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Non-conventional additions from agricultural waste

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ABSTRACT

Agricultural waste materials are usually dumped to landfill causing economic and environmental problems. The present work focuses on ash for partial cement replacement obtained from several agricultural wastes, either by incineration in the laboratory or directly from industries where the waste has been incinerated for energy production.

Agricultural waste materials tested were Almond shell Ash (AA), Olive Bagasse Ash (OBAa) grape Rachis/Pedicules ash (RPA), Chestnut peel ash (CA), Grape Bagasse Fly Ash (BGFA), Grape Bagasse Bottom Ash (BGBA) and Digested Filtering Waste (lees) from the wine industry (DFW). SEM and chemical analyses of these ashes are presented. Mortar with 10% cement replacement with each ash type was produced and compared to control mortar but none of the waste materials seem to be promising to use as a cement replacement material for structural concrete.

Keywords, additions, waste, pozzolan, cement.

INTRODUCTION

Increasing concern for environmental protection, energy conservation with minimal impact on economy have been motivating researchers to look for other alternatives for cement in the concrete industry. They provide environmentally safe, stable, and more durable and low cost construction materials. It is well known that production of cement (key binding component of concrete) is costly, consumes high energy, depletes natural resources and emits large amounts of greenhouse gases (mostly CO_2). It has been reported that the production of 1 ton of cement consumes about 4GJ of energy and requires about 1.7 tons of raw materials (limestone and shale) which leads to environmental degradation and pollution problems. Therefore concrete technology has focused on other alternatives which can be used as cement replacement materials in concrete. Researchers have been searching all the time for cheap and easily available cement replacement materials, like industrial and agricultural wastes which are pozzolanic in nature (Kaha et al, 2012).

These industrial and agricultural wastes are mostly the by-products of oil and coal burning by-products, slag, rice husk ash, bagasse, fly ash, cement dust, stone crusher dust, marble dust, brick dust, sewer sludge, glass, tires, etc. Million tons of these waste materials are abundantly available and discarded every year in the world. Recycling of such wastes as a sustainable construction material appears to be a viable solution not only for the pollution problem but also an economical option to design green buildings (Kaha et al, 2012)0.

Agricultural residues are primarily the stems, leaves and shafts of crops remaining in fields or at processing facilities after greater-value products of the plants (for example, grain, seeds, nuts, tubers, etc.) have been harvested. Agricultural residues are mostly generated at two different stages: after harvesting the main crop, such as rice in nut production; and after processing the plant in industrial operations, such as bagasse in olive oil industry. New technologies for value-added use of agricultural residues can generate industrial activities with major economic benefits to rural communities (Soroushian and Hassan, 2012).

The present work focuses on ash for partial cement replacement obtained from several agricultural wastes obtained from Portuguese industries. Waste materials were examined in terms of chemical and physical characteristics and mechanical properties of mortar containing 10% Portland cement replacement. Ash from agricultural wastes used as biomass in industries were Almond shell Ash (AA), Olive Bagasse Ash (OBAa), chestnut peel ash (CA), grape bagasse fly ash (BGFA), grape bagasse bottom ash (BGBA) and Digested Filtering waste (lees) from the wine industry (DFW). These last three are produced at a distillery in Portugal. Rachis/pedicules ash (RPA) was obtained in the laboratory by controlled incineration of rachis/pedicules, a waste material consisting of stems of grapes which causes concern to wine producers in the Douro region where Port wine is produced.

EXPERIMENTAL PROGRAM AND RESULTS

Chemical analysis of waste materials. Chemical analysis of most waste materials and of typical commercial Type I 42.5R Portland cement used are shown in Table 1.

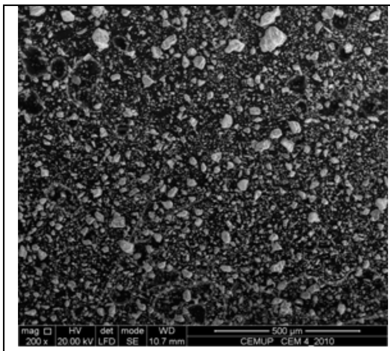
Scanning Electron Microscopy. Scanning Electron Microscopy (SEM) was carried out on agricultural waste samples, as well as, on cement. Some photos can be seen in Figure 1 to Figure 7.

Materials and Mortar Production. Typical commercial Type I 42.5R Portland cement was used. Seven mortar types were prepared following the procedure described in NP EN 196-1: a control mix with 100% cement (CTL), mixes with 10% of each agricultural waste material ground to sufficient fineness. CEN Reference sand for mortar production was used. Similar mortar workability, measured according to ASTM C 109/90 and ASTM C 230 was obtained for the different mortar types. Several test specimens were produced. After demoulding the following day, test specimens were cured in water at 20 ºC in a fog room until testing.

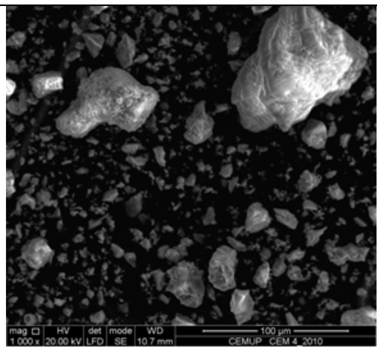
Table 1. Chemical composition of agricultural wastes.

Chemical composition (%)	Cement	BGBA	BGFA	DFW	RPA
LOI	2,61	35,95	8,84	68,89	13,90
Insoluble residue	1,33				
SiO_2	20,36	21,99	13,55	11,60	39,00
Al_2O_3	5,1	3,01	2,58	2,62	7,66
Fe_2O_3	3,12	1,44	1,33	0,84	2,87
CaO	62,72	14,72	28,80	9,60	13,54
MgO	1,81	2,36	5,00	1,44	6,67
Na_2O		0,38	0,38	0,29	1,25
K_2O		11,77	19,68	2,02	12,38
TiO_2		0,10	0,11	0,04	0,29
Na_2O eq		8,41	13,80	1,67	9,69
MnO		0,06	0,10	0,02	0,33
P_2O_5		35,95	17,93	2,17	1,91
SO_3	3,44	1,40		0,70	1,20
Cl	0,012				
Free lime	1,62				

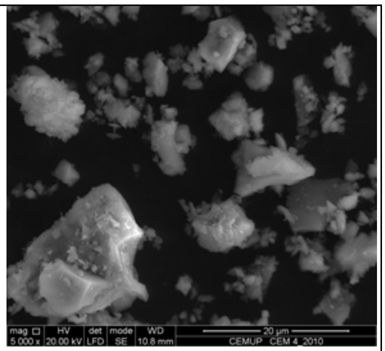
Scanning Electron Microscopy. Scanning Electron Microscopy (SEM) was carried out on agricultural wastes samples, as well as, on cement. Some photos can be seen in Figure 1 to Figure 7.



a) Cement 200 times enlarged

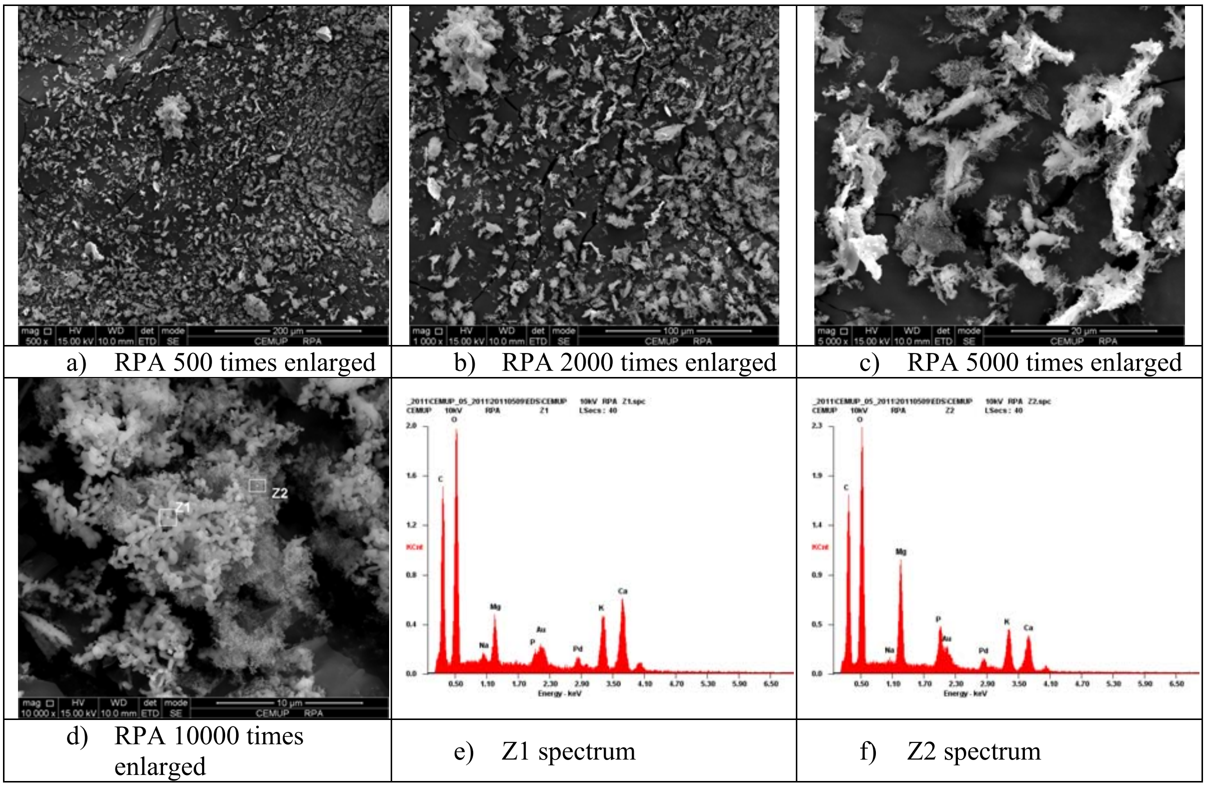


b) Cement 1000 times enlarged



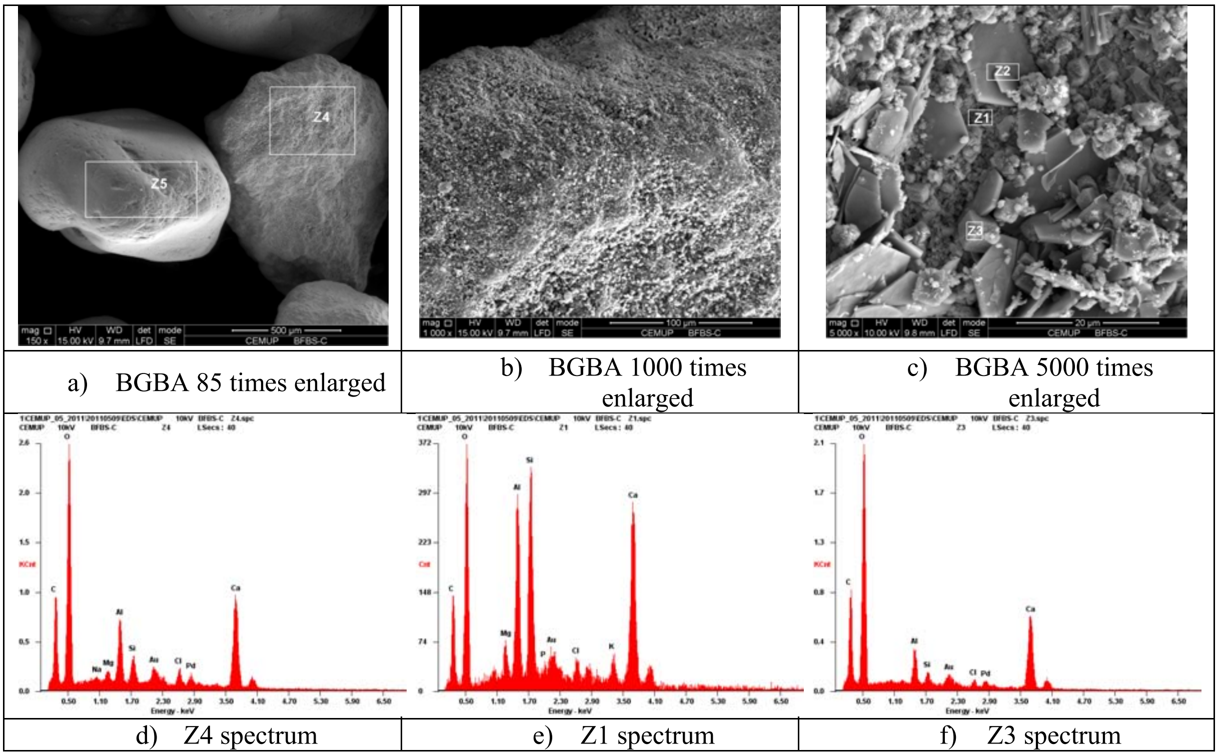
c) Cement 5000 times enlarged

Figure 1. SEM on cement.



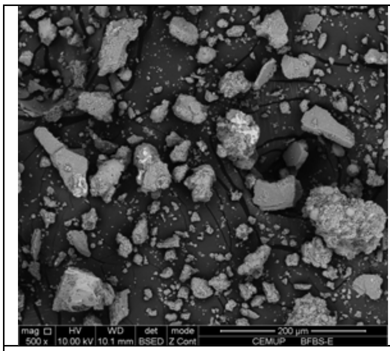
a) RPA 500 times enlarged
b) RPA 2000 times enlarged
c) RPA 5000 times enlarged
d) RPA 10000 times enlarged
e) Z1 spectrum
f) Z2 spectrum

Figure2. SEM on RPA.

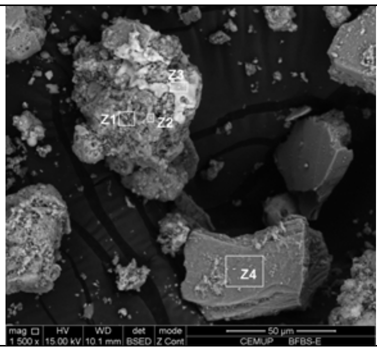


a) BGBA 85 times enlarged
b) BGBA 1000 times enlarged
c) BGBA 5000 times enlarged
d) Z4 spectrum
e) Z1 spectrum
f) Z3 spectrum

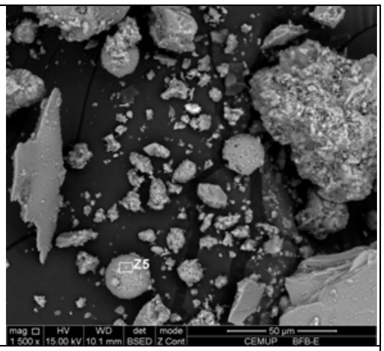
Figure 3. SEM on BGBA.



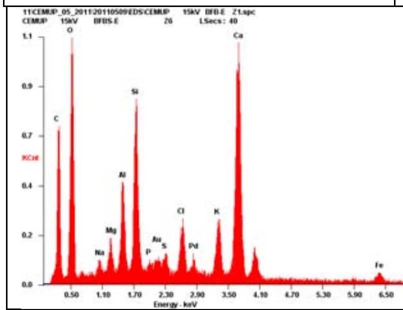
a) BGFA 500 times enlarged



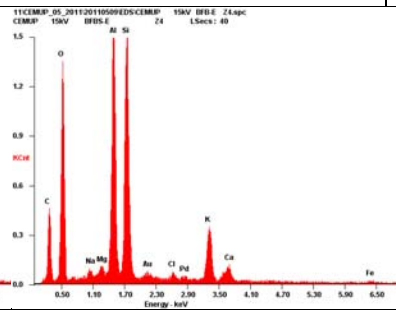
b) BGFA 1500 times enlarged



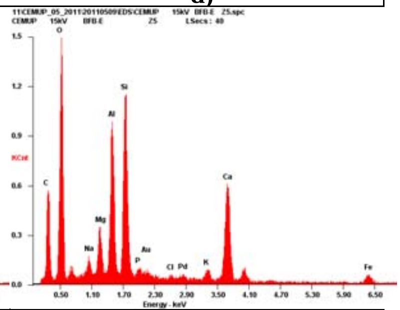
c) BGFA 1500 times enlarged
d)



e) Z1 spectrum

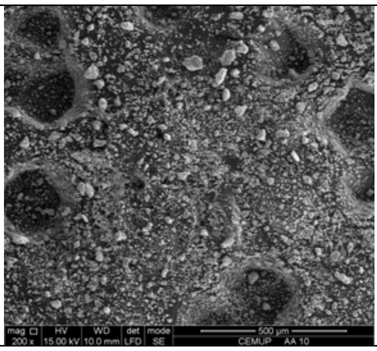


f) Z4 spectrum

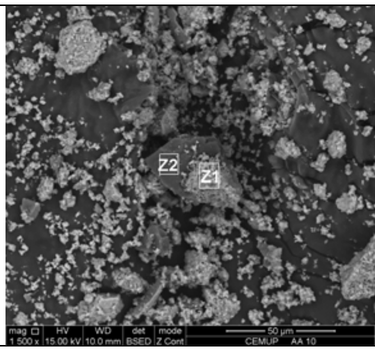


g) Z5 spectrum

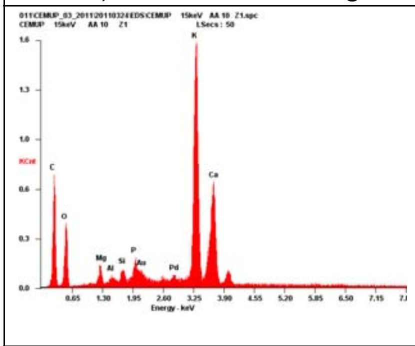
Figure 4. SEM on BGFA.



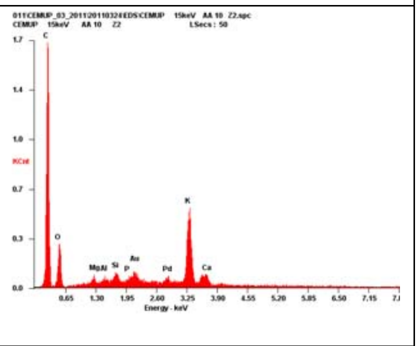
a) AA 200 times enlarged



b) AA 1500 times enlarged

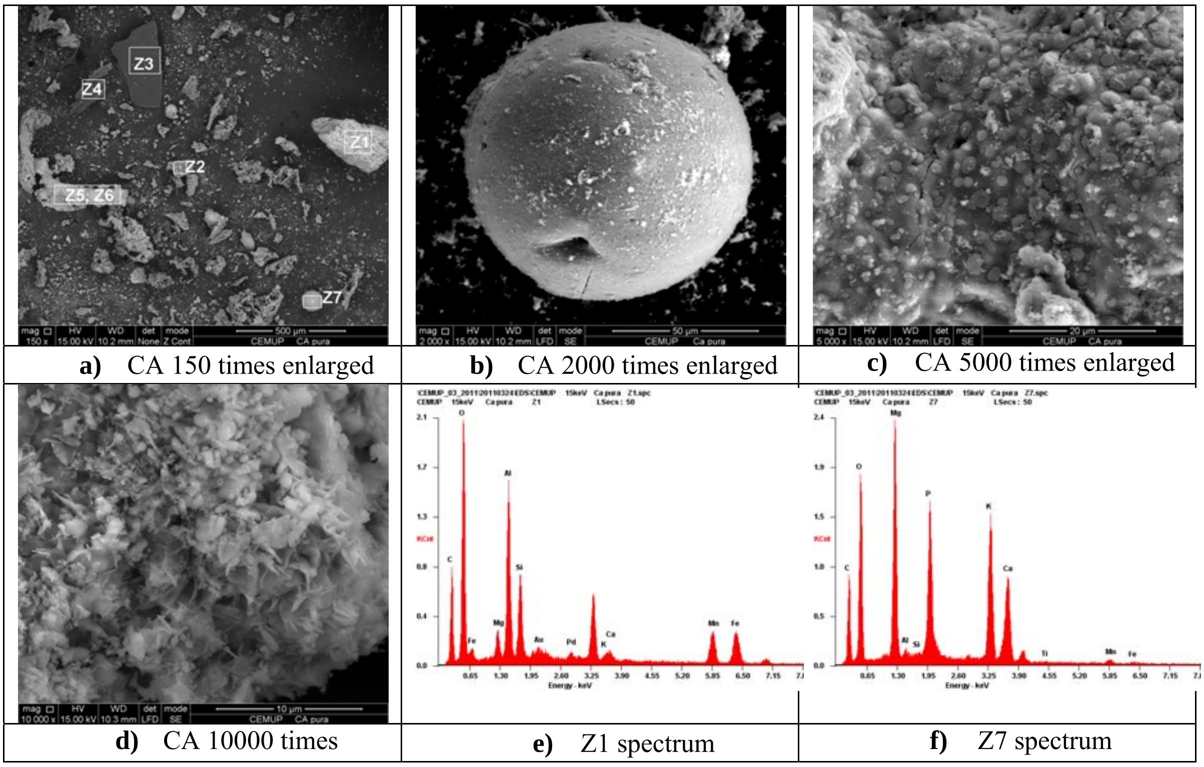


c) Z1 spectrum



d) Z2 spectrum

Figure 5. SEM on AA.



a) CA 150 times enlarged

b) CA 2000 times enlarged

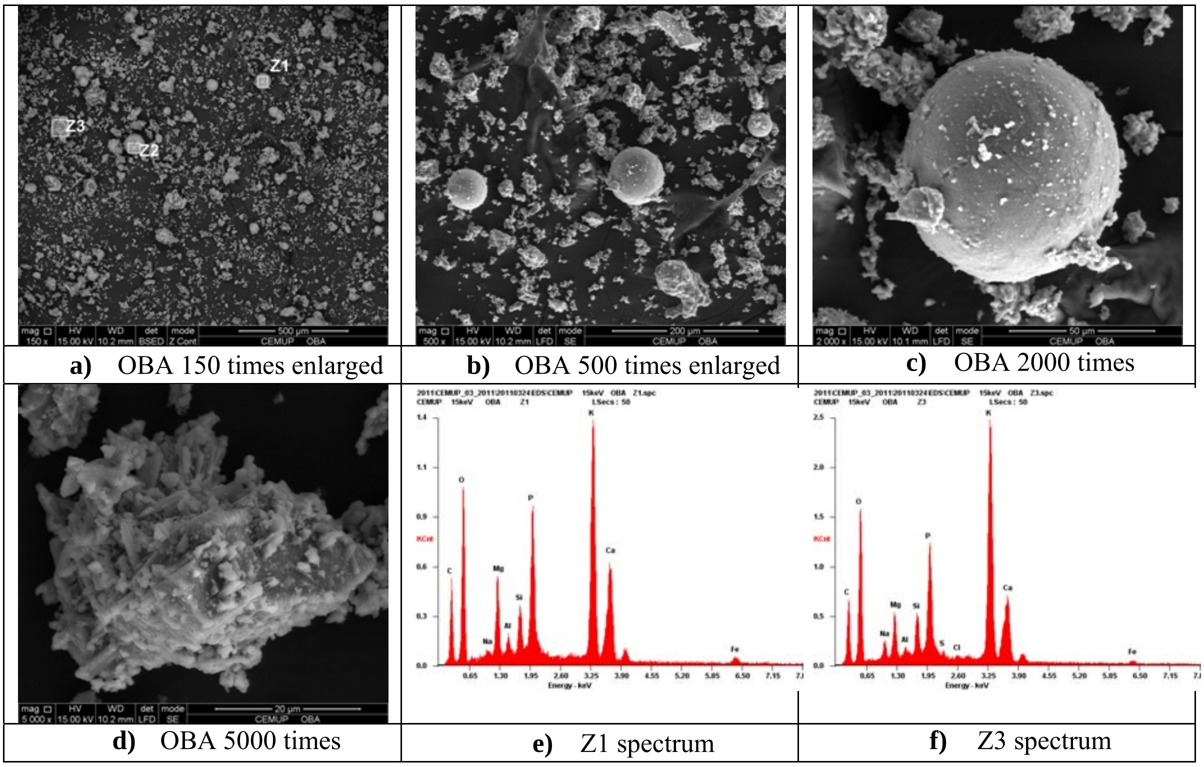
c) CA 5000 times enlarged

d) CA 10000 times

e) Z1 spectrum

f) Z7 spectrum

Figure 6. SEM on CA.



a) OBA 150 times enlarged

b) OBA 500 times enlarged

c) OBA 2000 times

d) OBA 5000 times

e) Z1 spectrum

f) Z3 spectrum

Figure 7. SEM on OBA.

Mortar strength. Flexural and compressive strength testing was undertaken at 28 days following the standard procedure in NP EN 196-1. Results are presented in Figure 8, as well as, activity indexes obtained in Figure 8. DFW and OBA showed no strength.

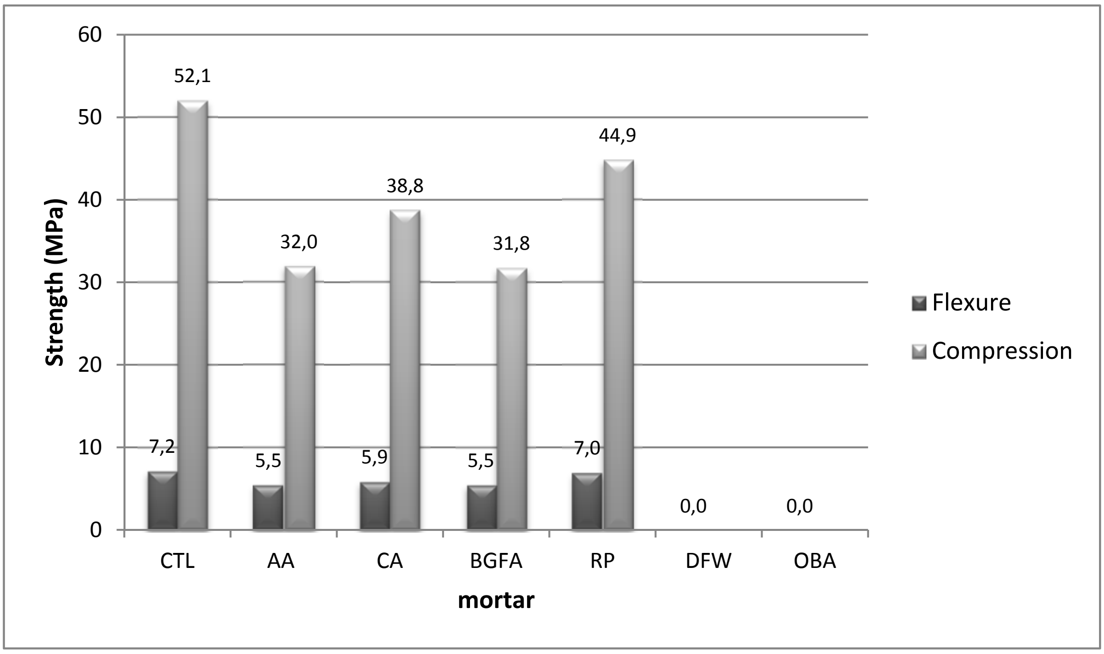


Figure 8. Compressive and flexural strength results.

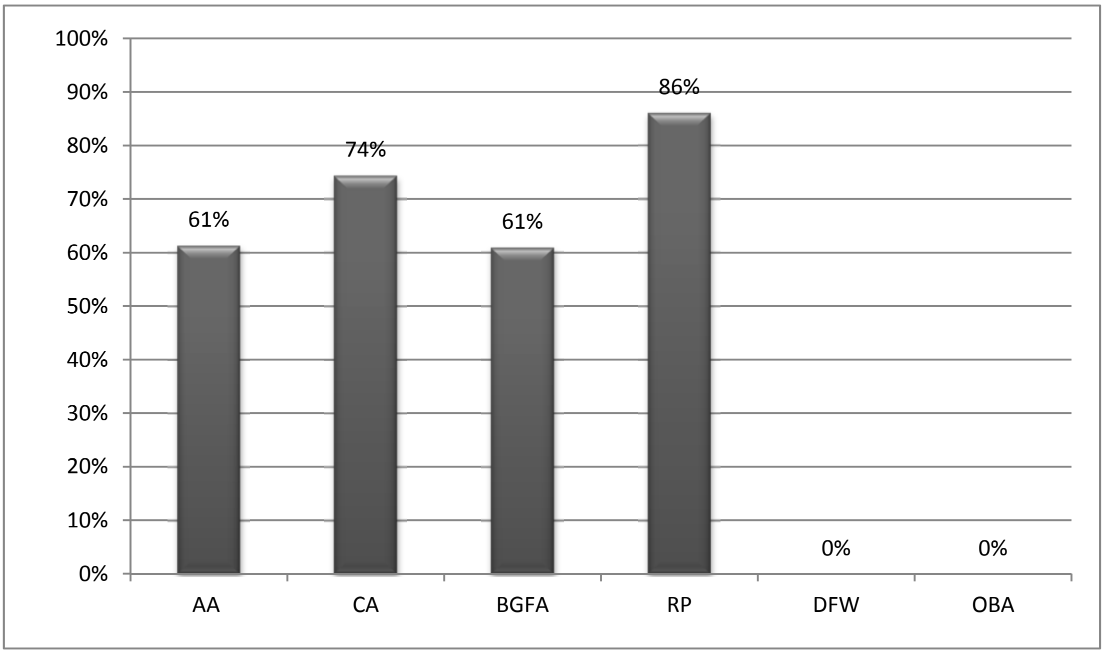


Figure 9. Activity indexes at 28 days.

DISCUSSION

Ashes from several agricultural wastes were examined as partial cement replacement materials for possible use in structural concrete.

Considering that no specific European standard covers materials such as these, properties were compared to requirements for fly ash according to European standard NP EN 450-1 and American standard ASTM C 618 (2012) for raw or calcined natural pozzolan, in Table 2. As can be observed BGBA, BGFA, DFW and RPA are not in accordance with these requirements: The sum of reactive oxides SiO_2+Al_2O_3+Fe_2O_3 are under the minimums required; SiO_2 is under the 25% limit except for RPA. Loss on Ignition (LOI) is too high for most of the ash types. In the case of DFW this is most probably due to the presence of organic matter which was detected visually in the ash. The limit for alkalis (Na_2O eq.) is exceeded in all cases except for DFW.

It must also be noted that BGBA and BGFA present a high amount of P_2O_5 which can be deleterious to concrete. According to (Uchikawa and Hanehara, 1997) and referring to clinker composition, when P_2O_5 exceeds 0.5% strength decreases with an increases in P content.

Regarding mechanical properties, at least 75% activity index at 28 days must be obtained when a pozzolan is incorporated in a cement binder. In the present study, only RPA mortar seems to comply with this limit. CA mortar activity index is close to this limit with activity index of 74%.

In terms of microstructure of these waste materials, SEM observations were carried out on most wastes. RPA particles showed irregular shapes, some elongated and forming agglomerates (Figure 2a),b) and c)). Furthermore, they seemed globular when observed at high magnifications (Figure 2d)). These particles presented calcium, potassium and magnesium as can be seen in spectrums obtained (Figure 2e) and f)) confirming chemical analysis.

Regarding BGBA, it could be concluded that the unground waste presented roughly rounded particles (Figure 3a)) some of which mainly composed of calcium and aluminium (Figure 3d)). Increasing magnification, it was observed that some particles were composed of slab crystals of almost perfect morphology, most probably, of Calcium Hydroxide (Figure 3f)), in accordance with (Metha and Monteiro, 2005), involving globular and dense structures with silicon, aluminium and calcium as main constituents. Generally these results confirmed chemical analysis. Chlorides were also found.

SEM observation of BGFA showed variable size and shape particles, some prismatic, some spherical and other slab like (Figure 4a)). Prismatic particles seemed less dense than other types (Figure 4b)). Slab like particles revealed silicon and aluminium as main components and calcium and magnesium in less amount (Figure 4e)). Spectrums carried out on spherical particles showed principally silicon and aluminium, however potassium was also found. Ponpon like structures seemed to be chemically variably composed. These general results for BGFA are in accordance with chemical analysis presented.

SEM observation on AA, showed that all particles presented similar appearance (Figure 5a)) and b)) but variable shape and composed essentially by potassium and calcium (Figure 5c) and d)).

CA particles observed in SEM, presented several forms and shapes, spherical, prismatic and slab-like (Figure 6a)). Spherical particles contained potassium, phosphorous, magnesium, calcium, silicon and sodium. Prismatic particles showed to be very different, presenting aluminium, silicon, calcium and magnesium. Chemical composition and morphology of particles showed to be variable.

Regarding OBA SEM observations, spherical particles were also found (Figure 7c)) with similar composition compared to spherical particles in CA as can be seen in spectrum of Figure 7e)). Ponpon-like structures were also identified and analogous combinations were found.

Only RPA mortar showed enough 28 day strength according to pozzolan requirements but chemical requirements were not fulfilled such as the sum of reactive oxides $SiO_2+Al_2O_3+Fe_2O_3$, although SiO_2 satisfies the minimum limit of 25%. RPA presented a LOI value over the limit although this may be due to the possible presence of calcium carbonate which is harmless. Nevertheless another drawback for RPA is the high K_2O content leading to an excessive Na_2O eq. This may deteriorate rheological properties, slightly retard setting and reduce strength (Uchikawa and Hanehara, 1997). It also can entail alkali-silica reactions in concrete if RP is used as a cement replacement material.

Table 2. Requirements in standards.

		Fly Ash (NP EN 450-1)	Coal fly ash and Raw or calcined natural pozzolan ASTM C 618
Chemical requirements	Cl	≤0,10%	
	SO_4	≤3,0%	
	SO_3	-	Class N ≤4,0% Class F ≤5,0% Class C ≤5,0%
	Free CaO	≤2,5%	
	Reactive CaO	≤10%	
	SiO_2	≥25%	
	$SiO_2+Al_2O_3+Fe_2O_3$	≥70%	Class N ≥70% Class F ≥70% Class C ≥50%
	NaO_2eq	≤5,0%	
	LOI	Class A ≤5% Class B 2%-7% Class C 4%-9%	Class A ≤10% Class B ≤6% Class C ≤6%
Physical requirements	Activity Index	≥75% at 28 days ≥85% at 90 days	≥75% at 7 days ≥75% at 28 days

CONCLUSIONS

This study aimed at assessing possible use of various agricultural wastes in cement based materials. The experimental study provided the following results:

Regarding mechanical properties only one of these wastes, RPA, presented enough strength to be incorporated in concrete as cement replacement. However in terms of chemical characteristics confirmed by SEM analysis, none of the studied materials can be considered as pozzolanic-cementitious materials according to requirements in ASTM C 618 as well as in the European standard EN 450-10. Besides, chemical composition of some of the waste materials showed presence of deleterious components for use in concrete.

ACKNOWLEDGMENTS

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