OUTSTANDING ASPECTS ON THE USE OF SPENT FCC CATALYST IN BINDERS

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Abstract

FCC is a waste material from petrochemical plants which has interesting properties for preparing binders. FCC is lightly grey in color, and white FCC-portland cements with L*≥85 can be prepared. FCC reactivity is enhanced by grinding and it is attributed to pozzolanic reaction towards lime. Stratlingite is the main hydrated product from pozzolanic reaction, and CSH and CAH are also formed. Reactivity of FCC is high, and low curing temperature does not affect this contribution to strength in hardened mixtures. Additionally, high strength concrete can be easily prepared, and compressive strength greater 100MPa can be reached. Mixtures with low w/b ratio showed good behaviour in carbonation tests.

Keywords: FCC, pozzolanic reactivity, lime binder, portland cement binder.

INTRODUCTION

Industrial activities and decontamination processes generate different types of residues and by-products. Most of them have chemical and physical characteristics for their reuse in binding materials based on hydraulic and non-hydraulic binders. Selected residues present special properties for their use in binders, such as silica fume: this material become a primary component for preparing high performance concrete. One of the most promising residues to be coverted as high-added value mineral admixture is the spent FCC catalyst. This component is generated as a waste material in refinery plants in which fluid catalytic cracking bed processes are working, being the waste classified as inert material from the environmental point of view. In the last decade, different research groups are developing studies on their reuse in cementing mixtures: Instituto de Ciencia y Tecnología del Hormigón (Polytechnical University of Valencia ICITECH, J.Payá et al. [1-4]) and Instituto Eduardo Torroja de Ciencias de la Construcción (CSIC, M. Frías et al. [5]) in Spain, Institute of Chemistry (Plock Branch of Warsaw University of Technology, B. Pacewska et al. [6-7]) in Poland, and National Yunlin University of Science and Technology (Taiwan, Su et al. [8]) in the Republic of China.

In the above mentioned reports, it has been demostrated the high reactivity of this residue (FCC) from the pozzolanic behaviour point of view, and varied mixes and their properties have been studied. In our research group, three projects have been developed concerning this material [9-11] and outstanding aspects from these studies are summarized in this paper.

EXPERIMENTAL

FCC wastes were collected from Spanish petrochemical plants. The composition of FCC was summarized in Table 1. Color measurements were carried out using a Minolta Chromameter CR-331C. Thermo- gravimetric analysis were obtained by means a Mettler Toledo 850 TGA thermobalance, working in air atmosphere, sealed aluminun crucibles with pinhole and 10ºC/min heating rate. Workability, setting and mechanical measurements were carried out according to the corresponding Spanish UNE standards. Carbonation treatments were carried out in a chamber with 75% humitidy and passing a 100%CO_2 current.

Table 1. Chemical composition ranges for FCC samples (percentage by weight).

SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO
45.5-49.6	42.7-47.5	0.5-0.8	<0.12	<0.21
SO_3	Na_2O	K_2O	TiO_2	LOI
<0.02	<0.5	<0.05	1.2-1.5	0.3-0.7

RESULTS AND DISCUSSION

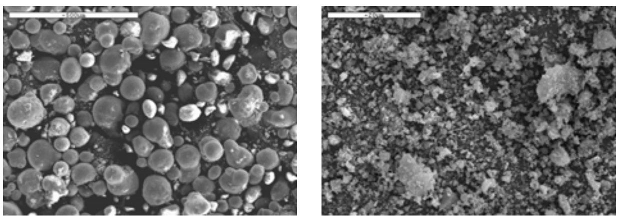
Outstanding physical properties

Whiteness is the most outstanding property: FCC would be used for manufacturing white Portland cements (WPC) because L* values for FCC were high, as can be seen in Table 2. Some black particles are observed due to the presence of carbon on the particle surface, being this carbon removed when calcining at 850ºC as showed L* values for FCC burned samples. Cements in which 20% by weight replacement of white portland cement yielded L values higher than the limit according to UNE83305:2007 (L*≥85).

Table 2. L* values for selected samples

Samp	WPC	FCC	FCC (850ºC)	80%WPC/20%FCC
L*	94.5	81.8-89.1	92.5-94.0	91.3-92.2

Another outstanding aspect is related to the relationship between reactivity and fineness (Figure 1 shows a comparison between original and ground FCC). Reactivity of original FCC must be achieved by grinding as can be seen in Table 3: Activity index AI at 28 days curing age (AI=Ri/Ro, being Ri the compressive strength for 30% FCC-replaced mortar and Ro for control mortar) is increased with ginding time.



(a) (b)

Figure 1. SEM micrographs for FCC samples: a) original; b) ground

Table 3. Activity Index AI values for 28-days mortars containing ground FCC samples (w/b=0,5, T=20ºC, 30% replacement CEM I-42.5R)

Grinding time(min)	0	5	10	20	40
AI	0.897	1.179	1.230	1.359	1.385

Outstanding properties of cementing fresh mixtures

FCC particles are porous and when they are ground become irregular in shape. Both factors have a strong influence on workability of pastes. In this way, water for normal consistency in pastes containing FCC is higher than those found for plain pastes. In Table 4, these values are summarized for WPC and ordinary Portland cement OPC pastes and the corresponding pastes in which a 20% of cement was replaced by FCC. Despite the greater amount of water in these pastes, setting times are slightly reduced compared to those found for plain pastes. This behavior suggests that FCC particles react with cement, increasing the number of contact points among particles.

Table 4. Normal consistency water (NCW) and setting times for pastes containing ground FCC.

Prop.	WPC	80%WPC/20%FCC	OPC	80%OPC/20%FCC
NCW (g)	146	172	155	171
Ts (min)	171	132	149	130
Tf (min)	202	181	178	163

Outstanding reactivity aspects of the pozzolan and the hydration products

The contribution to the strength in FCC- cement mortars could be attributed to pozzolanic reactivity ot this new mineral admixture, and is related to the high content of acid oxides (%SiO_2+%Al_2O_3>90%). Lime fixation can be monitored by TGA on hydrated lime-FCC and cement-FCC pastes. On one hand, reactivity of FCC towards $Ca(OH)_2$ is very high at early ages: 1/1 lime-FCC pastes showed 45% of fixed lime at 3 days curing time, and 60% at 7 days. Thermogravimetric DTG curves for lime-FCC pastes showed a main peak in the range 180-240ºC (See Figure 2, *peak2*) which was attributed to stratlingite (a CSAH hydrate). Also peaks corresponding to CSH (*peak1*) and CAH (*peak3*) were detected as secondary hydration products. *Peak4* was due to

$Ca(OH)_2$ decomposition, which was used for calculating lime fixation.

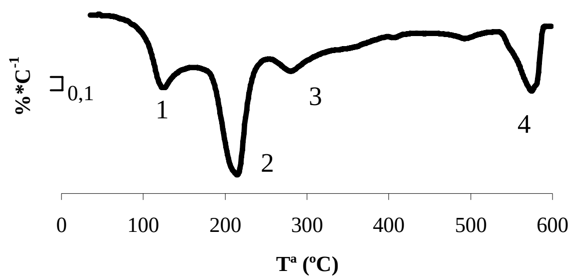


Figure 2. DTG curve for lime-FCC paste

Also, lime fixation in 15%FCC-85%OPC was great at early ages. Thus, 25% and 20% of lime fixation was observed at 3 and 7-day curing times respectively. In this case, lime fixation did not increase with time because an important release of portlandite is produced during the hydration of cement. Also, stratlingite was detected in DTG curves; this hydration product was identified by SEM, in particular for some well crystallized products (See Figure 3).

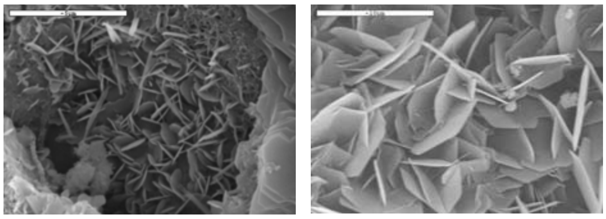
Outstanding performances in hardened binders

1. Curing temperature

It is well-known that a decrease in temperature implies a diminution in chemical reaction rate. In the cementing systems, it could be result in a low strength development. The use of FCC in OPC binders yielded good results when mixtures are cured at low temperatures. For instance, a good behaviour (See Table 5) was observed when 15% of cement was replaced by ground FCC and mortars cured at 5ºC: compressive strengths at 1 and 7-days curing ages were slightly higher in FCC-replaced mortars than those found for plain mortars, despite of lower cement content. A better behaviour was observed when FCC was added maintaining the cement content respect to plain mortar: for the same curing ages and temperature than above, large differences were found in compressive strength when 30% of FCC was added respect to cement content.

2. High strength concrete.

The preparation of high strength concrete could be carried out by reducing the water/binder ratio. The use of reactive mineral admixtures help to get this goal. FCC has shown excellent behavior in high strength concrete (15% cement replacement) as can be seen in Table 6. For instance, in WPC-concrete, a 27% increase in compressive strength was observed at 28-days (0.39 w/b, 20ºC). Also in OPC-concrete, a similar increase, 22%, was obtained at the same age (0.43 w/b, 20ºC).



(a) (b)

Figure 3. SEM micrographs for FCC containing binders showing stratlingite crystals: a) OPC binder; b) lime binder

Table 5. Compressive strengths (MPa) for plain cement mortar and FCC-mortars (T=5ºC, w/c=0,5)

Curing age	Plain mortar	FCC-Replaced (15%)	Fcc-Added (30%)
1 day	3.53	3.61	8.57
7 days	23.0	25.0	44.5

Table 6. Compressive strengths (MPa) for high strength concrete (T=20ºC, 15% FCC-replacement)

Cement	w/b ratio	Plain	FCC
WPC	0.39	81.5	104.1
OPC	0.43	71.5	87.3

3. Durability

Mortars prepared with 15% FCC showed different behavior in accelerated carbonation test, depending on the w/b ratio (See Table 7). Thus, for 0.5 w/b ratio, carbonation rate was higher than for plain cement mortar: due to the lack of alkaline reserve produced by the pozzolanic reaction of FCC, these mortar are easily carbonated. Probably, the reduction in portlandite in the matrix is not compensated by the denser structure produced by the pozzolanic reaction in order to prevent a fast carbonation of the mortar. In the case of mortars with low w/b ratio, the porosity becomes lower and very close: in this manner, the effect of the reduction of the portlandite content is not important because the penetration of CO_2 is prevented by the high density of the cementing paste.

Table 7. Carbonation rate (mm/year$^{0.5}$) for mortars.

Mortar	0.4 w/b ratio	0.5 w/b ratio
Plain	17.9	36.9
FCC (15%)	17.6	51.3

CONCLUSIONS

FCC is a waste with an interesting chance to be reused in cementing matrix, due to high pozzolanic reactivity and excellent properties in lime and portland cement blends. It would be converted from a waste to a primary material for high performance concrete.

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