Spent FCC catalyst for preparing alkali-activated binders: an opportunity for a high-degree valorization

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Abstract. Spent FCC catalyst is a waste from the petrochemical industry which has excellent pozzolanic properties, containing more than 90% silica and alumina. Its similarity to metakaolin creates interesting prospects for its use in the production of alkali-activated binders. In this study, the alkali activation of this residue, spent FCC catalyst, through mixtures with alkali hydroxide and silicate solutions (both sodium and potassium) has been carried out. The alkali cation had an important role in the nature of AA-FCC pastes: some differences in the mass loss in the thermogravimetric tests and in the X-ray mineral characterization were found. No significant differences in compressive strength were observed for mortars cured for 3 days in several conditions: room temperature and 65ºC. Prepared AA-FCC mortars had a compressive strength of about 65-70 MPa. Microstructural studies showed that an amorphous, dense and compact microstructure was obtained, independent of the activating solution and curing condition.

Introduction

Nowadays, the reuse of different types of wastes in construction is an ongoing research topic. Several studies deal with the use of agricultural and/or industrial wastes in Portland cement manufacturing, or even, as supplementary cementitious materials (SCMs), in the production of mortars and concrete. In both cases, there is a substantial reduction in the greenhouse gas emissions associated with Portland cement production. As previously mentioned, the main problem caused by the Portland cement industry comes from the associated CO_2 emission (decomposition of calcium carbonate, fossil fuel consume, and grinding process), representing 5-8% of global CO_2 emissions.

Otherwise, the reuse of wastes in the construction sector reduces landfill areas, diminishing the negative effects associated with this practice: diseases, soil contamination, water pollution, etc. Nevertheless, specific studies related to CO_2 emissions demonstrate that partial substitution of Portland cement alone can reduce CO_2 emissions from 886 kg to 660 kg after the production of 1 ton of Portland cement [1].

Hence, in recent decades, efforts are focusing on the production of alternative binders with low associated CO_2 emissions. Among these materials, calcium sulphoaluminate cements [2], belite cements [3] and alkali-activated binders [4-7] can be mentioned. Alkali-activated binders, in addition to reducing CO_2 emissions up to 80%, exhibit high compressive strength, good acid resistance and fire performance, and low shrinkage, when compared to Portland cement [7].

Alkali-activated binders are a network of SiO_4 and AlO_4 tetrahedra linked by sharing oxygen atoms. Positive ions such as Na^+, K^+, Mg^{2+} or Ca^{2+} must be present in the framework cavities to balance the charge deficiency of Al^{3+} compared to Si^{4+}. This linking forms a three dimensional network (chain and rings) of Si^{4+} and Al^{3+} in 4-fold coordination with oxygen [7-8].

In this paper, preliminary results about the use of spent FCC catalyst (spent FCC) as an aluminosilicate source in the production of alkali-activated cements are reported. Spent FCC is a waste material from the petrochemical industry which demonstrates excellent pozzolanic properties [9-10]. This inorganic material contains about 90% silica and alumina in its chemical composition.

Due to its similarity to metakaolin (a commercial and high reactive pozzolanic material, which is prepared from calcinations of kaolin at 700-800ºC, which consequently is a manufactured product and not a waste), spent FCC is generating very interesting and promising prospects for its use in the production of alkali-activated binders. It is important to state that the first paper related to the use of spent FCC as an aluminosilicate material in the production of alkali-activated binders was reported recently by Tashima et al. [11]. The authors assessed the viability of production of AA-FCC activated with sodium hydroxide and sodium silicate solutions. In that case, all systems were cured at 65ºC during 3 days with a high relative humidity (~95%). Hence, in this paper, spent FCC catalyst activation using potassium silicate solutions and the possibility of curing at room temperature by means of sodium silicate solutions are also assessed.

Experimental

Materials

Spent fluid catalytic cracking catalyst of petroleum (spent FCC) was obtained from BP OIL, Spain. Spent FCC is an inorganic material obtained as a waste from the petrol industry and petrol refineries. This waste material presents a high pozzolanic reactivity and a mean particle diameter of 17 μm, after grinding [9]. The chemical composition of spent FCC, determined by X-ray fluorescence, is summarized in Table 1.

Table 1. Chemical composition of spent FCC (wt%).

oxide (%)	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	other
FCC	46.04	47.47	0.58	0.17	0.11	0.30	0.02	5.31

Fig. 1 shows a scanning electron micrograph of the spent FCC used in this study. It can be noted that most of particles has an irregular form due to the dry milling process which reduces the particle size distribution of the original spent FCC. In some cases, the presence of spherical or spheroidal particles can be observed, indicating that not all particles were broken during the milling process.

Sodium and potassium hydroxide pellets (95% and 85% of purity, respectively) were supplied by Panreac S.A. A sodium silicate solution (waterglass, 28% SiO_2, 8% Na_2O, 64% H_2O) from Merck and a potassium silicate solution (21.5% SiO_2, 8.5% K_2O, 70% H_2O) from Kremer were also used for preparing alkali activating solutions. A siliceous sand with a specific gravity of 2.68 g.cm^{-3} and fineness modulus of 4.1 (UNE-EN 196-1) was used to prepare mortar samples.
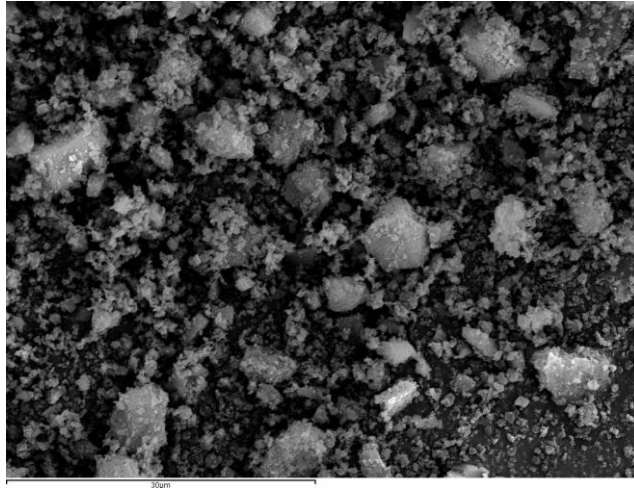
Fig. 1. SEM images of spent FCC particles after dry grinding process.

Tests performed on alkali-activated binders (AA-FCC).

Mechanical strength tests were carried out using a universal test machine following the procedures described in UNE-EN 196-1. The compressive strength test was performed obtaining an average of six values. Microstructural properties of alkali-activated (AA-FCC) systems were characterized using different instrumental techniques such as thermogravimetric analysis (TGA), X ray diffraction (XRD) and scanning electron microscopy (SEM). X ray diffraction (XRD, Philips PW1710 with Cu Kα radiation in 2θ range 5-55°) was used to characterize the crystalline phases in paste samples. Scanning electron microscopy (SEM, JEOL JSM-6300) was used to examine fracture surfaces. Thermogravimetric analysis (TGA, 850 Mettler Toledo thermo-balance) used 100 μL aluminum crucibles (sealed crucibles with a pinholed lid) and a nitrogen atmosphere. Samples were heated from 35 to 600°C at 10°C.min^{-1} to give total mass loss (%) data associated with the dehydration/dehydroxilation of AA-FCC.

Mix proportions

Activating solutions were prepared by mixing alkali hydroxide pellets with the required amount of water. After cooling down the temperature, the alkali silicate solution was added to adjust the concentrations of alkali cation (Na$^+$ or K$^+$), and SiO$_2$. The total Na$^+$ concentration was fixed in 10 kg.mol^{-1} and the total K$^+$ concentration was 9 kg.mol^{-1}. For Na-FCC system, the SiO$_2$/Na$_2$O molar ratio was constant (1.17). On the other hand, for K-FCC system, the SiO$_2$/K$_2$O molar ratio was fixed in 1.09. The H$_2$O/FCC ratio was 0.45 for Na-FCC and 0.40 for K-FCC.

The alkali activating solutions were prepared 30 minutes before their use to allow the solutions to cool down at room temperature. AA-FCC paste samples were produced by mixing spent FCC with the required amount of alkaline activating solution during three minutes. Then, paste samples were cast and stored both in ~95% RH at 65°C or at room temperature.

AA-FCC mortars were prepared by mixing spent FCC with activating solution for four minutes. Siliceous sand was then added to give a sand/spent FCC mass ratio of 3:1, and then mixed for another three minutes. The fresh mortar was cast in prismatic moulds (4x4x16 cm^3) and vibrated mechanically for 3 minutes to remove any air voids. The moulds were then sealed with a plastic film to avoid atmospheric carbonation and stored either in a thermal bath at 65°C or at room temperature. Mortars cured at room temperature were demoulded after 24 hours and stored in the same conditions for 3 days. Otherwise, mortars cured at 65°C were demoulded after 4 hours, and then stored at 65°C for 3 days.

Results and discussion

Mechanical strength studies

Fig. 2 shows the compressive strength results obtained for all mix proportions assessed, cured both at 65ºC and at room temperature for 3 days. Na-FCC mortars yielded 68 MPa when cured at 65ºC for 3 days. Comparing the compressive strength to a similar mortar cured at room temperature, it is observed that the curing conditions do not present any influence on the compressive strength of Na-FCC mortar for this curing age. For K-FCC a similar behavior is observed, which means, mortar samples cured at room temperature have 65.6 MPa in compression after 3 curing days and, mortar cured at 65ºC also present 66 MPa in compressive strength.

Comparing the activating solutions used, Na-FCC and K-FCC, both mortars had a similar compressive strength. The main difference of these mortars is the H_2O/spent FCC mass ratio, where Na-FCC had 0.45 and K-FCC had 0.40. Hence, it can be observed that sodium activating solutions even with a higher H_2O/spent FCC mass ratio present similar compressive strength to K-FCC. This can be explained by the fact that Na^+ is associated to the dissolution process of aluminosilicate materials, promoting the formation of higher amounts of monomers and dimmers, enhancing the mechanical properties of the alkali-activated system formed. Although K^+ activating solutions are characterized by a higher degree of gel formation [12], for AA-FCC systems it was observed that the dissolution process is a determinant factor in the alkali activation.
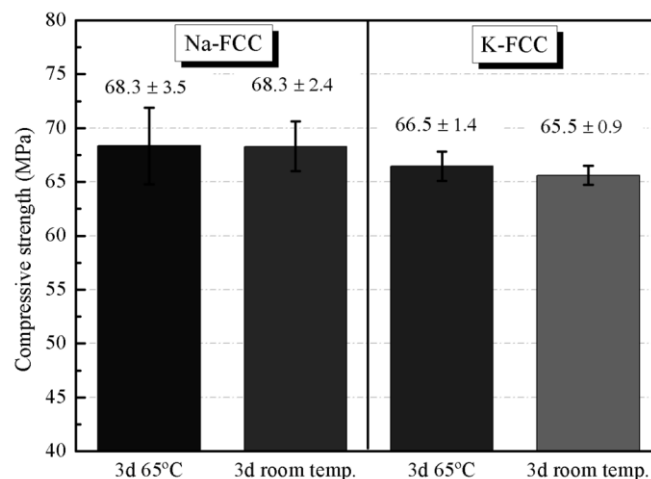

Fig. 2. Compressive strength values for both Na-FCC and K-FCC mortars, cured at 65ºC and at room temperature.

Thermogravimetric analysis studies

According to the thermogravimetric analysis (TGA), an important difference in the total mass loss is observed for Na-FCC and K-FCC cured under similar conditions. As can be noted in Fig. 3, in which the DTG curves are represented, the main mass loss occurs in the range of 130-300ºC, which is associated to the chemically bonded water and to the dehydroxylation of gel formed from the reaction of alkaline environment and reactive silica and alumina from spent FCC.
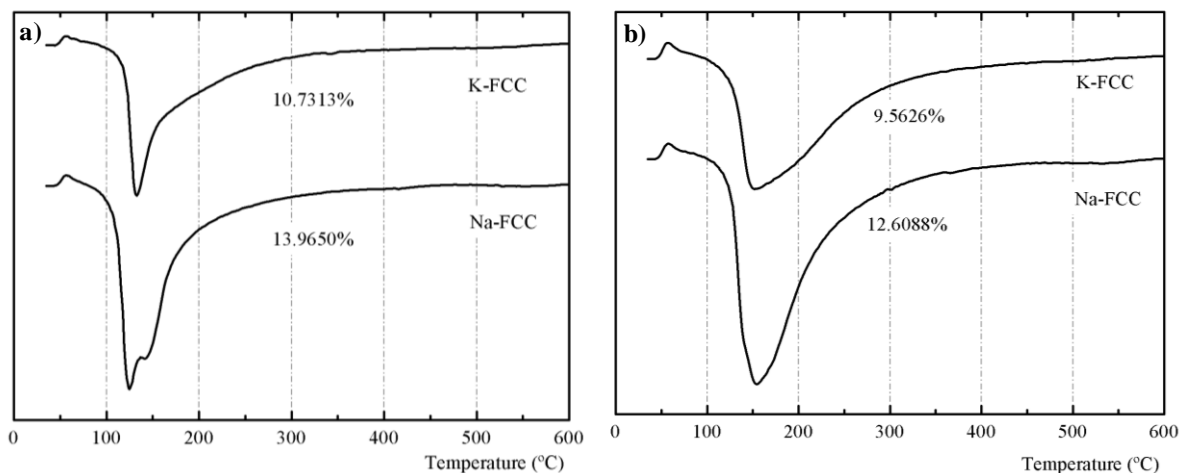
Fig. 3. DTG curves for all AA-FCC mixtures: a) room temperature; b) 65 °C with ~95%RH.

Important differences can be observed depending on the type of activating solution. While Na-FCC paste cured at 65 °C for 3 days presented ~12.5% mass loss, K-FCC paste with similar curing condition presented ~9.5% of total mass loss. The obtained results are consistent with the mechanical properties presented above. Although K-FCC systems have lower water content, the higher total mass loss yielded by Na-FCC can be attributed to the amount of gel products used for this system, when compared to K-FCC system.

The influence of curing conditions can also be noted by thermogravimetric analysis. For Na-FCC paste cured at room temperature for 3 days, ~14% mass loss is observed, indicating that the gel formed in this curing condition is still suffering a reordering of its nanostructure. Na-FCC cured at room temperature presented a peak related to the water associated to the aluminosilicate gel at ~120°C, while Na-FCC pastes cured at 65°C present this peak at 160°C. It indicates that AA-FCC when cured at 65°C present water or hydroxyl groups strongly bonded to the inorganic framework. Similar effects can be observed for K-FCC systems: for pastes cured at room temperature, ~11% of total mass loss is noted, while for a similar paste cured at 65°C, this mass loss was ~9.5%. Also, a DTG peak shift was observed when increasing the curing temperature, from 125 to 150 °C.

X-ray diffraction studies

Fig. 4 shows the X-ray diffraction patterns for both spent FCC and Na-FCC systems. As can be observed, spent FCC is an aluminosilicate material which presents in its structure some crystalline phases such as faujasite (PDFcard301380) and quartz (PDFcard331161). Others minor phases also can be detected, such as albite (PDFcard711152), kyanite (PDFcard11046) and wollastonite (PDFcard100489). A baseline deviation in the 17-32º 2θ range is observed, suggesting the presence of an important SiO_2/Al_2O_3 amorphous fraction.

When spent FCC reacts with sodium activating solutions, the X-rays diffraction for both pastes is significantly changed. The main crystalline phase (faujasite) present in spent FCC is totally dissolved by the activating solution and new zeolitic structures are formed: Na-P1 (PDFcard390219), herschelite (PDFcard191178) and hydroxysodalite (PDFcard311271). The formation of new structures characterized as zeolitic precursors are also reported in the literature [4;7-8]. Amorphous phases in the Na-FCC systems can be noted due to the baseline deviation in the 20-35º 2θ range. Comparing the mineralogy of similar pastes cured under different process, it means, when cured at room temperature versus cured at 65°C, no differences are observed on the mineralogy of these materials.

Fig. 5 shows the X-ray diffraction patterns of K-FCC systems cured at room temperature and at 65°C for 3 days. For AA-FCC pastes activated with potassium, the main crystalline phase present in spent FCC, (Faujasite) is also dissolved by the alkaline solution. In this case, a potassium zeolite-

type (PDFcard 220794) is formed as the main crystalline phase. The amorphous phases are also detected in XRD patterns and no important differences are observed between K-FCC pastes cured at room temperature and those cured at 65ºC. Again, a shift to a higher 2θ range for the deviation of the baseline is observed in the activated pastes.
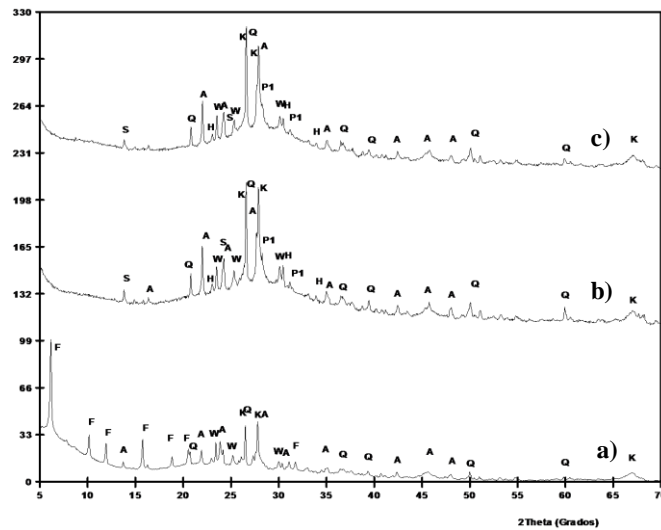

Fig. 4. X-ray diffraction patterns for spent FCC and Na-FCC systems: a) spent FCC; b) Na-FCC cured at room temperature; c) Na-FCC cured at 65ºC. Key: F: Faujasite; Q: Quartz; A: Albite; W: Wollastonite; K: Kyanite; P1: Na-P1 zeolite; H: Herschelite; S: Hydroxy-sodalite.
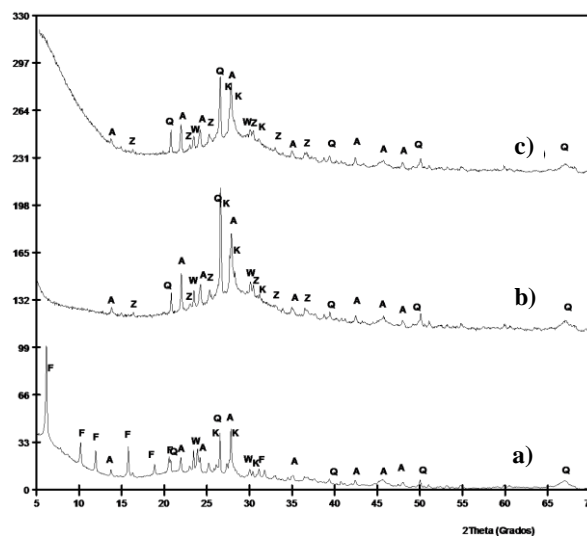

Fig. 5. X-ray diffraction patterns for spent FCC and K-FCC systems: a) spent FCC; b) K-FCC cured at room temperature; c) K-FCC cured at 65ºC. Key: F: Faujasite; Q: Quartz; A: Albite; W: Wollastonite; K: Kyanite; Z: potassium zeolite.

SEM studies

Fig. 6 shows the microstructure of fractured surfaces for Na-FCC pastes. Fig. 6a shows an Na-FCC paste cured at room temperature for 3 days. The presence of a dense-compact microstructure formed mainly by amorphous matrix can be seen with the presence of partially reacted spent FCC particle. For a similar paste cured at 65 ºC for 3 days (Fig. 6b), no differences can be seen when compared to the sample cured at room temperature.
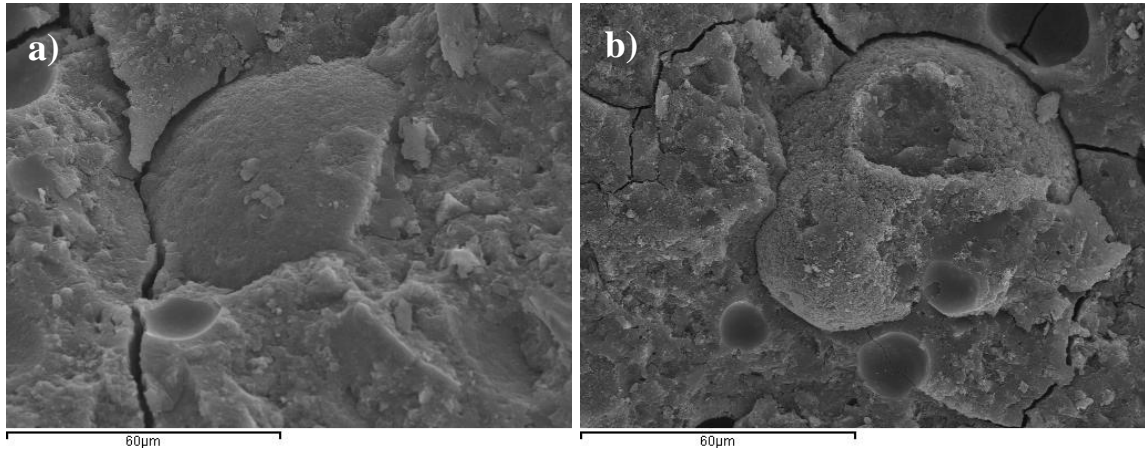
Fig. 6. SEM micrographs of Na-FCC pastes: a) cured at room temperature; b) cured at 65ºC.

The microstructure of potassium activated spent FCC is assessed in Fig. 7. Fig. 7a represents the microstructure of a K-FCC paste sample cured at room temperature for 3 days. A dense microstructure formed mainly by amorphous materials is observed. Compared to K-FCC pastes cured at 65 ºC for 3 days (Fig. 7b), no important differences were found.
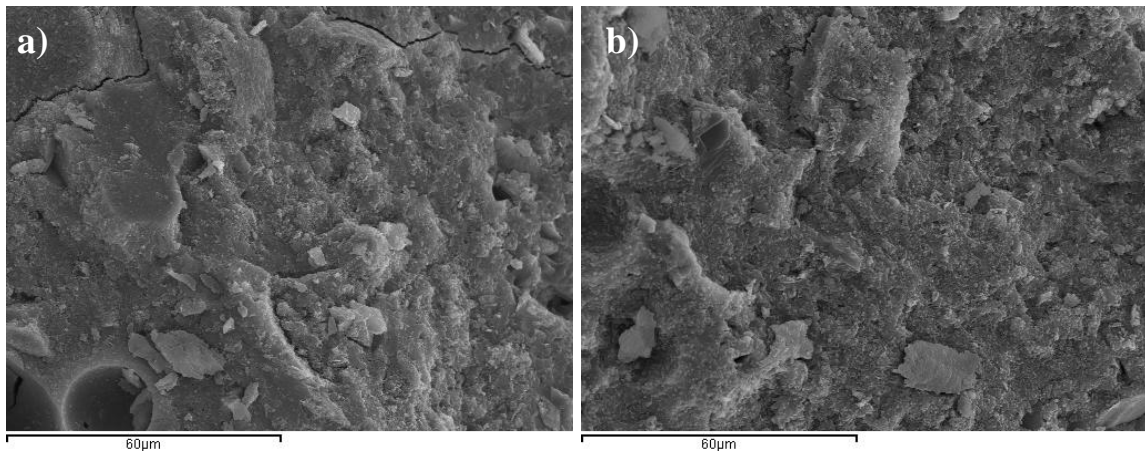

Fig. 7. SEM micrographs of K-FCC pastes: a) cured at room temperature; b) cured at 65ºC.

On the other hand, comparing Na-FCC to K-FCC samples, it can be noted that the microstructure of pastes prepared with sodium activating solutions are denser and more compact than with potassium activating solution. Probably, it is associated to the ability of sodium solutions to dissolve the aluminosilicate source materials. The microstructure`s features are also consistent with mechanical strength tests.

Conclusions

Alkali activation of spent FCC using both sodium and potassium activating solutions are reported, and it has been demonstrated that the alkali cation has an important role in the microstructure of AA-FCC: some differences in the mass loss in the thermogravimetric tests and in the X-ray mineral characterization were found for alkali-activated pastes. Comparing the compressive strength of mortars cured at room temperature and cured at 65ºC, no significant changes are observed for mortar cured for 3 days. AA-FCC mortars have a compressive strength of about 65-70 MPa after 3 curing days. Microstructural studies show that an amorphous, dense, and compact microstructure is obtained, independent of the activating solution and the curing condition.

Acknowledgments

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