Manufacture of copper slags alkali activated cements using olive pomace ash as an alternative alkaline activator.

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Abstract

This work assesses the feasibility of the development of alkaline activated cements using olive pomace fly ash as an alternative alkaline activator for copper slags activation. Cements in which copper slags were replaced by pomace fly ash (30-50 wt %) were manufactured and compared with cements obtained using a KOH commercial solution in the range of 4-8 M. Physical, mechanical and thermal properties of the cements were studied. The results showed that materials activated with olive pomace fly ashes reached higher mechanical properties than those activated with commercial activating solutions, KOH solutions. Therefore, this study demonstrates the feasibility of using pomace fly ash as a potential alkaline activator in the manufacture of alkaline activated materials and presents new sustainable materials, obtaining important economic and environmental advantages by using a waste as an alkaline activator.

Introduction

The manufacture of Portland cement entails the use of a large amount of energy resources and the use of fuels, which implies an environmental impact. In order to limit CO2 emissions, it is necessary to search for new alternative or green cements. The most promising green cements are alkali-cements or geopolymeric cements due to its properties and low environmental impact. These are non-Portland cements based only on natural minerals, waste or industrial by-products and an alkaline activator. However, commercial alkaline activators present environmental problems of some importance, as they are synthetic materials obtained through very expensive and highly polluting processes.

The common practice of storing biomass ashes in landfill constitutes an environmental risk as the land cannot be used for other purposes, because residues may contain toxic elements that can leach and contaminate the soil [1-3]. Therefore, the environmental problems caused by the storage of the waste, together with the increasing production of this type of ash [4], define the need to explore new sustainable valorisation routes for these wastes.

In Andalucía there are 1.4 millions Ha of olive grove. They produce around 4 million tons of olives [5] MAPA 2020). Olive cultivation and its industries produce by-product with high energetic value as: pomace, olive cake, olive stone and pruning. Ashes produced by the combustion of residues from olive grove are accumulated in landfills. These ashes are rich in alkalis, mainly in potassium.

In copper metallurgy, slags obtained are iron silicate. Transformations of the raw materials result in the production of silicates, in particular fayalite (SiO_2) FeO, which is a chemically stable iron silicate. A smelter producing 310,000 mt/year of anodes consumes 1,000,000 mt/year of copper concentrate and as by-products produces 900,000 mt/year of sulphuric acid and 300,000 mt/year of slag [6]. These slags are used in heavy concrete, industrial floor mortar manufacture, cement manufacture, road construction and other building materials [6].

The present study investigates the manufacture of new alkaline activation binders with near zero carbon footprint by activating copper slag (70-50 wt %) with pomace fly ash (30-50 wt %) as an alternative alkaline activator to commercial alkaline activators. As a reference, the slags were also activated with a solution (4 M and 8 M) of KOH commercial.

Materials and methods

Copper slags (CS) were used as a precursor of alkali activated cements. They were provided by Atlantic Copper S.A.U., located in Huelva (Spain). The by-product copper slags were crushed in a ball mill and sieved to a particle size of less than 0.100 mm. The alkaline activator used was olive pomace fly ash (OPA) from Energía de la Loma S.A. plant in Villanueva del Arzobispo, Jaén (Spain). The ashes were sieved to a particle size of less than 0.063 mm. Besides, 4 M and 8 M solutions were prepared using GlobalChem KOH commercial (85 % purity). Chemical composition of raw materials can see in the Table 1.

Table 1. Chemical composition of raw materials: copper slags (CS) and olive pomace ash (OPA).

	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	MnO	Na_2O	K_2O	TiO_2	P_2O_5	SO_3	LOI
CS	27.65	2.04	62.18	1.25	0.38	0.03	0.63	0.56	0.21	0.04	0.90	0.00
OPA	1.86	0.38	0.67	5.33	0.81	0.02	0.19	52.08	0.05	1.62	6.81	24.93

The ashes were mainly composed of K_2O (52.08%), the main component of the olive pomace, and to a lesser extent of SO_3 (6.81%) and CaO (5.33%). The ashes also had a high percentage of unburned as indicated by the high Loss of Ignition (LOI: 24.93 %).

In this study, three different mixtures were designed, using CS as a precursor (70-50 wt %) and OPA as an alternative alkaline activating solution. As a reference, alkali-activated cements activated with solutions of KOH (4 M and 8 M) were produced. The solid/water ratio was set to 0.2 for all samples. The different compositions are presented in Table 2. Raw materials, CS and OPA, were mixed at a slow speed in the dry state for 2 minutes using a planetary kneader. Water, for samples using ash as an alkaline activator or commercial KOH activating solution is then added to the mixture or to the copper slag respectively. The paste is mixed for 90 seconds. With the help of a scraper, the material adhering to the walls is removed and homogenized again for another 60 seconds. Then, the alkali activated paste is poured into 60x10x10 mm moulds and stirred on a shaking table to remove air. Subsequently, the pastes are cured in an oven at 80 °C for 7 days. After the first curing period, they are demoulded and left in the air under atmospheric conditions until the age of 28 days.

Table 2. Composition of alkaline activated cements.

Sample	CS (g)	OPA (g)	H_2O (g)	KOH (g)	M (mol/l)
70CS-30OPA	252	108	90	-	-
60CS-40OPA	216	184	90	-	-
50CS-50OPA	180	180	90	-	-
100CS-4MKOH	336.2	-	90	23.8	4
100CS-8MKOH	312.5	-	90	47.5	8

Physical and mechanical properties of the specimens were studied. The bulk density was determined according to ASTM 642-13 [7]. Flexural and compressive strength were obtained according to UNE-EN105-11 standard [8]. The alkali activated cements were characterized by Fourier Transform Infrared Spectroscopy (FTIR) using a Vertex 70 Bruker equipment. The degree of reaction of binders were determined according to Fernández-Jiménez et al. [9].

Results and discussion

Binders using ash as an alternative activating agent, shown bulk density values between 1514 kg/m^3 and 1809 kg/m^3 for 70CS-30OPA and 50CS-50OPA, respectively, after 28 days of curing (Figure 1). Therefore, a higher bulk density value was obtained to a lower proportion of copper slag, even though the real density of copper slags 3833 kg/m^3 was higher than olive pomace fly ash 2546 kg/m^3. This may be due to the higher amount of geopolymer gel formed according to the degree of reaction which was 92.2 % for the 70CS-30OPA cements, increasing to 95.0 % for the 50CS-50OPA specimens. The binders activated with a commercial KOH solution shown much higher bulk density values than the binders that use ash as an alternative activating agent, 2353 and 2431 kg/m^3, for 100CS-4MKOH and 100CS-8MKOH cements, respectively. The higher bulk density of these cements was in accordance with the higher real density of the copper slag. As for the influence of the curing time, it was observed that the bulk density increased with curing time, indicating an advance of the geopolymerization reaction.

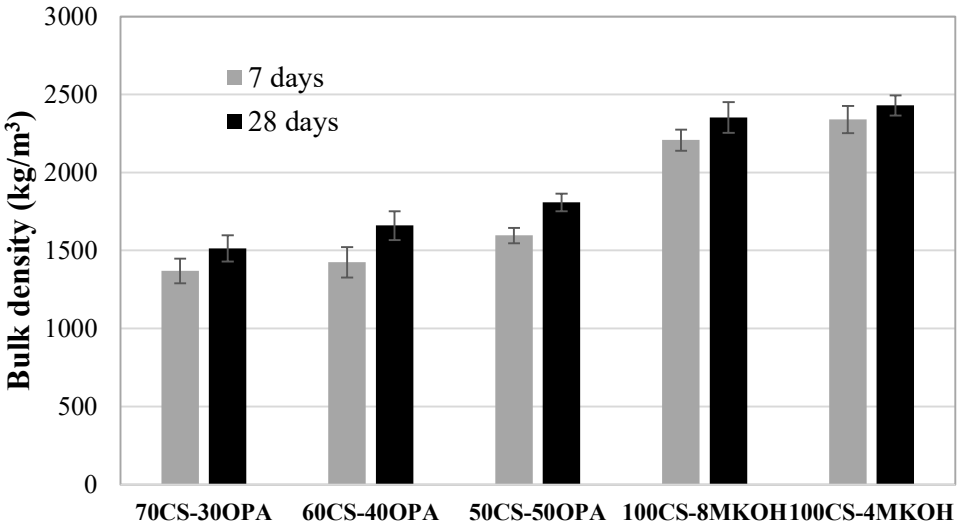

Figure 1. Bulk density of the alkali activated cements after 7 and 28 days of curing.

Regarding the mechanical properties of the cements, it can be observed that the flexural strength increases with the curing time from 7 to 28 days, according to the bulk density data (Figure 2). It can be noticed that the 50CS-50OPA binders presented flexural strength values of 6.4 MPa, similar to those obtained for the binders manufactured using an 8 M solution of commercial KOH, 6.8 MPa. In addition, all cements using OPA as an alkaline activator showed higher flexural strengths than those using a 4 M solution of commercial KOH

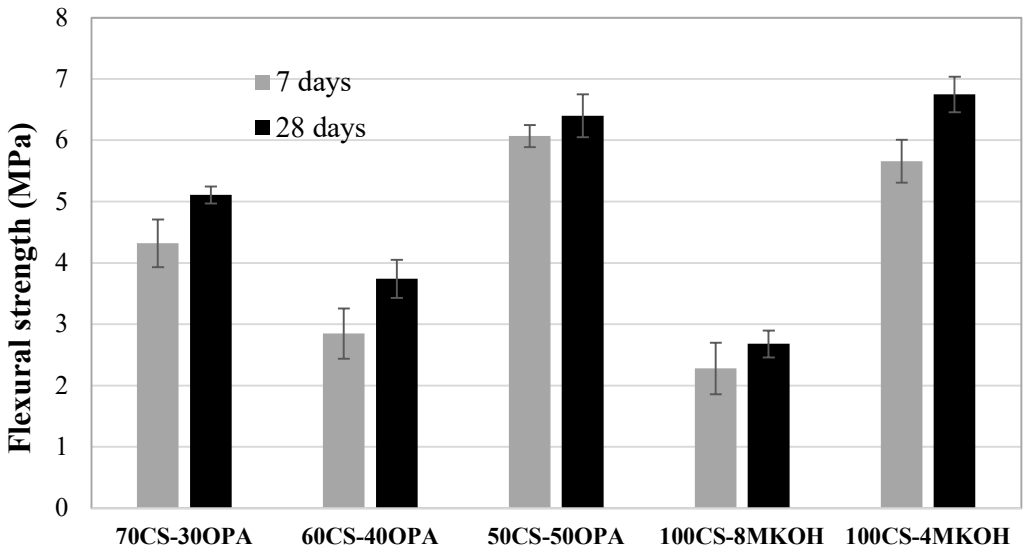

Figure 2. Flexural strength of alkali activated cements after 7 and 28 days of curing.

As for the compressive strength, like the flexural strength, it increased with curing time except for the 70CS-30OPA specimens where the compressive strength remained constant (Figure 3). For binders using OPA as an alternative activator, an increase in compressive strength was observed to higher amount of OPA, with values between 7.5 MPa for the 70CS-30OPA specimens and 14.0 MPa for the 50CS-50OPA cements. The values obtained for the specimens were similar but slightly lower than those obtained with an 8 M solution of commercial KOH, which reached 17.1 MPa after 28 days of curing. However, in all specimens using OPA as an alternative activator, higher compressive strength values were obtained than when using a 4 M solution of commercial KOH. The highest compressive strength may be related to the highest amount of geopolymer gel formed, as well as to the increased density.

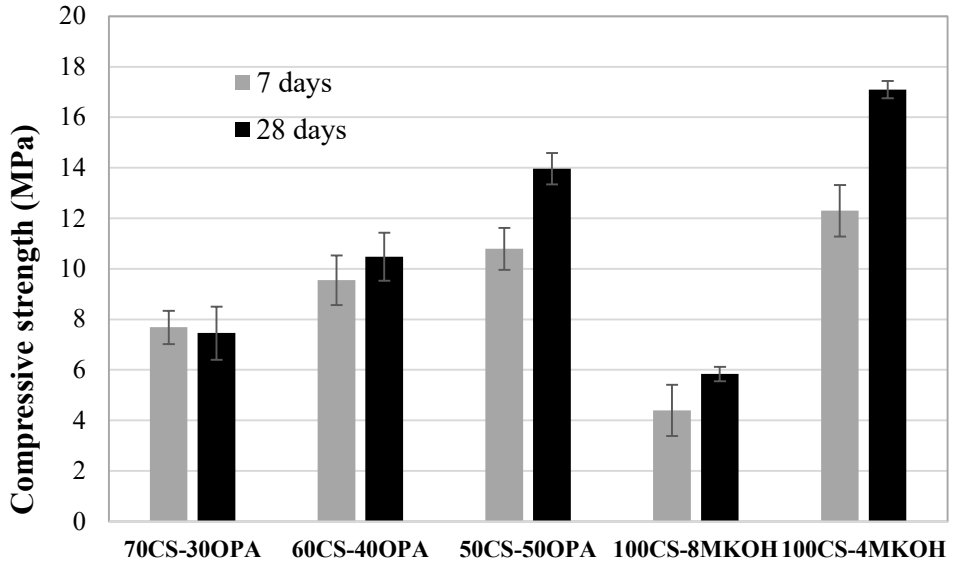

Figure 3. Compressive strength of alkali activated cements.

The FTIR spectra of the manufactured binders are presented in Figure 4. It can be seen how the FTIR spectra of the cements activated with olive pomace fly ash differed from the FTIR spectra of those using solutions of the commercial activator KOH. The absorption bands centred at approximately 3300 and 1625 cm^{-1} correspond to the bending of the H-O-H and O-H bonds of water molecules [10]. This band corresponds to water molecules from crystallisation or absorption of reaction products [11]. These bands did not appear in the precursors (CS and OPA) show the geopolymerization reaction of alkaline activation products and water in the paste. This band is slightly higher as the OPA content increases, indicating the formation of more gel according to the degree of reaction. The bands of the pastes centred at 1412 and 874 cm^{-1} indicate the presence of the CO_3^{2-} group formed from the reaction between unreacted potassium ions present in the OPA precursor reacting with atmospheric CO_2 producing carbonation of the activated cement with alternative alkalis [12]. The band associated with the asymmetric stretching vibration of the Si-O-T (T=Si or Al) bonds in the slags, centred at 856 cm^{-1}, shifted to higher frequencies, reaching values at 28 days of curing between 956 cm^{-1} for the fly ash-activated binders and 904 cm^{-1} for those activated with commercial KOH solution. This indicates the development of new K-A-S-H gels in all the manufactured binders.

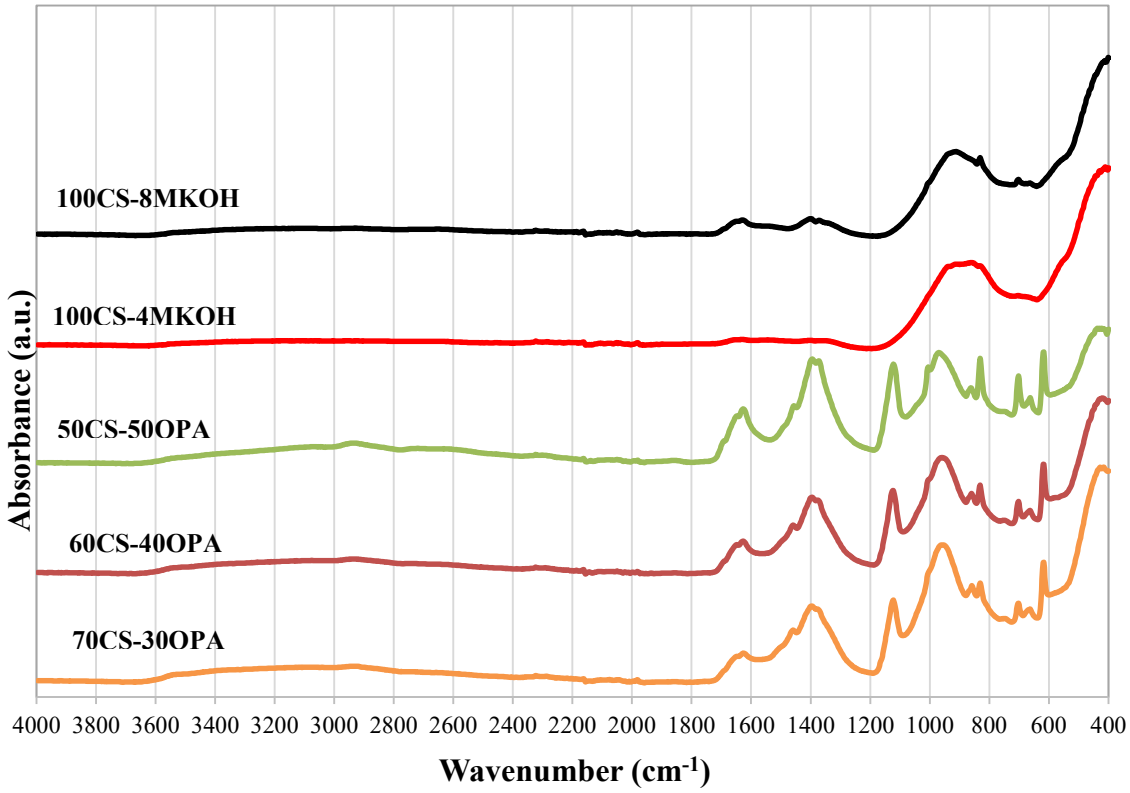

Figure 4. FTIR spectra of the alkali activated cements after 28 days of curing.

Conclusions

This study demonstrates the viability of pomace fly ash as an alternative alkaline activator for binders with copper slag as a precursor. The results indicate that cements with the optimum technological properties are the 50CS-50OPA one, which have similar properties to those manufactured with an 8 M solution of commercial KOH. For the 50CS-50OPA specimens prepared using ash waste, bulk density values of 1809 kg/m^3 and flexural and compressive strengths of 6.4 and 14.0 MPa, respectively, were obtained after 28 days of curing. Furthermore, if binders with an almost zero carbon footprint want to be obtained, it is necessary to replace commercial activators with significant economic and environmental disadvantages with alternative activators from waste, such as OPA, in order to move closer to a circular economy.

Acknowledgements

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