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Biomass ashes to produce an alternative alkaline activator for alkali-activated cements.

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Abstract

In the last decade, herbaceous and agricultural biomass have been used as an alternative energy source. As consequence, large amounts of residual ashes containing potassium (potassium-rich ashes) have been generated. Olive biomass ash (OBA) and almond shell ash (ABA) have been successfully used as alkali source in the alkaline activation of ground granulated blast furnace slag (BFS). This study focuses on the production of new and alternative alkaline activators for BFS systems using nutshell ashes (NBA), mango seed-bark ashes (MBA) and hazelnut shell ashes (HBA). The chemical and mineralogical composition of these ashes were assessed and, the mechanical and microstructural properties of BFS pastes activated with NBA, MBA and HBA were evaluated. The results indicated that all assessed materials are potassium-rich ashes differing mainly on the amount of CaO and P_2O_5. The compressive strength of BFS pastes yielded about 26 MPa and, according to FESEM/EDS analysis, K_2O (in the range 8.03-24.33%) replaces chemical bounded Ca^{+2}, forming C-(K)-A-S-H gel.

Keywords: Biomass ash, valorisation, alkali-activated cement, blast furnace slag, chemical composition, high potassium ashes.

1. Introduction

The United Nations adopted 17 Sustainable Development Goals (SDGs) to make social, economical and environmental improvements. As Hickel indicates, there is a difficult balance to achieve economic objectives simultaneously with environmental ones [1]. SDG 13 indicates, "Take urgent action to combat climate change and its impacts". Fossil fuel combustion is the principal cause of global warming. In 2018, 89% of all CO_2 emissions came from fossil fuels and industry [2]. Using biomass as renewable energy is one of the best solutions to eliminate fossil fuels. Depending on the source of biomass, the corresponding ashes have different compositions. Herbaceous and agricultural biomass ashes (HABA) offer higher K_2O quantities [3], being good candidates for activating ground granulated blast furnace slag (BFS) due to the moderate alkaline environment required for its activation.

The main reaction product formed by the alkaline activation of BFS using hydroxide solutions (NaOH, KOH) is a C-A-S-H gel, where Na^+ or K^+ replace chemically bounded Ca^{+2}, forming C-(M)-A-S-H gel.

Few publications about potassium-rich ashes (olive biomass ash – OBA and almond shell biomass ash – ABA) activating BFS are found in the literature [4-6]. Soriano et al. [6] assessed the use of ABA as an alkaline activator in one-part BFS systems. The mortars containing 20wt.% of addition of ABA presented 36.4 MPa after 7 curing days at 65 ºC. Similar mortar activated with 8 molal of commercial KOH solution yielded 21.2 MPa.

All studies mentioned above reported technical and environmental advantages of using potassium-rich ashes for BFS systems, including enhancement on mechanical and microstructural properties, reduction on landfilling and consequent valorisation of biomass ashes [4-6].

Hence, this paper aims to study the potential of using different HABA such as nutshell biomass ash (NBA), mango biomass ash (MBA) and hazelnut shell ashes (HBA) as alkali-source for alkali-activated cements. The chemical and mineralogical composition of biomass ashes were assessed and, alkali-activated BFS pastes activated with potassium-rich ashes were characterised through compressive strength, thermogravimetric analysis and FESEM/EDS.

2. Experimental

2.1. Materials

BFS, supplied by Cementval-SA (Puerto de Sagunto, Spain), was used as a precursor material. ABA, supplied by Borges Agricultural & Industrial Nuts (BAIN), was used as a reference potassium-rich ash and, its characterisation has been previously reported [6].

Shell and seeds from hazelnuts, nuts and mangos were put inside a cylindrical steel container, with perforations in the base and were calcined throughout a self-combustion process (in this process the combustion was initiated using gas-fuel through the base during the first minute and, afterwards, the process took place by self-combustion of the biomass).

2.2. Methods

Biomass ashes were characterised by X-ray diffraction (equipment: Brucker ADX D8 Advance) and by an EDS analysis with field emission scanning electron microscopy (equipment: ULTRA 55-Zeiss with EDS analyser). Alkali-activated pastes were prepared using a fixed water/binder ratio of 0.4, where the binder was composed of 25 wt.% of biomass ash and 75 wt.% of BFS (proportion was selected based on the literature [7]). Pastes (1x1x6 cm^3), cured in the first 7 days at 65 ºC and afterwards during 28 days at 20 ºC, were assessed throughout compressive strength test (12 specimens, INSTRON universal machine - model 3382), thermogravimetric analysis (Mettler Toledo TGA 850 thermobalance) and FESEM/EDS analysis.

3. Results and Discussion

3.1. NBA, MBA and HBA characterisation

ABA is mainly composed of K_2O and CaO at 46.08% and 18.73%, respectively, and the main components of BFS are SiO_2 and CaO (30.53% and 40.15%, respectively) [6]. The chemical compositions of ashes were determined by the EDS analysis and are summarised in Table 1.

The oxides components calculated by EDS were corrected with the value obtained by loss on ignition (L.O.I) at 700 ºC.

Table 1. Chemical composition of NBA, MBA and HBA (wt.%)

	MgO	Al_2O_3	SiO_2	P_2O_5	SO_3	K_2O	CaO	Cl^-	others	L.O.I
NBA	5.80	-	0.53	5.87	1.53	37.33	34.01	0.73	-	14.20
MBA	10.66	-	1.32	22.94	3.97	38.21	8.26	0.85	0.16	13.63
HBA	6.27	0.20	0.74	4.38	3.05	31.81	30.02	0.07	0.14	23.21

The main component of all the ashes was potassium oxide. Both NBA and HBA had a similar composition, with CaO as their second principal component. Their composition came close to those obtained by ABA. MBA had a considerable amount of P_2O_5. The low chloride content for all ashes assessed do not limit their use on reinforced BFS-activated concrete.
All the ashes, except ABA, have calcite as the main peak in XRD (Fig. 1). Fairchildite and buetschilite confirmed the presence of calcium-potassium carbonates. Sulphates appeared in the form of arcanite, α-potassium sulphate and gypsum and, they were also reported in HBA by Gogebakan et al. [8]. The presence of hydroxylapatite and kovdorskite was related to phosphate phases.

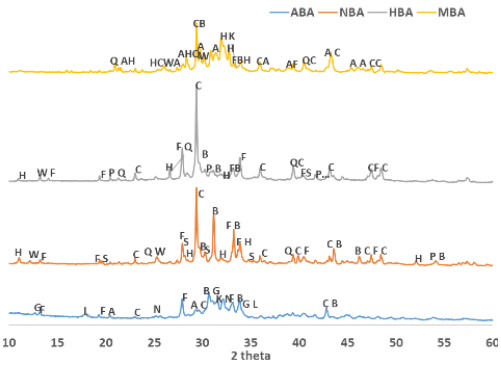

Fig. 1. XRD patterns of ABA, NBA, HBA and MBA (C: calcite-$CaCO_3$; A: arcanite-K_2SO_4; L: portlandite-$Ca(OH)_2$; F: fairchildite-$K_2Ca(CO_3)_2$; B: buetschilite- $K_2Ca(CO_3)_2$; N: anhydrite-$CaSO_4$; K: kovdorskite-$Mg_2(PO_4)(OH).3H_2O$; G: gypsum-$CaSO_4.2H_2O$; Q: quartz-SiO_2; H: hydroxylapatite-$Ca_5(PO_4)_3(OH)$; S: silvine-KCl; P: α-potassium sulphate-αK_2SO_4; W: wollastonite-$CaSiO_3$).

Fig. 2 shows FESEM micrographs of ashes, enhancing the presence of small particle size with irregular shape. In the same way, some few larger particles with dense, compact and presenting a superficial roughness can be observed.

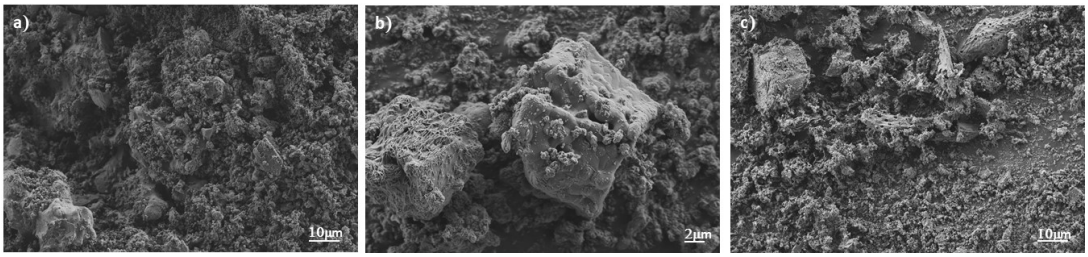

Fig. 2. FESEM micrographs of potassium-rich ashes: a) NBA; b) MBA; c) HBA.

3.2. *One-part 100 % waste-based paste characterisation*

Compressive strength tests performed for BFS pastes yielded 29.98, 25.05, 26.85 and 27.21 MPa for the pastes with ABA, NBA, MBA and HBA, respectively. These results come close

to those of the pastes analysed by Alonso et al. [5], who obtained values of around 30-35 MPa in the pastes with 70% BFS and 30% of OBA cured for 24 h at 45 ºC or 85 ºC, and for 27 days at ambient temperature. Hence, the mechanical results indicate the potential of using these potassium-rich ashes for activating the BFS system.
After the compressive strength test, the samples were immersed in acetone to stop activation reactions. Then they were dried at 65 ºC in an oven and employed to analyse reaction products. The thermogravimetric analysis confirmed the presence of the typical hydrates for BSF-activated paste with potassium activators [4, 6]. These products were mainly C-A-S-H and C-(K)-A-S-H gels, and hydrotalcite. The total mass loss percentages within the range between 35 ºC and 600 ºC were 12.74%, 12.22% and 12.35% for the BFS pastes activated with NBA, MBA and HBA, respectively. These results indicates that similar hydrates were formed independently on the potassium-rich ash used.
Figure 3 shows the FESEM micrographs at 2000x magnification. All pastes presented a dense structure and, according to the EDS analysis, potassium is present on the composition of reaction products indicating the formation of C-(K)-A-S-H gels. For pastes containing NBA, MBA, HBA the amount of K_2O in the structure is in the range 8.03-14.75%, 9.29-24.33% and 12.45-14.48%, respectively.

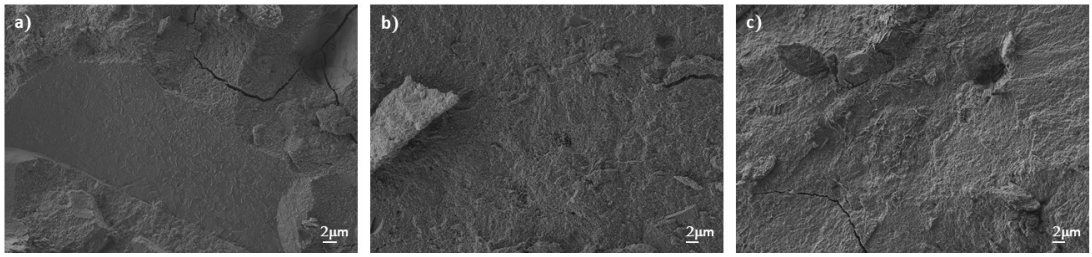

Fig. 3. FESEM micrographs (2000x magnification) of the BFS-activated pastes: a) NBA; b) MBA; c) HBA.

Conclusions
The study performed allows to obtain some important conclusions:
- The chemical characterisation of NBA, MBA and HBA indicates their potential of using as alkaline activators of BFS systems due to the presence of K_2O on their composition (about 35% for all ashes assessed).
- The compressive strength results of BFS pastes yielded about 26 MPa, independently on the ash used.
- The microstructural analysis performed through thermogravimetric analysis and FESEM/EDS showed a dense, amorphous, compact structure.
- C-(K)-A-S-H gels were identified as the main hydrated products formed in the reaction.

Acknowledgements
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