strength measurements were performed according to EN-196-1 [9] and EN-196-3 [13] standards.

3. Results and discussion

The characteristics of FC3R-blended cements (B, C, D and E) were studied and compared with the control cement (A). Some chemical, physical and mechanical properties for A–E cements were determined and the results are discussed in this section.

3.1. Chemical characteristics

LOI, IR, SO_3 and chloride contents were determined for all the cements. The obtained results are summarized in Table 2.

Cements containing FC3R (B, C, D and E) did not present very different LOI and chloride parameters with respect to the control cement (A). The SO_3 contents decreased with the increase of FC3R percentage in the

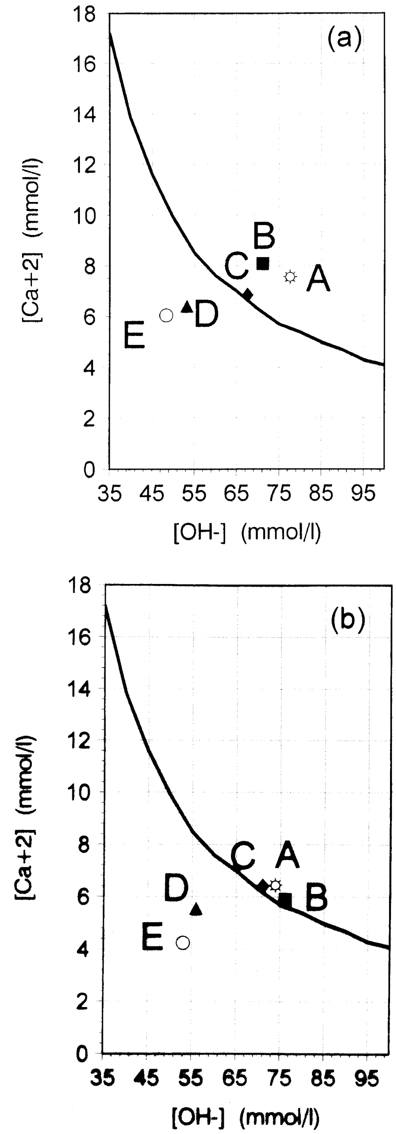

Fig. 1. OH^- and Ca^{2+} concentrations obtained from Fratini's test: (a) 8 days test; and (b) 15 days test.

Table 3
Chemical parameters in pozzolanicity determination for FC3R-blended cements

Cement	8 days at 40°C		15 days at 40°C	
	$[OH^-]$ (mmol/l)	$[Ca^{2+}]$ (mmol/l)	$[OH^-]$ (mmol/l)	$[Ca^{2+}]$ (mmol/l)
A	77.6 ± 0.3	7.55 ± 0.11	73.9 ± 0.4	6.44 ± 0.04
B	71.2 ± 0.3	8.09 ± 0.08	76.2 ± 0.2	5.91 ± 0.08
C	67.5 ± 0.2	6.84 ± 0.04	71 ± 1	6.42 ± 0.08
D	53.3 ± 0.1	6.41 ± 0.07	55.9 ± 0.5	5.56 ± 0.11
E	48.4 ± 0.1	6.03 ± 0.04	53.1 ± 0.7	4.23 ± 0.06

Table 4
Constancy of volume and setting time for FC3R-blended cements

Cement	FC3R content (%)	Water for defined[a] consistency (%)	Distance between needles (mm)	Initial set (min)	Final set (min)
A	0	29.5	0.8	120	158
B	6	30.9	0.1	124	164
C	10	31.8	< 0.1	114	160
D	15	33.0	0.1	102	152
E	20	34.2	0.2	94	145

[a] Defined as the water required to give a paste in which a flat-ended Vicat plunger 1 cm in diameter, weighing 300 g, when released at the surface of the paste penetrates to a point 5–7 mm from the bottom of a Vicat mould filled to a depth of 40 mm.

Table 5
Flexural and compressive strength for mortars prepared with A–E cements

Cement	FC3R (%)	Flexural strength, R_f (MPa)			Compressive strength, R_c (MPa)		
		2 days	7 days	28 days	2 days	7 days	28 days
A	0	6.20 ± 0.30	7.59 ± 0.05	9.50 ± 0.30	33.0 ± 1.0	46.0 ± 1.0	52.0 ± 3.0
B	6	5.60 ± 0.20	8.16 ± 0.10	9.60 ± 0.40	31.4 ± 0.7	46.0 ± 1.0	58.0 ± 3.0
C	10	5.64 ± 0.15	8.10 ± 0.50	9.54 ± 0.11	30.9 ± 0.3	49.0 ± 1.0	62.0 ± 2.0
D	15	5.20 ± 0.30	8.13 ± 0.10	9.30 ± 0.40	29.7 ± 0.5	49.8 ± 0.7	64.6 ± 0.9
E	20	5.10 ± 0.05	7.70 ± 0.20	7.94 ± 0.09	27.7 ± 0.3	48.6 ± 0.6	64.2 ± 1.2

cement; SO_3 content in FC3R was very low and the active addition diluted the control cement. On the contrary, the IR parameter increased with the increase of FC3R content, suggesting that FC3R contained a significant quantity of material insoluble in hydrochloric acid and potassium hydroxide.

Another important parameter in pozzolan-blended cements is the property called pozzolanicity. This parameter was measured according to Fratini's method [12] by the determination of calcium cation (Ca^{2+}) and hydroxyl anion (OH^-) contents for water in contact with the tested cement after 8 or 15 days at 40°C. Ca^{2+} and OH^- contents in water for this test are summarized in Table 3.

In general, a decrease of OH^- and Ca^{2+} concentrations in solution was observed when FC3R content in cement was increased, suggesting the active role of FC3R addition towards calcium hydroxide released from the hydration of cement. The OH^- and Ca^{2+} concentrations are plotted on calcium hydroxide saturation curve in Fig. 1. A, B and C cement points were above the Ca^{2+}/OH^- saturation curve, indicating that the release of calcium hydroxide from cement became more important than calcium hydroxide fixation by active FC3R and the solutions were saturated in $Ca(OH)_2$. However, both 8 days and 15 days tests for D and E cements yielded lower Ca^{2+} and OH^- concentrations and, consequently, their plotted points appeared below calcium hydroxide saturation curve. This behavior found for D and E cements demonstrate the pozzolanic activity of FC3R. Thus, positive pozzolanicity was observed only for cements with highest FC3R contents (15% and 20%).

3.2. Physical characteristics

Constancy of volume and setting times for FC3R-blended cements were determined. From these data summarized in Table 4, several observations may be made: Firstly, the amount of water needed to give a predefined consistency increases as the FC3R content is increased. This increase from 29.5% to 34.2% may be attributed to the adsorption of water on FC3R particles. The loss in workability of mortars containing FC3R [7] by mortar flow measurements has been reported recently, and the behaviour of pastes confirms this aspect.

In the second place, no expansion on hydration was observed using Le Chatelier needles [13]. FC3R did not contain a significant amount of dangerous species (e.g. magnesium sulphates) for expansive processes. Conse-

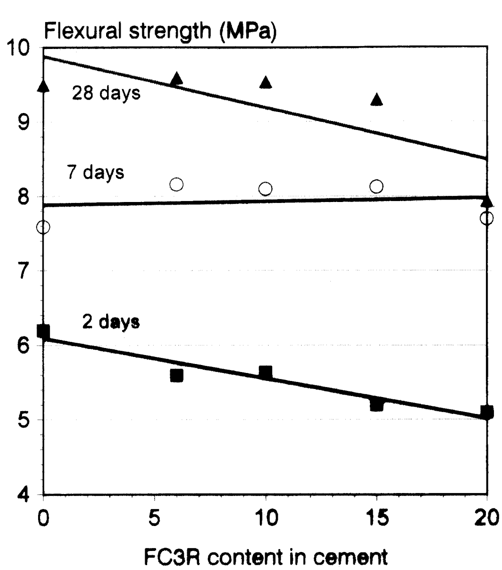

Fig. 2. Flexural strength of cements at several curing ages.

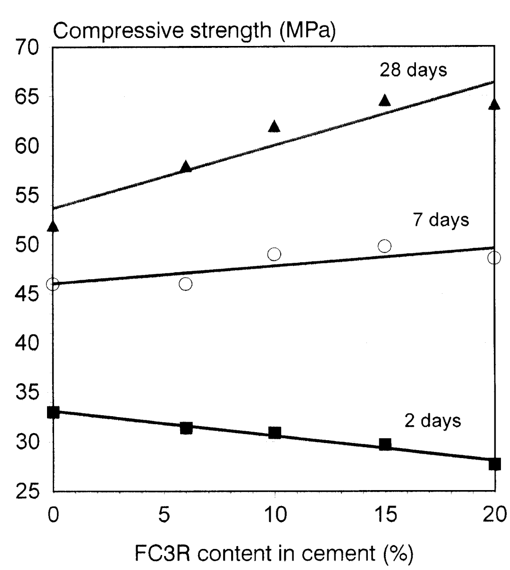

Fig. 3. Compressive strength of cements at several curing ages.

quently, the distance between indicator needles was always lower than 10 mm, demonstrating volume stability in relation to internal attack processes.

Additionally, in the third place, initial and final setting times are noticeably influenced by the presence of FC3R in cements. The initial and final setting times became shorter probably because the sulphate content in blended cement (see Table 2) decreased with the FC3R content by dilution effect.

3.3. Mechanical characteristics

The study of the behavior of FC3R-blended cements was carried out from the mechanical point of view, by preparing $4 \times 4 \times 16$ cm specimens. These mortars, immersed in water and cured at 20°C, were tested [9] by measuring flexural (R_f) and compressive (R_c) strengths at 2, 7 and 28 days ages. Mechanical strength data are summarized in Table 5 and shown in Figs. 2 and 3.

The R_f value after 2 days of curing showed a dependence in the FC3R content, suggesting that very limited pozzolanic reaction at this age. However, for 7 and 28 days of curing time, R_f values for mortars made with FC3R-blended cements were similar to the control mortar made with A cement, indicating the active role of FC3R. Mortar prepared with E cement, (highest FC3R content, 20%) yielded anomalous R_f values at 28 days.

The compressive strength values (R_c) for FC3R-blended cements clearly showed the pozzolanic activity of the FC3R. Fig. 3 plots R_c values for mortars cured for 2, 7 and 28 days at 20°C. Again, a decrease of R_c with the substitution of Portland cement by FC3R was observed for early age (2 days). In general, R_c values for 7 day and 28 day mortars containing FC3R were higher than those of the control mortar. A clear dependence was observed for 28 days of curing time R_c values: compressive strength of mortars increased with the percentage of replacement, demonstrating the pozzolanic activity of FC3R.

An alternative way for revealing pozzolanic contribution of FC3R would be the calculation of the strength gain SG [14]. This parameter was given as follows:

$$SG_i = R_i - \left(R_o \frac{w_{cem}}{w_{binder}}\right)$$

where R_i was the compressive strength of FC3R-blended cement mortar, R_o the compressive strength of control mortar at the same age, w_{cem} the cement content and w_{binder} the sum of cement and FC3R contents. Fig. 4 shows SG values for B, C, D, and E cements.

SG values for cements at 2 days of curing time were very low, suggesting the role as inert material for FC3R replacement. SG values for 7 days of curing time increased with percentage of substitution of Portland cement by FC3R, yielding SG values greater than 10 MPa for D and E cements. SG values for 28 days of curing time were very

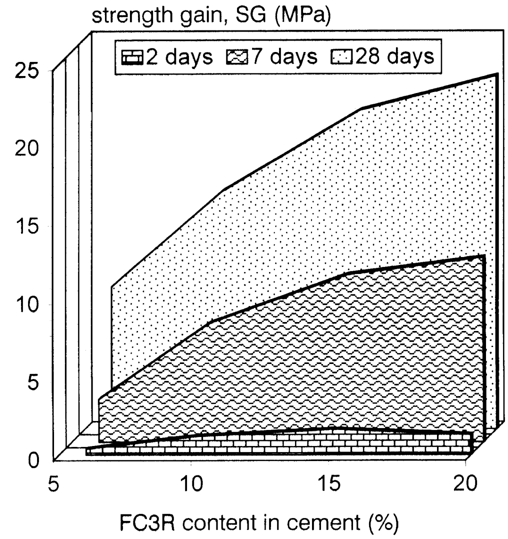

Fig. 4. Strength gain (SG) values for prepared FC3R blended cements at several curing ages.

high (from 9 to 22 MPa), which were much greater than those found for fly ashes [14].

4. Conclusions

1. The suitability of preparing blended cements using FC3R has been demonstrated.
2. FC3R-blended cements prepared by replacing 6–20% of an OPC fulfilled European standards (EN) regarding chemical, physical and mechanical properties.
3. Pozzolanic cements containing FC3R can be prepared with replacing percentages in the 15–20% range.
4. FC3R is presented as a good pozzolanic material. Some important aspects such as durability, chemical resistance and long-term behavior of mortars should be investigated in the future.

Acknowledgments

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