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Biomass fly ash effect on fresh and hardened state properties of cement based materials



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ABSTRACT

Cement pastes and mortars were prepared by replacing ordinary Portland cement with different dosages of biomass fly ashes (0, 10, 20 and 30% BFA) whilst in dry condition. The effect of BFA on the flow behaviour (spread on table and rheology), setting time, temperature of hydration and electrical resistivity was studied in this experimental research. Increasing the amount of BFA in the compositions required extra dosage of water, as a result of particles fineness, tendency for agglomeration and retention/absorption of water molecules. As a consequence, the relative amount of free water diminishes and the flowability is poorer. The introduction of BFA also led to an increase in setting time, while the resistivity obtained from the impedance measurements tends to be lower than the reference paste (ash-free). The higher concentration of mobile species in the pore solution, namely sodium ions introduced by the ash, explains that tendency. The hydration temperature of cement pastes tends to decrease with the level of cement to ash replacement. Between the two tested ashes (from grate and fluidized sand bed furnaces), differences in particle size and shape, in the amount of residual organic matter and concentration of inorganic components define minor changes in the workability and setting behaviour. Therefore, the introduction of biomass fly ashes affects the hardened state features but do not compromise them.

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1. Introduction

Considerable researches have been conducted worldwide on the use of waste materials to avert an increasing toxic threat to the environment, or to streamline present waste disposal techniques by making them more affordable. It follows that an economically viable solution to this problem should include utilization of waste materials for new products rather than land disposal. Up to now, the use of additives and substitutes to Ordinary Portland Cement (OPC) has been one of the most successful ways to decrease the $\rm CO_2$ emissions generated by cement and concrete producers, and amongst those industrial wastes have got a wide attention [1–8]. Based on the physical, chemical and morphological properties, it is reported that biomass fly ash, an industrial by-product of thermal

* Corresponding author. E-mail address: victorf@ua.pt (V.M. Ferreira). power industries, has a substantial potential for use as a pozzolanic mineral admixture and/or as an activator/binder in cement-based materials [9–12]. The biomass ash was tested in several applications [13], including Controlled Low Strength Materials (CLSM), low and medium-strength concrete, masonry products, roller-compacted concrete pavements (RCCP), materials for road base, and blended cements. Several other research efforts are underway to use the ash as adsorbent, raw material for ceramics, etc [14–18].

Compared to coal fly ash, where significant research has already taken place and high use are already reported in several countries [19,20], commercial utilization of biomass ash is not so widely reported. Currently, most of the biomass ash produced in thermal power plants is either disposed of in landfill or recycled on agricultural fields or forest, and often this goes on without any form of control. Therefore, this paper details an experimental research on the effect of the biomass fly ashes characteristics on the fresh state properties, using different techniques such as, flow table, rheology, setting time, temperature of hydration and electrical resistivity.

2. Experimental

2.1. Materials

An ordinary Portland cement (OPC) CEM I 42.5 R, certified in accordance with the NP EN 197-1:2001 was used in this paper. Its chemical composition determined by XRF analysis is listed in Table 1. The aggregate was siliceous sand with particle size distribution between 0.15 and 4.75 mm, while the superplasticizer, SP (Sikament 300 Plus), was used to adjust the plasticity of fresh mortars.

The biomass fly ashes (BFA) used in this work were generated from distinct combustion technologies. The biomass fly ash (BFA1) was collected in the electrostatic precipitator of a thermal power plant that uses a grate furnace to burn wood or forest biomass residues from logging activities. The fly ash BFA2 is generated in a co-generation plant, associated with paper—pulp production that burns mainly eucalyptus bark in a bubbling fluidized bed combustor.

A detailed characterization of these biomass fly ashes is reported elsewhere [12]. Both ashes are heterogeneous mixtures of particles with distinct sizes and shapes. The overall particle size distribution of the ashes cut at 1 mm was typically below 100 μm ; the mean particle size is 52.92 μm (BFA1) and 16.04 μm (BFA2). The specific surface areas and bulk density of BFA1 and BFA2 are, respectively: 40 m^2/g , 2.59 g/cm^3 ; and 8 m^2/g , 2.54 g/cm^3 . The organic contents of the ashes, estimated by firing at 525 °C, were 14% (BFA1) and 7% (BFA2), revealing the higher efficiency of the fluidized bed combustion. The chemical composition of the ashes is given in Table 1. The contents in alkaline species (Na, K) are significant, being higher in BFA2. This ash is also richer in CaO and shows lower amounts of silica and alumina. The BFA were sieved at 75 μm and dried at 60 °C before incorporation in the mortars.

2.2. Testing procedures

Several cement pastes and mortars were prepared by replacing ordinary Portland cement (OPC) by distinct amounts of BFA in dry condition. A set of compositions were prepared by incorporating BFA ranging from 0, 10, 20 and 30% by weight percentage of the binder. Mortars were prepared with water/binder (W/B) between 0.55 and 0.65 (weight ratio) considering the demand of water for

Table 1XRF analysis of cement and biomass fly ashes.

Element	BFA1	BFA2	CEM		
	(Wt. %)				
Loss on ignition (1000 °C)	25	20	1.66		
SiO ₂	41	28	19.74		
Al_2O_3	9.3	6.2	4.74		
Fe ₂ O ₃	2.6	2.2	2.69		
CaO	11.4	25.4	63.54		
MgO	2.3	5	2.42		
Na ₂ O	0.9	3.3	0.19		
K ₂ O	3.9	3.2	1.02		
SO ₃	_	_	3.11		
TiO ₂	0.4	0.3	_		
MnO	0.3	0.7	_		
P_2O_5	0.9	0.9	_		
Cd	1.0 mg/kg	1.3 mg/kg	_		
Pb	191 mg/kg	12 mg/kg	_		
Cu	99 mg/kg	27 mg/kg	_		
Cr	47 mg/kg	73 mg/kg	_		
Hg	<1 mg/kg	<1 mg/kg	_		
Ni	35 mg/kg	27 mg/kg	_		
Zn	376 mg/kg	34 mg/kg	_		

higher amounts of fly ash substitution. The cement to aggregate ratio was taken as 1:3 in all mortars tested.

The components were weighed and mixed thoroughly in a laboratory mixer (CONTROLS, 65-LS). The mixing procedure includes: (i) addition of water to the dry powder mix; (ii) mixing for 1 min at a low rotation speed of (~60 rpm); (iii) stopping for one minute to gather the mix into the centre; (iv) mixing again for 2 min at a higher rotation speed (~120 rpm). The complete mortar formulations are listed in Table 2.

Initially, the flow table (Fig. 1) and rheometer were used to characterize the workability/consistence and the rheological behaviour of mortars in the fresh state. The consistency of mortars was determined using the standard EN 1015-3:1999. The rheological behaviour of fresh mortars was evaluated in a Viskomat PC Rheometer (Fig. 1). The torque gives an indication of flow resistance and it can be measured as function of time and rotation speed profile. This procedure allows to set up a relationship between shear stress (or torque) and strain (rotation speed) and the to estimate the rheological parameters, namely the yield stress and plastic viscosity. The rotation speed, time and torque data are sampled by a data acquisition system. The total testing time ranged from 15 to 60 min, depending on the biomass fly ash content. The rheometer maximum speed (N) used was 100 rpm and at every 5 min the speed was brought to zero, maintained for 30 s, and then it was enhanced for 30 s up to 100 rpm. The yield stress (g) and the plastic viscosity (h) were obtained from the Bingham's model and using the down curve, since it shows a regular behaviour [21]. The Bingham model is represented by:

$$\tau = \tau_0 + \mu_p \cdot \gamma \tag{1}$$

where τ (Pa) is the shear stress, τ_o (Pa) is the yield stress, μ_p (Pa s) is the plastic viscosity and γ (s⁻¹) is the shear rate. The Bingham model may be also expressed through torque, T (N mm) as a function of rotation speed, N (min⁻¹–1) by the equation (2):

$$T = g + h \cdot N \tag{2}$$

where g (N mm) and h (N mm min) are directly proportional to the yield stress and plastic viscosity, respectively [22,23].

The setting times of the mortars were measured using an automated VICAT apparatus using the standard NP EN 196-3:2006, while the temperature of hydration was measured using a quasi-adiabatic calorimeter.

The microstructure of the fly ash was studied using an environmental scanning electron microscopy — ESEM (Phillips Electro Scan 2020) equipped with a Peltier cooling. The ESEM microscope was operated in wet mode, using water vapour as the imaging gas. A gaseous ion detector was used with a sample chamber pressure of 5 Torr for imaging and 15 Torr when flooding. The chamber was flooded 3 times after loading the sample. The images were obtained with a close up detector with a working distance of 1 mm.

Table 2Mix proportions used for biomass fly ash cement mortars.

Sample code	Composition	BFA	Cement	SP	W/B	Sand
		(g)				
Ref 1	CEM 42.5 R Type 1	0	400	3.00	0.55	1200
10BFA1	90% CEM + 10% BFA1	40	360	3.00	0.55	1200
20BFA1	80% CEM + 20% BFA1	80	320	3.00	0.60	1200
30BFA1	70% CEM + 30% BFA1	120	280	3.00	0.65	1200
10BFA2	90% CEM + 10% BFA2	40	360	3.00	0.55	1200
20BFA2	80%~CEM + 20%~BFA2	80	320	3.00	0.55	1200
30BFA2	70%~CEM + 30%~BFA2	120	280	3.00	0.60	1200

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