Cemento adicionado con un residuo del proceso de craqueo catalítico (FCC): hidratación y microestructura

Blended cement containing fluid catalytic cracking catalyst residue (FCC): hydration and paste microstructure

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Resumen

El presente trabajo estudia el efecto de la incorporación de un residuo procedente de la industria petroquímica denominado catalizador gastado del craqueo catalítico (FCC) en la hidratación y microestructura de pastas cementicias. Se utilizan como materiales de referencia, además del cemento portland (OPC), dos tipos de adición de alto desempeño, metacaolín (MK) y humo de sílice (HS). La caracterización de los productos de hidratación se realizó por medio de difracción de rayos X (DRX), análisis termogravimétrico (TG), microscopía electrónica de barrido (SEM) y resonancia magnética nuclear (NMR). Se complementa este estudio con la evaluación de la resistencia mecánica a compresión de morteros a edad hasta de 90 días. Los resultados indican que los principales productos de hidratación en las pastas adicionadas con FCC son silicato cálcico hidratado (CSH), aluminatos cálcicos hidratados (CAH) y silicoaluminatos cálcicos hidratados (CASH). Pastas con 10% de FCC reportan un consumo de cal del 61% a edad de 360 días de curado, valor muy superior al reportado por las adiciones de MK y HS en la misma proporción, esto indica una mayor reactividad del FCC, que incluso se manifiesta a edades tempranas. Cabe anotar que, considerando el factor de dilución, la incorporación de un 10% de FCC como reemplazo del cemento contribuye a la resistencia del material adicionado en órdenes de hasta un 30%. Esto es un indicativo del uso potencial de este residuo como material suplementario en mezclas cementicias.

Palabras Clave: Catalizador gastado de Craqueo Catalítico, Cementos Adicionados, Productos de Hidratación, Resistencia mecánica a compresión

Abstract

The effect of the incorporation of a petrochemical industry waste, named spent fluid catalytic cracking (FCC) in the hydration process and microstructure of cement paste, was studied. Portland cement (OPC) pastes, with and without addition of meta-kaolin (MK) and silica fume (SF), were used as reference materials. The characterization of the type of hydration products was performed by using X-ray diffraction (XRD), thermo-gravimetric analysis (TG), scanning electron microscopy (SEM) and nuclear magnetic resonance (NMR). This study is complemented with the evaluation of compressive strength of blended cement mortars up to 90 days of curing. The main products of hydration in cement pastes, added with FCC, were calcium silicate hydrate (CSH); calcium aluminate hydrates (CAH) and hydrated calcium aluminosilicates (CASH). The addition of 10% of FCC reports lime consumption from 61% to 360 days of curing; this value is higher than the ones reported by the additions of MK and HS in the same percentage of addition. This indicates a higher reactivity of the FCC, which is manifested even at early ages. It should be noted that, considering the dilution factor, the addition of 10% FCC as cement replacement contributes to the strength of the blended material in the order up to an additional 30%. This is indicative of the potential use of this waste as supplementary material in cementitious mixtures.

Keywords: Fluid Catalytic Cracking Catalyst, Blended Cement, Hydration Products, Compressive Strength

1. Introduction

In the construction sector worldwide, Portland cement is the main cementitious material. However, its production requires the use of high temperatures, high energetic consumption, as well as the employment of fossil fuels and high consumption of natural resources, which affect environmental sustainability. Therefore, such process is considered as highly pollutant. This situation has led the scientific community and producer companies to consider the use of other less-pollutant energetic sources and, to incorporate blended material as a partial replacement of cement. In that sense, different kinds of blended material have been analyzed, considering that their addition to cement represents an economic, ecologic and technical solution (Carrasco et al., 2005).

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Such blended material may come from different sources, either natural (pozzolans, limestone), natural and activated by temperature (clay, meta-kaolin) or from industrial by-products (fly ashes, high furnace slag or rice husk) (Kumar and Monteiro, 2006). It is important to highlight that some of such products are considered as industrial waste materials. Their use as blended products has some environmental and economical benefits, since waste material is not dumped into a garbage deposit, thus increasing their aggregate value. Generally, blended products may contribute by modifying green mortars and concrete behavior, as well as their performance in the long term (ACI 201). Some alternative materials work as micro-fillers by increasing cement paste density and by delivering a dense and homogeneous microstructure in the paste-aggregate transition zone. They contribute to the permeability reduction, to increase mechanical properties and, in general, they facilitate the production of blended mortars and concretes of proper mechanical and durability properties. In some countries, specifications and standards have incorporated blended products by admitting them as part of the so-called blended cements.

Over the past few years, the use of a fluid catalytic cracking material has been reported (FCC, English initials). This residual material comes from petrochemical industry, where the virgin catalyst is used to refine crude for gasoline and other fuels production. The worldwide production is estimated in 400,000 tons/year approximately (Zornosa et al., 2008), which is mainly used by some refineries as inert element for roads paving and filling, as well as refill or aggregate for cement blocks. In Colombia the generation of FCC catalyst residue is estimated in 15,000 tons per year. In spite of being in contact with products of the petrochemical industry and, although some heavy metals have been found in its structure, this material is not environmentally dangerous; therefore, it is classified as an inert solid residue (Torres et al., 2012).

The FCC is a semi-crystal material formed by particles of spherical or spheroid shape, of highly porous nature, thus providing an increased specific surface which is quite typical of high reactivity (Chen et al., 2004; Paya et al., 2009; Tseng et al., 2005). The chemical composition of this spent catalyst is quite similar, no matter what its origin is. It is mainly formed by Al_2O_3 within a range of 37 – 46% and, SiO_2 within a range of 47 – 58%. It has an average particle size ranging from 60-70 μm (Chen et al., 2004; Tseng et al., 2005; Torres et al., 2009; Paya et al., 2003; Paya et al., 2003a; Pinto et al., 2007).

Different studies suggest that the optimum FCC percentage, as cement blended material, is between 10 and 15%, values that increase cement compressive strength from 10% to 26%, respectively (Chen et al., 2004; Paya et al., 2009; Tseng et al., 2005). It is important to indicate that such increases may be observed at early ages, due to the effects of blended material on the acceleration reactions during the hardening process.

Although it is demonstrated that this is a highly reactive element, it is possible to increase its reactivity by means of thermal or mechanical activation processes (Paya et al., 2000). Furthermore, some researchers have demonstrated that blended mortars and cements with 20% FCC have a proper behavior, when facing chlorides and sulfates attacks (Pacewska et al., 2000; Zornosa, 2007).

The purpose of the present paper is to analyze the micro-structural development and the hydration process of blended cement pastes at 10% and 20% FCC, as replacement for cement in the same proportions; consequently two widely studied pozzolans have been employed as reference materials: one of aluminum nature (meta-kaolin, MK) and the other of siliceous nature (silica fume, SF) containing 10% of blended material.

2. Materials and experimental procedure

2.1 Materials

For the execution of this study, a fluid catalytic cracking residue (FCC) was employed, which was supplied by a Colombian petro-chemical industry. Its physical and chemical characteristics are shown by Table 1.

Tabla 1. Características químicas y físicas de los materiales utilizados

Table 1. Chemical and Physical Characteristics of employed material

Características/ Characteristics	FCC	MK	HS/ SF	Cemento/ Cement (OPC)
Composición química, %/ Chemical composition, %				
Oxido de Sílice, SiO_2 / Silicon Dioxide, SiO_2	44,13	53,00	>90,00	19,43
Oxido de Aluminio, Al_2O_3 / Aluminum Oxide, Al_2O_3	46,06	43,80	-	4,00
Oxido de Hierro, Fe_2O_3 / Iron Oxide, Fe_2O_3	0,81	0,43	-	3,61
Oxido de Calcio, CaO / Calcium Oxide, CaO	0,52	0,02	-	64,46
Oxido de Magnesio, MgO / Magnesium Oxide, MgO	-	0,03	-	1,52
Oxido de Potasio, K_2O / Potassium Oxide, K_2O	0,11	0,19	-	0,39
Oxido de Titanio, TiO_2 / Titanium Oxide, TiO_2	0,67	1,70	-	0,34
Pérdidas por ignición, LOI/ Loss by Ignition, LOI	6,50	0,46	6	2,58
Propiedades Físicas/ Physical Properties				
Densidad (Kg/m^3)/ Density (Kg/m^3)	2,63	2,60	2,01	3,15
Tamaño medio de partícula (μm)/ Average particle size (μm)	16,15	1,20	0,20-0,50	23,00

Table 1 shows that FCC is mainly formed by aluminum and silica in almost 90% and its average particle size is 16.15 μm . Other materials employed by this study, in addition to the non-blended Portland cement (OPC), are Silica Fume (SF) and Meta-kaolin (MK), which characteristics are included in the same Table 1. They were used as reference material, for comparison purposes only.

Figure 1 shows the pictures from scanning electron microscopy (SEM) for the FCC. It is demonstrated that particles have a spherical or spheroid shape, with a high porosity, which provides a high specific surface reflected by a high reactivity.

Figura 1. Micrografía SEM del catalizador gastado del craqueo catalítico (FCC)

Figure 1. Scanning Electron Microscopy (SEM) for the spent Fluid Cracking Catalyst Residue (FCC)

2.2 Blended pastes preparation and employed techniques

In order to monitor the hydration process, Ordinary Portland Cement pastes (OPC) were elaborated with and without blended materials. Pastes were prepared with a water/binder ratio (w/B) of 0.35% and the replacement of cement by FCC, in the proportion of 10% and 20%. Besides non-blended Portland cement (OPC), cements were used with addition of meta-kaolin (MK) and silica fume (SF) in a proportion of 10%, as reference materials. The samples were cured at room temperature in saturated water with $\text{Ca}(\text{OH})_2$ during different periods comprising 7, 28, 90, 180 and 360 days. When curing stage was completed, the samples were grinded and “frozen” by using acetone and ethanol, so as to avoid the progress of reactions. Finally the materials were characterized by their mineral and micro-structural composition by using the thermo-gravimetric analysis (TG), x-ray diffraction (DRX), nuclear magnetic resonance (NMR) and scanning electron microscopy (SEM) analyses. Furthermore, the mechanical compressive strength for FCC blended cements was also assessed.

3. Discussion and results analysis

3.1 Study by means of Thermo-gravimetric analysis – Portlandite consumption

The thermo-gravimetric analysis (TG/DTG) was carried out by a TA Instrument device SDT Q600, at heating speed of $10^\circ\text{C}/\text{min}$, under a nitrogen atmosphere with a flow of 100 ml/min by employing an alumina crucible. Figure 2 shows the DTG curves of reference paste (100% OPC) and pastes blended with FCC, MK, SF at different curing ages, 7, 28, 90, 180 and 360 days.

The peak number 1 on Figure 2, located at a temperature between $115\text{--}120^\circ\text{C}$, corresponds to the dehydration of calcium silicate hydrate (CSH) and, it is overlapped with peak number 2 corresponding to ettringite, which is located at a temperature ranging from $100\text{--}180^\circ\text{C}$.

Peak 3 in the range of 180-240°C is attributable to the dehydration process of calcium aluminate hydrates (CAH) and; hydrated calcium aluminosilicates (CASH). Finally peak number 4, around 400°C, corresponds to the de-hydroxylation of calcium hydroxide (CH), and a minor peak in the area at 700°C corresponds to the decomposition of blended carbonate for the test sample. It can be observed that as long as material hydration progresses some changes take place on the DTG graph. Such changes are provoked by the increase of hydration products.

Figura 2. Curvas DTG a diferentes edades de curado. a) 7 días, b) 28 días, c) 90 días, d) 180 días y e) 360 días
Figure 2. DTG curves at different curing ages. A) 7 days; b) 28 days; c) 90 days; d) 180 days and; e) 360 days

As from seven (7) curing days, it is observed that peak 3 is higher for FCC and MK blended pastes, due to the high alumina content (Table 1) and the progress of pozzolanic reactions. This behavior matches with the one reported by other researches (Pacewska et al., 1998; Pacewska et al., 2000; Borrachero et al., 2002; Dweck et al., 2008). DTC graphs allow us to conclude that hydration products obtained from FCC addition are quite similar to the ones reported by the reaction between meta-kaolin, silica fume and cement.

By analyzing the peak around 400°C, corresponding to the dehydration of calcium hydroxide (CH), it is observed that blended samples contain less amount of calcium hydroxide in comparison to non-blended samples, throughout all curing ages, therefore, proving the pozzolanic nature of FCC, MK and SF. In general, 10% FCC blended cement shows a lower amount of CH, in comparison to the ones containing MK and SF at the same percentage, thus showing a higher reactivity by FCC.

The progress of dehydration of blended cement is associated to the pozzolanic activity of blended material, which can be confirmed by the calcium hydroxide activity consumption assessed from the weight loss calculation between 400 and 500°C on Figure 2. Affixed lime percentage reported by FCC, MK and SF, due to pozzolanic reaction, was calculated by means of the Equation 1 (Tseng et al., 2005; Paya et al., 2003; Zhang et al., 2012).

$$\% \text{ cal fijada} = \frac{(CH)_0 - (CH)_p}{(CH)_0} * 100 \quad (1)$$

Where $(CH)_0$ is the initial amount of $Ca(OH)_2$ contained by the paste OPC/FCC and; $(CH)_p$ is the amount of $Ca(OH)_2$ in the same paste, at a given age.

The results obtained by Equation 1 are presented by Table 2, which shows that 10% FCC blended cement at has the greatest reactivity, throughout different curing ages under study. Consequently, at 7, 28, 90, 180 and 360 curing days, consumptions of 38.84%, 44.07%, 46.46%, 57.71% and 61.44%, are reported respectively. Generally, such values are higher than the ones reported by MK and SF blended pastes. It is important to mention that the 20% FCC addition also reports higher lime consumption in comparison to other blended pastes, excepting for 90 and 180 days of curing, where the consumption was slightly lower. This behavior is in line with the one reported by other researchers (Torres et al., 2009; Pacewska et al., 1998; Pacewska et al., 2002). The values here presented explain some unusual results reported by former studies regarding curing ages up to 28 days (Trochez et al., 2010).

Tabla 2. Porcentaje de cal fijada para cada tipo de adición
Table 2. Percentage of affixed lime for each blended material

Consumo de Cal (%) Lime consumption (%)	7 días 7 days	28 días 28 days	90 días 90 days	180 días 180 days	360 días 360 days
10% FCC	38,84	44,07	46,46	57,71	61,44
20% FCC	32,17	33,65	37,03	42,89	47,22
10% MK	28,39	33,19	38,87	43,81	45,77
10% HS/ SF	20,29	25,89	29,34	33,91	33,30

Above results are in line with the ones obtained from mechanical compressive strength (see Figure 3), highlighting the performance of 10% FCC paste.

Figura 3. Resistencia de los morteros con y sin adición
Figure 3. Mortars pastes compressive strength, with and without addition

3.2 NMR - ^{29}Si analysis on hydrated pastes

The ^{29}Si Nuclear magnetic resonance technique (NMR) is used to identify the level of silicate polymerization on the hydrated paste. The obtained spectrum signals depend on the length and angle of the Si-O-Si link, as well as on the adjacent atoms. Initially, the cement anhydrous phases correspond to Q0 (-66 a -74 ppm), where the silicon atom does not share oxygen with adjacent atoms. As long as hydration progresses, polymerization takes place delivering dimers (Q1, -75 a -82 ppm) or chains (Q2, -85 a -95 ppm), making room for CHS. The replacement of Si in the tetrahedron by aluminum atoms (Qn (xAl)) displaces the spectrum signal towards more positive values. Figure 4 show the NMR ^{29}Si spectrums on the reference paste and 10% FCC, MK and SF blended pastes at ages of 1, 7 and 90 curing days. All spectrums contain non-reactive anhydrous cement components at close resonances ranging from -71.3 ppm and -73.3 ppm attributable to belite (C3) and alite (C2), respectively. The spectrums also contain wide resonances, still unresolved, with peaks pertaining to Qⁿ tetrahedrons of calcium silicate hydrate (CSH) (Kjorth et al., 1988; Brough et al., 1994; Cong et al., 1998).

This phase resonances are originated in the SiO_4 tetrahedrons groups located at the end of chains (Q^1 , a -78ppm), at the center chains (Q^2 , a -85 ppm) and, located at bridging position (Q^{2p} , a -82 ppm). Finally there is a peak at -81 ppm, pertaining to the resonance of a SiO_4 tetrahedron and AlO_4 tetrahedron as the closest neighbor (Q^2 (1Al)) (Richardson et al., 1993; Andersen et al., 2003).

Figura 4. Espectro NMR ^{29}Si de muestra de cemento hidratado a: a). 1 día (Cem-Ref) b). 7 días (Cem-Ref) c). 90 días (Cem-Ref) d). 1 día (Cem-FCC) e). 7 días (Cem-FCC) f). 90 días (Cem-Ref) g). 1 día (Cem-MK) h). 7 días (Cem-MK) i). 90 días (Cem-MK) j). 1 día (Cem-HS) k). 7 días (Cem-HS) l). 90 días. C2: silicato bicálcico (SC_2), C3: silicato tricálcico (SC_3)

Figure 4. NMR ^{29}Si spectrum of hydrated cement sample at: a). 1 day (Ref-Cem) b). 7 days (Ref-Cem) c). 90 days (Ref-Cem) d). 1 day (FCC-Cem) e). 7 days (FCC-Cem) f). 90 days (Ref-Cem) g). 1 day (MK-Cem) h). 7 days (MK-Cem) i). 90 days (MK-Cem) j). 1 day (SF-Cem) k). 7 days (SF-Cem) l). 90 days. C2: bicalcium silicate (SC_2), C3: tricalcium silicate (SC_3)

By raising curing ages, a decrease of peaks C2 and C3 is observed, followed by an increased amount of SiO_4 , Q^1 , $\text{Q}^2(1\text{Al})$, Q^2 and Q^{2p} , which correspond to the CSH phase, thus confirming the progress of hydration process. Particularly, the highest reaction level is observed on FCC and MK blended pastes at 90 curing days. It is worth mentioning that in such a case, $\text{Q}^2(1\text{Al})$ units are highly increased. Such behavior is derived from the high percentage of Al_2O_3 available in the chemical composition of such blended pastes, in comparison to pattern pastes and SF pastes. By increasing the replacement level of Si by Al in bridging positions, in the CSH chain, may lead to the acceleration of Belite hydration speed (Andersen et al., 2004).

3.3 NMR - ^{27}Al analysis on hydrated pastes

NMR ^{27}Al studies on hydrated cement pastes allow us to monitor calcium aluminate hydration phases, by means of the observation of combined tetrahedral Al samples, Al (IV); and octahedral, Al (VI) (Andersen et al., 2003; Faucon et al., 1998; Faucon et al., 1998a). Figure 5 presents NMR ^{27}Al spectrums of blended pastes at 1, 7 and 90 curing days, where a signal of about 13 ppm is available for all the spectrums corresponding to Al(VI) of ettringite (Brunet et al., 2010). The presence of such phase is proven by the results obtained from DRX analysis. On the other hand, a resonance close to 74 ppm, which is attributed to the Al(IV) added to CSH chains, shall be considered. The replacements of Si by Al in the chain tetrahedrons are supported by the observation of $\text{Q}^2(1\text{Al})$ on NMR ^{29}Si . This behavior is prominent at 90 curing days, as much for reference pastes as for different blended pastes. Some researches state that the Al(IV) resonance of tri-calcium aluminate (C_3A) on anhydrous cement is close to 80 ppm, followed by displacement of lower values during the progress of hydration process, mainly as a consequence of Al(IV) in the tetra-calcium ferro-aluminate (C_4AF). This behavior was observed in all analyzed spectrums (Brunet et al., 2010).

Figura 5. Espectro NMR ^{27}Al de muestra de cemento hidratado a: a). 1 día (Cem-Ref) b). 7 días (Cem-Ref) c). 90 días (Cem-Ref) d). 1 día (Cem-FCC) e). 7 días (Cem-FCC) f). 90 días (Cem-Ref) g). 1 día (Cem-MK) h). 7 días (Cem-MK) i). 90 días (Cem-MK) j). 1 día (Cem-HS) k). 7 días (Cem-HS) l). 90 días

Figure 5. NMR ^{27}Al spectrum of hydrated cement sample at: a). 1 day (Ref-Cem) b). 7 days (Ref-Cem) c). 90 days (Ref-Cem) d). 1 day (FCC-Cem) e). 7 days (FCC-Cem) f). 90 days (Ref-Cem) g). 1 day (MK-Cem) h). 7 days (MK-Cem) i). 90 days (MK-Cem). 1 day (SF-Cem) k). 7 days (SF-Cem) l). 90 days

3.4 X-ray diffraction analysis

Figure 6 present the results of X-ray diffraction technique. This Figure shows that all diffraction patterns are similar; however the intensity of blended products is different.

Figura 6. Difractogramas de pastas de OPC adicionadas con FCC, MK y HS. a) 7 días, b) 28 días, c) 90 días, d) 180 días y e) 360 días. E: Etringita, CA: CAH10, C: Ca(OH)₂, C3: Silicato tricálcico (SC3), C2: Silicato bicálcico (SC2)

Figure 6. Diffraction graphs of OPC pastes blended with FCC, MK and SF. a) 7 days, b) 28 days, c) 90 days, d) 180 days and e) 360 days. E: Etringite, CA: CAH10, C: Ca (OH)₂, C3: Tricalcium Silicate (SC3), C2: Bicalcium Silicate (SC2)

The observed hydration products are: calcium silicate hydrates, ettringite and portlandite, which confirm the results obtained by TG / DTG and NMR techniques. Bicalcium silicates (C2) and Tricalcium silicates (C3) were also observed in all the analyzed pastes, which show a decrease throughout curing ages, thus evidencing a progressive advance of hydration process. It is worth highlighting that the ability of such silicates is lower for 20% blended pastes. This behavior is attributed, by Garcia de Lomas et al. (2007), to the dilution effect provoked by the higher percentage of replacement carried out.

In relation with curing ages, the same behavior was observed for the portlandite peak, located at a value of 2θ around 17.8. At early ages, a marked decrease is observed for FCC and MK blended pastes, which behavior is due to similarities of chemical composition. At 90 curing days, blended samples show a significant portlandite decrease in comparison to pattern pastes, thus matching the results reported by Hsu et al. (2001). Reduced peak intensity, located at a value of 2θ around 8.6, corresponds to the ettringite phase.

3.5 Scanning electron microscopy analysis

Figure 7 presents the SEM micrographs of reference cement pastes and FCC, MK and FS blended pastes cured at 3 days. Such micrographs confirm the presence of hydration products found by the X-ray diffraction analysis. Small needles are observed in the reference cement pastes and SF blended pastes, thus indicating the formation of ettringite; however, FCC and MK blended pastes have a higher amount of ettringite and they contain calcium aluminate hydrates of hexagon shape, due to a high content of Al_2O_3 . In general all pastes show the formation of calcium silicate hydrate gel.

Figura 6. Micrografías SEM de pastas hidratadas a 3 días de curado. a) OPC, b) OPC-FCC, c) OPC-MK y d) OPC-HS. (E: Ettringita, CA: CAH_{10} , C: $Ca(OH)_2$)

Figure 6. Photomicrograph of SEM hydrated pastes at 3 curing days a) OPC, b) OPC-FCC, c) OPC-MK and d) OPC-HS. (E: Ettringite, CA: CAH_{10} , C: $Ca(OH)_2$)

4. Conclusions

Based on the results of the current research:

- The potential of FCC as pozzolanic material was proven in Portland cement matrixes, showing the highest reactivity in 10% blended samples, with a proportion of affixed lime of 61% at 360 curing days. This value exceeds the ones reported by FS and MK blended pastes at the same percentage.
- By means of different characterization techniques, it was determined that the main hydration products for FCC blended cement are: calcium silicate hydrate (CSH), ettringite, calcium aluminate hydrates (CAH) and hydrated calcium aluminosilicates (CASH).
- It is worth mentioning the possibility of using up to a 20% FCC in replacement of Portland cement, as this mixture presents a similar behavior as 10%MK and 10%SF blended pastes.

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