Replacement of metakaolin with fly ash in metakaolin-based geopolymers

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Coal is the most complex and most abundant fossil fuel in the world. The thermoelectric plants in Spain, generate more than 9.5 million tonnes of wastes per year with only 20% of them are used for different applications (Ecoba, 2020). In addition, coal-fired power plants produced approximately 33 million tonnes of CO_2 in 2016, significantly lower than 48 million tonnes of CO_2 produced in 2015 (The Spanish Electrical System, 2016).Coal fly ash mixed with heavy metals and toxins are currently stored in landfills and ash lagoons (Ahmaruzzaman, 2010) Thus, it can result a risk to the surrounding environment causing significant environmental impacts. A considerable effort is being made worldwide on research concerning the reuse of coal combustion fly ashes as a source of alternative raw materials to produce new materials, such as cement, concrete, zeolites, glass-ceramics, adsorbents for cleaning of flue gas, lightweight aggregate, road subbase, clay bricks and geopolymers (Toniolo and Boccaccini, 2017; Thomas et al., 2017).

One of the most promising building materials are geopolymers A geopolymer is a cementing material resulting from an alkaline activation process, which consists of an inorganic chemical reaction, at room temperature or slightly high, between a solid material of silicoaluminous origin, which will be the precursor, mixed with a high alkalinity solution, called activator (Davidovits, 2008). The reaction begins when the aluminosilicate is contacted with the alkaline activator solution, giving rise to a new structure formed by polymer chains. Such chains arise due to the polycondensation of silicate and aluminate ions, alternatively joined by sharing oxygen atoms, forming tetrahedral units called sialate.

In this study, coal fly ash (CFA) (0-100 wt %) was used to evaluate the potential of using this waste as a source of aluminosilicates for the synthesis of geopolymers to replace metakaolin (MK). The alkaline activator used was a solution of sodium hydroxide (NaOH) in a concentration of 10 mol/l and sodium silicate (Na_2SiO_3). Different geopolymer compositions have been prepared at various molar ratios Si / Al depending on the percentage of coal fly ash added to the metakaolin precursor (25, 50, 75 and 100 wt %). Furthermore, as a reference, geopolymers were synthesized using only metakaolin as the raw material. (Table 1). The raw materials, metakaolin (MK) and coal fly ash (CFA) were mixed at a slow speed in the dry state for 5 minutes using a planetary kneader. The alkaline solution is then added to the mixture for 2 minutes. Finally, the paste is homogenized for 10 minutes at fast speed. The geopolymeric precursors are poured into cylindrical moulds 35 mm in diameter and beaten on a shaking table to remove air. Subsequently, pastes are cured in a humid chamber at 60 ° C and saturated humidity for 1 day. After the first curing period they are demoulded and left in the air in atmospheric conditions for 7 and 28 days.

Table 1. Paste labels, Si/Al and Na/Si molar ratios, quantities of raw materials used

Sample	Si/Al Mola ratio	Na/Si Molar ratio	MK (g)	CFA (g)	Na_2SiO_3 (g)	H_2O (g)	NaOH (g)	M (mol/l)
100MK	1.45	0.51	450	0	300	195	80	10
75MK-25CFA	1.66	0.51	337.5	112.5	300	195	80	10
50MK-50CFA	1.94	0.52	225	225	300	195	80	10
25MK-75CFA	2.34	0.53	112.5	337.5	300	195	80	10
100CFA	2.94	0.53	450	0	300	195	80	10

The geopolymers have been characterized by Fourier Transform Infrared Spectroscopy (FTIR) and X-ray diffraction (XRD). The physical and mechanical properties of the specimens have been studied in terms of the substitution of metakaolin by coal fly ash and curing time. The XRD and FTIR analysis confirm the formation of

the C-S-H geopolymeric gel for all MK-CFA proportions at 1, 7 and 28 days of curing. The proportion of gel decreasing slightly as the CFA residue content in the materials increases and increases slightly for a cure time of 1 to 7 days, indicating a geopolymerization reaction progress. Longer cure times, barely produce changes, indicating that the geopolymerization process has concluded after 7 days of curing. Geopolymers with values of apparent density between 1475 and 1590 kg / m^3, an apparent porosity between 17.74 and 11.20 % and a water absorption between 11.7 and 7 % have been obtained for a curing time of 7 days. The bulk density increased and the apparent porosity and water absorption decrease as greater amounts of CFA residue are added. Apparent densities decreased with the curing time reaching values between 1379 kg / m^3 and 1430 kg / m^3. Increasing the curing time of 28 days results in a slight decrease in bulk density, and an increase in apparent porosity and water absorption, possibly due to a greater evaporation of the liquid phase. The geopolymers have compressive strength values between 21.5 and 18 MPa after 7 days of curing and 22.2 and 19 MPa after 28 days of curing. It is observed that the incorporation of CFA produces a slight decrease of the mechanical properties, probably due to the smaller amount of geopolymeric gel formed, being the influence of the small curing time, due to the almost complete formation of the geopolymeric gel after 7 days of curing .

The results indicate that the replacement of the CFA residue by MK in the synthesis of geopolymers can be a satisfactory solution for the recovery of waste that results in sustainable construction materials that can be an alternative to conventional Portland cement.

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