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# Refluxed rice husk ash/NaOH suspension for preparing alkali activated binders

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## Abstract

Geopolymers simultaneously containing two waste materials have been developed: Fluid catalytic cracking catalyst (FCC), as mineral admixture and Rice Husk Ash (RHA) for preparing alkaline activator. Alkaline activators were prepared by refluxing aqueous mixtures of ground or original RHA with NaOH. All mortars with alkaline activator containing RHA showed compressive strength (cured at 65°C for one day) in the range of 31-41 MPa, which was similar to control mortar prepared using an equivalent mixture of NaOH and water glass. Refluxing times between 30 and 240 minutes yielded good performance mortars. This new way of valorisation would imply economic and environmental benefits in geopolymer production.

Keywords: FCC, RHA, Geopolymer, Waste materials

## 1. Introduction

The reaction of an aluminosilicate mineral admixture with a highly concentrated aqueous alkali hydroxide and/or silicate solution produces an alkali aluminosilicate structure called geopolymer (1). This type of material can provide comparable performance to conventional cementitious binders, with an additional environmental advantage: an important reduction of greenhouse gas emissions (2). Alkali-activated cements usually consist of two components: a mineral admixture

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(with vitreous silica and alumina component) and an alkaline activator solution. Caustic alkalis or alkaline salts are normally used as alkaline activators in alkali-activated cement and concrete (3). In particular, the use of water glass becomes the most critical item in terms of environmental and economic points of view (4). Some industrial by-products and wastes alone or combined, as coal fly ash, rice husk ash, metakaolin, fluid catalytic cracking catalyst and hydrated carbonated cement have been used as cementitious components in alkali-activated cements (4-8). In this paper, the fluid catalytic cracking catalyst residue (FCC) is tested as an aluminosilicate source in the production of geopolymeric binder (7), using the rice husk ash (RHA) as a source for preparing the alkaline activator. FCC and RHA have been successfully used as supplementary cementitious materials (SCM) in Portland cement-based binders (9,10).

In this research, a mixture of RHA, NaOH and water was boiled in a reflux system to dissolve silica and to obtain sodium silicate solution. This mixture was used as an alkaline activator instead of commercial water glass, which is usually used in the manufacture of most of the geopolymers. Thus, in our research, two waste materials were used to produce alkaline activators: FCC as an aluminosilicate source and RHA as a silica source. Soluble silica in RHA and mortar strength results were compared with quartz in order to study the influence of silica crystallinity.

## 2. Experimental

### 2.1 Materials and Techniques

FCC is an aluminosilicate with a high pozzolanic reactivity and a mean particle diameter of 17.1  $\mu\text{m}$  (supplied by OMYA Clariana S.A.). RHA was supplied by DACSA S.A. and had a mean particle diameter of 62.3  $\mu\text{m}$ . After grinding, the mean particle diameter was reduced to 20.3  $\mu\text{m}$ . Sikron M-500 (siliceous flour, quartz) was supplied by Sibelco with a mean diameter of 7.7  $\mu\text{m}$ . In table 1, the chemical compositions of FCC, RHA and Sikron are shown. Sodium hydroxide (98% purity) supplied by Panreac S.A. and commercial water glass (28%  $\text{SiO}_2$ ; 8%  $\text{Na}_2\text{O}$ ; 64%  $\text{H}_2\text{O}$ ) from Merck were used in the preparation of alkaline solutions.

Table 1. Chemical composition in mass percentage of FCC, RHA and Sikron

Sample	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO	SO <sub>3</sub>	K <sub>2</sub> O	LOI	Na <sub>2</sub> O	P <sub>2</sub> O <sub>5</sub>	TiO <sub>2</sub>	Cl <sup>-</sup>
FCC*	47.76	49.26	0.60	0.11	0.17	0.02	0.02	0.51	0.31	0.01	1.22	-
RHA*	85.58	0.25	0.21	1.83	0.50	0.26	3.39	6.99	-	0.67	-	0.32
SIKRON**	99.2	0.40	0.05	0.02	-	-	0.05	0.27	-	-	0.03	-

\*Analyzed in ICITECH laboratory \*\*Supplied by Sibelco

Three different samples were used for the preparation of alkaline activator solution: original RHA (O-RHA), ground RHA (G-RHA), and Sikron (Quartz). Soluble silica was calculated by a gravimetric method as follows: a mixture of 3g of NaOH, 2.9 g of RHA or Sikron was suspended in 10 mL of deionised water. The mixture was boiled in a reflux system for different times (5 to 240 min), after which it was filtered, washed with hot water, and dried at 60°C before being weighed. The weight difference between untreated and treated samples was considered soluble silica, although small quantities of other products may have also been dissolved.

Mechanical strengths (flexural and compressive) of mortars were obtained by using a universal testing machine, according to UNE-EN-196-1 standard. Thermogravimetric analyses (TGA) were performed in a TGA 850 Mettler- Toledo thermobalance under air atmosphere, using alumina crucibles, and a heating rate of 20°C min<sup>-1</sup>, from 35°C to 1000°C. Microscopic studies were carried out by means of JEOL JSM-6300 Scanning Electron Microscopy.

## 2.2 Dosage and curing conditions

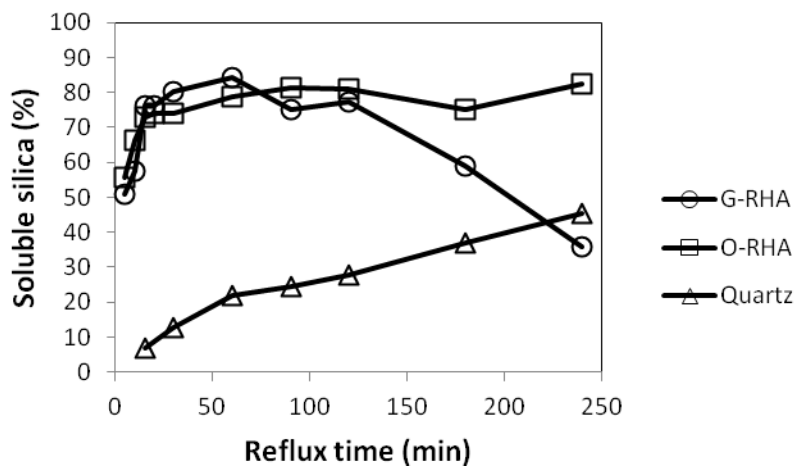
Two different geopolymeric mortars with the same sodium content, which were based on FCC, were prepared; the first one used a mixture of 81 g of NaOH, and 78.6 g of silica sample (O-RHA, G-RHA or Quartz) suspended in 270 mL of deionised water as an alkaline activator. The mixtures were refluxed from 15 to 240 min and cooled before use. For the second geopolymeric mortar, the activator dissolution was prepared using a mixture of water glass/NaOH with a SiO<sub>2</sub>/Na<sub>2</sub>O molar ratio equal to 1.17. This second geopolymeric mortar was taken as the control

mortar. In both cases, 450 g of FCC as a cementitious material was used. All mortars tested presented a water/FCC ratio of 0.60 and a sand/FCC ratio of 3. Mortars were tested in bending and compression modes after 1 day of curing at 65°C in a high relative humidity (RH 95-100%).

### 3. Results and Discussion

In Figure 1, soluble silica versus reflux time is shown. For O-RHA and G-RHA, for the first 60 min, an increase of soluble silica with reflux time was produced. At this time, approximately 80% of the sample was dissolved; no significant differences were observed until 120 min reflux time. For longer reflux times, a decrease in soluble silica occurred for G-RHA. However, for the O-RHA samples, the soluble silica remained constant at approximately 80%.

Figure 1. Soluble silica content (%) versus reflux time. Original Rice Husk Ash (O-RHA), Ground Rice Husk Ash (G-RHA) and Sikron (Quartz).



In order to understand this finding, both residues (O-RHA and G-RHA) obtained by reflux for 240 min were analysed by SEM (see Figure 2a). Important differences between residues were found: in the G-RHA residue, a gel structure was observed, indicating that the jellification process of  $\text{Na}_2\text{SiO}_3$  occurred.

Figure 2a. SEM micrographs from residues refluxed for 240 minutes of Ground Rice Husk Ash (G-RHA, left) and Original Rice Husk Ash (O-RHA, right)

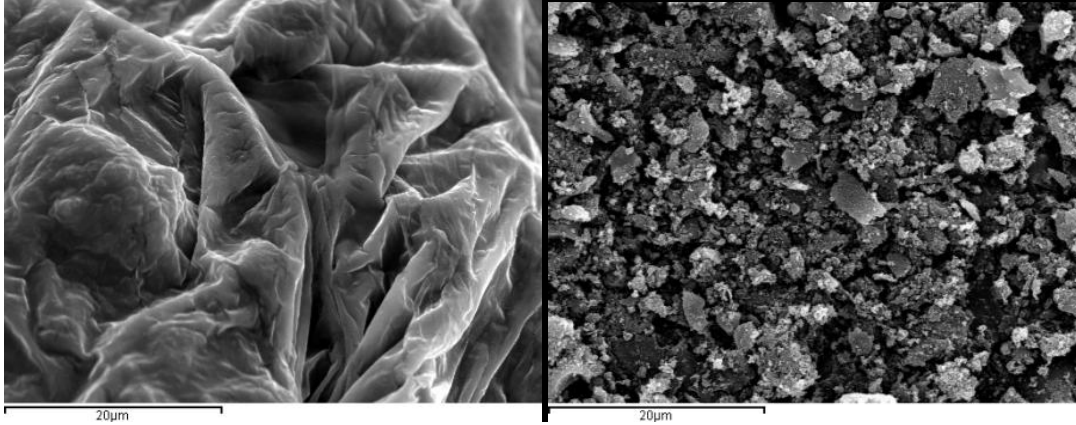
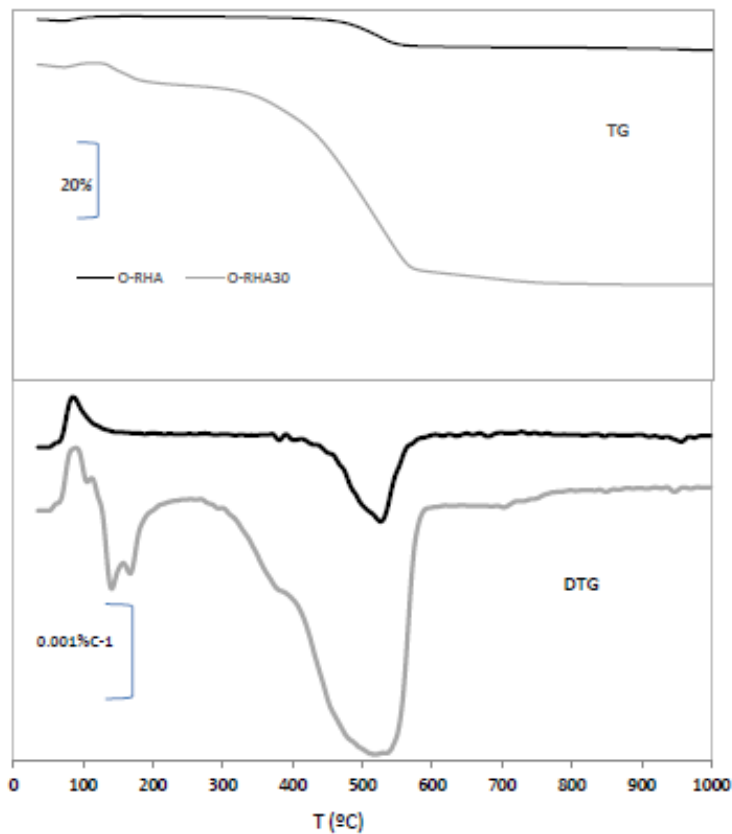


Figure 2b. TG and DTG curves from original rice husk ash (O-RHA) and residues refluxed for 30 minutes of original rice husk ash (O-RHA30)



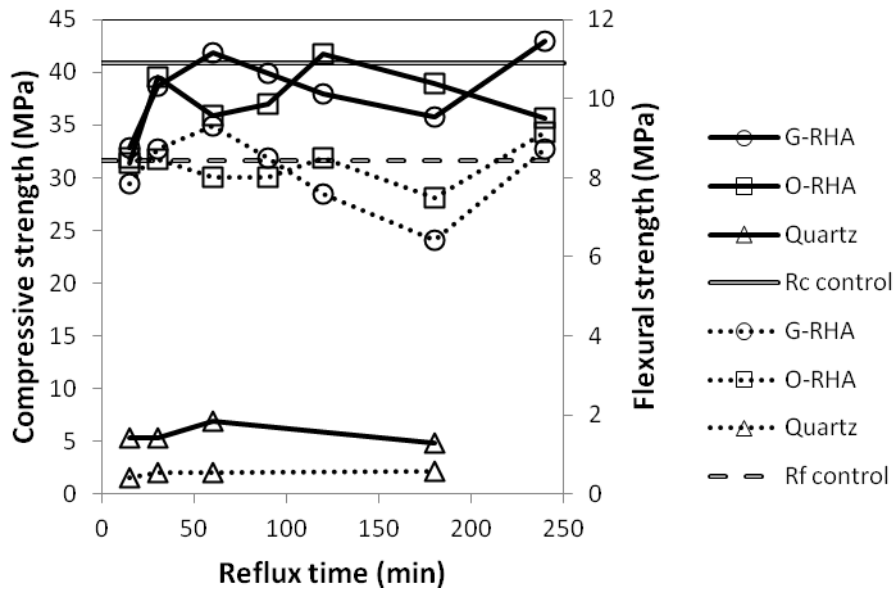
This process could explain the results obtained in the soluble silica values (Figure 1). In the jellification process, a significant amount of water could have been retained in the gel structure; this water cannot be totally eliminated by filtering and drying. As a result, when a filtered/dried

sample is weighed, the gel produced was weighed together with the non-dissolved silica. A thermogravimetric analysis (Figure 2b) for O-RHA samples and the insoluble residue from the reflux of O-RHA for 30 minutes was made (O-RHA30). Two significant differences were found: in the thermogram for residue from reflux, a loss of mass at approximately 150°C was observed, which was probably due to the formation of the gel by the reaction of silica present in RHA and the added sodium hydroxide. This loss of mass was not found in the thermogram for the O-RHA sample. Secondly, in the 350-600°C range, and in both samples, a loss of mass due to carbon oxidation processes took place, but this loss of mass was much higher for the insoluble residue than for the O-RHA sample (41.7% and 6.3% respectively). This suggests that carbon present in O-RHA is not dissolved when attacked with sodium hydroxide, and remains in the insoluble residue, thereby increasing its carbon concentration.

For Quartz samples, a linear increase of dissolved sample with refluxing time is observed, but the amount of soluble silica was much lower than that found for RHA samples. This fact can be explained by taking into account the crystallinity of quartz: the more crystallised a sample, the more difficult it will be to dissolve.

Control mortar, prepared using a mixture of water glass and NaOH, yielded 40.9 MPa in compression and 8.45 MPa in bending mode. In Figure 3, the strengths of mortars versus reflux times are shown. All mortars prepared with alkaline activators containing RHA (original and ground) showed a compressive strength higher than 30 MPa, and in general, no significant differences were observed between activating solutions prepared with O-RHA and G-RHA. A very low compressive strength was obtained in mortars with quartz due to the low soluble silica content. It is noteworthy that for 240 minutes of reflux time, soluble silica for G-RHA was lower than those found for O-RHA (see figure 1); however, compressive strengths for both mortars were similar. This suggests that the jellification process does not appear to have an influence on mortar strength.

Figure 3. Influence of reflux time on mortar strength. Flexural strength (dotted lines). Compressive strength (solid lines). Double lines are used for control mortar.



The most relevant result of this set of experiments is that compressive strength of control mortar was very similar to that found for mortars prepared using refluxed RHA samples, except in the case of the lowest reflux time (15 min). These results confirm, firstly, that is possible to prepare a geopolymer using two waste materials: FCC as a cementitious component and RHA as a part of the alkaline activator. Secondly, the compressive strength of this geopolymer is very similar to those found for geopolymers prepared using a mixture of commercial water glass and NaOH (control mortar).

#### 4. Conclusions

Alkaline activators for geopolymer synthesis can be prepared by reflux mixtures of ground or original RHA with NaOH. The effectiveness of the process depends on reflux time. Activation of FCC by a mixture of RHA/NaOH produced mortars with a compressive strength in the range of 31-41 MPa, which is similar to the compressive strength of control mortar prepared using a mixture of commercial water glass and NaOH. These results would promote the possibility of using two waste materials in alkali-activated cements simultaneously: RHA for the alkaline



activator and FCC as the cementitious material, thereby reducing the economic and environmental cost of geopolymers production.

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