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Study of the binary system fly ash/sugarcane bagasse ash (FA/SCBA) in SiO_2/K_2O alkali-activated binders

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ABSTRACT

Due environmental problems related to Portland cement consumption, many studies have been performed to diminish its use. One solution is the development of alkali-activated binders, which can decrease CO_2 emissions and energy consumption by 70% when compared to Portland cement production. In addition, an alkali-activated binder presents mechanical properties similar to Portland cement mixtures, which turns into an interesting material in civil construction. Aluminosilicate-based materials are important raw materials to produce the alkali-activated binders. Therefore, two residues are presented as an aluminosilicate source in this study: fly ash (FA) and sugarcane bagasse ash (SCBA). Both residues were obtained from a combustion process to generate energy, the former from coal and the latter from the bagasse of the sugarcane industry. In addition, the alkaline activating solution is an important factor to achieve improved mechanical properties. In this context, this study investigated the influence of four different SiO_2/K_2O molar ratios (0, 0.36, 0.75 and 1.22) in the activating solution with a constant water content, and three FA/SCBA binder proportions (75/25, 50/50 and 25/75). Microstructural characterization was carried out by X-ray diffraction, Fourier transform infrared spectroscopy, thermogravimetric analysis, scanning electron microscopy, mercury intrusion porosimetry, pH and electrical conductivity measurements to study the evolution of the reaction process. The compressive strength of mortars was assessed in order to determine the optimum SiO_2/K_2O molar ratio and FA/SCBA ratio. The tests showed that a SiO_2/K_2O molar ratio of 0.75 and FA/SCBA proportion of 75/25 provided the best mechanical properties.

1. Introduction

New materials are being researched worldwide in order to reduce Portland cement consumption. Three main problems are related to the production process of Portland cement: the emission of CO_2 (this hydraulic binder is responsible for 5–8% of global greenhouse gas emissions) [1], energy requirements, and the use of non-renewable materials. In this context, alkali-activated binders (also called geopolymers or inorganic polymers) appear to be an interesting solution in terms of abovementioned problems. An alkali-activated binder is a well-cemented composite obtained through the chemical reaction between an aluminosilicate source with an amorphous structure and a highly concentrated alkaline solution [2,3]. The product formed from this reaction is a three-dimensional tetrahedral structure of aluminate and silicate, where the alkali metal from the solution balances the global negative charge from Al^{3+} four-fold oxygen coordination [4].

When the production of Portland cement is compared to that of alkali-activated binders, several environmental advantages are highlighted. In terms of gas emissions, the production of one ton of Portland cement clinker releases 0.8 tons of CO_2 into the atmosphere [5], whereas some alkali-activated binders emit only 0.184 tons of the greenhouse gas to produce the same amount of binder [6]; this represents a reduction of over 70% [7]. In terms of energy requirements, alkali-activated binders require 70% less when compared to Portland cement [8]. The most interesting aspect of alkali-activated binders is that the aluminosilicate sources that have been researched are usually residues [9,10], whereas one ton of Portland cement requires 2.8 tons of non-renewable raw material (clay and calcium carbonate, among others) [11]. In addition to the environmental advantages, the technological benefits of alkali-activated binders are their high

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compressive strength and durability, which are similar to or better than the characteristics of Portland cement [12].

Several aluminosilicate sources are being studied to produce alkali-activated binders such as fly ash from thermoelectric power plants [10,13], metakaolin [14], spent fluid catalytic cracking catalysts [9], blast-furnace slag [15] and others. In addition, residues from the agroindustry are being researched in alkali-activated binders, such as rice husk ash [16]. Recently, interesting studies have been carried out on binary systems (the presence of two aluminosilicate sources in the mixture as mineral precursors) to improve the mechanical properties of a single-precursor binder; good cementing materials have been produced from these mixtures [17–19]. In this context, this study investigated a binary system consisting of fly ash/sugarcane bagasse ash (FA/SCBA) as an aluminosilicate source for alkali-activated binder production. Both fly ash (FA) and sugarcane bagasse ash (SCBA) are residues of energy generation, the former from coal combustion and the latter from bagasse combustion. Due to the available amount of those residues, civil construction appears to be a suitable choice to valorize these wastes.

Fly ash generation is estimated at over 500 million tons per year [20]. This waste is used to partially replace Portland cement as a pozzolanic material [21], and studies on alkali-activated binders are being carried out [22]. On the other hand, one problem related to sugarcane bagasse ash is its increased production in Brazil. Sugarcane production has expanded by 154% in the last 15 years in this country, reaching 654 million tons in 2014 [23]. Bagasse represents one quarter of sugarcane mass [24], and 80% of this by-product is burned in order to generate energy [25]. After the burning process, approximately 2.5% (by mass) of the bagasse remains as ashes, called sugarcane bagasse ash [26]. Nowadays, this waste is being researched as a pozzolanic material [27], but there are fewer studies on its use in alkali-activated binders [28,29].

In general terms, the alkaline activation of fly ashes requires the use of high waterglass and sodium hydroxide concentrated solutions. Typically, the sodium concentration is in the range of 10–15 M to obtain suitable compressive strength development [30]. The partial replacement of FA by SiO_2-rich pozzolans could improve the hardening process of fly ashes in the alkali-activation process [31]. Then, under these conditions, the concentration of the activator could be reduced, with corresponding savings in expensive reagents used for preparing these mixtures. With this purpose, we present here the role of SCBA in FA alkali-activated systems.

In this paper, alkali-activated binders were obtained from a binary system of FA/SCBA as the aluminosilicate source, activated by a solution of potassium hydroxide and potassium silicate. This study was carried out in two sections: in the first part, the influence of the SiO_2/K_2O molar ratio to select the optimum solution was assessed, and in the second part, different proportions of FA/SCBA were assessed in order to achieve the best mechanical performance. Evolution of the reaction process was assessed in pastes by Fourier transformed infrared spectroscopy (FTIR), thermogravimetric analysis (TGA), X-ray diffraction (XRD), pH/electrical conductivity measurements and mercury intrusion porosimetry (MIP). The compressive strength test for mortars was performed in order to select the optimum SiO_2/K_2O molar ratio in the solution and the optimum FA/SCBA proportion in the binder.

2. Materials and methods

2.1. Materials

Fly ash (FA) was supplied by Infraestructuras Balalva, Spain. This ash was ground in an industrial ball mill for 10 h in order to enhance its reactivity. Sugarcane bagasse ash (SCBA) was taken from a settling lagoon at Destilaria Generalco S/A, close to General Salgado, Brazil. In this factory, the bagasse was burnt to obtain energy, and the ash generated was collected using a scrubber. The resulting suspension was mixed with water from sugarcane washing, and afterwards it was poured into the lagoon. The settled solids were retrieved from the lagoon. Afterwards, the sugarcane bagasse ash was dried at 105 °C and milled for 20 min in a ball mill in order to increase its reactivity [28]. This original ash (non-calcined ash), in a first approach, was tested for preparing geopolymeric mixtures. However, some problems in setting and hardening were observed, since the residue presents a high amount of organic matter [28]. Thus, in order to remove it, the original ash was calcined at 650 °C for 2 h. Then, the obtained calcined ash was used for geopolymeric mixtures (named SCBA for the rest of the manuscript). The chemical compositions of FA and SCBA are shown in Table 1. The crystalline compounds present in FA were mainly quartz (SiO_2, PDF card# 331161) and mullite ($3Al_2O_3.2SiO_2$, PDF card# 150776), whereas for SCBA there were mainly quartz and calcite ($CaCO_3$, PDF card# 050586). The particle size distribution and derivative granulometric curves of FA and SCBA are shown in Fig. 1. The mean particle diameter (D_{mean}) and ninety percent passing size (D_{90}) for FA were 9.11 and 40.18 μm, respectively, whereas the SCBA values for D_{mean} and D_{90} were 18.47 and 61.31 μm, respectively. SEM images of FA and SCBA particles are shown in Fig. 2. SCBA particles (Fig. 2a and b) had an irregular shape, but some particles showed a specific shape (prismatic, see Fig. 2a) [32]. Fly ash (Fig. 2c and d) presented as spherical particles, although some irregular particles were produced during the milling process.

In the preparation of the alkaline solutions, potassium hydroxide and potassium silicate were used as alkaline reagents. Potassium hydroxide pellets (85% purity) were supplied by Panreac SA, and the potassium silicate solution (waterglass, 8.5 wt% K_2O, 21.5 wt% SiO_2 and 70.0 wt% H_2O) was supplied by Kremer. For mortar specimens, siliceous sand with a fineness modulus of 4.1 and a specific gravity of 2680 kg/m^3 was used.

2.2. Preparation of alkali-activated binders

Studies on alkali-activated binders were performed in two sections. In the first part of the study (Section 1), the SiO_2/K_2O molar ratio in the solution was varied in order to identify the optimum value, and the FA/SCBA proportion was held constant at 50/50 by mass. In the second part of the study (Section 2), only this optimized solution was used, and the FA/SCBA proportion was varied in order to achieve the best mechanical properties. In both studies, tests were carried out on pastes and mortars. The H_2O/K_2O molar ratio was held constant at 13.89 and the water/binder (as the sum of FA and SCBA) ratio was 0.45. For mortars, sand was used at a sand/binder ratio of 3/1 by mass.

Four solutions were assessed in the first section of the study, where the SiO_2/K_2O molar ratios evaluated were 0 (S1), 0.35 (S2), 0.75 (S3) and 1.22 (S4). The FA/SCBA proportion was held constant at a ratio of 50/50. The optimum SiO_2/K_2O molar ratio selected for the second section was 0.75 (S3). In the subsequent part of the study, the FA/SCBA proportions assessed were 75/25, 50/50 and 25/75. Table 2 summarizes the alkali-activated binders studied in each section. The specimens were named according to the solution used (S1, S2, S3 and S3) and the FA/SCBA proportion (75/25, 50/50 and 25/75).

In the preparation of paste and mortar specimens, the alkaline activators (potassium hydroxide and potassium silicate) were dissolved in the water and the binder (FA/SCBA) was added to the solution, then allowed to reach room temperature. For mortars, the binder was mixed with the alkaline solution for 4 min and then