CHARACTERIZATION OF BIOMASS ASH, FLY ASH AND NATURAL ZEOLITE FROM SERBIA AS SCM

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Summary: *One of the possible solutions for reducing the environmental impact of concrete industry represents the utilization of the supplementary cementitious materials. For that purpose some of the alternative materials from Serbia, such as biomass ash, fly ash and natural zeolite, are characterizated, their class of pozzolanic activity and activity index are determined and presented in this paper. Based on those results, it can be concluded that this characterized materials can be used as supplementary cementitious materials in the cement composites.*

Keywords:*Alternative materials, class of pozzolanic activity, activity index*

1. INTRODUCTION

Concrete is the largest volume building material used for almost all infrastructure developments [1]. In a term of ecology, the production of Portland cement (PC), which is a main concrete binder, is a responsable for 5-8 % of the global CO_2 emission [2]. One of the possible solutions for reducing the environmental impact of concrete industry represents the application of supplementary cementitious materials (SCM) [1]. The presence of such materials influences the amount and type of hydrates formed in blended cement systems as well as their volume, porosity and finally the durability of the cement-based composites [3].
Some of the alternative materials from Serbia, which can be utilized as SCM, are biomass ash (BA), fly ash (FA) and natural zeolite (NZ). NZs are natural aluminosilicate minerals, while BA and FA present solid industrial by-products (BA is the agricultural by-product and FA is one of the by-products of coal combustion in thermal power

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plants). The average quantity of biomass wastes in Serbia is estimated to almost 13 million tons per year. The individual sector utilizes about 50 % of straw, while a large one utilizes only 20% [4]. Moreover, there are six coal-burning power plants in Serbia and about 200 million tons of FA are deposited at the landfill areas of totally 1.500 hectares [5]. Finally, the high quality zeolite deposits are widespred in Serbia (e.g. Igroš, Jablanica 1 and Zlatokop) [6].
This paper deals with the characterization of BA (precisely wheat straw), FA ans NZ as SCM and their comparison.

2. MATERIALS AND METHODS

2.1. Materials and mixtures

For the purpose of characterization of BA, FA and NZ as SCM (Figure 1) the following component materials were used:

- Ordinary Portland cement (CEM I 42.5R, *Lafarge-BFC* Serbia) in accordance with standard EN 197-1 [7] (the chemical composition of used CEM I 42.5R is shown in Table 1 [8]);
- Biomass ash - wheat straw ash (Mitrosrem - Sremska Mitrovica);
- Fly ash from thermal power plant *Nikola Tesla B* (PPNT B);
- Natural zeolite from a quarry in Igroš (Brus, Serbia) with particle size less than 125 μm;
- Slaked lime, *Krečana doo*, Čelinac, B&H, in accordance with standard SRPS B.C1.020 [9];
- CEN standard sand in accordance with standard SRPS EN 196-1 [10];
- Deionized water.

CEM I 49.5 R | Biomass ash | Fly ash | Natural zeolite

Figure 1. Samples of PC, BA, FA and NZ

Table 1- Chemical compositions of used PC [8]

Sample	Chemical composition [%]											
CEM I 42.5 R	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Free CaO	Na_2O	K_2O	NO	Cl^-	L.I.*
	20.98	5.51	2.58	61.96	2.50	3.60	1.11	0.22	0.74	0.37	0.03	1.35

* Loss on ignition

In order to determine the pozzolanic activity of BA, FA and NZ according to SRPS B.C1.018 [11], standard mortar bars were prepared with pozzolanic material, slaked lime and standard sand, with following mass proportions: msl:mpm:mqs =1:2:9 (where are: msl – mass of slaked lime; mpm – mass of pozzolanic material; mss – mass of CEN standard sand). Mixutes and the amount of used deonized water are shown in Table 2.

Table 2- Mortar mixture proportions for determination of the pozzolanic activity class

Mixture	Slaked lime (g)	Pozzolanic material (g)			Standard sand (g)	Deionized water (g)
		BA	FA	NZ		
Pozz-BA	150	300	-	-	1350	300
Pozz-FA	150	-	300	-	1350	270
Pozz-NZ	150	-	-	300	1350	300

For the purpose of determination of BA, FA and NZ activity index according to SRPS EN 450-1 [12], reference and three blended cement mortar mixtures were made, and their compositions are shown in Table 3.

Table 3- Mortar mixture proportions for determination of the activity index

Mixture	CEM I 42.5R (g)	Pozzolanic material (g)			Standard sand (g)	Deionized water (g)
		BA (MP)	FA	NZ		
BA (MP)	337.5	112.5	-	-	1350	225
FA	337.5	-	112.5	-	1350	225
NZ	337.5	-	-	112.5	1350	225

3. METHODS

3.1. Chemical analysis

The chemical compositions of BA, FA and NZ powder samples were determined in accordance with SRPS EN 196-2 [13].

3.2. Physical properties

Loose balk density of PC, BA, FA and NZ powder samples was obtained via procedure described in standard SRPS B.C8.042 [14].
True density of PC, BA, FA and NZ powder samples was determined according to SRPS B.B8.032 [15].
For the determination of PC, BA, FA and NZ fineness, the following methods were used: *Blaine* method in accordance with standard SRPS B.C8.024 [16] and air-jet sieving method in accordance with standard SRPS EN 933-10 [17]
Standard consistency, the setting times and the soundness (*Le Shatelier*) of blended cement pastes were examined according to SRPS EN 196-3 [18].

3.3. Pozzolanic activity

The classes of BA, FA and NZ pozzolanic activity were determined based on 7 day compressive (R_c) and flexural (R_f) strength of mortar bars, prepared and examined in accordance with SRPS B.C1.018 [11]. After compacting, specimens were hermetically packed and cured 24h at 20±2°C, and then 5 days at 55±2°C. After cooling of specimens in next 24h at 20±2°C, their flexural strength (R_f) and compressive (R_c) strengths were determined.

3.4. Activity index

Activity index of BA, FA and NZ was obtained via procedure described in standard SRPS EN 450-1 [12], while the preparation of standard mortar bars (Figure 2) and determination of the compressive strength were carried out in accordance with SRPS EN 196-1 [10].

PC BA FA NZ

Figure 2. Reference and blended cement mortar specimens

4. RESULTS AND DISCUSION

4.1. Chemical analysis

The chemical compositions of BA, FA and NZ powder samples are shown in Table 4. Standard SRPS EN 450-1 [12] prescribs that the sum of the contents of silicon dioxide (SiO_2), aluminium oxide (Al_2O_3) and iron oxide (Fe_2O_3), determined in accordance with SRPS EN 196-2 [13], shall not be less than 70 % by mass. According to the obtained results, it can be noticed that NZ is characterized with the highest amount of these oxides: 76.09%, followed by FA and BA with: 74.92 % and 70.98 %, respectively, while CEM I 42.5 R has just about 29 % of those oxides. However, BA has the highest amount of SiO_2 and the lowest amount of Al_2O_3, NZ has medium values, while FA has the lowest amount of SiO_2 and the highest amount of Al_2O_3. Therefore, the ratios of SiO_2 and Al_2O_3 (S/A ratio) in BA, FA and NZ are 61.72, 2.69 and 4.95, respectively.

Table 4- Chemical compositions of BA, FA and NZ

Sample	Chemical compositions [%]												
BA	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Free CaO	Na_2O	K_2O	-	Cl^-	L.I.*	S/A ratio
	69.13	1.12	0.73	5.78	2.50	0.20	0.14	0.11	13.03	-	0.06	5.18	61.72
FA	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	TiO_2	Na_2O	K_2O	-	MnO	L.I.*	S/A ratio
	50.07	18.58	6.27	11.16	1.40	2.86	0.51	0.62	1.76	-	0.03	6.66	2.69
NZ	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	TiO_2	Na_2O	K_2O	FeO	P_2O_5	L.I.*	S/A ratio
	62.30	12.59	1.20	4.80	1.94	0.05	0.22	0.70	0.63	0.23	0.016	11.06	4.95

* Loss on ignition

Based on the presented results it can be seen that the sulphate (SO_3) content in BA, FA and NZ is less than 3 % by mass, the content of Na_2O less than 5.0 % and the content of magnesium oxide (MgO) is less than 4.0 %, which is in accordance with SRPS EN 450-1 [12].
The loss on ignition of BA, FA and NZ was determined in accordance with the principles of the method described in SRPS EN 196-2 [13]. Based on the obtained results (Table 4), it can be concluded that BA and FA belong to category B, while NZ exceeds the upper limit value for C category for approximately 2% (the limits of the categories are given in standard SRPS EN 450-1 [12]).

4.2. Physical properties

Some of the basic physical properties of PC, BA, FA and NZ powder samples, as well as their corresponding pastes, are examined and presented in Table 4.

Table 4- Physical properties of PC, BA, FA and NZ powder samples and pastes

Material properties:	CEM I 42.5R	BA	FA	NZ
Loose balk density (g/cm^3)	0.982	0.677	0.604	0.720
True density (g/cm^3)	3.126	2.380	2.313	2.312
Fineness - *Blaine* method (cm^2/g)	4188.6	5800.0	10212.5	5392.8
Fineness - Air-jet sieving method (%)	4.9	10.5	18.1	50.0
Paste properties:	CEM I 42.5R	BA	FA	NZ
Standard consistency (%)	29.0	30.6	35.0	40.4
Initial setting time (min)	241	210	475	242
Finish setting time (min)	348	320	523	273
Soundness - *Le Shatelier* (mm)	0.5	0.5	0.0	0.5

It can be seen that BA, FA and NZ have lower values of loose balk density and true density than that of PC. Furthermore, the specific surface area, determined by *Blaine*

method, appears to be the highest for FA (10212.5 cm^2/g), than for BA (5800.0 cm^2/g) and for NZ (5392.8 cm_2/g), while PC has the lowest value (4188.6 cm_2/g), which is in accordance with obtained standard consistency of their corresponding pastes, taking to account zeolite's ability to gain water by over 30% of its dry mass [19].
Based on results of air-jet sieving, BA belongs to category S, FA to category N, while NZ has fineness of 50 % (the upper limit for category N is 40 %), according to SRPS EN 450-1 [12]. The longest setting times has FA, the shortest initial setting time has BA, while NZ has the shortest finish setting time. Finally, determined values of soundness for PC, BA, FA and NZ blended cement pastes are in accordance with SRPS EN 197-1 [20].

4.3. Pozzolanic activity

The class of pozzolanic activity of BA, FA and NZ was determined based on 7 day compressive and flexural strengths of mortar bars and the results are given in Table 5.

Table 5- Class of BA, FA and NZ pozzolanic activity

Pozzolanic material	R_f (MPa)	R_c (MPa)	Class
BA	3.30	10.30	10
FA	4.30	22.81	15
NZ	2.74	9.11	5

These classes are used to measure pozzolanic activity based on the strength of mixtures containing potential pozzolanic material and lime. Testing of pozzolanic properties showed that FA has the highest pozzolanic activity - class 15, BA has a lower pozzolanic activity - class 10, while NZ belongs to class 5. High pozzolanic activity of FA can be attributed to its high content of SiO_2, Al_2O_3 and Fe_2O_3, as well as its high specific surface area, as presented in prevoius chapters. A higher class of pozzolanic activity should lead to the better reactivity of these materials in cement-based composites: mortar and concrete.

4.4. Activity index

Activity index is calculated as a ratio (in percentage) of the compressive strength of standard mortar bars, prepared with 75% of PC and 25% of pozzolanic material, by mass, to the compressive strength of standard mortar bars prepared with 100% cement, tested at the same age. Results are illustrated in Figure 3.

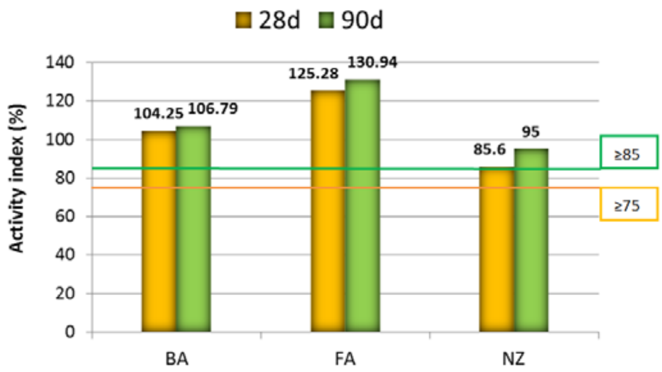

Figure 3. Activity index of tested pozzolanic materials at the age of 28 and 90 days

According to the criteria given in standard SRPS EN 450-1 [12], the activity index at 28 days shall not be less than 75%, while at 90 days shall not be less than 85%. All tested pozzolanic materials fulfil the requested criteria. In addition, BA and FA achieved higher compressive strength in relation to the reference mortar. At the age of 28 days, as the pozzolanic reaction has not been activated yet, strength increase can be attributed to filler effect of small particles of these materials. At the age of 90 days, FA and BA strength increase can be attributed to their pozzolanic activity via their high specific surface area and total oxides content.

5. CONCLUSION

Based on the results of presented study, the following can be concluded:

- BA, FA and NZ have pozzolanic activity, due to their high content of SiO_2, Al_2O_3 and Fe_2O_3 (more than 70%) and high specific surface areas.
- In a term of air-jet sieving, BA belongs to category S, FA to category N, while in a term of the loss on ignition of BA and FA belong to category B.
- The activity indexes of BA, FA and NZ are in accordance with their pozzolanic activity classes.
- FA has the highest activity index and belongs to Class 15, then BA has the medium activity index and belongs to Class 10, while NZ has the lowest activity index and belongs to Class 5, and in this regard FA, BA and NZ can be used as SCMs.

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КАРАКТЕРИЗАЦИЈА ПЕПЕЛА БИОМАСЕ, ЛЕТЕЋЕГ ПЕПЕЛА И ПРИРОДНОГ ЗЕОЛИТА ИЗ СРБИЈЕ КАО ДЦМ

Резиме: *Једно од могућих решења за смањење утицаја индустрије бетона на животну средину представља коришћење допунских цементних материјала. У ту сврху је урађена карактеризација изабраних алтернативних материјала из Србије, као што су пепео биомасе, летећи пепео и природни зеолит, одређена је њихова класа пуцоланске активности, као и индекс активности, а резултати су приказани у овом раду. На основу датих резултата може се закључити да се испитани материјали могу користити као допунски цементни материјали у цементним композитима.*

Кључне речи: *Алтернативни материјали, класа пуцоланске активности, индекс активности*