Preliminary studies on the use of sugar cane bagasse ash (SCBA) in the manufacture of alkali activated binders

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Abstract. Alkali activated binders require the addition of a mineral-rich amorphous silica and alumina. This paper proposes the use of a mineral residue from the burning of sugar cane bagasse. The alkali activated mixtures were prepared containing binary mixtures of sugar cane bagasse ash (SCBA) and other mineral admixtures: fly ash (FA) or blast furnace slag (BFS). As alkaline activators, mixtures of alkali (Na⁺ or K⁺) hydroxide and alkali (Na⁺ or K⁺) silicate were used. Alkali-activated pastes and mortars containing binary systems SCBA/FA or SCBA/BFS were prepared and cured at 65 ºC. Microstructural properties of these alternative binders were assessed by means of TGA, SEM, XRD and pH measurements. Mechanical strength of mortars was performed after 3 and 7 days at 65 ºC. Compressive mechanical strengths of these mortars were in the range 30-55 MPa, showing the good mechanical performance achieved by the alkali activation. Microstructural studies suggested the development of stable matrices and the formation of typical gel.

Introduction

Nowadays, the reuse of industrial and agricultural wastes as raw material in the production of new products is essential for the sustainable development. It can contribute on the reduction of landfill areas and also diminish the carbon footprint caused by the industry. The civil construction is one of the most important industrial sectors that generates large amounts of waste and contributes significantly to the greenhouse gas emissions. According to estimates, the cement industry is responsible for about 5-8% of global CO₂ emissions.

In general terms, the production of 1 tonne of clinker Portland generates ~1.0 tonne of CO₂. Although Brazilian cement industry have a low CO₂ emission (approximately 560 kg of CO₂ per tonne of Portland cement), the use of wastes in the production of blended mortars and concrete could reduce the consumption of Portland cement and, consequently, diminishing the CO₂ emission for a similar volume of concrete produced.

Among the waste materials that can be used as construction material, fly ashes and silica fume have already been accepted as supplementary cementitious materials (SCM) for the production of mortars and concrete. Nevertheless, other waste materials also present a high potential to be used for this propose, such as rice husk ash [1-2], sewage sludge ash [3], fluid catalytic cracking catalyst residue [4-5], ceramic wastes [6].

Another interesting alternative to reduce the carbon footprint associated to the Portland cement production is the use of alternative binders with low CO₂ emission. Among these alternative binders that have been studied in deep in the last decades, alkali-activated materials require an
especial attention due to its low CO₂ emission associated, up to 80% less than Portland cement. Additionally, these binders can present good compressive strength and durability, even higher than Portland cement ones [7-8].

Taking into account all the issues related to the reduction of carbon footprint of cement industry and the reduction of landfill areas required for wastes, there are many papers related to the use of sugar cane bagasse ash (SCBA) as supplementary cementitious materials in the production of blended Portland cement or concrete [9-10]. In most of cases, SCBA can be considered as a high reactive pozzolanic material [11-12].

Many interesting studies on reusing of waste from agricultural and food industry activities are being carried out [13], especially on high volume generated wastes, such as rice husk, palm-oil shell, wheat straw and sugar cane derived wastes. Thus, the production of sugar cane in Brazil is higher than 500 Mton per year, and part of the bagasse generated in the extraction of sugar is usually exploited in furnaces for obtaining heat and water vapor. In Brazil, more than 130 Mton of bagasse is reused in this way, yielding a final waste of 3Mton of ashes (SCBA).

No bibliographic references have been found about the use of SCBA in the production of alkali-activated binders. Hence, in this paper, a preliminary study to assess the viability on the use of SCBA in the production of alkali-activated systems is shown. This would be one of the ways to be followed for valorization of SCBA in the construction industry, and for this purpose, binary mixtures with blast furnace slag (BFS) or fly ash (FA) have been proposed.

Experimental

Materials. Blast furnace slag (BFS) was supplied by Cementval SL (Sagunto-Valencia, Spain). This material was ground in a laboratory ball mill (alumina balls) for 30 minutes. The mean particle diameter was 21.4 μm. Derivative granulometric curve is depicted in Fig. 1. Chemical composition is given in Table 1. Fly ash (FA) was supplied by Infraestructuras Balalva SA (Onda-Castellón, Spain). This material was ground in an industrial ball mill (steel balls) for 10 hours. The mean particle diameter was 15.6 μm. Derivative granulometric curve and chemical composition are shown in Fig. 1 and in Table 1, respectively.

Sugar cane bagasse ash (SCBA) was collected from a settling lagoon in Destilaria Generalco S/A., close to General Salgado city (São Paulo – Brazil). In this factory, the sugar cane bagasse was burnt in a furnace for obtaining heat. The generated ash was collected using a scrubber. The resulting suspension was mixed with the water from sugar cane washing, and then was poured into the lagoon. The settled solid was taken from the lagoon, dried at 105°C and, finally, it was ground in a laboratory ball mill (steel balls) for 20 minutes. The mean particle diameter was 26.8 μm. Derivative granulometric curve is depicted in Fig. 1. Chemical composition is given in Table 1. This ash presented a high content of unburned material (32.2%). Fig. 2 shows the thermogravimetric derivative curve for the ash, in which an important amount of material is lost in the 450-650°C range. The corresponding DTA curve shows the presence of a main exothermic process at this temperature range related to the oxidation of organic matter and carbon. The ash (SCBA) was used in natura for mixtures with BFS. However, because initial tests showed that it did not work (difficulties in the setting process) by mixing with FA, the ash in this case was previously calcined at 650°C for 2 hours (c-SCBA).

The Potassium hydroxide (85% purity) and sodium hydroxide (98% purity) were supplied by Panreac AS. The Potassium silicate solution, supplied by Kremer, had the following chemical composition (by mass): 8.5% K₂O, 21.5% SiO₂ and 70% H₂O. Sodium silicate solution was supplied by Merck, with a density of 1.35 g/cm³ and a pH between 11 and 11.5. Its chemical composition (by mass) was: 8% Na₂O, 28% SiO₂ and 64% de H₂O.
Mix proportions and curing procedures. Two types of mixtures were prepared: pastes and mortars. Pastes were prepared mixing the binder and the corresponding activating solution. Mortars were prepared by addition of natural sand using a binder/sand ratio of 1/3. Mixtures containing SCBA and BFS were prepared by mixing 15% SCBA and 85% BFS. The binder (SCBA+BFS) was mixed with the activating solution, and a water/binder ratio of 0.45 was selected. The activating solution was prepared using sodium hydroxide and sodium silicate, and it had 5 mol Kg\(^{-1}\) of sodium cation, and presented a SiO\(_2\)/Na\(_2\)O molar ratio of 1.46.

Mixtures containing c-SCBA and FA were prepared by mixing 25% c-SCBA and 75% FA. The binder (c-SCBA+FA) was mixed with the activating solution, and a water/binder ratio of 0.45 was selected. The activating solution was prepared using potassium hydroxide and potassium silicate, and it had 8 mol Kg\(^{-1}\) of potassium cation, and presented a SiO\(_2\)/K\(_2\)O molar ratio of 0.65.

Pastes were stored in sealed plastic bottles at 65°C for 3 and 7 days. Mortars were cast in 160mmx40mmx40mm prismatic molds (according to UNE-EN-196-1 standard), which were stored for 4 hours at 65°C in a water vapor saturated plastic box. Then, specimens were demoulded and
stored in the plastic box until mechanical test. Three prismatic specimens were tested, after 3 and 7 days of curing at 65°C, in 3 points bending, and then the six portions obtained were tested in compression. Flexural strength (R_f) value was calculated as a mean of three data and compressive strength (R_c) values were calculated as a mean of six data.

Figure 2. Derivative thermogravimetric and differential thermal analysis curves for SCBA in natura. Note: Exothermic events are upwards.

Physico-chemical characterization procedures. XRD diffractograms were collected by means Philips PW1710 diffractometer, using Cu-Kα wavelength, and 40 kV and 20 mA, in the 2θ range 5-70°. Scanning electron microscopy (SEM) studies were carried out in a JEOL JSM-6300: samples were covered with gold. A pHmeter Crison micropH2001 was used for measuring alkalinity of pastes: 1 g of paste was ground and 10 mL of deionized water was added. After 10 minutes of continuous magnetic stirring, the pH was measured. Three pH measurements were carried out, the final value being a mean of these three data. Thermogravimetric Analysis (TGA) was performed in a TGA 850 Mettler-Toledo thermobalance. Pastes were analyzed under nitrogen atmosphere, using pin-holed aluminium sealed crucibles, with a heating rate of 10°C min⁻¹, from 35°C until 600°C.

Results and Discussion

Characterization of SCBA. This ash presented a high proportion of unburned organic matter and carbon, resulting 67.80% of inorganic components. In the inorganic fraction, SiO₂ was the main compound (46.3%). CaO content in the inorganic fraction was also important (23.9%). Part of the calcium was in the carbonate form: from DTG curve (Fig. 2) the calculated amount of calcium carbonate (CaCO₃) was 18.8%.

The SCBA was mineralogically characterized by means of XRD analysis. The corresponding diffractogram is depicted in Fig. 3. It can be noted that the main mineral was quartz. Also, peaks belonging to calcite, hematite, sanidine and wollastonite were identified. It is noteworthy that the baseline of the diffractogram had no deviation in the 2θ range 20-35°, suggesting that the proportion of crystalline fraction is important. In fact, in the same Fig. 3, SCBA diffractogram is compared to the BFS and FA ones. For both mineral admixtures, background level and deviation baseline are more evident than those observed for SCBA.

The particle morphology of ground SCBA is shown in Figs. 4a and 4b. It can be seen that particles are irregular in shape, finding many types of particles (Fig. 4a). Most of particles showed rough surfaces and in some cases accessible porosity was identified (Fig. 4b). Also SEM
micrographs were taken for calcined SCBA at 650°C (c-SCBA). Figs. 4c and 4d showed that there were not important changes in the morphology (size, shape and surface roughness) of the particles when SCBA is calcined. The morphology of BFS and FA particles are also showed in Figs. 4e and 4f respectively.

**Figure 3.** XRD diffractograms for: a) BFS; b) SCBA; c) FA. (Key: Q: Quartz; C: Calcite; W: Wollastonite; M: Mullite; S: Sanidine; H: Hematite)

**SCBA-BFS mixture.** A mixture containing 15%SCBA and 85% BFS was prepared and activated with an alkaline solution (sodium hydroxide plus sodium silicate, 5 mol·Kg⁻¹ of sodium cation, and 1.46 SiO₂/Na₂O molar ratio). This paste set at 65°C in less than 1 hour, probably due to the hydraulic behavior of BFS. The paste was cured for 3 and 7 days at 65°C and then characterized by means TGA, pH, SEM and XRD.

TG curves for SCBA+BFS pastes cured at 65°C for 3 and 7 days are depicted in Fig. 5a. In both curves, a continuous decreasing in mass was observed, with 20.0% total mass loss for 3 days and 17.9% for 7 days. This behavior means that the alkaline activation from 3 to 7 days produces a condensation process of OH groups, releasing water. The corresponding DTG curves (Fig. 5b) show a main peak centered at 135-145°C. A displacement at high temperatures of the right shoulder in the DTG curve is observed when increasing the curing time. This behavior suggests that there is a reorganization in the network and remaining H₂O/OH groups are more strongly bonded.

Paste cured after 3 days had a pH=12.72, and the value slightly increased at 12.85 after 7 days of curing at 65°C. Both pH values are much lower than the initial pH of alkaline activating solution (higher than 14). This behavior means that an important part of hydroxyl anions were chemically reacted with mineral admixture (SCBA+BFS) for producing the new matrix. The slight increase in pH with curing time could be related to the diminution in mass loss measured by TG analysis: the elimination of OH groups must release more sodium hydroxide into the gel pores.

SEM micrographs of SCBA+BFS pastes are shown in Fig. 6. A dense matrix is observed (Fig. 6a), which is the consequence of the activation of the mineral admixture. In some cases, large pores are found (Fig. 6b).
XRD pattern of the paste cured for 3 days at 65ºC is shown in Fig. 7a. The most important peaks present in this paste are those corresponding to quartz and to calcite, which were found for SCBA. This result means that an important part of SCBA did not react, probably this part corresponds to the crystallized fraction. The baseline deviation in the 2\(\Theta\) range 25-37º belongs to the amorphous fraction of the paste, and it is a mismatch to those found for BFS.
Finally, mechanical strengths were measured. The $R_c$ after 3 days was $53.5\pm2.0$ MPa, and after 7 days it was very similar, $51.2\pm0.4$ MPa. However, $R_f$ values were sensitive to the increase in curing time, and thus after 3 days it was $5.31\pm0.37$ MPa whereas after 7 days it was $2.94\pm0.65$ MPa. This decrease in $R_f$ value could be attributed to the change in the reorganization of OH groups and/or recrystallization processes.

**SCBA-FA mixture.** Different attempts for setting SCBA-FA mixtures were unsuccessful, probably due to the high amount of unburned organic matter. However, when SCBA was calcined at 650°C for removing this undesirable matter (yielding c-SCBA), the alkali activation of c-SCBA+FA mixture was successful. Thus, mixtures containing 25% of c-SCBA and 75% of FA were reacted using an alkali activating solution (potassium hydroxide plus potassium silicate, 8 mol Kg$^{-1}$ of potassium cation, and 0.65 SiO$_2$/K$_2$O molar ratio). The paste was cured for 3 and 7 days at 65°C and then characterized by means TGA, pH, SEM and XRD. TG curves for c-SCBA+FA pastes cured at 65°C for 3 and 7 days were recorded, and depicted in Fig. 8a. In both samples, the mass decreased continuously with the increasing heating temperature, with 11.7% total mass loss for 3 days sample
and 12.1% for 7 days. Thus, there is a slight increase in the total combined water, due to the reaction progress from 3 to 7 days of curing. The corresponding DTG curves (Fig. 8b) show a main peak centered at 135-140°C. No important change was observed with the curing time.

Figure 7. XRD diffractograms for pastes cured for 3 days at 65°C: a) SCBA+BFS; b) c-SCBA+FA. (Key: Q: Quartz; C: Calcite; W: Wollastonite; M: Mullite; S: Sanidine; H: Hematite)

Figure 8. Thermogravimetric results for alkali activated c-SCBA+FA pastes after curing 3 and 7 days at 65°C: a) TG curves; b) DTG curves.
Paste cured after 3 days had a pH=12.49, and this value slightly decreased to 12.37 after 7 days of curing at 65ºC. This behavior also means that an important part of OH− was combined with the mineral admixture (c-SCBA+FA) in the formation of the new cementing matrix. The slight decrease of pH with curing time could be related to the increase in the amount of the combined OH/H₂O groups accordingly to the TG data.

SEM studies showed (Fig. 9) that most of fly ash particles reacted partially, finding spherical particles with attacked surfaces. XRD diffractogram for 3-days cured paste is shown in Fig. 7b. It can be noted that the observed peaks belong to the minerals present in the admixtures: mullite and quartz for FA, and calcite and quartz for c-SCBA. In this case, the baseline deviation for the paste is a shift to higher 2Θ values: from 20-30º for FA to 25-35º for the activated admixture after 3 days of curing.

Also, the mechanical properties of prepared mortars were determined. The R_c after 3 days was 33.5±1.8MPa, and, after 7 days, was slightly higher, 36.4±0.85MPa. This increasing of R_c could be attributed to the larger amount of combined OH/H₂O groups accordingly to the TG analysis. R_f values slightly changed with curing time, and thus, after 3 days, it was 4.41±0.98MPa whereas after 7 days it was 3.19±0.85MPa.

Conclusions
This study demonstrates the feasibility of using sugar cane bagasse ashes (SCBA) by mixing with fly ash (FA) or blast furnace slag (BFS) in alkaline activated pastes and mortars. In the case of SCBA+FA mixtures, removal of unburned matter must be previously carried out to yield good performance. Compressive mechanical strengths of these mortars were in the range 30-55 MPa, showing the good mechanical performance achieved by alkali activation. Microstructural studies suggested the development of stable matrices and the formation of typical amorphous gels.

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