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# New geopolymeric binder based on fluid catalytic cracking catalyst residue (FCC)

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## Abstract

This paper provides information about the synthesis and mechanical properties of geopolymers based on fluid catalytic cracking catalyst residue (FCC). FCC was alkali activated with solutions containing different $SiO_2/Na_2O$ ratios. The microstructure and mechanical properties were analysed by using several instrumental techniques. FCC geopolymers are mechanically stable, yielding compressive strength about 68MPa when mortars are cured at 65ºC during three days. The results confirm the viability of producing geopolymers based on FCC.

**Keywords:** FCC, geopolymer, alkali-activated binder

## 1. Introduction

The geopolymerization process is a chemical reaction between an aluminosilicate material and a high alkaline solution, under controlled curing conditions to form NASH gel and some zeolitic structures [1,2]. The first systematic research  related to alkali activated materials was carried out in 1957 by Glukhovsky [3]. After that, a lot of efforts have been made in this area, such us the  research done by Palomo et al. [4,5], Davidovits [6,7] and van Deventer et al. [8–10].

Geopolymers have many advantages over Portland cement, such as similar or higher compressive strength, better fire resistance and more durability [11]. Otherwise, these materials can be considered a low $CO_2$ emission binder due to its reduction up to 80% in the $CO_2$ emission, when compared to Portland cement [12].

Most of the studies related to alkali activated binders are based on blast furnace slag, fly ashes and metakaolin. However, other aluminosilicate materials can also be used as raw material in the geopolymerization process [8,13]. In this paper, the fluid catalytic cracking catalyst residue (FCC) is tested as an aluminosilicate source in the production of geopolymeric binders. This material is a high reactive aluminosilicate one obtained as a byproduct from the petroleum industry. FCC has been successfully used as a supplementary cementitious material (SCM) in Portland cement binders [14].

In general terms, studies about FCC compare its properties with metakaolin (MK) due to their similar chemical composition. Payá et al. [15] concluded that FCC presents higher pozzolanic reactivity at an early age curing than MK, whereas MK has high reactivity for long time curing. Another advantage of using FCC is its low water demand, compared to MK. It allows to produce binders with lower water/binder ratio and, consequently, with higher compressive strength than MK binders. As previously reported [14,15], FCC showed high pozzolanic reactivity when mixed with Portland cement, due to a chemical combination with portlandite $Ca(OH)_2$. In this study we evaluate the role of FCC in a different environment, alkaline too, with the absence of calcium ions, but sodium ions.

Transferring this knowledge to alkali activated systems, it is important to observe that geopolymers based on MK present high $H_2O/Na_2O$ ratio. For these binders, the ultimate compressive strength achieved is in the range of 7.03-13.13MPa [16].

In this paper, the fluid catalytic cracking catalyst residue (FCC) is tested as an aluminosilicate source in the production of geopolymeric binders.

## 2. Experimental

### 2.1. Materials and techniques

The spent fluid catalytic cracking catalyst of petroleum (FCC) was used as a raw material in alkali activated binders. FCC is an aluminosilicate material (46.04% $SiO_2$, 47.47% $Al_2O_3$, 0.58% $Fe_2O_3$, 0.11% CaO, 0.17% MgO, 0.30% $Na_2O$, 0.02% $K_2O$ and some other impurities) with a high pozzolanic reactivity and a mean particle diameter of 17.1μm (after grinding) [14]. Sodium hydroxide (98% purity) supplied by Panreac S.A. and waterglass (28% $SiO_2$; 8% $Na_2O$; 64% $H_2O$) from Merck were used in the preparation of alkaline solution.

Ultimate mechanical strengths of mortars were obtained by using a universal testing machine, according to UNE-EN-196-1 standard. Flexural strength was obtained as a mean of three values whereas compressive strength was calculated as a mean of six values. Thermogravimetric analyses (TGA) were performed in a TGA 850 Mettler-Toledo thermobalance under nitrogen atmosphere, with pin-holed aluminium sealed crucibles, and a heating rate of 10ºC.min$^{-1}$, from 35ºC until 600ºC. XRD patterns were collected in a Philips diffractometer PW1710 with Cu-Kα radiation, under routine conditions of 40Kv and 20mA, in the 2Θ range 5-55º. Microscopic studies were carried out by means of Scanning Electron Microscopy, by using a JEOL JSM-6300. Water/binder suspensions were monitored at different ages by electrical conductivity and pH measurements: a Crison microCM2201 conductimeter and a Crison micropH2001 pH-meter were used (Alkali-resistant pH-electrode Crison 5204 was used). The analysis was performed using 1g of geopolymer paste and a 10ml of deionized water. A continuous stirring was performed during 10 minutes before the measurement, and then the electrodes were submerged.

### 2.2. Dosage and curing conditions

Some geopolymeric mortars based on FCC were prepared with an NaOH solution as alkaline activator to verify the viability of using FCC in geopolymeric binders.  All mortars tested presented a water/FCC ratio of 0.60 and a sand/FCC ratio of 3. Compressive strength values of mortars were in the range 1-16MPa after 7 curing days at 65ºC in high relative humidity (RH~100%). Specifically, mortar activated using 5 molal of NaOH solution yielded 1.20MPa, using 7.5 molal yielded 3.40MPa and 10 molal yielded 15.17MPa. The best result was observed for the highest NaOH concentration. Mortar activated using 10 molal NaOH was also tested after 3 curing days in the same conditions: the compressive strength was 16.46MPa. This behaviour suggests that the activation using only NaOH did not improve mechanical properties due to the lack of silicate anions in the activating solution. Additionally, an increase in the curing time did not produce better mechanical behaviour.

Thus, a new set of alkaline solutions based on mixture of sodium silicate and sodium hydroxide solution were tested in order to increase their mechanical properties. The total $Na^+$ concentration was fixed in 10 molal, varying the amount of dissolved $SiO_2$. The alkaline solution compositions are listed in Table 1. For this set of mortars, samples were cured for 3 days at 65ºC in high relative humidity (RH~100%). As it can be observed, the $SiO_2/Na_2O$ molar ratio was in the range 0-1.46.

Table 1. Alkaline activating solutions of geopolymers based on FCC.

## 3. Results and Discussion

Mechanical strength values of geopolymers with different $SiO_2/Na_2O$ ratio are shown in Figure 1. For alkaline solutions with $SiO_2/Na_2O$ ratio lower than 0.4, both mechanical strengths, compressive and flexural, are significantly low. However, for higher $SiO_2/Na_2O$ ratios, an improvement in mechanical properties is observed. This behaviour suggests the importance of dissolved $SiO_2$ in these systems. Thus, flexural strength higher than 10MPa was obtained for $SiO_2/Na_2O$ ratio in the 0.8-1.5 range. Concerning compressive strength, the maximum value (68.34MPa) was obtained for $SiO_2/Na_2O$ ratio of 1.19. The results suggest that the activation of this aluminosilicate requires the use of a mixture of waterglass/NaOH.

Figure 1. Mechanical strength for geopolymers based on FCC using different $SiO_2/Na_2O$ ratio.

The nature of the geopolymeric gel generated by reaction of FCC and alkaline solution was tested by means of TG, SEM and XRD studies. Thermogravimetric analysis of FCC pastes which use activating solutions with different $SiO_2/Na_2O$ ratios were carried out for 1-day and 3-days curing times at 65ºC. A continuous loss of weight was observed from 100ºC, finding a peak centered at 140-160ºC in the DTG curve, typical of geopolymeric gels [17].This loss of weight is associated to the volatilization of water molecules and/or $OH^-$ groups from the products formed in the geopolymerization process. The increase in the loss of weight with curing time (e.g., from 13.3% to 15.13% for AA-FCC0.88 paste) is attributed to the progress of geopolymeric gel formation.

The geopolymerization reaction was also monitored by means of the electrical conductivity and pH values of the paste with $SiO_2/Na_2O$ ratio of 1.9 (see experimental section). The pH of the paste diminished strongly in the first 2 hours, from 13.01 to 12.49. This fact is related to the dissolution of the $Al_2O_3/SiO_2$ framework of the FCC. From 2 hours to 7 days, the pH decreases from 12.49 to 12.42. These results suggest that the alkaline media attacks the mineral addition easily. In the same way, the electrical conductivity of paste suspensions was measured: thus, an important decrease from 23.1 to 12.77microS/cm was observed for the first 2 hours of reaction. The decrease in electrical conductivity was from 12.77 to 7.3 microS/cm for the period 2hours-7days; this means that the measurements in electrical conductivity showed higher sensitivity than pH measurements. The decrease in electrical conductivity was related to the chemical combination of $Na^+$, $OH^-$ groups and silicate anions in the geopolymeric matrix.

XRD patterns were measured (see figure 2) for FCC and for two activated pastes: 0 and 1.17 $SiO_2/Na_2O$ ratio (after 3 days of curing at 65ºC). FCC was an aluminosilicate-based mineral addition with some crystallized compounds: acid-faujasite (in sodium form $Na_2Al_2Si_4O_{12}.8H_2O$, PDFcard-391380) is identified as the main mineral compound. A baseline deviation was observed in the 17-32º 2Θ range, suggesting the presence of an important of $SiO_2/Al_2O_3$ amorphous fraction. When FCC reacted with alkaline solution, XRD pattern changed, demonstrating the evolution of the mineral addition. After the chemical reaction, quartz ($SiO_2$, PDFcard-331161) and albite ($NaAlSi_3O_8$, PDFcard-090466) were the main crystalline identified compounds. Probably, these crystalline compounds are generated from the decomposition of faujasite. However, in both pastes, amorphous materials are the most important fraction after the chemical reaction, and an evident baseline deviation in the 25-35º 2Θ range was observed. This means that the amorphous fraction in the FCC was transformed after the chemical activation process.

Figure 2. XRD patterns for FCC and geopolymers based on FCC.

Some SEM micrographs of geopolymers based on FCC are shown in Figure 3. Figure 3a presents a detailed view of microstructure of AA-FCC0. A porous matrix and the presence of partially reacted FCC are observed. Nevertheless, AA-FCC0.88 paste (Figure 3b) has a dense-compact microstructure characterized as a geopolymeric gel, in amorphous state.

Figure 3. SEM micrographs of alkali activated FCC pastes cured at 65ºC during 3 days: a) AA-FCC 0; b) AA-FCC 0.88.

## 4. Conclusions

FCC is an inorganic industrial waste that can be used for preparing geopolymers. Activation of FCC by NaOH/waterglass mixture at 65ºC let us produce a stable binder and mortars with compressive strength in the range of 8.52-68.34MPa.

Microstructural studies have revealed that increasing the $SiO_2/Na_2O$ ratio, an amorphous, dense-compact microstructure can be obtained.

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Figure 1. Mechanical strength for geopolymers based on FCC using different $SiO_2/Na_2O$ ratio.

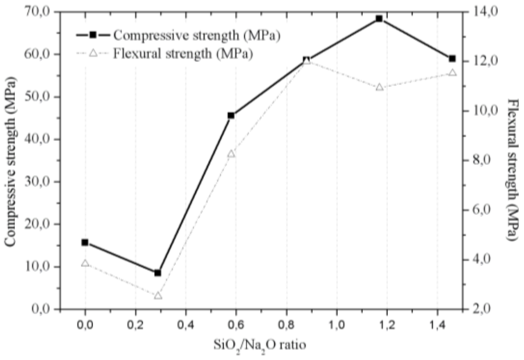

Figure 2. XRD patterns for FCC and geopolymers based on FCC.

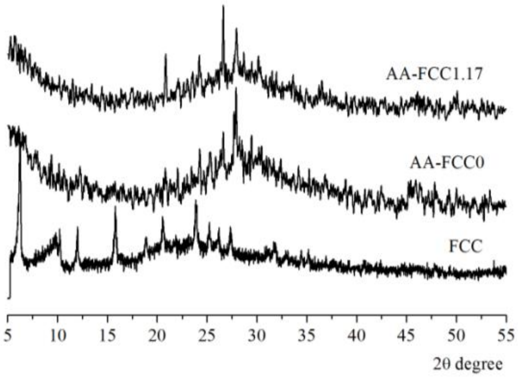

Figure 3. SEM micrographs of alkali activated FCC pastes cured at 65ºC during 3 days: a) AA-FCC 0; b) AA-FCC 0.88.

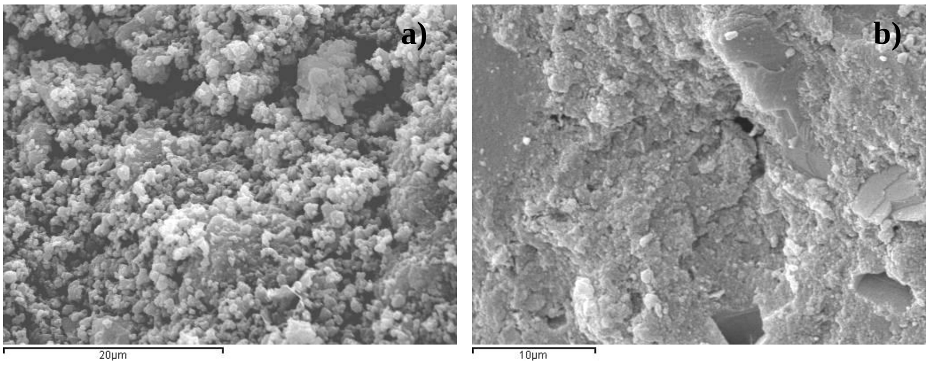

Table 1. Alkaline activating solutions of geopolymers based on FCC.

| | $Na_2O$ (mol) | $SiO_2$ (mol) | $H_2O/Na_2O$ | $SiO_2/Na_2O$ |
|---|---|---|---|---|
| AA-FCC 0 | 1.35 | 0 | 11.11 | 0 |
| AA-FCC 0.29 | 1.35 | 0.39 | 11.11 | 0.29 |
| AA-FCC 0.58 | 1.35 | 0.79 | 11.11 | 0.58 |
| AA-FCC 0.88 | 1.35 | 1.18 | 11.11 | 0.88 |
| AA-FCC 1.17 | 1.35 | 1.58 | 11.11 | 1.17 |
| AA-FCC 1.46 | 1.35 | 1.97 | 11.11 | 1.46 |