Pergamon

Cement and Concrete Research 29 (1999) 1773–1779

CEMENT AND CONCRETE RESEARCH

Fluid catalytic cracking catalyst residue (FC3R) An excellent mineral by-product for improving early-strength development of cement mixtures

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Received 18 March 1999; accepted 19 July 1999

Abstract

A "new" industrial by-product obtained from the fluid catalytic cracking (FCC) process in petrol refinery is studied for construction uses. This by-product, named as fluid catalytic cracking catalyst residue (FC3R), is composed of original spherically shape particles and fragments produced in the catalytic process (30–0.1 μm) that present highly irregular morphologies. FC3R presented a very high specific surface area that produced a decrease in workability of cement-based mortars containing FC3R. Workability of FC3R-cement mortars can be increased using a superplasticizer. Replacement of cement by ground FC3R in mortars produced a very important increase in compressive strength that exceeds plain cement mortar, probably due to pozzolanic reaction. Ground FC3R can be used for preparing cements with excellent mechanical properties.

Keywords: Pozzolan; Mortars; Mechanical strength; Fluid catalytic cracking catalyst; SEM

1. Introduction

Extensive investigations on the use of mineral admixtures in Portland cement mixtures have been carried out [1–6]. Natural and artificial mineral admixtures have been used (e.g., low-calcium and high-calcium fly ashes, silica fume, blast furnace slag, steel slag, copper, nickel and magnesium slags, volcanic ashes, diatomaceous earth, opaline rock, rice husk ash, phosphogypsum, titanogypsum, municipal solid waste incineration residues, fluid gas desulphurization residues, mining and quarrying wastes, and demolition wastes). Some of these materials are active mineral products possessing pozzolanic activity or/and cementicious properties.

The reuse of industrial by-products in concrete production offers many benefits such as: (1) environmental benefits from diminution of natural resource mining, prevention of disposal problems, energy saving, and reduction of carbon dioxide emissions; (2) economic benefits because by-products may be low-cost materials and they can be used to replace higher-cost materials and significant refuse costs can be avoided; and (3) technological advantages, improving several properties of fresh and hardened mortars and concretes, as early and long-term strength development, sulphate resistance, and rheologic properties.

Petroleum industries and particularly petrol refineries obtain specific or selected molecular-weight fractions using fluid catalytic cracking (FCC) processes. Frequently, used catalyst consists of inorganic silica-alumina-based compounds with "very open" atomic structures (zeolite type). The catalytic activity of these products has a short lifetime and the "old inactive" catalyst may be replaced by the "new active" catalyst. Thus, significant quantities of fluid catalytic cracking catalyst residue (FC3R) are produced, causing waste disposal problems. Several attempts at reuse of this residue in ceramic industry [7] in replacing kaolin as a raw material in the preparation of ceramic frits are underway.

Chemical composition and atomic structure of FC3R may be appropriate for use in mortar and concrete production. To the best of our knowledge, the first reference concerning the use of FC3R in cement and concrete production appeared in 1997 [8]. Recently, Pacewska et al. have studied some properties of cement pastes containing a spent catalyst from catalytic cracking in a fluidized bed [9].

The present paper describes preliminary and recent results on the possibility of use of FC3R in mortar production and the contribution of this "new" mineral admixture to strength development of mortars.

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PII: S0008-8846(99)00164-7

Table 1
Chemical composition of FC3R (percentages in weight)

SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	LOI
48.2	46.0	0.95	<0.01	<0.01	0.50	<0.01	1.50

2. Methods

The source of FC3R was BP-Oil España S.A. refinery in Castellón (Spain). The color of the material was white or very slightly grey. Chemical composition of FC3R is given in Table 1. Analytical-grade toluene (Panreac) was used for specific gravity determination. A laboratory ball mill (Gabbrielli Mill-2) was used for grinding FC3R: 300 g of original FC3R were introduced into the bottle-mill containing 98 balls of alumina (18 mm diameter). A melamine-based product (Melcrete M-200) was used as superplasticizer agent. Characteristics of cement, sand, and water were previously reported [10].

Mortars were prepared as follows: water and cement were mechanically mixed at slow speed for 30 s; after that, sand was slowly added over a 30-s period, and the resulting mortar was stirred for another 30 s at medium speed. The mixer was stopped to let the mortar stand for 90 s; subsequently, superplasticizer (when used) was added, mixed for 60 s at high speed, followed by adding FC3R and mixing for 60 s. Microphotographs were obtained by scanning electron microscopy (JEOL JSM-6300, equipped for microanalysis by energy dispersive X-ray).

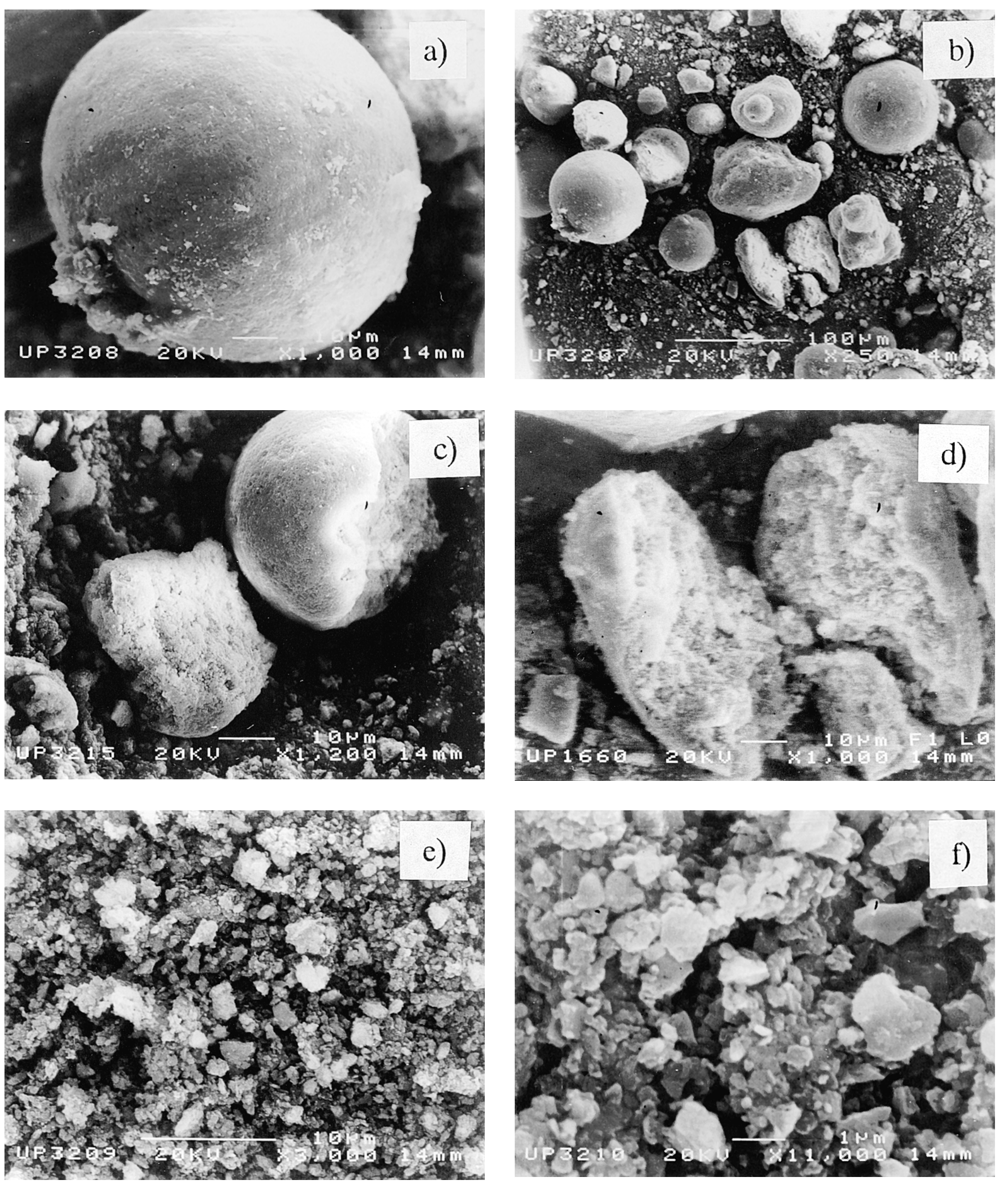

Fig. 1. Scanning electron microphotographs of FCCR: (a) typical spherical FCC catalyst particle; (b) general view of FC3R; (c and d) FC3R irregular particles showing internal porous structure; (e and f) general views for ground FC3R40.

3. Results and discussion

3.1. General characteristics of FC3R

FCC catalyst used in petroleum cracking process contains largely spherical or spheroidal shape particles (Fig. 1a), ranging from 100 to 20 μm in diameter. However, when this material is removed after use, the particle size has been significantly altered. Thus, FC3R is composed of original spherical particles and their fragments (ranging in size from 30 to 0.1 μm) that had highly irregular morphologies (Fig. 1b). FC3R particles showed a very porous appearance as the microphotographs in Fig. 1c and 1d indicate.

The specific gravity values of this material revealed the high porosity of particles; in this sense, 2.45 was the specific gravity value for original residue (named as FC3R0), whereas its bulk specific gravity was only 0.863. Zeolite-type compounds are open framework aluminosilicates, containing polyhedral cavities that are connected by wide windows and channels. For this reason, FC3R particles can absorb water easily and will act as a water-demanding product in cement-FC3R mixtures; thus, a loss of FC3R-cement mixture workability will occur.

To enhance the fineness of FC3R, samples were ground several times (from 5 to 120 min) using a laboratory ball mill. The original spherical and spheroidal particles were totally broken down and particle fineness was spectacularly increased. The microphotographs in Fig. 1e and 1f represent two views of a sample ground for 40 min (named as FC3R40), showing that main part of particles were less than 2 μm in diameter. However, specific gravity values for ground samples ranged from 2.45 to 2.51, indicating that structural cavities and channels into original FC3R0 particles are still accessible after the grinding treatment.

FC3R can be considered as a ceramic mixture of silicon and aluminum oxides (Table 1) in an open framework structure; thus, a lot of silicon and aluminum atoms are at the external surface of crystals (the most obvious boundary of a crystal). Surface atoms are not bonded to the maximum number of nearest neighbors, giving rise to a high surface energy. FC3R was found to have an extremely high specific surface area, about 83000 m^2/kg, indicating the presence of a high quantity of boundary silicon and aluminum atoms, which would act as acidic centers. In this manner, the framework structure will have a large concentration of highly acidic sites in which pozzolanic reaction would take place. Additionally, when materials with high specific surface area are used in concrete formulations, kinetic aspects could be involved; for example, acceleration of cement hydration process because each particle acts as a "nucleation site" for precipitation of cement hydration products. Also, microstructure aspects must be taken into account because this type of material could improve the microstructure of the hydrated cement pastes in the transition zone.

3.2. Flow behavior of FC3R-cement mortars

The presence of connected polyhedral cavities in the zeolite FC3R structure permits the absorption of water molecules, resulting in a water demand when this material is added to cement mixtures. Workability of mortars was determined by means of the flow table method [11]. Spreading of the mortar cone was designated as flow table spread (FTS). Fig. 2 shows FTS values for different FC3R-cement mixtures. To enhancing their workability, a water-soluble melamine-based superplasticizer was used to obtain workable mixtures with 0.45 to 0.5 water/cement + FC3R ratios. Fig. 2 indicates that the substitution of cement by FC3R results in a remarkable reduction of FTS. Moreover, there is no FTS differences between original and ground FC3R, suggesting that the effect on workability of increasing fineness by grinding is much less important than the internal

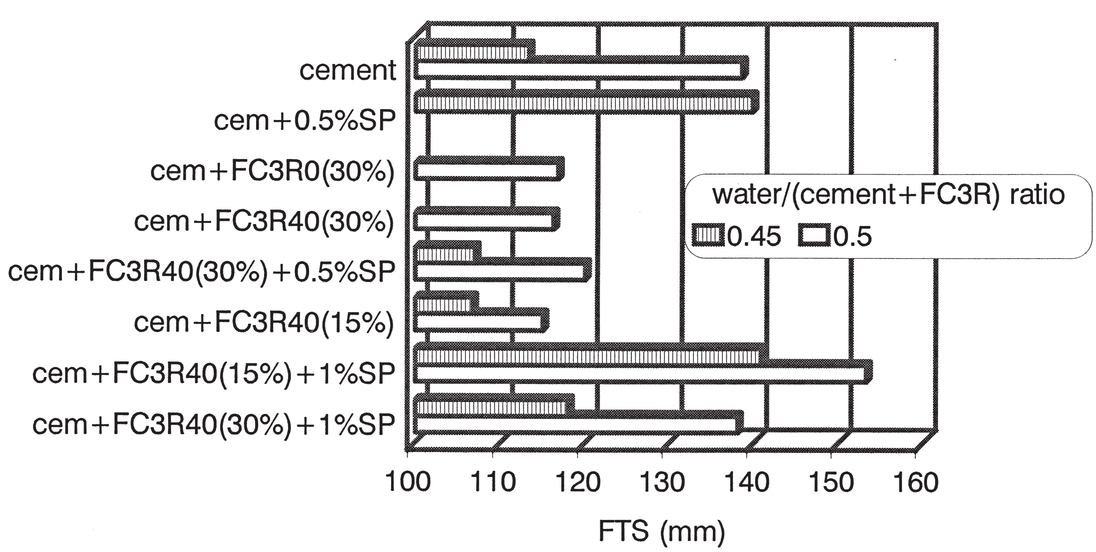

Fig. 2. FTS values for different FC3R-cement mortars.

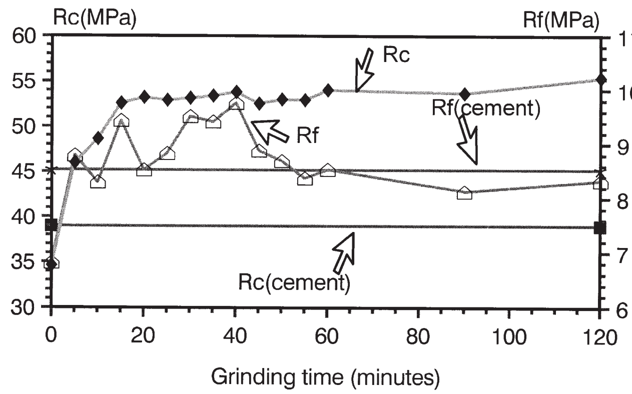

Fig. 3. Rf and Rc strength values for FC3R-cement mortars: the influence of grinding time of FC3R (28-day curing time; 20°C; 30% replacing percentage).

water absorption effect. Mortar mixes also were prepared with superplasticizer [superplasticizer (SP) dosage of 0.5 and 1% by weight of cement + FC3R]. Addition of superplasticizer improves flowability of mortars, in some cases yielding FTS values greater than or similar to that of plain cement mortar.

3.3. Early strength development of FC3R-cement mortars

To study the influence of various parameters such as FC3R fineness, curing time, curing temperature, and FC3R/cement ratio on strength of FC3R-cement-based mortars, several series of mortar mixes were prepared.

3.3.1. The influence of FC3R fineness (series A)

Plain cement mortar was prepared by mixing 1350 g of natural sand, 450 g of cement, and 225 mL of water (0.5 water/cement ratio). FC3R-containing mortars were prepared by replacing a 30% (by weight) of cement. The FC3R-used materials were original (FC3R0) or ground samples (from 5 to 120 min grinding time). Fig. 3 plots flexural (Rf) and compressive (Rc) strength of 28-day cured mortars (at 20°C) vs. grinding time. Grinding enhances the mechanical properties of FC3R-containing mortars, since Rc of FC3R-cement mortars were all higher than 45 MPa when ground FC3R was used, whereas plain cement mortar yielded less than 40 MPa. On the other hand, Rc increased with grinding time only until 20 min. Flexural strength data showed a more erratic behavior, but in general, Rf values for FC3R-cement mortars were similar to or greater than plain the cement mortar one, except for nonmechanically treated min-

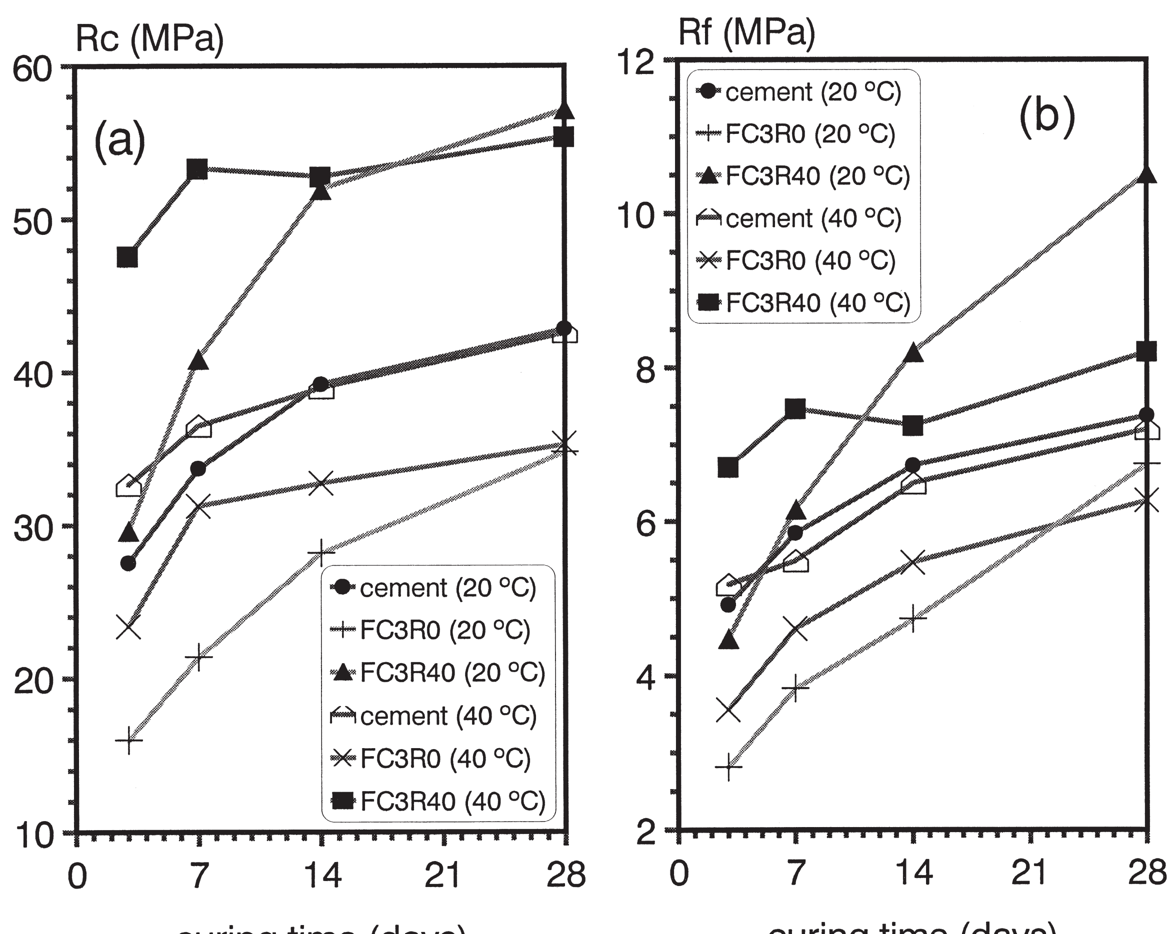

Fig. 4. Mortar strength values for series B. The influence of curing time and curing temperature on: (a) compressive strength and (b) flexural strength.

eral admixture FC3R0. These experimental results suggest that ground FC3R mineral admixture is an effective active material probably due to pozzolanic reaction between hydrated lime from cement hydration and some components of FC3R.

Despite the fact that FC3R0 showed high specific surface area and thus a large concentration of acidic sites, mortar strength values were low. This fact can be due to pozzolanic reactions being restricted to acidic sites nearest to external surface of particles, since cement hydration products and hydrated lime-FC3R products seal off channels. Thus, internal acidic sites do not react further and pozzolanic reaction is delayed. When ground FC3R is used, channels are reduced in length, and the majority of acidic sites are available to react with hydrated lime.

3.3.2. The influence of curing time and curing temperature (series B)

Mortars were prepared as above but only original FC3R0 and 40 min of grinding time FC3R40 samples were used as the replacing admixture. Figs. 4a and 4b show Rc and Rf strength development of mortars, respectively. In this case, it is noted that when FC3R0 is used, Rc and Rf values for both curing temperatures (20 and 40°C) were always lower than those of plain cement mortar strengths. However, grinding of FC3R markedly enhances strengths in such a way that at 7-day curing time, FC3R40-containing mortar strengths clearly exceed plain mortar strengths. Moreover, when curing temperature was raised from 20 to 40°C, a significant gain was observed for 3- and 7-day curing times. Finally, 28-day curing time strength values confirm high pozzolanic activity of FC3R for both curing temperatures.

3.3.3. Influence of cement/FC3R ratio (series C and D)

Series C mortars were prepared by replacing a given percentage, in weight, of cement by FC3R40 (5, 10, 15, 20, 25, and 30%). Series C1 samples were prepared with 225 mL of water without superplasticizer. Series C2, C3, C4, and C5 were prepared with 225, 200, 175, and 150 mL of water, respectively, containing superplasticizer (1% of the total amount of cement + FC3R40 was added for all these series). Series D was prepared varying the FC3R40/(FC3R40 + cement + sand) ratio from 0 to 0.075, maintaining the water volume at a constant level of 225 mL, replacing cement (se-

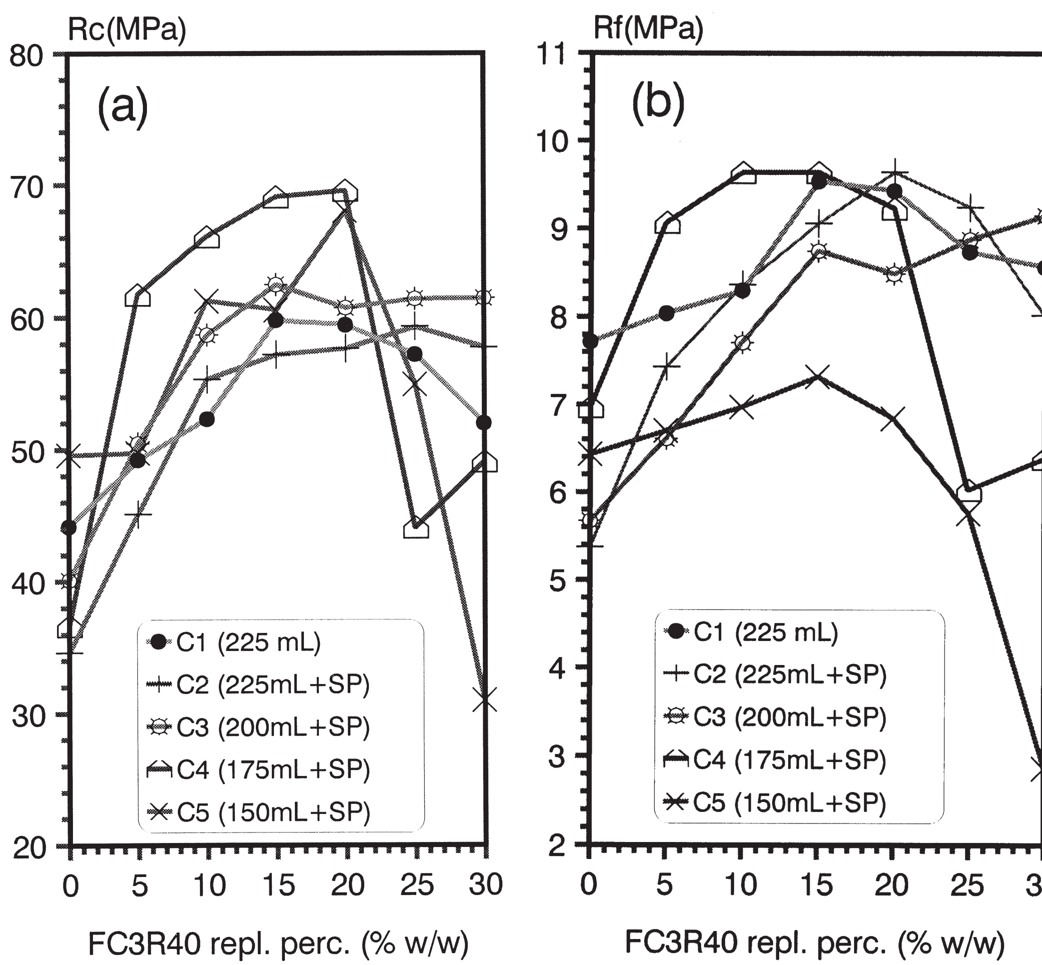

Fig. 5. Mortar strength values for series C. Substitution of part of cement by FC3R40: (a) compressive strength and (b) flexural strength (SP = superplasticizer).

ries D1) or replacing sand (series D2). Figs. 5 and 6 represent strength values for series C and D, respectively.

In general, three facts must be emphasized. Firstly, maximum strength values were found for 15 to 20% replacement percentages of cement by FC3R40, probably due to two reasons: (1) prepared mixes containing the highest replacement percentages (25 and 30%) were less workable and specimens showed high porosity, and (2) reduction of cement content implied less free calcium hydroxide from calcium silicates hydration. Secondly, diminution of water/(cement + FC3R40) ratio increased strength, except for series C5, probably due to low workability of these mortars; very high compressive strength values were obtained for 15 and 20% replacement percentages in series C4. Finally, series D revealed that when sand was partially replaced by FC3R40 a continuous increase of compressive strength with substitution was observed. This fact is in good agreement with available hydrated lime from cement hydration: in this series, hydrated lime is present in enough quantity for pozzolanic reaction development and therefore strength increases.

4. Conclusions

1. Workability of mortars containing cement-FC3R mixtures is lower compared to cement plain mortar. The main reason for this behaviour is the extremely high specific surface area presented by FC3R that produces high water absorption.
2. Grinding enhances pozzolanic properties of FC3R. Rc increases with grinding time up to 20 min; higher grinding times do not produce significant increases. All the mortars containing FC3R gave Rc higher than plain mortar except for nonmechanically treated mineral admixture FC3R0.
3. The behaviour in relation to Rf was more erratic, but in general, Rf values for FC3R-cement mortars were similar to or greater than those of plain cement mortar, except, again, for FC3R0.
4. When FC3R0 is used, Rc and Rf values for 20 and 40°C curing temperatures were lower than plain cement mortar strengths; however, grinding process markedly enhances strengths that exceed plain mortar

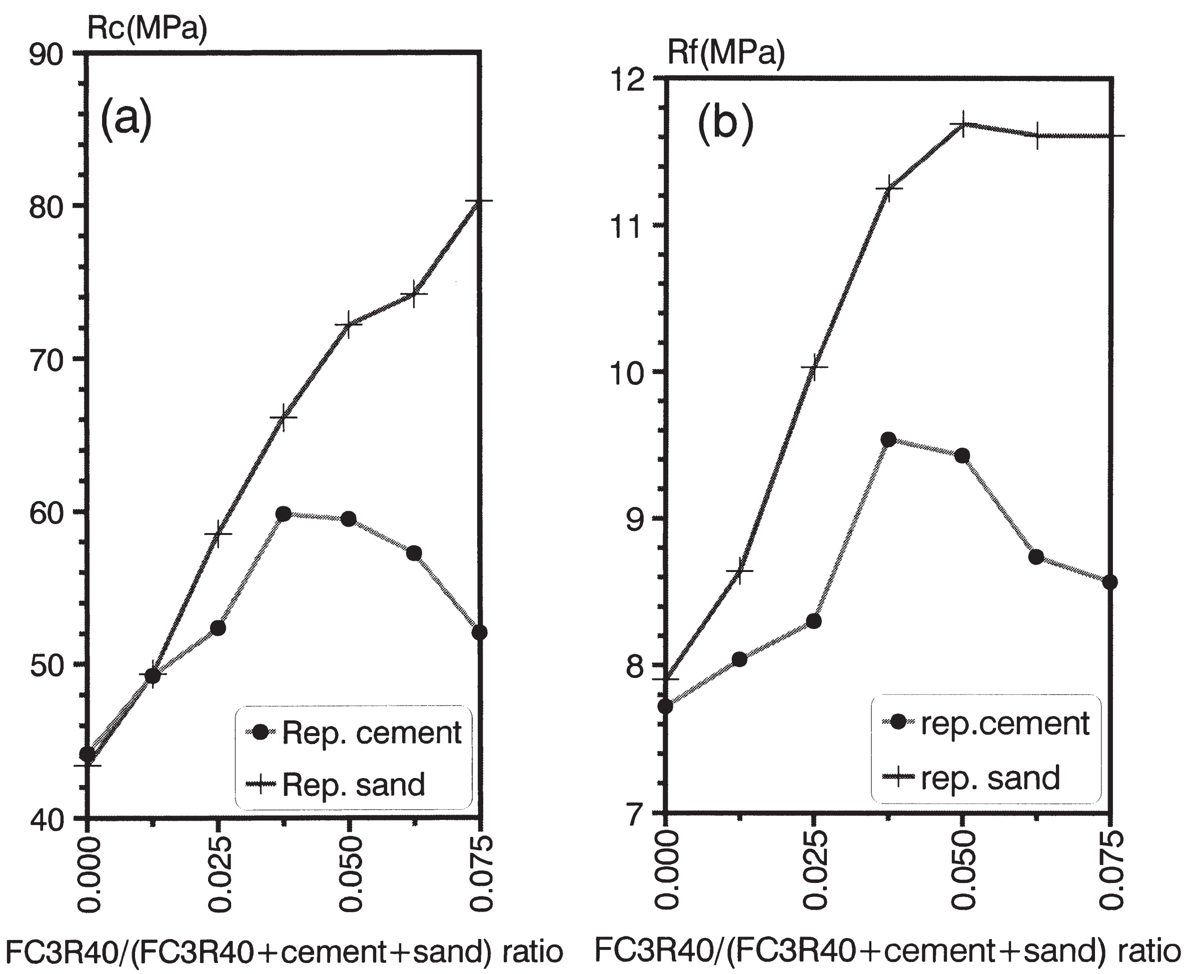

Fig. 6. Mortar strength values for series D. Comparisons between cement replacement and sand replacement by FC3R40: (a) compressive strength and (b) flexural strength.

values for 3-day curing time for both curing temperatures.

5. When sand is partially replaced by FC3R40, a continuous increase of compressive strength with substitution was observed.

Acknowledgments

This work was supported by BP Oil España S.A. Thanks are given to Manuel Planes (technician in charge of the Electron Microscopy Services of the Polytechnic University of Valencia).

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