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# Cement equivalence factor evaluations for fluid catalytic cracking catalyst residue

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ABSTRACT

Fluid catalytic cracking catalyst residue (FC3R) is a waste material that can be used as a Portland cement replacement in pastes, mortars, and concrete. The flow table results show that FC3R is a water demanding addition; nevertheless, this effect can be compensated with the use of superplasticizers. The pozzolanic activity of FC3R was studied observing the mechanical strength evolution with time. Pastes and mortars with FC3R incorporated show higher mechanical strengths than control specimens, indicating the pozzolanic activity of the waste. Cement equivalence factor (*k*-factor) evaluations were carried out. The *k*-factor values for the FC3R pastes and mortars were always greater than one, indicating that in order to maintain the same compressive mechanical strength of the control specimen it is sufficient to replace cement with a smaller amount of catalyst residue, due to the high pozzolanic activity of FC3R. There is a strong agreement between the *k*-factor values obtained in pastes and mortars.



## 1. Introduction

Fluid catalytic cracking catalyst residue (FC3R) is an inorganic waste material, generated in the petrol industry, specifically in the fluid catalytic cracking process. The approximate world generation of waste catalyst at the end of 1994 was of a little under a thousand tons a day [1], rising in the last decade to little more than 3000 tons per day [2,3]. Recent studies reported the contribution to the gain of mechanical strength in mortars and concretes with FC3R incorporated [2–8]. Some others studied the FC3R pozzolanic activity, measured in terms of lime fixation, in lime pastes as well as in cement pastes [4,9–12]. The pozzolanic activity is largely attributed to the zeolitic structure of the catalyst residue, as reported for other zeolites [13,14]. Antiohos et al. [3] reported FC3R cement equivalence factor values (*k*-factor), but only using a single water/binder ratio of 0.5. Those studies confirmed the high pozzolanic activity of FC3R. The use of FC3R incorporated into hydraulic binders has been seen as an excellent pozzolanic material. However, although the FC3R market value is worthless in these moments, the challenge is to optimise the amount of cement replacement due the low FC3R generation volume.

The present study introduces the use of small paste specimens to evaluate compressive mechanical strength development, and compare those results with the ones found in mortars, in order to validate this technique. If the correlation between both specimens (pastes and mortars) is high, the use of pastes would be beneficial in terms of reducing specimen preparation time.

Other advantages are not having to use fine aggregate, and consequently, using less material.

The *k*-factor values were compared to those obtained for metakaolin (MK) in a study on pastes and these were then compared to silica fume (SF) on mortars. MK is a thermally activated aluminosilicate, which reacts with calcium hydroxide to produce similar gel type products such as hydrated calcium silicate obtained from cement hydration, hydrated calcium aluminate and calcium aluminosilicate. It has been reported that substitution of cement in the range of 5–15% by MK produces significant increases in the compressive strength for high performance concretes and mortars, in particular, at early ages [15,16]. On the one hand, the reason to compare SF in mortars was because SF is commonly used as pozzolan for obtaining high strength composites. On the other hand, the FC3R was compared with MK on pastes because this is a material with similar chemical composition and because FC3R had positive results for whiteness. This property is also true for MK, but not for SF.

The aim of this work is to determine the cement equivalence factor for FC3R and to compare these equivalence factors in pastes and mortars.

## 2. Experimental procedure

The catalyst residue (FC3R) was supplied by BP OIL España S.A. (Castellón, Spain). It was ground for twenty minutes in order to obtain an optimal pozzolanic activity [9]. Metakaolin (MK, from Met-

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**Table 1**
Chemical composition and physical properties of Portland cement and pozzolans, %.

| Material | OPC | FC3R | DSF | MK |
|---|---|---|---|---|
| $SiO_2$ | 19.6 | 48.2 | 91.1 | 52.1 |
| CaO | 62.63 | <0.01 | 0.48 | 0.07 |
| $Al_2O_3$ | 5.3 | 46.0 | 0.2 | 41 |
| $Fe_2O_3$ | 3.56 | 0.95 | 0.14 | 4.32 |
| MgO | 2.1 | <0.01 | 0.19 | 0.19 |
| $Na_2O$ | 0.1 | 0.5 | – | 0.26 |
| $K_2O$ | 1.15 | <0.01 | 0.5 | 0.63 |
| $SO_3$ | 3.6 | 0.04 | 0.14 | – |
| LOI | 1.99 | 1.5 | 6.69 | 0.6 |
| Relative density | 3.05 | 2.42 | 2.08 | 2.50 |
| Specific surface area ($cm^2$/g) | 4000 | 11500 | 1200 | 14000 |
| Volume average diameter ($\mu$) | 15.01 | 19.96 | 54.44 | 5.84 |

**Table 2**
Mixtures for the workability study.

| | Control | 15% FC3R |
|---|---|---|
| Water/binder ratio ($w/b$) | (0.35–050) | (0.35–050) |
| OPC (g) | 450 | 382.5 |
| Water (g) | (450*($w/b$))-(S*0.8) | (450*($w/b$))-(S*0.8) |
| FC3R (g) | 0 | 67.5 |
| Aggregate (g) | 1350 | 1350 |
| Superplasticizer, S (g) | S (0–31.5) | S (0–31.5) |

**Table 3**
Adjustment parameters for the effect of superplasticizer percentage on mortar workability according to a linear model (Eq. (1)).

| $W/c$ | Control | | | 15% FC3R | | |
|---|---|---|---|---|---|---|
| | $\alpha$ | $\beta$ | $R$ | $\alpha$ | $\beta$ | $R$ |
| 0.50 | 38.22 | 122.15 | 0.99 | 39.52 | 112.56 | 0.99 |
| 0.45 | 9.77 | 120.25 | 0.97 | 7.65 | 121.33 | 0.98 |
| 0.40 | 7.88 | 105.55 | 0.92 | 5.85 | 104.23 | 0.93 |
| 0.35 | 1.16 | 101.65 | 0.94 | 0.62 | 100.00 | 0.99 |

astar) was used in cement pastes as a comparative pozzolanic material, whereas densified silica fume (DSF from Ferroatlántica) was used for the mortars. Finally, ordinary Portland cement from CEMEX (CEM I 52.5 R, Buñol, Spain) was used. Data on the chemical composition and physical properties of the pozzolans, as well as the cement, are shown in Table 1. For studies on workability and mechanical strength in mortars, a new-generation superplasticizer was used, namely Glenium 22 from Bettor (density 1.05 g/$cm^3$, viscosity at 20 °C was 60 cps, dry residue of 20%). The mortars were prepared with siliceous aggregate, supplied by Caolines Lapiedra (Lliria, Spain), pre-mixed to obtain a fineness modulus of 3.51. Preparation of the mortars for the workability and the mechanical strength studies was carried out according to UNE-EN 196-1:2005 standard [17]. Table 2 shows mortars mix proportions for the workability studies. The influence of superplasticizer on the performance of FC3R mortars was also studied. To determine compressive mechanical strength on cement pastes, as reported in [12], test specimens of $1 \times 1 \times 6$ cm (based on the Köch-Steinegger method [18]) were used. Tables 3 and 4 show mix proportions

**Table 4**
Mix formulations for the $k$-factor study in pastes.

| Paste | Control, FC3R, MK |
|---|---|
| Curing temperature (°C) | 20 |
| Water/binder (%Superplasticizer)[a] | 0.25 (2.00); 0.30 (1.50); 0.35 (1.00); 0.40 (0.50); 0.45 (0.25); 0.50 (0.00); 0.55 (0.00) |
| Pozzolan substitution (%) | 15 |
| Curing time (days) | 3, 7, 14, 28, 90 |

[a] %Superplasticizer is reported to binder content.

for the pastes and the mortars, in the $k$-factor study. For mortars, aggregate/binder ratio was 3/1, being the binder the sum of cement and pozzolan.

## 3. Results and discussion

### 3.1. Workability studies on mortars

Control mortars and FC3R replaced mortars (15% of cement weight) were prepared using different water/binder ratios according to Table 2.

Fig. 1 shows the results obtained on the flow table for mortars. Singular values of workability less than 110 mm were not represented, except for 0.35 water/binder ratio. The following can be observed:

- For all water/binder ratios, mortars substituted with FC3R decrease workability with respect to the control mortar. This can be explained based on the zeolitic type structure of the spent catalyst [19,20], which results in a greater water demand. Additionally, a high specific surface area was found for this material (Blaine fineness 11,500 $cm^2$/g).
- In general, as the percentage of superplasticizer increases, the value of the workability for a given water/binder ratio also increases.
- Experimental data were adjusted to a linear model according to Eq. (1). Table 3 shows these results. It can be observed that the straight trend lines used to adjust experimental data satisfactorily represent the behavior of mortars with respect to % of superplasticizer addition (see the $R$ values in Table 3).

$$\text{Workability (mm)} = \alpha\%\text{Superplasticizer} + \beta \quad (1)$$

### 3.2. Studies on mechanical strength and the evaluation of k-factor in cement pastes

There are previous reports on pozzolanic activity of FC3R, by means of thermogravimetric analyses and by the evaluation of mechanical strengths [2–8,9–12]. Thus, this study is focused on determining the $k$-factor, for which it was necessary to carry out tests on different water/binder ratios, as shown in Table 4. As can be observed on this table, FC3R was compared to MK because they have similar chemical compositions. Table 5 shows the results of compressive mechanical strength on cement pastes from this study. In general, the order of strength is FC3R > MK > Control. For the three types of mixtures, typical behavior can be observed

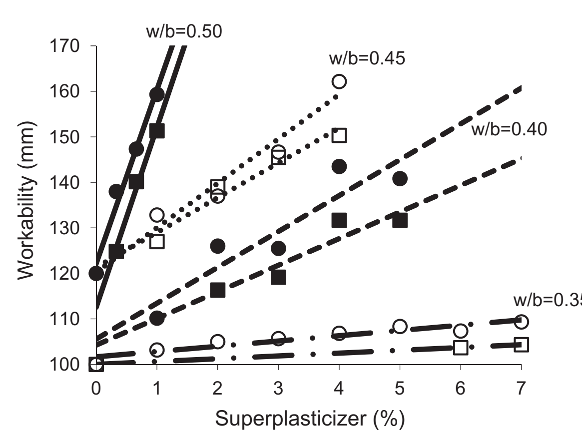


**Fig. 1.** Effect of water/binder ratios and superplasticizer percentage on mortars workability (key: circle for control mortar; square for 15% FC3R mortar).

with respect to curing time and water/binder ratio. That is, it can be observed a gradual increase in Rc as the curing time increases, and a decrease in Rc as the water/binder ratio increases. However, for both FC3R and MK, Rc values are greater than the corresponding control pastes. Only at 3 days of curing time MK paste yielded lower strength than Control paste, indicating that a slower development of pozzolanic activity of MK compared with the catalyst residue at the earliest ages. For example, for the $w/b$ = 0.40–7 days of curing time, the paste with 15% FC3R has a mechanical strength of 68.4 MPa, whereas 63.4 MPa was observed for the MK and 53.6 MPa for the control paste. When the curing time increases for the same $w/b$ ratio, this reactivity order is maintained: at 90 days of curing time, mechanical strength is 100.9 MPa for the FC3R paste, 93.4 MPa for the MK paste and 72.7 MPa for control paste.

For the evaluation of the contribution of a pozzolan to compressive strength, the $k$-factor is calculated. This $k$-factor represents the amount of cement that can be substituted in a paste or mortar by a pozzolan to obtain the same value of mechanical strength. The $k$-factor can be obtained from the following relationship [21]:

$$(w/c)_r = \frac{w}{c_x + k \cdot d_x} \tag{2}$$

where $d_x$ is the amount of pozzolan (addition), $c_x$ is the amount of cement, $(w/c)_r$ is the water/cement ratio without addition, $w$ is the water content to comply the same strength ($R_x = R_r$, being $R_x$ the compressive strength for pozzolan/cement mixture and $R_r$ for control mortar) requirement in both mortars (or pastes).

Thus, solving for the $k$-factor:

$$k = \frac{1}{(d_x/c_x)}\left[\frac{(w/c)_x}{(w/c)_r} - 1\right] \tag{3}$$

where $(w/c)_x$ corresponds to the water/cement ratio in the sample with the addition.

Based on this definition, the process to evaluate $k$ is as follows:

**Table 5**
Average compressive strength of cement pastes.

| Paste | W/b | Curing time (days) 3 Rc (MPa) | 7 | 14 | 28 | 90 |
|---|---|---|---|---|---|---|
| Control | 0.25 | 96.35 | 108.24 | 107.80 | 110.01 | 131.53 |
| FC3R | | 113.13 | 121.03 | 128.01 | 124.22 | 126.28 |
| MK | | 83.69 | 106.25 | 107.03 | 114.84 | 129.54 |
| Control | 0.30 | 76.64 | 88.45 | 86.04 | 102.35 | 108.68 |
| FC3R | | 86.08 | 96.58 | 104.52 | 108.37 | 113.46 |
| MK | | 68.23 | 85.83 | 90.99 | 90.11 | 105.94 |
| Control | 0.35 | 64.03 | 71.34 | 75.80 | 85.60 | 87.76 |
| FC3R | | 72.52 | 89.13 | 96.94 | 107.25 | 108.05 |
| MK | | 58.11 | 80.30 | 81.59 | 93.28 | 91.63 |
| Control | 0.40 | 47.98 | 53.66 | 59.78 | 66.00 | 72.70 |
| FC3R | | 49.45 | 68.44 | 71.83 | 75.31 | 100.94 |
| MK | | 45.33 | 63.41 | 86.44 | 84.85 | 93.41 |
| Control | 0.45 | 45.73 | 54.29 | 57.72 | 61.45 | 77.91 |
| FC3R | | 47.61 | 65.91 | 75.07 | 81.14 | 96.73 |
| MK | | 44.15 | 64.23 | 64.19 | 71.64 | 74.43 |
| Control | 0.50 | 34.18 | 39.65 | 43.65 | 50.96 | 57.00 |
| FC3R | | 35.87 | 50.18 | 58.60 | 62.03 | 68.91 |
| MK | | 34.50 | 47.90 | 54.88 | 60.52 | 56.66 |
| Control | 0.55 | 26.64 | 31.02 | 39.30 | 47.24 | 51.61 |
| FC3R | | 31.32 | 42.75 | 52.27 | 54.35 | 63.25 |
| MK | | 29.69 | 44.49 | 49.34 | 58.36 | 61.19 |

1. Determine the variation of compressive strength with respect to the water/cement ratio for mixtures with and without added pozzolan. Notice that for the $k$-factor study, the $w/b$ ratio is used for the addition of pozzolan, not for the substitution (according to its definition); thus, $(w/c)_x$ must be obtained from Table 3, according to

$$(w/c)_x = (w/c)_r \cdot \frac{450.0}{382.5} \tag{4}$$

2. Obtain adjustment equations correlating compressive strength $R$ and water/cement ratio as:

$$R = R_0 + \frac{h}{(w/c)} \tag{5}$$

where $R_0$ and $h$ are parameters from the adjustment of the equation.

3. Given that the definition of $k$ establishes that $R_r = R_x$, $R_r$ can be calculated for a given $(w/c)_r$ value and, consequently $(w/c)_x$ could be obtained (see Fig. 2).
4. The values of $(w/c)_r$ and $(w/c)_x$ obtained in step 3 are used, in Eq. (3), to obtain $k$ values.

A physical interpretation of the $k$-factor is the following:

- $0 < k < 1$: implies that a greater amount of pozzolan must be added with respect to the amount of cement substituted to obtain the same strength, maintaining the same water/cement ratio, and therefore reducing the water/binder ratio.
- $k = 1$: implies that pozzolan must be added in the same amount of substituted cement to obtain equal strength.
- $k > 1$: implies that a smaller amount of pozzolan must be added with respect to substituted cement to obtain equal strength.

In Table 6 the correlation parameters of Eq. (5) for each curing time are shown, along with the mean relative percentage error ($e_{rm}$), calculated as follows:

$$e_{rm}(\%) = \frac{\sum_{i=1}^{n}\left(\frac{|R_{c,exp} - R_{c,theo}|}{R_{c,exp}}\right)_i}{n} \times 100 \tag{6}$$

where $n$ is the total number of pastes for each curing time.

From Table 6, it is clear that the adjustment achieved is very acceptable (average mean relative percentage error of 5.3%).

Table 7 shows the $k$-factor values for FC3R and MK. The following considerations can be made:

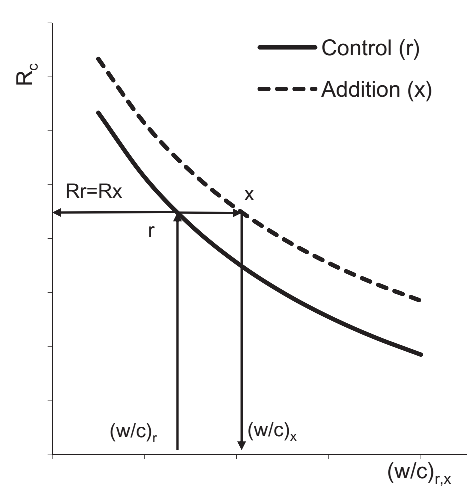


**Fig. 2.** Exemplifying the definition of the factor $k$.

**Table 6**
Correlation parameters of Eq. (5) for cement pastes study.

| Paste | Time (days) | $R_0$ | $h$ | $e_{rm}$ (%) |
|---|---|---|---|---|
| Control | 3 | −29.48 | 31.83 | 3.77 |
| FC3R | | −37.60 | 43.85 | 4.45 |
| MK | | −19.34 | 30.91 | 4.38 |
| Control | 7 | −33.55 | 36.60 | 4.42 |
| FC3R | | −34.88 | 51.62 | 8.23 |
| MK | | −6.98 | 33.30 | 3.85 |
| Control | 14 | −17.72 | 31.36 | 2.96 |
| FC3R | | −19.12 | 46.19 | 5.62 |
| MK | | −6.37 | 36.04 | 5.28 |
| Control | 28 | −9.03 | 30.01 | 4.92 |
| FC3R | | −10.43 | 41.94 | 6.26 |
| MK | | −4.91 | 38.49 | 6.52 |
| Control | 90 | −17.53 | 37.26 | 3.73 |
| FC3R | | 11.15 | 33.86 | 9.74 |
| MK | | 5.52 | 36.18 | 5.08 |

- The $k$-Factor for FC3R is, in general, greater than for MK for all $w/b$ ratios and for all the curing times studied, with the exception of the 0.50 and 0.55 in 7, 28 and 90 curing days.
- For FC3R, at a fixed curing time, $k$ decreases as the $w/b$ ratio increases (as reported in the literature for SF [22] and for FA [23]); whereas for MK, the behavior is the opposite. Since MK is more water demanding than the spent catalyst, when maintaining the same level of superplasticizer (optimized for the FC3R) a less workable paste would be obtained for the MK, thus yielding a better development of the mechanical strength when $w/b$ is increased.
- The maximum $k$ values (at a fixed $w/b$) for FC3R were reached at 14 curing days; this indicates the time of maximum pozzolanic activity. As for the MK, the maximum $k$ values were reached at different $w/b$ ratios. In particular, for 0.55–0.50, the maximum $k$ value is reached at 7 days, whereas for 0.45–0.25 $w/b$ ratios, it is reached at 28 days.
- The $k$ values for FC3R are always greater than 1; therefore, cement can be replaced with a smaller amount of pozzolan to obtain the same strength, maintaining the same water/cement ratio.
- The $k$ values for MK are also greater than 1, with the exception of those corresponding to 3 days (0.50–0.25 of $w/b$) and 7 days (0.25–0.30) which are smaller than 1. Thus, in those conditions it is necessary to substitute cement for a larger amount of pozzolan to obtain the same strength.

### 3.3. Studies on mechanical strength and evaluation of k-factor in cement mortars

The values of compressive strength for cement mortars, manufactured according to Table 8, are tabulated in Table 9. The following considerations can be made:

- Compressive mechanical strength increases as $w/b$ ratio decreases.
- Compressive mechanical strength increases as curing age does, from 3 to 90 days, with stabilization or slight decrease between 90 and 365 days.
- For almost all $w/b$ ratios and curing times, the mortars containing spent catalyst outperform the control ones; the latter outperform silica fume ones as well, except in the case of $w/b = 0.40$. The low DSF reactivity observed is attributable to the degree of densification of the material [24].

As in the study of cement pastes, the correlation parameters were also obtained for the study of mortars using Eq. (5). Table 10 displays the values of these parameters and the mean relative percentage error calculated with Eq. (6), showing again a very acceptable fit (average relative mean error equal to 5.9%).

The cement pastes (specimens of $1 \times 1 \times 6$ cm) were constructed under similar conditions to those of mortars (the only change is the percentage of superplasticizer added). The compressive strength data obtained for mortars and pastes, for the controls and for the FC3R replaced mixtures, can be correlated, as it is shown in Fig. 3. An acceptable relationship of the experimental data obtained by both methods can be observed. It can be seen that as the mechanical strength increases, the difference between the mortar and the paste increases. This behavior is because the mortar has an interface paste–aggregate. When the mechanical strength is

**Table 7**
$k$ Factor values for cement pastes study as a function of curing time and water/binder ratio.

| Time (days) | Pozzolan | $(w/b)_r$ | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | 0.25 | 0.30 | 0.35 | 0.40 | 0.45 | 0.50 | 0.55 |
| 3 | FC3R | 1.67 | 1.58 | 1.50 | 1.42 | 1.34 | 1.26 | 1.18 |
| | MK | 0.31 | 0.42 | 0.53 | 0.64 | 0.76 | 0.88 | 1.00 |
| 7 | FC3R | 2.25 | 2.25 | 2.22 | 2.21 | 2.20 | 2.18 | 2.17 |
| | MK | 0.63 | 0.93 | 1.25 | 1.60 | 1.99 | 2.43 | 2.92 |
| 14 | FC3R | 2.59 | 2.57 | 2.55 | 2.53 | 2.52 | 2.50 | 2.48 |
| | MK | 1.49 | 1.64 | 1.79 | 1.95 | 2.11 | 2.29 | 2.47 |
| 28 | FC3R | 2.16 | 2.14 | 2.12 | 2.11 | 2.09 | 2.07 | 2.05 |
| | MK | 1.86 | 1.91 | 1.97 | 2.02 | 2.08 | 2.14 | 2.19 |
| 90 | FC3R | 2.37 | 2.28 | 2.20 | 2.12 | 2.03 | 1.96 | 1.88 |
| | MK | 0.84 | 1.09 | 1.36 | 1.64 | 1.96 | 2.30 | 2.67 |

**Table 8**
Mix formulations for the $k$-factor study in mortars.

| Mortar | Control, FC3R, DSF |
|---|---|
| Curing temperature (°C) | 20 |
| Water/binder (%Superplasticizer)[a] | 0.35 (5.00); 0.40 (3.00); 0.45 (1.00) 0.50 (0.33); 0.55 (0.00) |
| Pozzolan substitution (%) | 15 |
| Curing time (days) | 3, 7, 14, 28, 90, 365 |

[a] %Superplasticizer is reported to binder content.

**Table 9**
Average compressive strength on cement mortars study.

| Mortar | W/b | Curing Time (days) | | | | | |
|---|---|---|---|---|---|---|---|
| | | 3 | 7 | 14 | 28 | 90 | 365 |
| | | $R_c$ (MPa) | | | | | |
| Control | 0.35 | 52.04 | 64.16 | 62.07 | 68.09 | 78.64 | 81.58 |
| FC3R | | 64.01 | 78.71 | 78.6 | 82.18 | 82.99 | 84.47 |
| DSF | | 40.02 | 51.51 | 56.91 | 56.71 | 61.98 | 73.09 |
| Control | 0.4 | 47.56 | 61.3 | 56.4 | 61.96 | 72.02 | 71.15 |
| FC3R | | 51.63 | 69.44 | 76.2 | 78.4 | 85.39 | 85.34 |
| DSF | | 41.57 | 55.12 | 60.74 | 68.8 | 80.79 | 76.36 |
| Control | 0.45 | 47.77 | 50.58 | 56.29 | 63.7 | 64.87 | 59.85 |
| FC3R | | 47.14 | 62.47 | 68.91 | 79.81 | 78.76 | 71.2 |
| DSF | | 29.99 | 28.67 | 45.55 | 54.72 | 57.68 | 47.62 |
| Control | 0.5 | 40.14 | 43.97 | 49.1 | 53.08 | 55.17 | 50.61 |
| FC3R | | 39.81 | 52.47 | 60.74 | 67.78 | 69.57 | 65.89 |
| DSF | | 29.25 | 35.75 | 45.78 | 47.88 | 45.78 | 43.27 |
| Control | 0.55 | 29.65 | 38.84 | 43.13 | 45.58 | 50.58 | 45.84 |
| FC3R | | 32.53 | 45.86 | 53.54 | 59.36 | 60.74 | 58.77 |
| DSF | | 26.77 | 29.91 | 34.5 | 44.81 | 45.28 | 44.65 |

**Table 10**
Correlation parameters of Eq. (5) for cement mortars study.

| Mortar | Time (days) | $R_0$ | $h$ | $e_{rm}$ (%) |
|---|---|---|---|---|
| Control | 3 | −0.56 | 19.25 | 7.58 |
| FC3R | | −1.91 | 25.2 | 5.33 |
| DSF | | −13.08 | 24.9 | 5.63 |
| Control | 7 | −12.87 | 28.44 | 2.44 |
| FC3R | | −14.83 | 39.29 | 2.01 |
| DSF | | −27.32 | 37.03 | 13.96 |
| Control | 14 | 17.47 | 15.61 | 2.93 |
| FC3R | | −1.15 | 36.4 | 3.26 |
| DSF | | 15.57 | 16.95 | 8.73 |
| Control | 28 | 28.27 | 13.94 | 6.45 |
| FC3R | | 23.84 | 25.85 | 4.52 |
| DSF | | 22.02 | 14.22 | 8.01 |
| Control | 90 | −1.41 | 28.6 | 2.02 |
| FC3R | | −2.23 | 40.74 | 3.98 |
| DSF | | −15.77 | 38.88 | 11.44 |
| Control | 365 | −2.1 | 27.87 | 4.39 |
| FC3R | | −8.34 | 43.43 | 4.25 |
| DSF | | −11.87 | 32.43 | 10.83 |

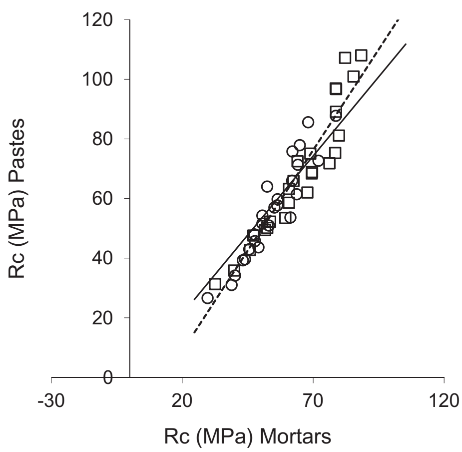


**Fig. 3.** Compressive mechanical strength correlation between pastes and mortars. Key: ○ control mortar; □ 15% FC3R mortar, solid line-adjustment with $a$ = 0, dashed line-adjustment with $a \neq 0$.

**Table 11**
$k$ Factor values for cement mortars study as a function of curing time and water/binder ratio.

| Time (days) | Pozzolan | $(w/b)_r$ | | | | |
|---|---|---|---|---|---|---|
| | | 0.35 | 0.40 | 0.45 | 0.50 | 0.55 |
| 3 | FC3R | 1.57 | 1.55 | 1.52 | 1.50 | 1.47 |
| | DSF | 0.30 | 0.15 | 0.00 | −0.14 | −0.27 |
| 7 | FC3R | 1.97 | 1.95 | 1.92 | 1.90 | 1.87 |
| | DSF | 0.60 | 0.47 | 0.34 | 0.22 | 0.10 |
| 14 | FC3R | 3.66 | 3.28 | 2.93 | 2.61 | 2.31 |
| | DSF | 0.24 | 0.20 | 0.17 | 0.13 | 0.10 |
| 28 | FC3R | 3.79 | 3.66 | 3.53 | 3.40 | 3.28 |
| | DSF | −0.67 | −0.76 | −0.85 | −0.94 | −1.03 |
| 90 | FC3R | 2.33 | 2.32 | 2.30 | 2.29 | 2.28 |
| | DSF | 0.89 | 0.75 | 0.62 | 0.49 | 0.37 |
| 365 | FC3R | 2.52 | 2.44 | 2.35 | 2.27 | 2.19 |
| | DSF | 0.21 | 0.12 | 0.03 | −0.06 | −0.14 |

high, it fails in the interface rather than in the cementitious matrix. Since the paste does not contain this interface, higher mechanical strength values are obtained in pastes. The solid line in Fig. 3 is the adjustment considering an intercept equal to zero, while the

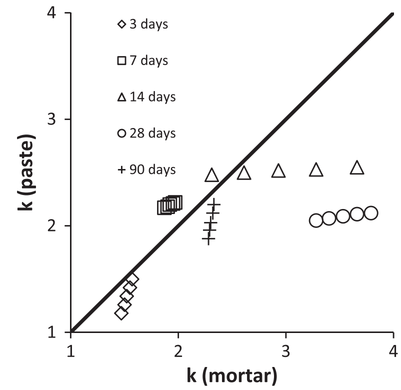


**Fig. 4.** Comparison of FC3R $k$ factor values for cement pastes and mortars.

dashed line in the same figure corresponds to the adjustment considering a non-zero intercept. The correlation factor is equal to 0.93 in the first case and to 0.95 in the second case. This adjustment follows the equation (intercept equal to zero):

$$R_{c,pastes} = 1.06 \cdot R_{c,mortars} \tag{7}$$

The slope is practically equal to 1, showing the equivalence of both methods. This fact highlights the usefulness of obtaining compressive strength from pastes rather than from mortars, given the smaller amount of material used, the advantage of not having to use aggregate, the shorter preparation time, an easier handling, and a less volume. When using the adjustment with non-zero intercept, the equation is $R_{c,pastes} = 1.35 \cdot R_{c,mortars} - 18.17$.

The values of $k$-factor in the mortar study are shown in Table 11. The following observations can be made:

- $k$-Factor for FC3R is much higher than that found for DSF in all $w/b$ ratios and in all curing times studied.
- The behavior of $k$-factor with respect to the $w/b$ ratio for a fixed curing time is linear (due to the type of adjustment used); and for a fixed curing time, $k$ decreases as the $w/b$ ratio increases (as reported for densified silica fume [22] and for fly ash [23]).
- $k$ Values (at a fixed $w/b$) for FC3R increase with curing time, reaching a maximum between 14 and 28 curing days, indicating the time for maximum pozzolanic activity; while DSF shows two $k$ maximum values, at 7 and 90 days, and a minimum at 28 days.
- $k$ Values for FC3R are always greater than 1, meaning that cement could be substituted for a smaller amount of pozzolan to obtain the same strength, as long as the same water/cement ratio is maintained.
- $k$ Values for DSF are all less than 1, contrary to what is reported in the literature. This can be explained due the degree of densification of the tested DSF [24] and to the high dosage of superplasticizer. In our case, the cement would have to be substituted for a larger amount of pozzolan to obtain the same strength. Negative values have no physical meaning, which can be interpreted as an inert addition.

Fig. 4 compares $k$-factor values obtained for mortar and cement pastes containing FC3R. In general, $k$ values obtained from mortars are greater than those obtained from pastes, with the exception of those in 7 curing days (though the difference is so slight that can be neglected). Observed differences are probably due to the different geometry used between the pastes and mortars, as well as the mathematical adjustments carried out with the linear equation model used (Eq. (5)). In FC3R mortars greater cement replacement by pozzolan compared to pastes (higher $k$ factor values) is allowed.

This means that for a given curing time, we can replace more cement by FC3R in the mortar to maintain the same mechanical strength than in the control specimen (only cement), compared to the paste (as has been previously explained since the latter does not contain the interface paste–aggregate). This effect is more evident when the curing time increases (generally higher *k* factor values were found in mortars than in pastes) reaching a maximum at 14 days for pastes, and a maximum between 14 and 28 days for mortars, which shows the curing time for maximum FC3R pozzolanic activity. This can be explained because in the paste, in the absence of aggregate, contact between the portlandite and pozzolan is favored, facilitating the pozzolanic reaction.

## 4. Conclusions

From the results obtained in this study, the following conclusions can be drawn:

1. Mortars substituted with 15% of fluid catalytic cracking catalyst residue (FC3R) show a decrease in workability with respect to the control mortar for all the studied water/binder ratios. This behavior is attributed to the zeolitic type structure of the catalyst residue. As the percentages of addition of superplasticizer increases, the workability also increases. Experimental data were satisfactorily adjusted by straight lines, representing the behavior of the mortars with respect to the percentage of addition of superplasticizer.
2. Regarding the study of mechanical strength in cement mixtures, upon comparing FC3R with the control, MK and DSF, it can be concluded that with FC3R higher compressive mechanical strength at short curing times is obtained, except for the MK at longer curing times. Nevertheless, in all cases, the FC3R mechanical strength is always higher than the control mixture and DSF containing mixture.
3. *k*-Factor values from the study of cement pastes for FC3R are in general greater than those for MK, and always greater than 1, which implies that a smaller amount of catalyst residue can be used to replace cement in order to obtain the same strength. The maximum *k* values for FC3R are registered at 14 curing days, indicating the age of maximum pozzolanic activity, whereas the maximum pozzolanic activity for MK occurs in the range of 14–28 days of curing time.
4. When comparing compressive mechanical strength data obtained in pastes and mortars, a good correlation was observed, confirming the great advantage of working with prismatic 1x1x6 cm test specimens for pastes instead of mortars.
5. The FC3R *k*-factor values obtained from the mortar study are greater than 3.5, between 14 and 28 curing days, indicating the age of maximum pozzolanic activity for FC3R.
6. *k*-factors obtained for mortars and pastes are, in general, very similar. However, *k*-values in mortars are slightly greater. The greatest difference can be observed at 14 curing days for mixtures with low $w/b$ ratios, as well as at 28 curing days for all $w/b$ ratios.

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## References

[1] Meyers RA. Handbook of petroleum refining processes. 2nd ed. McGraw Hill; 1996.
[2] Hsu K-C, Tseng Y-S, Ku F-F, Su N. Oil cracking waste catalyst as an active pozzolanic material for superplasticizer mortars. Cem Concr Res 2011;31:1815–20.
[3] Antiohos SK, Chauliara E, Tsimas S. Re-use of spent catalyst from oil-cracking refineries as supplementary cementing material. China Particuol 2006;4(2):73–6.
[4] Pacewska B, Bukowska M, Wilinska I, Swat M. Modification of the properties of concrete by a new pozzolan. A waste catalyst from the catalytic process in a fluidized bed. Cem Concr Res 2002;32:145–52.
[5] García M, Sánchez MI, Frías M. Pozzolanic reaction of spent fluid catalytic cracking catalyst in FCC-cement mortars. J Therm Anal Calorim 2007;90(2):443–7.
[6] Tseng YS, Huang CL, Hsu KC. The pozzolanic activity of a calcined waste FCC catalyst and its effect on the compressive strength of cementitious materials. Cem Concr Res 2005;35:782–7.
[7] Payá J, Monzó J, Borrachero MV, Velázquez S, Soriano L. Study on the properties of different spent sillicoaluminous catalysts and their use in cementing mixtures. In: 8th CANMET, Las Vegas; 2004. p. 513–527 [Supplementary papers].
[8] Chen H, Tseng Y, Hsu K. Spent FCC catalyst as a pozzolanic material for high-performance mortars. Cem Concr Compos 2004;26(6):657–64.
[9] Caputo D, Liguori B, Colella C. Some advances in understanding the pozzolanic activity of zeolites: the effect of zeolite structure. Cem Concr Compos 2008;30(5):455–62.
[10] Rosell-Lam M, Villar-Cociña E, Frías M. Study on the pozzolanic properties of a natural Cuban zeolitic rock by conductometric method: kinetic parameters. Constr Build Mater 2011;25(2):644–50.
[11] Payá J, Monzó J, Borrachero MV, Velázquez S. Evaluation of the pozzolanic activity of fluid catalytic cracking catalyst residue (FC3R). Thermogravimetric analysis studies on FC3R-Portland cement pastes. Cem Concr Res 2003;33:603–9.
[12] Payá J, Monzó J, Borrachero MV, Velázquez S, Bonilla M. Determination of the pozzolanic activity of fluid catalytic cracking residue. Thermogravimetric analysis studies on FC3R-lime pastes. Cem Concr Res 2003;33:1085–91.
[13] Payá J, Monzó J, Borrachero MV, Velázquez S. Chemical activation of pozzolanic reaction of fluid catalytic cracking residue (FC3R) in lime pastes. Part I: thermal analysis. Adv Cem Res 2004;16:123–30.
[14] Payá J, Monzó J, Borrachero MV, Velázquez S. The chemical activation of pozzolanic reaction of fluid catalytic cracking catalyst residue (FC3R) in lime pastes. Adv Cem Res 2007;19:93–6.
[15] Ponn CS, Lam L, Kou SC, Wong YL, Wong R. Rate of pozzolanic reaction of metakaolin in high-performance cement pastes. Cem Concr Res 2001;31:1301–6.
[16] Fernández R, Nebreda B, de la Villa R, García R, Frías M. Mineralogical and chemical evolution of hydrated phases in the pozzolanic reaction of calcined paper sludge. Cem Concr Compos 2010;32(10):775–82.
[17] UNE-EN 196-1. Métodos de ensayo de cementos. Parte 1: Determinación de resistencias mecánicas; 2005.
[18] Köch A, Steinegger H. A rapid test method for cements for their behaviour under sulphate attack. Zement Kalk Gips 1960;7:317–24.
[19] Payá J, Monzó J, Borrachero MV. Fluid catalytic cracking catalyst residue (FC3R). An excellent mineral by-product for improving early-strength development of cements mixtures. Cem Concr Res 1999;29:1773–9.
[20] Zornoza E, Garcés P, Monzó J, Borrachero MV, Payá J. Compatibility of fluid catalytic cracking catalyst residue (FC3R) with various types of cement. Adv Cem Res 2007;19(3):117–24.
[21] Payá J, Borrachero MV, Monzó J, Ordóñez LM, Bonilla M, Mellado A. Cenizas de Cáscara de Arroz (CCA) Obtenidas en Condiciones de Combustión no Controlada: Posibilidades de Uso en Hormigones. In: Proceedings of III Congreso Nacional de Materiales Compuestos, Málaga (Spain); 1999. p. 501–8.
[22] Alaejos MP, Fernández YM. El Coeficiente de Eficacia del Humo de Sílice. Construcc 1999;49(253):57–63.
[23] Bijen J, Van Selst. Cement equivalence factors for fly ash. Cem Concr Res 1993;23:1029–39.
[24] Martínez-Velandia D, Payá J, Monzó J, Borrachero MV. Effect of sonication on the reactivity of silica fume in Portland cement mortars. Adv Cem Res 2011;23:23–31.