ONE-PART BLAST FURNACE SLAG MORTARS ACTIVATED WITH ALMOND-SHELL BIOMASS ASH: A NEW 100% WASTE-BASED MATERIAL

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Abstract

The use of almond-shell biomass ash (ABA) as an alkali source in one-part blast furnace slag (BFS) mortars activation was investigated for the first time. The chemical composition of ABA revealed high alkalinity ash to be composed mainly of K_2O and CaO. The one-part 100% waste-based mortars and pastes were studied by mechanical and thermogravimetric tests. The compressive strength values of the newly designed materials were higher than the mortars fabricated with commercial products (36.4 *versus* 21.2 MPa). The formation of C-S-H/(C,K)-A-S-H gels took place in the thermogravimetric studies. The use of ABA in mortars proved an interesting alternative to chemical reagents in alkali activated cements.

Keywords: Alkali-activated material; Blast furnace slag; Almond-shell biomass ash; Alternative potassium source; Biomass valorization

1. Introduction

When preparing alkali-activated mortars, raw materials with a strong alkalinity are generally used as activators, and one environmental-friendly alternative is to use biomass ash that is rich in potassium or calcium. Peys et al. studied rich potassium biomass ash in systems with metakaolin, where they used it as the precursor material[1]. These authors employed three biomass types: wood ash from a mixture of oak and beech, corn cob ashes and cotton ashes. The best results were obtained with corncob ashes.

In 2017, Font et al. [2] studied the use of olive-stone biomass ash (OBA) as an alkali source for preparing alkali-activated materials (AAM). They performed physico-chemical characterisations, and a compressive strength of 29.9 MPa was obtained for the mortars cured at 65ºC for 7 days. De Moraes Pinheiro et al. [3] compared mortars with BFS activated with NaOH and KOH at different concentrations (from 4M to 12M) and mortars with several replacement (15-35%) and addition (5-25%) percentages of OBA cured at 65ºC for 7 days. Better results were obtained when substituting BFS for OBA within the 20-35% range compared to the BFS mortars activated with KOH. The 25% OBA addition yielded the highest compressive strength (38.4 MPa).

Alonso et al. [4] studied the behaviour of BFS and coal fly ash (CFA) samples activated with olive biomass fly ash (OBFA) and olive biomass bottom ash (OBBA). They studied the chemical, mineralogical and radiology characterisations of olive samples, and radiological and mechanical results in pastes with BFS and CFA. These authors concluded that only BFS obtained good results when developing compressive strength, and samples met European legislation criteria in radiology terms.

The world's almond production has increased worldwide, from 1.03 MMT in 2014/2015 to 1.3 MMT in 2018/2019 [5]. Almond fruit represents 25% of the total weight because the shell makes up the remaining 75% [6]. Almond shells are frequently used as fuel, producing ash as waste (about 2% per mass of biomass). The recovery of waste is obviously essential for the development of a sustainable circular economy. As far as we are aware, no research has been conducted on using almond-shell ash as an alkali source for AAM preparations.

This paper presents a preliminary study of the waste obtained by almond-shell calcination. The obtained ash was almond-shell biomass ash (ABA). The aim of this research was to characterise the ash and study, for the first time, its behaviour in BFS matrices. One-part ABA/BFS mortars were compared to the mortars activated with BFS and KOH alkali solutions.

2. Materials and Methods

2.1. Materials

Blast furnace slag (BFS) was supplied by Cementval-SA (Puerto de Sagunto, Valencia, Spain) and was milled in a ball mill for 30 minutes to obtain a mean diameter of 26 µm. Almond-shell biomass ash was supplied by Borges Agricultural & Industrial Nuts (BAIN) (Altura, Castellón, Spain) (Table 1 shows their chemical compositions). The original ABA was milled in a ball mill for 20 minutes before use, and 85% purity potassium hydroxide (KOH) was employed as the alkaline reagent (Panreac SA) in the control mixes.

2.2. Methods

- ABA characterisation: X-ray fluorescence (XRD, Philips Magic Pro XRF), pH of the solid suspension in deionised water (Crison micro PH2001 pH meter), particle size distribution (PSD, Malvern Instrument Mastersizer 2000), X-ray diffraction (XRD, Bruker AXD D8 Advance) and field emission scanning electron microscopy (FESEM, ULTRA 55-ZEISS) with samples covered by carbon.

- Two control samples were developed by mixing BFS with aqueous solutions of KOH with several molalities, 4M and 8M, and a water/solid ratio = 0.40 (for mortars 450 g BFS, 180 g water, the corresponding quantity of KOH and 1350 g standard siliceous sand [7]). For ABA containing mixtures, the milled ash was first dry-mixed with BFS and then mixed with still water: a) 20% replacement of BFS (20R sample) with a water/solid ratio = 0.40 (for mortars 360 g BFS, 90 g ABA, 180 g water and 1350 g sand); b) 20% addition (20A sample) with a water/solid ratio = 0.34 (a reduction in water/solid ratio occurred because 90 g ABA were added to 450 g BFS, maintaining the same quantities of water and sand than 20R). Prismatic specimens (4x4x16 cm^3) were cured at 65ºC and 100% RH, and characterised after 3 and 7 days. The compressive strength of six samples was tested by a universal testing machine [7]. Pastes were assessed by thermogravimetric analyses (TGA) within the 35-600ºC temperature range at a 10ºC/min heating rate and in an N_2 atmosphere (TGA850 Mettler-Toledo thermobalance). Sealed aluminium 100 µL crucibles (with pin-holed lids) were used for the analysis.

Table 1
Chemical composition of BFS and ABA (wt%)

Material	Oxide composition (%)										
	SiO_2	CaO	Al_2O_3	Fe_2O_3	Na_2O	MgO	K_2O	P_2O_5	SO_3	Others	LOI*
BFS	30.53	40.15	10.55	1.29	0.87	7.43	0.57	0.26	1.93	0.89	5.53
ABA	0.64	18.73	0.19	0.47	0.37	1.68	46.98	1.74	0.68	0.52	28.00

*Loss on ignition

3. Results and Discussion

3.1. ABA characterisation

Almond-shell biomass ash is composed mainly of K_2O (46.98%). The second main compound is CaO (18.73%; see Table 1). The amount of K_2O in ABA was higher than that reported in OBA by Font et al. (32.16%), de Moraes Pinheiro et al. (32.12%) and Alonso et al. (17.31%) [2–4].

The pH obtained for the suspension of ABA in deionised water (10-minute stirring) was 10.8 for a mix with a ABA:water ratio of 0.40. This value was significantly lower than that found in OBA (13.5 for an OBA:water ratio of 0.47). This means that alkaline compounds in ABA are not easily dissolved.

After the ABA milling treatment, the resulting mean particle was 18.8 µm and the 10%, 50% and 90% passing diameters (d_{10}, d_{50} and d_{90}) were 2.3, 12.3 and 45.2 µm, respectively.

The main peaks observed in the XRD patterns for ABA were the crystalline phases of fairchildite ($K_2Ca(CO_3)_2$), bütschilite ($K_2Ca(CO_3)_2$) and calcite ($CaCO_3$). The portlandite ($Ca(OH)_2$) and arcanite (K_2SO_4) peaks were not marked. Some traces of anhydrite ($CaSO_4$) and kovdorskite ($Mg_2(PO_4)(OH).3H_2O$) were found.

Figure 1 shows the FESEM images of the original ABA (125 µm sieving) (Fig. 1a) and ground ash (Fig.1b). In the original ash, a mixture of very large smooth-surface particles (c.a. 70-120 µm) and small rough-surface particles (c.a. 10-30 µm) was found. The detail of the small rough-surface particles showed a crystalline topography (the EDS analysis revealed that potassium (59.8%) and calcium (11.6%) were major elements). The image of the ground ABA (Fig. 1b) shows some large particles (c.a. 20-30μm) with porous and non-porous smooth surfaces and small rough particles (enlarged in Fig. 1a).

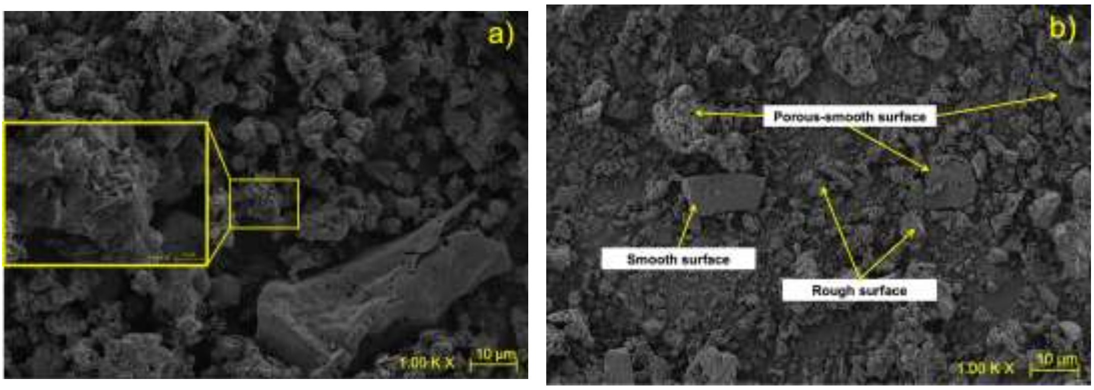

Fig. 1. FESEM images: a) original ABA after 125 μm sieving; b) ABA after milling

3.2. *One-part 100% waste-based mortars and pastes characterisation*

The results of the mechanical tests of mortars (20R, 20A, 4M and 8M) after 3 and 7 curing days are shown in Fig. 2. It is noteworthy that the 100% waste-based systems (BFS activated by ABA) yielded a higher compressive strength than the control ones (KOH was employed for BFS activation). The evolution of mechanical behaviour between days 3 and 7 was also more marked for samples 20R (11 MPa gain) and 20A (3 MPa gain) than for samples 4M and 8M (both increased by 2 MPa).

After 3 days, the replacement system (20R) yielded 21.7 MPa, which is a lower compressive strength than that obtained for the addition system (20A). The replacement system (20R sample) yielded 10 MPa more than the 8M control sample, and the 20A sample almost doubled the compressive strength compared to 8M (36.4 MPa). The ABA results were similar to those obtained in the OBA systems studied by de Moraes Pinheiro et al. [3] at 7 curing days. For the replacement system, the 20R-ABA mortar yielded 32.6 MPa compared to 26.0 MPa obtained for the 20R-OBA mortars. With the addition system, the 20A-ABA mortar yielded 36.4 MPa *versus* 34.7 MPa in the 20A-OBA mortar. The higher potassium content of ABA was responsible for better mechanical performance.

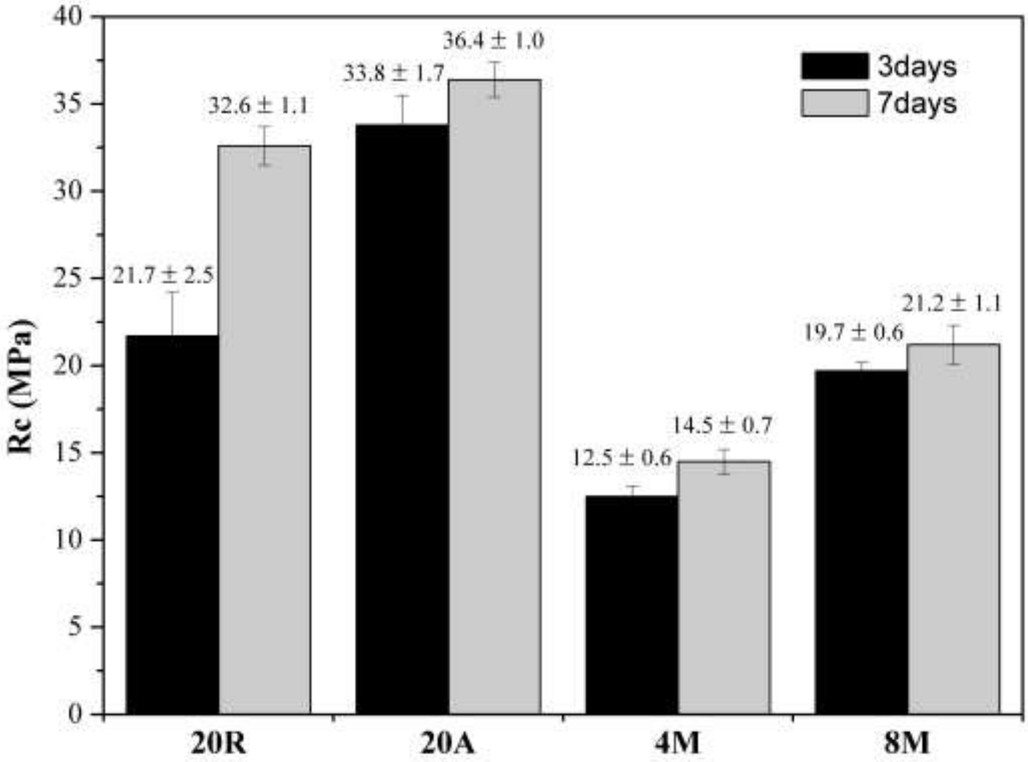

Fig. 2. Compressive strength of mortars after 3 and 7 curing days at 65ºC.

The derivative thermogravimetric curves (DTG) and the total mass loss within the 35-600ºC temperature range (wt-%) for pastes 4M, 8M and 20R (after 3 and 7 curing days at 65ºC) are shown in Fig. 3. The same mean peaks of mass losses (PK-1, PK-2 and PK-3) were obtained for the control samples and the 100% waste-based one (20R sample). PK-1 was the main peak in all the pastes and was associated with gel dehydration C-S-H and (C,K)-S-H [8]. PK-1 for sample 20R was centred at 133-134ºC, but at 145-154ºC in the pastes with KOH. This difference suggests a slight change in gel composition.

PK-2 corresponds to the dehydration of gels C-A-S-H and (C,K)-A-S-H, and PK-3 corresponds to the dehydration of hydrotalcite [3]. PK-3 was more intense in the control pastes (4M and 8M). The presence of hydrotalcite was confirmed by X-ray diffraction in all the pastes. The total mass loss was more marked in the control pastes than in paste ABA, but this behaviour was not related to strength development.

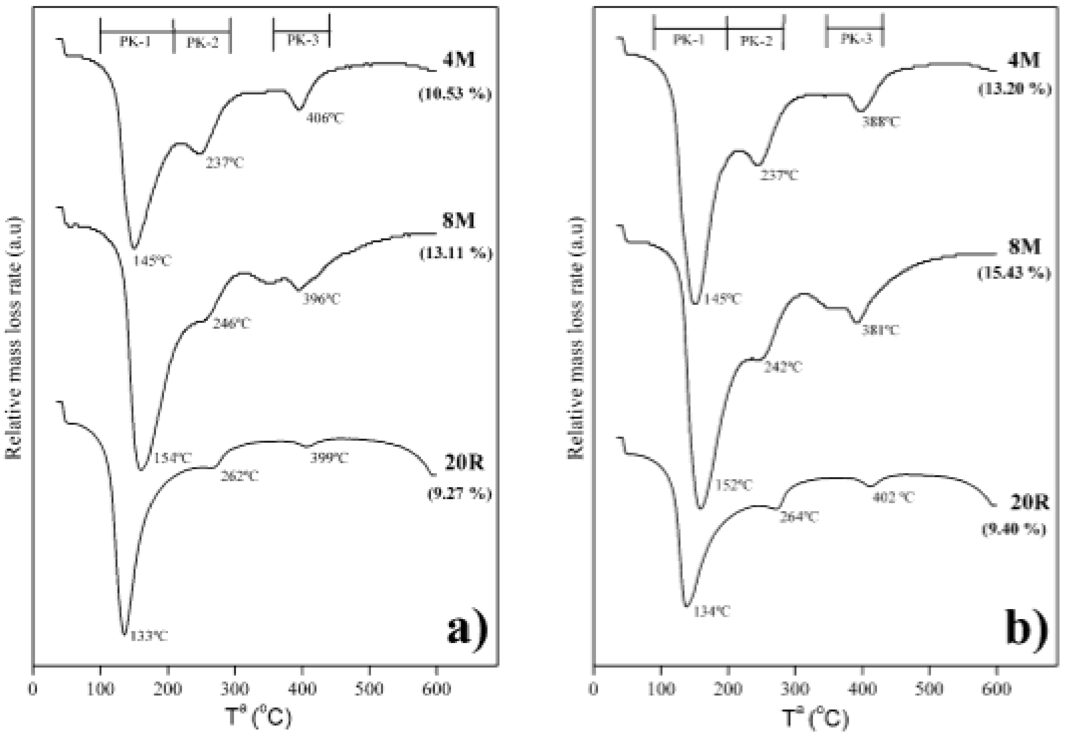

Fig. 3. The DTG curves of 20R, 4M and 8M cured at 65ºC: a) 3 day and b) 7 days. The values in brackets indicate the total mass loss within the 35-600ºC temperature range (wt-%).

4. Conclusions

The ash obtained from almond-shells (ABA) is a good candidate for preparing 100% waste-based alkali-activated systems based on BFS. A 71.7% gain strength was obtained for the mortar 20A *versus* the control mortar KOH-8M after 7 curing days. This investigation reveals the potential of a new biomass residue valorization, the ABA, as commercial reagent replacement in the preparation of AAM.

Acknowledgements

We wish to thank Borges Agricultural & Industrial Nuts for supplying ash and the Electronic Microscopy Service at the UPV. This research was supported by MINECO (Project RTI2018-097612-B-C21).

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