Rheology and packing density of biomass fly ash/Portland cement mixtures

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Abstract

Paper deals with rheological properties and packing density of fresh mixtures of Portland cement and biomass fly ash. Water demand of paste of normal consistency increases with increase of replacement level of biomass fly ash for Portland cement. Up to 5 wt.% contents of biomass fly ash yield stress and plastic viscosity values decrease, while at contents higher than 5 wt.%, the opposite trend was revealed. Biomass fly ash compared to Portland cement has proportionally lower content of particles with size of tens and first single digit numbers of microns. Deficiency in this region at higher contents of biomass fly ash in cement mixtures results in deflection from ideal packing density curve. Based on modeling of the curve, it was found that ideal cumulative particle size distribution is lacking particles with size around 1 μm.

Keywords

biomass fly ash, cement, setting, rheology, packing density

Introduction

Properties of biomass fly ash (BFA) in cementitious systems has been studied by several authors. Even though the biomass combustion is well-established technology for power and heat production, the environmental management of the ash as a by-product is still a challenge. Quality and quantity of the ash were affected by the biomass used [1], weather it is wood, bark, herbaceous biomass or agriculture waste [2]. In the current trend of power generation, emergence of biomass (forestry and agricultural waste) fueled power plant seems to be a promising source of renewable energy with low operational cost coupled with continuously renewable fuel [3]. A major portion produced (approximately 70 %) of the wood waste ash produced is land-filled as a common method of disposal [4, 5].

In the Czech Republic, tens of heat and power plants produce the biomass fly ash in various quantities. Integration of the biomass ashes within the natural cycles has continuously become a necessity on the national level. One of the possible ways is to use BFA as admixture for Portland cement (PC). There are two main scientific approaches how to characterize BFA in cementitious system; BFA as a partial cement replacement material and BFA as a filler. Several authors studied possibilities of use of various BFA in cementitious systems in terms of strengths [6] and hydration [7], but only a few information has been written about workability [8], rheology and packing density. Data on workability of woody BFA quantified by slump tests provided by has shown little reduction or increase in the mix workability, limited setting delay and moderate compressive strength reduction when ground unwashed or washed woody BFA was used at cement replacement levels of 15 wt.% or 30 wt.%.

According to the European Waste Catalogue and hazardous residues list [9], both bottom ash and fly ash coming from the combustion of untreated wood are classified as non-hazardous wastes.

Particle packing is fundamental to concrete. The packing should be optimized in order to use less binder, that would have been normally required in the concrete. By application of suitable particle packing models to the entire concrete mix, the particle size distribution (PSD) of the entire mix can be adjusted in order to achieve mobility in the fresh state and adequate properties when hardened. Due to the fact that the ingredients of a concrete mix are particles with continuous size distributions, a model should be based on packing of continuous size distributions. The concrete flow and self-compacting ability in the fresh state are usually in conflict with optimal packing [10]. The conflict can be solved by introduction of fine particles i.e. by BFA, silica fume, calcined clays etc. in size of cement and below, into a concrete mix.

Materials and methods

Used BFA is filter ash from biomass combustion (Veolia Energie ČR, a.s. Heating plant Krnov). BFA is by-product of grate boiler combustion with 3.72 MPa, operating temperature 445 °C and 35 t/hr. Electrical and thermal power of the boiler is 4900kW and 28 000 kW. Wood chips as basic fuel is used with pellets, sawdust, corn meal, chopped crops as the additional fuel in heating plant. PC is CEM I 52.5 N from manufacturer Českomoravský cement, a.s. (HEIDELBERG Cement Group). PC was replaced by 5, 10, 15 and 20 % of BFA. Chemical parameters of BFA are shown in Table 1.

Volume density was determined according to ČSN EN 1097-3. Specific surface area of BFA and PC was measured by N_2 absorption according to the Brunauer-Emmett-Teller theory (BET). Nitrogen was used as the adsorbate. The results were compared with the TiO_2 standard. Results of BET and volume density are shown in Table 2. Phase composition determined by X-ray diffraction with Rietveld refinement is given in Table 3.

Measurement of particle size distribution was carried out by a laser diffraction method using CILAS 920L laser particle size analyzer. In laser diffraction particle size analysis, a representative cloud or ensemble of particles passes through a broadened beam of laser light which scatters the light onto Fourier lens. This lens focuses the scattered light onto a detector array and, using an inversion algorithm, a particle size distribution is inferred from the collected diffracted light data.

Size range of particle size analyzer is 0.3 – 400 μm, dispersing medium: isopropyl alcohol. Before the measurement, every sample was treated with ultrasound (60 s). PSD of PC and BFA is given in Figure 1. Cumulative particle size distribution was evaluated by EMMA software that calculates and displays the particle size distribution of a mixture of components. The curves of all samples were correlated to modified Andreassen model for ideal packing density with q-value 0.35 and volume density given in Table 2. Relatively long list of minerals was found in BFA by Rietveld refinement X-ray diffraction method (Table 3). Both high contents of amorphous phase and silica in BFA are promising in terms of pozzolanic activity and use of BFA as supplementary cementitious material (SCM). The high content of SO_3^{2-} on BFA must be balanced by addition of gypsum as the setting retarder. High content of CaO is associated with calcite when all free lime is carbonated during water treatment of BFA.

Table 1. Chemical parameters of BFA

sample	SiO_2	CaO	Na_2O	K_2O	MgO	Fe_2O_3	Al_2O_3	Cl^-	SO_3^{2-}	LOD	LOI
	wt. %										
BFA	19.39	22.01	0.43	9.66	4.15	4.15	6.16	1.93	8.35	1.64	23.41

Table 2 Volume density and BET of PC and BFA

sample	vol. density	BET
	kg/m^3	m^2/g
BFA	176	9.5
PC	1380	6.3

Table 3 Phase composition of BFA (Rietveld analysis XRD)

phase	wt. %
Qartz	4.8
Calcite	10.9
Hematite	3
Magnetite	0.2
Anhydrite	4.2
Albite	1.9
Muscovite	2.8
Dolomite	1.1
Rutile	0.3
Microcline	3.5
Arcanite	2.1
Biotite	2.0
Sylvine	2.2
Halite	0.2
Periclase	2
Thenardite	3.7
Syngenite	8.4
Amorphous phase	46.7

Rheological measurements were carried out on rotational rheometer DHR-1 (TA Instruments). Thixotropy (Pa/s) as a time-dependent rheological property was calculated following stability of the paste test [11]. The thixotropic behaviour was determined by delineating the area (A_{thix}) between the curves formed by the points of the static yield stress ($\tau_{o,s}$) and the dynamic yield stress ($\tau_{o,d}$) at different shear rates $\dot{\gamma}$ (Figure 2). Where T_{max} is function of $\tau_{o,s}$ and T_{min} of $\tau_{o,d}$. The extent of shear rate was 25-150 (s^{-1}), with steps 25, 50, 75, 100, 125 and 150 (s^{-1}) Eq. (1).

$$A_{thix} = \int_{25}^{150} T_{max}\, d\dot{\gamma} - \int_{25}^{150} T_{min}\, d\dot{\gamma} \qquad (1)$$

Yield stress and plastic viscosity were calculated from flow curves using Bingham model Eq. (2). Where τ_0 is yield stress, μ is plastic viscosity and $\dot{\gamma}$ is shear rate.

$$\tau = \tau_o + \mu\dot{\gamma} \tag{2}$$

All rheological tests were done at 25 °C. The geometry of coaxial cylinders was used for testing. Normal consistency for each sample was determined and the rheological testing was done at the same consistency for all samples. The course of the setting was evaluated by needle penetration test (Tussenbrock test). This test basically measures when the hydrating cement paste develops some finite value of resistance to penetration which is expressed by threshold shear stress τ_{thold} (kPa) in time.

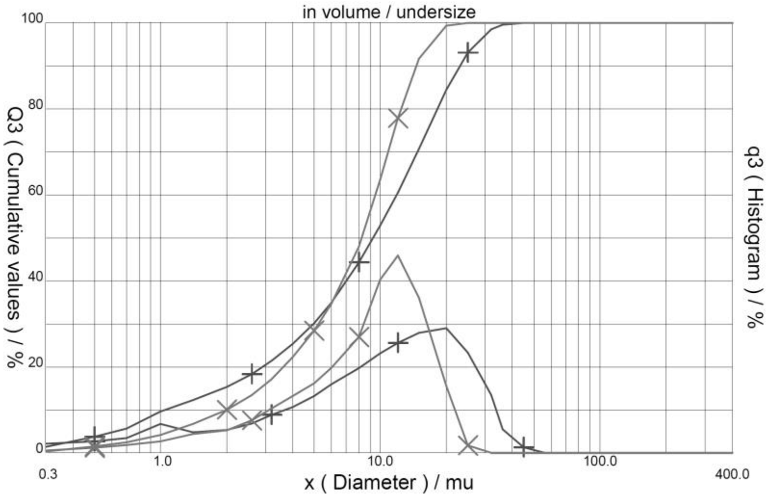

Fig. 1 PSD of PC 52.5N (+) and BFA (×)

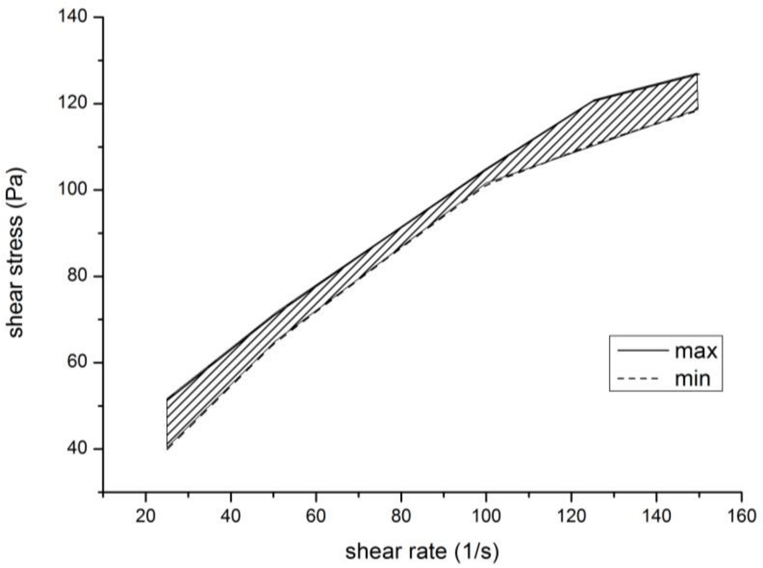

Fig. 2 Thixotropy (Pa/s) as the delineated area between curves of static and dynamic yield stress

Results

Consistency and setting

Water demand of BFA/PC blended cement pastes increases proportionately with the level of cement replacement by BFA. Higher water demand of pastes with BFA relative to PC is mainly affected by higher specific surface area of BFA compared to OPC particles [3, 12-14]. Setting and all rheology test were carried on samples with same consistency which was linearly dependent on content of BFA in the mixture (Table 4). Particle size distribution of BFA and PC is given in Figure 1.

The course of setting was monitored by Tussenbrock test. Some analogy to Tussenbrock test can be found with Vicat (ASTM C191) or Gillmore (ASTM C266) needle tests [15] which give results of initial and finish setting times, but are insufficient in characterizing the course of the setting. Besides the Tussenbrock test, there are alternatives for characterization of the course of setting i.e. state of art modeling of the setting with VCCTL software [16, 17]. Relatively week bonds that are associated with formation of outer C-S-H products and ettringite (Aft) during initial hydration can be broken during setting of cementitious system. The well interconnected structure of newly formed hydrates shows increasing resistance to penetration as the setting proceeds.

Table 4 Consistency of PC/BFA mixtures

	PC/BFA				
	100/0	95/05	90/10	85/15	80/20
w/c	0.4	0.45	0.49	0.54	0.58

BFA has dilution effect on hydration, which means the amount of formed hydrates is proportionally lower compared to reference pure PC paste. Based on results, it is evident that BFA has retarding effect on setting. Start and end of setting were determined from τ_{thold}/time curves to find the role of BFA content in studied mixtures. Prolonged workability times and more important slower heat development of PC/BFA mixtures was already discussed in previous studies [3]. The lower heat release during early hydration can reduce thermal expansion risk in massive constructions. Results of setting are given in Figures 3 and 4.

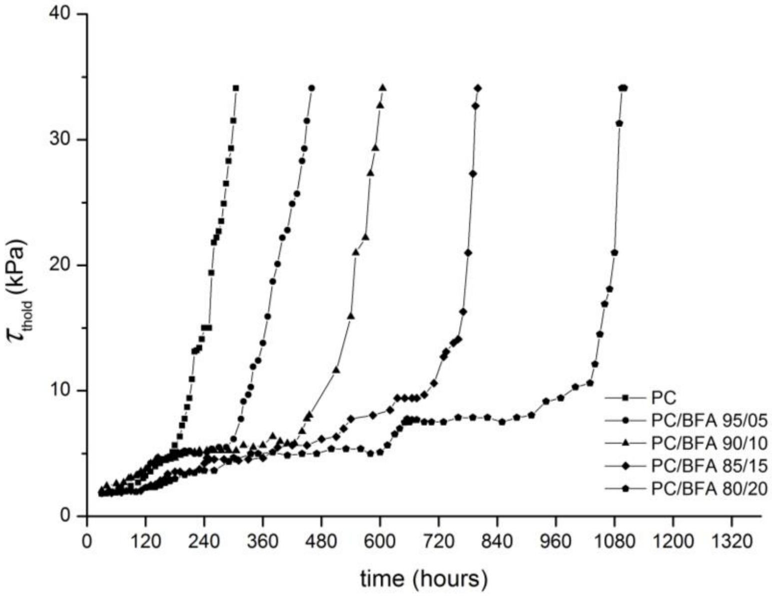

Fig. 3 Setting of mixtures with BFA

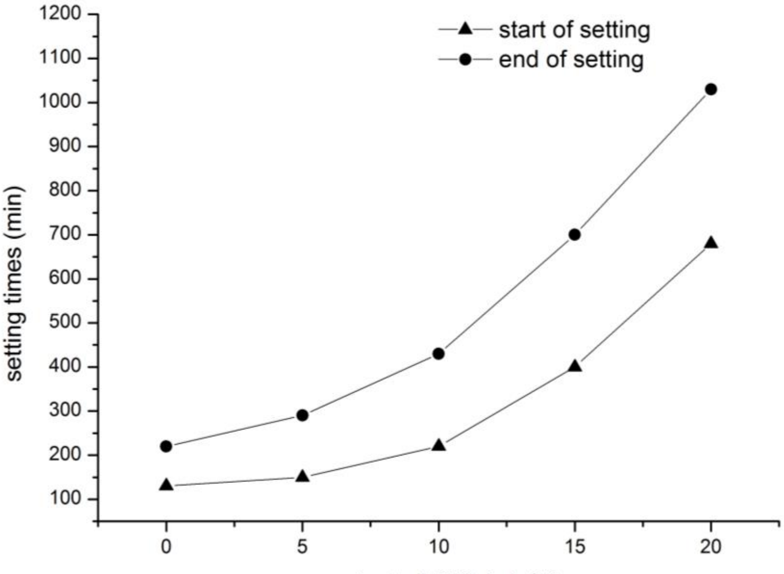

Fig. 4 Start and end of setting of BFA mixtures

All samples show viscoelastic properties of highly concentrated water solutions that can be characterized as a Bingham fluid. Hysteresis loops of flow curves shear stress vs. shear rate were constructed in the region of 0,1-150 s^{-1}. Yield stress (Pa) and plastic viscosity (Pa.s) were calculated from hysteresis flow curves using Bingham model. Since normal consistency of the PC/BFA paste increases with increasing content of BFA, the rheological testing was carried out on samples of same consistency. The inter-particle forces which determine the yield stress are composed of the Van der Waals, electrostatic and steric forces, which are all determined by the particle conformations, surface charges and medium chemistry [18]. Samples with BFA, similarly to reference sample of pure PC, show shear-thinning behaviour in the tested shear rate region. Broad range of bonds are expected from the gradual shape of viscosity/shear rate curves. At higher shear rates (above 25 s^{-1}) the hydrodynamic effect gradually prevails. Values of yield stress and plastic viscosity decrease up to 5 wt. % of BFA, while opposite trend was revealed for higher contents of BFA (Figure 5). The decrease of yield stress provides a possible way to workability enhancement for the mixture with small amount of BFA.

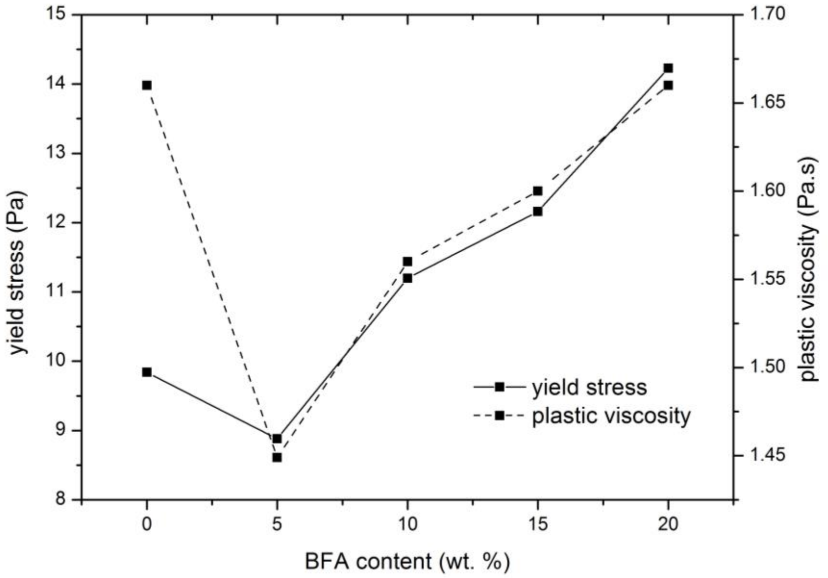

Fig. 5 Rheological parameters of PC/BFA mixtures

It was previously concluded, that the water/solid volume ratio is not directly related to yield stress, but instead it is more important how the particles pack. In situations where the particle packing increases due to a broader PSD, less water is needed to fill the voids between the particles, the excess water efficiently separates the particles, reducing flocculation and resulting in lower yield stress [19-21].

Despite the time-dependent rheological parameters can be determined from single flow hysteresis curve, the different approach was chosen for evaluation of thixotropy [11]. This approach allows a better assessment of rheological behavior and stability of the PC/BFA system during the initial hydration and more closely approximates the main use of this material, which is self-compacting concrete.

Thixotropy increase with increased content of BFA shows in this case the poorer stability of fresh mixtures (Figure 6). Thixotropy or structural build-up is closely related to formation of week bonds during formation of gelatinous and crystalline hydration phases. These phases are AFt (ettringite) and outer C-S-H hydrates. Week bonds are broken during shearing. High content of alkalis is expected to ruin the sulfate balance of the system.

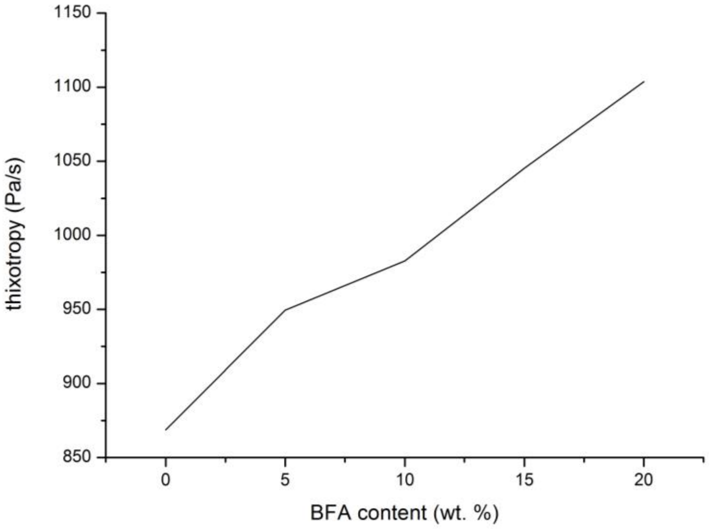

Fig. 6 Thixotropy of PC/BFA mixtures

Packing density

Compared to PC, BFA has proportionally lower content of particles with size below 10 microns. This deficiency at higher contents of BFA in cement mixtures causes deflection from ideal packing density curve (Figure 7). Number of methods can be used for characterization of packing density. Despite the fact that new methods are purposed recently, there is so far, no generally accepted method of packing density measurement. The packing characteristics of the cementitious materials have great influence on the performance of a concrete mix, especially strengths [21].

PSD of PC and BFA at various replacement levels were correlated with modified Andreassen model, as the “ideal” PSD curve for packing density. Modeling of the curve with various admixtures showed that cumulative particle size distribution can be improved by addition of another admixtures, i.e. finely ground blast-furnace slag, silica fume or metakaolin. The statement of the previous study [22] has shown, that sawdust ash, when used as a supplementary cementitious material, decreases the early strength gain of concrete, but when small amount of metakaolin was added to sawdust-ash concrete, the detrimental effects on early-age strength gain was counteracted. Other authors [12] published positive role of woody BFA at a cement replacement level up to 16% by total binder weight on pore structure and its refinement when using in combination with small amounts of silica fume, hence, reducing the chloride diffusivity of mortar mixes produced.

Based on results of rheological testing and modeling of ideal packing density, it can be purposed to use only amounts up to 5 wt.% of woody BFA in PC mixtures. There is a possibly to improve the PC/BFA packing density by addition of admixture with complementary particle size, which means compensate the lack of fine particles in the mixture. With increased replacement level of BFA, the deficiency in particles with size around 1 μm was revealed (Figure 7).

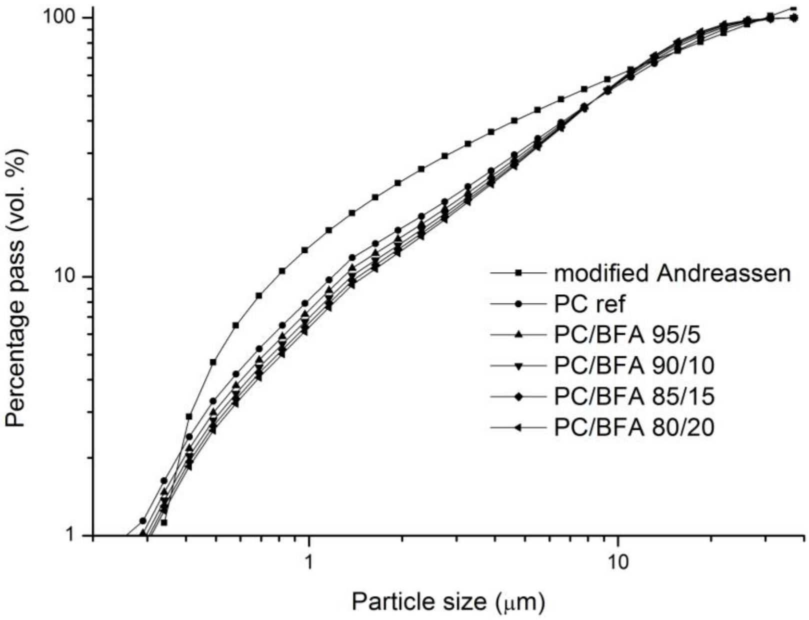

Fig. 7 Correlation of modified Andreassen model with PC/BFA mixtures

Conclusions

Evaluation of possibility of reuse of BFA at different replacement levels as a supplementary cementitious material was studied. For achieving same consistency of mixtures, water demand increases with increasing level of BFA. At the same consistency, setting of PC/BFA pastes is retarded gradually with increasing level of BFA. Used penetration method allows to monitor both setting times and the course of the setting. PC/BFA pastes show shear-thinning behaviour similarly to pure PC reference paste in the tested shear rate region. Broad range of bonds is characterized by the continuous shape of viscosity/shear rate curves. With regards to reference sample, yield stress and plastic viscosity decrease up to 5 wt. % of BFA and increase continuously for higher contents of BFA. Small amounts of BFA improve workability of PC/BFA fresh pastes. The lower stability of fresh mixtures with high content of BFA is characterized by poorer thixotropy and thixotropy rebuilt, which becomes more evident at higher contents of BFA. Based on correlation of rheological testing and modeling of ideal packing density, it can be assumed that only small amounts of woody BFA can improve the performance of PC/BFA mixtures. Further improvement towards ideal packing of particles can be provided by addition of fine admixtures with complementary particle size to PC/BFA mixtures. Deficiency in particles with size around 1 μm was revealed with increasing level of BFA.

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Standards:
ASTM C191
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