POZZOLANIC REACTION OF A SPENT FLUID CATALYTIC CRACKING CATALYST IN FCC-CEMENT MORTARS

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This work presents the relation between the pozzolanic activity, the hydration heat and the compressive strength developed by blended mortars containing 10 and 35% of a spent fluid catalytic cracking catalyst (FCC).

The results show that, in comparison with 100% Portland cement mortar, a mortar with 10% FCC increases the hydration heat all over the period of testing. This hydration heat increasing is due to the pozzolanic effect, therefore the resulting compressive strength is higher than the reference mortar. Whereas, in a mortar with 35% of FCC, the hydration heat is higher than 100% PC mortar, until 10 h of testing. After this age, the substitution degree predominates over the pozzolanic activity, showing in this case, lower hydration heat and developing lower compressive strength than 100% PC mortar.

Keywords: *compressive strength, heating, hydration heat, pozzolanic reaction, spent fluid cracking catalyst*

Introduction

It is well known that finely divided materials can accelerate the portland cement (PC) hydration. Moreover, if the material shows high pozzolanic activity, the heat produced during the hydration is higher in the blended mortars than in the equivalent reference (a typical example is silica fume (SF)) [1–3]. Due to this fact, an increase in the hydration heat released can have a negative effect on the performance (durability) of the mortars and concretes, mainly due to volume changes (shrinkage) and microcrack formation.

The pozzolanic materials react with calcium hydroxide released in the hydration of PC, increasing the hydration heat due to the exothermic effect of the pozzolanic reaction. This fact is more evident in materials with high pozzolanic activity such as SF, which produces an increase in the hydration heat evolution of blended mortars compared to the 100% PC mortars. Nevertheless, materials with low initial activity, like fly ash (FA), diminish the hydration heat [3], as well as natural pozzolanic materials [4].

Later, Sanchez Rojas *et al.* [1], studied the opaline rock (OR), fly ash (FA) and silica fume (SF). In this work a quick method of detection and quantification of pozzolanic activity with time and the method of Langavant calorimeter was used to control the hydration heat of mortar [5] collected in the Spanish Standard [6]. The results reported that both methods offer similar data on the behavior of the considered materials, since there was a good correlation between both, despite the fact that they are different methods based on the observation of different properties and effects.

At the moment, other alternatives to these materials are being investigated using clayey materials. A typical example is kaolin, that upon a controlled calcination produces metakaolinite (MK) [7], whose properties as a pozzolanic material have been previously exposed [7–10]. Furthermore, Frias *et al.* [11], studied the pozzolanic activity of MK in the heat evolution of mortars with different percentage of cement substitution by MK. The results showed that the MK has similar behavior to SF, generating more heat than the reference mortar.

Recently, the researches are being focusing on an industrial waste coming from the petroleum industry, the fluid catalytic cracking catalyst (FCC). There are several references which corroborate that this residue acts as a very active pozzolan from short curing ages in mortars as well as concretes and with a very good durability [12–20]. However, there is few information about its influence on the hydration heat.

In a previous paper, Payá *et al.* [21] have studied the evaluation of the hydration heat of a type I white cement with a mixture prepared from a substitution of a 15% by mass of FCC, with special characteristics, among of them, the initial FCC was submitted to a previous treatment, a grinding. The registry of the released heat took place in a conduction calorimeter concluding that the FCC mainly accelerates the process of hydration of a white cement at the first moments of reaction (0.6–6 min) without generating higher hydration heats at longer times than the control.

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Despite this study there is a lack of information in this field. Therefore it would be necessary deeper studies about the influence of this industrial waste in the developed heating, because this fact plays an important role in the durability of the blended matrixes, and moreover to observe the evolution of this property, the heating, with different percentages of additions, in order to recommend the ideal percentage in function of the final application of the commercial cement.

Consequently, the present article shows the heat developed in mortars with a substitution of 10 and 35% by mass of FCC. The results obtained in the present paper are important since they provide data to enable an assessment of temperature rise in mortars and concretes to be made in practice, which has an important effect on the engineering properties, mainly on durability, as mentioned previously.

Experimental

Materials and methods

The materials used in this study were: cement, sand and a fluid catalytic cracking catalyst (FCC).

- Base cement: According to the European Standard [22], the base cement was a CEM I/42.5 R cement, with a clinker content equal or above 95%, and could contain up to 5% additional components.
- Sand: The sand used has a silica content of more than 98% and maximum particle size of less than 2 mm.
- Fluid catalytic cracking catalyst (FCC): A spent catalyst (without previous treatment) provided by the company Repsol YPF, whose composition is shown in Table 1. X-ray diffraction (XRD) pattern (Fig. 1), shows an amorphous material with crystalline compound presence that corresponds to a hydrogen aluminum silicate.

The mixed cement were prepared in a high speed powder mixer to ensure homogeneity of the materials treated without disturbing their granulometry. Mixtures were made up by mass to the following compositions (Table 2).

These cement mixtures were used to prepare standardized mortars with sand/binder proportion 3/1 and water/binder of 0.5.

In this work, as in other studies carried out by the authors, an accelerated method was used to study the pozzolanic activity of these materials. This method follows the reaction between the material and a saturated lime solution with time. The test is based on putting the sample in contact with the saturated lime solution at 40±1°C for 2 h and 1, 7 and 28 days. At the end of that time the CaO concentration in the solution was established. The fixed lime (mmol L^{-1}) was obtained by the difference between the concentration in the saturated lime solution and the CaO found in the solution in contact with the sample, at the end of the given period.

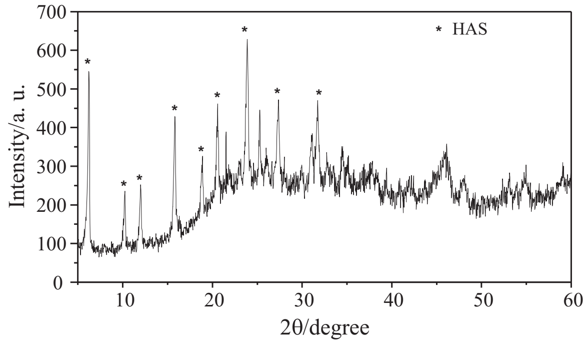

Fig. 1 XRD patterns of FCC

The method given for determining hydration heat in the Spanish Standard [6] is based on the Langavant Calorimeter. This semi-adiabatic method consists of quantifying the heat generated during the cement hydration, introducing a mortar, just mixed, in a Dewar flask, (which is used as a calorimeter). In order to quantify the heat released by the tested mortar, is compared to a thermically inert mortar (minimum three months old). Therefore, heating (°C) is defined as the difference between the temperature of the tested mortar and the temperature of the inert mortar. This value of heating was used to calculate the hydration heat developed by the test sample (Eq (1)):

$$q=\frac{C}{m_c}\theta+\frac{1}{m_c}\int_0^t a\theta \mathrm{d}t \qquad (1)$$

where q is hydration heat (amount of heat given off in J g^{-1} of binder), m_c is the mass of cement in the testing specimen in g, t is the length of the hydration in h, C is the total thermic capacity of the calorimeter and the testing mortar (J °C), a is the global thermic transmission coefficient (J h^{-1} °C^{-1}), and θ is the heating of the testing mortar at the instant t in °C.

Mortars samples were prepared, cured and their compressive strength measured at the curing ages of 2, 7 and 28 days according to the standard UNE-EN 196-1 [23]. The mixes were cast into specimens with the size 4·4·16 cm. The mortars were removed from the molds after 24 h of curing, and the samples were kept in water until the testing age.

Table 1 Chemical composition for FCC/%

Material	L.O.I	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	K_2O	RI
FCC	4.10	42.12	51.27	0.37	0	0.99	0	0.40	0.17	0.53

Table 2 Mixtures compositions

Dosage/kg (UNE-EN 196-9)	
Cement or binder	0.350
Sand	1.050
Water	0.175
Total mass	1.575
Mixtures	
Reference mortar	100% Portland cement (PC)
Binder	90% PC / 10% FCC 65% PC / 35% FCC

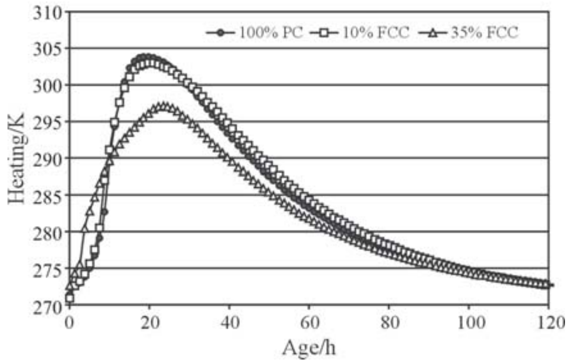

Fig. 3 Heating over time for FCC blended cements mortars

Results and discussion

Pozzolanic activity

The results obtained for the pozzolanic activity are shown in Fig. 2. It is observed that at 2 h FCC show high pozzolanic activity, since it has fixed significant amounts of lime (mmol L^{-1}). This high pozzolanic activity at first ages that FCC presents can be due to the chemical composition of the pozzolanic material (content of acid components: Si, Al, Fe), which plays an important role, but mainly, the crystallinity degree of this material. Thus, FCC displays a low degree of crystallization, leading to a high reactivity with lime.

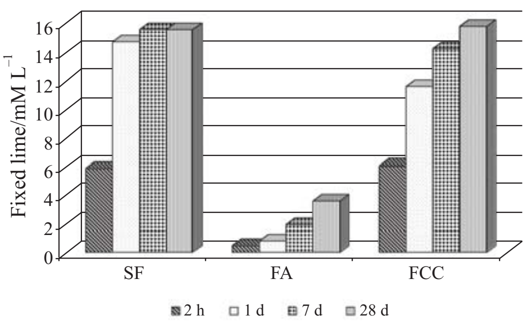

Fig. 2 Pozzolanic activity: fixed lime over time

It can be emphasize, how the FCC shows a 3% higher pozzolanic activity than SF at the age of 2 h, equaling itself practically at 28 days. At this age, FA, also shows lower pozzolanic activity than FCC (92% lower), due to its low activity at early ages [4], FA hardly shows reaction with lime before 28 days.

Heating

Figure 3 represents the evolution of heating for the different mortars analyzed. The results show that the maximum heating happens between 19 and 23 h of hydration and depends on the amount of FCC added.

The fact of replacing cement by a mineral addition, gives rise to a series of considerations that one must take into account. On the one hand it is necessary to consider the influence of substituting PC by additions (effect of dilution) and on the other hand the pozzolanic effect of the material added, that can generate an increase or decrase of the heat developed in the blended mortar with respect to the control.

The graph shows how at first ages (until 10 h), mortars with an addition of 10 and 35% of FCC present a major heating than the reference mortar, this heating is as much greater as greater is the percentage of cement replaced by FCC. This phenomenon displays that the pozzolanic effect predominates on the dilution effect. This fact is in agreement with the pozzolanic activity results previously mentioned.

This increase in the heating might be due to the adsorption of Ca^{2+} ions onto the surface of pozzolana may possibly favor their removal from the solution and this would accelerate the hydration of alite [23]. As happens with natural pozzolans, that the dominant period is shortened and result in an acceleration of the clinker hydration [24].

After 10 h of hydration, an inflexion point is observed, from which a temperature increase is not observed and the decrease of the 'heating' is proportional to the amount of cement replaced. Not only in a 10% FCC mixture but in a 35% FCC mixture, both effects are determining; in the mixture with 10% of FCC the 'heating' diminishes 2.4% and in the mixture with a substitution of 35% this diminution is 23.4% with respect to 100% mortar PC. Therefore, the dilution effect obtained does not correspond with the amount of cement replaced, demonstrating that the substitution effect predominates on the addition since at these ages the FCC pozzolanic activity diminishes.

Evaluation of the hydration heat

Figure 4 shows the hydration heat (J g^{-1} of binder) for 100% PC, 10% FCC and 35% FCC mortars.

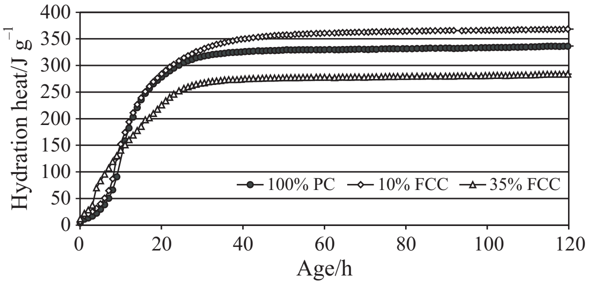

Fig. 4 Hydration heat over time for FCC blended cements mortars

In the case of a mortar with a substitution of a 10% FCC, the pozzolanic activity is the main factor observed, showing higher hydration heat than the 100% PC mortar, during the length of time that the test lasts, five days.

This fact is also observed in a mortar with a 35% FCC substitution at the first 10 h of testing. Nevertheless, from this point, 10 h of hydration, a cement substitution by 35% of FCC diminishes the hydration heat produced with respect to the reference mortar predominating the substitution degree on the pozzolanic activity.

This phenomenon can be clearly seen in Fig. 5 which represents the evolution of the hydration heat of mortars with FCC relative to the reference mortar, with the reference point of zero being assigned to the hydration heat developed by the 100% PC mortar. This graph covers the first 80 h of the test, when the pozzolanic materials often produce an increase in hydration heat in comparison to the base cement.

It can be seen that a 10% of FCC substitution, displays, in all the measurement interval, higher hydration heat than the 100% PC mortar.

Beyond 10 h, the mortar with a 35% of FCC substitution, presents a decrease on the hydration heat in respect to the reference mortar. The positive values obtained at the first 10 h of testing would indicate that the hydration process is favored until that moment.

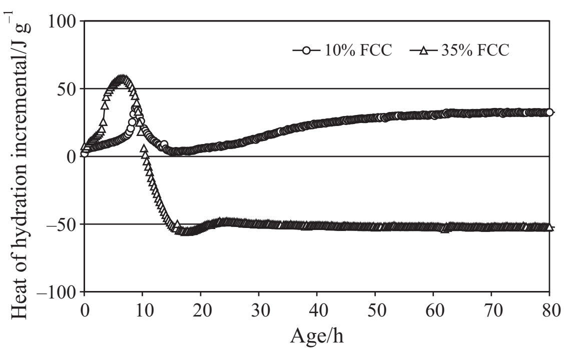

Fig. 5 Heat of hydration incremental over time for FCC blended cements mortars

Therefore, after 10 h of hydration, the substitution percentage of cement counteracts the heat coming from the pozzolanic reaction, predominating the substitution effect on the pozzolanic effect.

This decrease of the hydration heat might be caused because at these high substitution levels the pozzolanic activity may be inhibited due to the reduced availability of portlandite (CH). In the same manner that occurred to a mortar with 30% SF, as reported Frias *et al.* [11].

Compressive strength of hardened mortars

Figure 6 shows the effect of FCC on the compressive strength of mortars (W/B=0.5) cured at 2, 7 and 28 days. In general, the compressive strength of mortars is increased with time. Mortar with 10% of FCC present higher compressive strength value than PC and 35% FCC mortar.

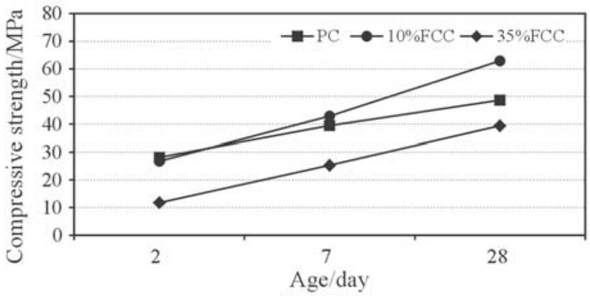

Fig. 6 Compressive strength for FCC blended cement mortars

Normally, replacement of cement in mortars by mineral admixtures would reduce the mechanical properties of the resulting materials due to the dilution effect produce by the substitution of part of the cement [26]. In contrast, the compressive strength of materials would be increased if the inorganic fillers could increase the rate of cement hydration and generate a pozzolanic reaction [1, 27]. The compressive strength of a 10% FCC mortar is at 7 and 28 days, 8 and 22.5%, respectively higher than that the reference mortar, because of the contribution of increasing the rate of cement hydration and generating a pozzolanic reaction overcomes the dilution effect. On the contrary, for 35% FCC mortar, the dilution effect becomes dominant, therefore the compressive strength is 36 and 19% lower at 7 and 28 days, respectively, than the reference mortar. The results obtained of the compressive strengths for these mortars are according to the data obtained for the hydration heat, this is, in a 10% FCC mortar the pozzolanic effect predominates over the dilution effect, and for a 35% FCC mortar, is the substitution degree of the predominant effect.

Conclusions

From the results presented in this paper, the following conclusions can be established:

- FCC is highly pozzolanic industrial waste at first ages, slightly greater than SF and significantly higher than FA (2 h). This has been confirmed by the tests carried out on pozzolanic activity.
- The pozzolanic activity results (fixed lime, Fig. 2) showed that the capacity for fixation lime for FCC is at 2 h, 3 and 92% higher, and at 28 days, 1 and 77% higher, than SF and FA, respectively.
- According to the heating definition, mortars with 10 and 35% addition of FCC, can reach higher 'heating', at first ages, with respect to the control mortar, due to their high pozzolanic activity, prevailing the pozzolanic reaction over the substitution degree. After 10 h of hydration both additions present a heating less than the 100% PC mortar.The predominant effect, in this case, is the substitution degree. The maximum temperatures reached inside mortars are 53°C for mortar with 10% of FCC and 47°C for mortar with an addition of 35% FCC.
- The hydration heat produced by a mortar with an addition of 10% FCC is greater than a mortar 100% PC, whereas for an addition of 35% FCC, at first ages, presents the same behavior, at longer ages the hydration heat observed is less than the reference mortar.
- Respect to the data of compressive strength obtained, it can be concluded that at 28 days, with a 10% FCC mortar the pozzolanic activity is the effect that predominates, since these blended mortars present higher compressive strength that the reference one. In contrast, a 35% FCC mortar have lower compressive strength than the Portland cement mortar, this denotes that the substitution degree is the predominant effect.
- Finally, it has to be pointed out that, although the FCC is a highly pozzolanic material, it is important to select the most suitable percentage of FCC based on the final application of these blended mortars.

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