IMPACT OF BY-PRODUCTS ON CHARACTERISTICS OF GEOPOLYMER MORTAR MIXTURES

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Summary: *This paper researched physical-mechanical characteristics of geopolymer mortar mixtures based on fly ash, with addition of waste aluminosilicate materials such as red mud, biomass ash, silica dust and waste ceramic tiles. Four mixtures are made with the same 90:10 ratio of mass of fly ash and other binders, while on one mixture is made with fly ash only. The quantities of other materials required for making of geopolymer mortars such as the quantity and type of aggregate, aluminosilicate activators and water are constant. All mixtures are cured in the same laboratory conditions, at the temperature of 95°C for 24 hours, and afterwards the specimens are cured at the temperature of 22°C until the testing. The goal of this research is determining how the same water/binder and binder/agreggate ratio affects the physical-mechanical characteristics of geopolymer mortar mixtures made of various waste materials.*

Keywords: *Geopolymer mortar, fly ash, byproducts, physical-mechanical characteristics*

1. INTRODUCTION

It is known that production of traditional concretes and components required for their making considerably contributes the environment pollution and creation of greenhouse effect. Since a large amount of cement is used when making concrete, it would be of

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great importance to find an alternative material which would be more eco friendly and which would reduce the CO_2 emission [1]. New composite materials, which, in terms of their physical and mechanical characteristics correspond to traditional concrete composites, are called geopolymers [2]. Geopolymer is an inorganic alumino-hydroxide polymer synthesized from predominantly silicon and aluminium materials of geological origin and industrial by-product material [3]. Geopolymers are created by activating alumino-silicate materials which in interaction with highly alkaline solutions (such as NaOH or KOH alkali and silicate compounds such as Na2SiO3 or K2SiO3) form a solid a compact structure [4]. As binders, various industrial by-products containing oxides of silicon and aluminum in amorphous form [5] such as fly ash (FA), silica fumes (SF), ground granulated blast furnace slug (GGBFS), red mud (RM), biomass ash (BA), palm oil etc. Geopolymers are characterized by a reaction called polymerization, which is conditioned by the factors such as the chemical composition of binders and alkali compounds, water content and curing condition [6]. As opposed to the traditional Portland cement materials, geopolymers do not require the C-S-H phase for matrix formulation and building strength, but rather the polycondensation process of silica and alumina binders to achieve the strength level that is required [7]. During the geopolymer hardening, the N-A-S-H phenomenon of the gel phase (N—Na_2O; A—Al_2O_3; S—SiO_2; H—H_2O) is characteristics, and it occurs as a result of alkali activation of the amorphous portion of the binding material. Fly ash and other aluminosilicate reactivity can be proved by testing physic-mechanical characteristics, which depend on the chemical composition of the binder, but also on the curing conditions [8].
Therefore, the subject of this paper was to study influence of different byproduct materials on physical-mechanical properties of geopolymer mortar mixtures, synthesized of aluminosilicate binders based on low-calcium FA and its partial substitutional binders such as RM, BA, SF and CT blends activated by temperature curing in order to determine mixture of optimal mechanical characteristics.

2. EXPERIMENTAL PROGRAMME

2.1. MATERIALS

The following binding materials are used in this paper:

1. Fly ash (FA) from power plant Kostolac “B” from Kostolac, Serbia;
2. Red mud (RM) by-product of the Bayer process of aluminum production by “Kombinat aluminijuma” from Podgorica , Montenegro;
3. Biomass ash (BA) crated in thermal treatment of beech wood processing;
4. Silica fume (SF), Sika, Switzerland;
5. Granit ceramic tiles (CT) generated in demolition during reconstructions.

Chemical composition of used FA binder is given in Table 1, while physical properties of used binder materials are determined according to the standing standard SRPS B.C1.018:2015 [9] and they are displayed in Table 2. Pulverization of CT binder is performed using the laboratory ball-mill, while sifting of this material as well as FA and BA is performed with laboratory sifting through the sieve with 0,09 mm openings.

Table 1. Chemical composition (wt%) of the raw binder materials

Chemical compounds	SiO_2	Fe_2O_3	Al_2O_3	CaO	MgO	SO_3	P_2O_5	TiO_2	Na_2O	K_2O
FA	51,68	11,58	20,16	7,43	2,41	1,02	0,12	1,04	0,8	1,04

The used alkali activator is obtained by combining sodium hydroxide – (SH) in flakes form (Oltchim, Romania, p.a. 98,5%), and Sodium silicate – (SS) in liquid form (Galenika-Magmasil d.o.o. Serbia, content SiO_2 – 26.70%, Na_2O – 13.30% and H_2O – 60%). The concentration of SH solution used in this research is 10 molarity (M) and it is obtained by dissolving of flakes in water.

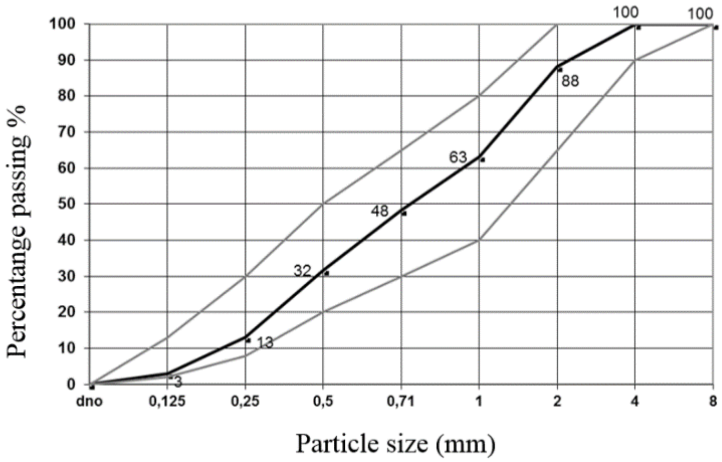


Figure 1. Particle size distribution of used aggregate

Sand for aggregate from the South Morava river is sifted through 2 mm sieve mesh. Particle size distribution of the used aggregate is determined according to the SRPS ISO 6274:1998 standard [10]. The percentage (%) of aggregate passing through the characteristic sieve openings (mm) is displayed in Figure 1. Other chemical admixtures are not used for making of the tested geopolymer mortar mixtures.

2.2. PREPARATION OF GEOPOLYMER MORTAR

For the purposes of this research, five geopolymer mortar mixtures are made and tested. One mixture is made with fly ash only (labeled as „FA“), while in the remaining geopolymer mortar mixtures, f 1/10 of mass of FA is substituted with solid binders such as RM, BA, SF and CT (labeled as „FA-RM“, „FA-BA“, „FA-SF“ and „FA-CT“, respectively). Mortar mixtures are made using binding materials and sand in mass ratio 1:3. The amount of extra water is determined using the flow table in „FA“ mixture, and it was maintained constant in other mixtures, too. The mix proportions of the tested mixtures are displayed in Table 3.

Making of geopolymer mortar mixtures is performed in the laboratory rotary mixer. Firstly, binder, alkaline liquid and water are mixed for 5 minutes. After the paste is obtained, dry sand is added, and for the purpose of obtaining a compact mortar, the mixing continues for 5 minutes. After mixing, mortar specimens are cast into 4 x 4 x 16 metal moulds. The moulds are then covered with fire-resistant glass and sealed with rubber to prevent loss of moisture from the specimens. 24 h after making, samples are cured at 95ºC for the next 24 h, after which they are demoulded and wrapped into a plastic foil. Samples are stored at the laboratory temperature of around 22ºC until the testing.

Table 2. Physical properties of constituent materials

Material	Properties	
FA	Density: 763 kg/m3 % of sieve passage 0.09mm: 90,9 Color: dark	
RM	Density: approx. 2700 kg/m3 % of sieve passage 0.09mm: 99 Color: red	
BA	Density: approx. 2400 kg/m3 % of sieve passage 0.09mm: 100 Color: light grey	
SF	Density: 737 kg/m3 % of sieve passage 0.09mm: 99,8% Color: dark grey	
CT	Density: approx. 801 kg/m3 % of sieve passage 0.09mm: 100 Color: sienna	

Table 3. Mix design of geopolymer mortar mixtures

Mixture	FA [g]	RM [g]	BA [g]	SF [g]	CT [g]	SH/SS	W/B	B/S
FA	450	-	-	-	-	0,19	0,45	1:3
FA-RM	405	45	-	-	-	0,19	0,45	1:3
FA-BA	405	-	45	-	-	0,19	0,45	1:3
FA-SF	405	-	-	45	-	0,19	0,45	1:3
FA-CT	405	-	-	-	45	0,19	0,45	1:3

Fly ash (FA), Red mud (RM), Biomass ash (BA), Silica fume (SF), Granit ceramic tiles (CT), Sodium silicate (SS), Sodium hydroxide (SH), Binder (B), Sand (S)

2.3. PREPARATION OF GEOPOLYMER MORTAR

Physical-mechanical characteristics of geopolymer mortar mixtures are tested in the fresh and hardened states.
Density is tested on the fresh mixtures, according to the SRPS EN 1015-6:2008/A1:2008 standard [11] and workability according to the SRPS EN 13395-1:2010 standard [12].
On the hardened specimen prisms, having dimensions 40 x 40 x 160 mm at the age of 3, 7 and 28 days are tested density, compressive strength and flexural strength according to the SRPS EN 196-1:2018 standard [13]. For each mortar mixture, a total of nine prisms are made. Three mortar prisms are tested at each sample age.

3. EXPERIMENTAL RESULTS AND DISCUSSION

According to the chemical analysis of fly ash, the total content of $SiO_2 + Al_2O_3 + Fe_2O_3$ is 83,42%, while the content of CaO is 7,43%. According to the standard ASTM:C618-12a [14], FA is divided in two classes. The used FA belongs to the F, class i.e. to low-calcium FA, with the CaO content lower than 10%. The dark color of the FA binder is a result of high percentage of contained Fe_2O_3. The ratio of silicates and aluminates (SiO_2/Al_2O_3) in FA is 2,56.

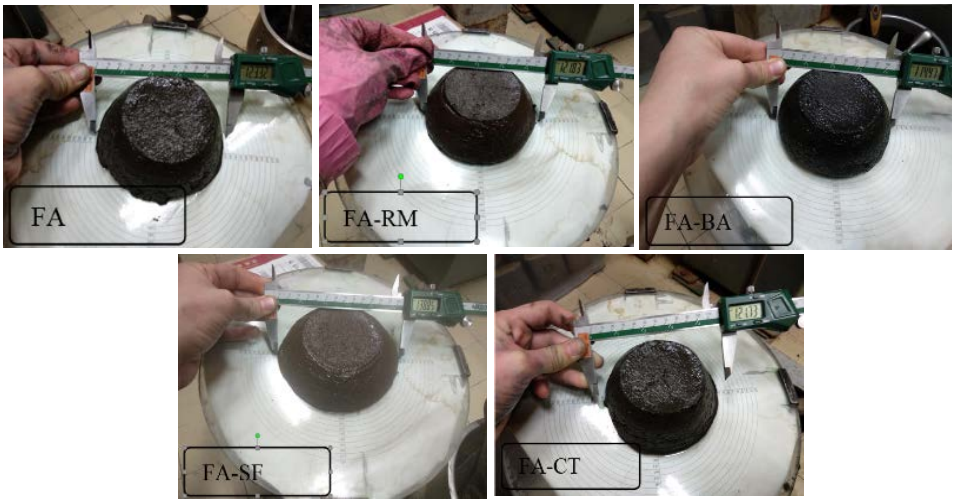


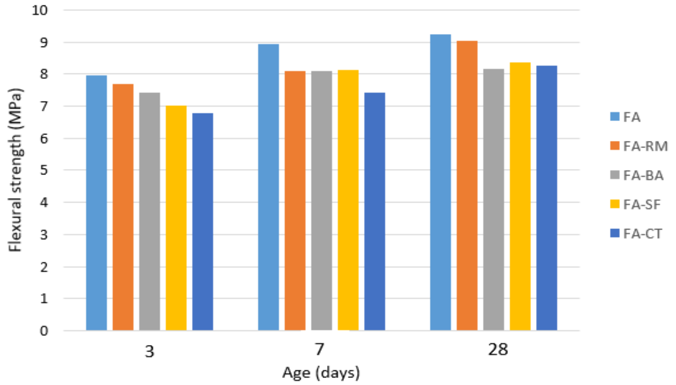
Figure 1. Samples of fresh mortar mixtures after the workability test

The workability test is conducted at the room temperature of 21–23ºC. The test of mortar mixtures is performed using the standard conical mold installed on the middle of the test flow table. After filling up, the conical mould is removed, and the flow table is lifted up and down according to the instructions in the standard [12]. Flow values are then measured in two perpendicular directions. The used alkali compounds led to creation of a sticky mass due to high viscosity of sodium silicate. The appearance of samples after testing of workability using the flow table are presented in Figure 1.

Table 4. The results of workability test and bulk density

Mixture	Flow Value [mm]	Fresh bulk density [kg/m^3]	Bulk density at the age of 3 days [kg/m^3]
FA	125	2120	2095
FA-RM	120	2165	2158
FA-BA	115	2150	2145
FA-SF	140	2140	2131
FA-CT	120	2130	2122

The results of workability test and bulk density of fresh and hardened mortar are given in Table 4. The hardened mortar specimens in the shape of prism are tested according to the procedure described by the standard [13]. The flexural strength value is obtained by calculating the arithmetic mean of flexural values of three tested specimens at their age of 3, 7 and 28 days. In a similar manner, the compressive strength is obtained by calculating the mean values of six tested specimens. The results of flexural and compressive strength of tested specimens are displayed in Figure 2 and 3.



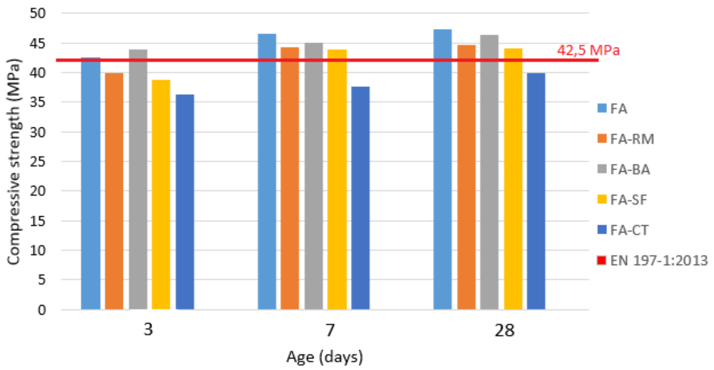


Figure 2 and 3. Compressive and flexural strength of geopolymer mortar mixtures

The workability test results indicated that with the change of the binder admixture, the Flow value changes, too. All tested mortar mixtures, except “FA-SF“, have a stiff consistence, which according to the standard should be lower than 140mm [12]. The tested mortar mixture labeled as “FA-SF” (140 mm) made only with SF has the highest flow value. This mixture is at the very beginning of the border which defines plastic consistence (conditioned between 140 – 200 mm).
The bulk density test results of fresh mortar mixtures indicate that the bulk density of the tested gepolymer mixtures is within the range from 2120 kg/m^3 to 2165 kg/m^3, while in case of the hardened specimens, it is in the range from 2095 kg/m^3 to 2158 kg/m^3. The lowest bulk density value is exhibited by the mixture labeled as “FA” i.e. the mixture made of fly ash only, while the mixture labeled as “FA-RM”, in which 10 % of fly ash mass is replaced with red mud, has the highest value. The highest variation of bulk density in the observed period from the making to the testing at the sample age of 3 days is observed in the mortar mixture labeled as “FA” and it is 1,8 %, while in other mixtures this variation is lower than 1 %.
The flexural strength test results at the sample age of 3, 7 and 28 days are displayed in Figure 2. It can be concluded that the samples labeled with “FA” have the highest value of flexural strength. The value of tested flexural strength of samples of this mixture at the sample age of 3 days is 7,98 MPa. The compressive strength of the samples of this mixture is the highest at measuring performed at the age of 7 and 28 days when it was 8,94 MPa and 9,25 MPa, respectively. The lowest measure value of flexural strength at the age of 3 and 7 days is recorded for the samples of the mixture labeled as “FA-CT” (6,80 MPa and 7,43 MPa, respectively), where 10% of binder mass is substituted with waste ceramic tiles. Yet, the lowest value of flexural strength at the specimen age of 28 days is recorded for the samples labeled as “FA-BA” (8,17 MPa) which is for 1% lower than the samples of the mixture labeled as FA-CT. By observing the diagram, it can be seen that the specimens, as early as at the age of 3 days exceeded 80% of the flexural strength measured at 28 days. Also, in the observed period between 3 and 28 days of testing, an increase of strengths is noticeable, but they are small in comparison to the achieved initial values of specimens measured at the age of 3 days.
According to the compressive strength test results, displayed in Figure 3, the highest value of compressive strength at the sample age of 3 days is recorded for the specimens labeled as “FA-BA” i.e. the mixture where 10% of fly ash is replaced by biomass ash. The compressive strength of this mortar mixture is around 3,5% higher than the compressive strength of the samples made with fly ash only as binder. The lowest values of compressive strength at this specimen age are measured for the “FA-CT” mixture (36,34 MPa). At the specimen age of 7 and 28 days the highest value of compressive strength is measured for the specimens of the mixture labeled as “FA” which are 46,51 MPa and 47,30 MPa, respectively. At the sample age of 28 days, the samples labeled as “FA-BA”, ”FA-RM” and “FA-SF” have up to 6 % lower values of measured compressive strength in comparison with the samples of the mixture labeled as “FA”, while those for the samples of the “FA-CT” mixture are around 15% lower. Also, in the observed period from 3 to 28 days of testing, there is an increase of compressive strength, but they, as in the flexural strength tests, are small in respect to the achieved initial sample values measured at the age of three days. By comparing the obtained values of compressive strengths of the samples at the age of 28 days to the standing values from the EN 197-1:2013 standard [15], it is noticed that all mixtures except “FA-

CT" meet the basic requirements stipulated by the standard for composition, specifications and conformity of common cements.

4. CONCLUSIONS

According to the obtained characteristics, it can be concluded that geopolymer mortars based on FA originating from coal-fired electric plant „Kostolac B" with the addition of red mud, biomass ash and silica fume can be an alternative to cement mortar. Environmental and economic advantages of using geopolymer material are reflected in using the waste materials, for which the emission of CO_2 during its conversion from a by-product into a binding material is minimal. Commercial application of such mortars can directly cause reduction of disposed waste and the end price of products.
It is necessary to confirm the results obtained in this way with the mixtures which set in natural ambient, and with concrete mixes with more extensive tests of physical and mechanical characteristics.

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REFERENCES

[1] P. Nath, P. K. Sarker: Effect of GGBFS on setting, workability and early strength properties of fly ash geopolymer concrete cured in ambient condition. *Construction and Building Materials*, **2014**, vol. 66, p.p.163-171.
[2] G. Gorhan, G. Kurklu: The influence of the NaOH solution on the properties of the fly ash-based geopolymer mortar cured at different temperatures. *Composites: Part B*, **2014**, vol. 58, p.p. 371-377.
[3] A. Islam, U. J. Alengaram, M. Z. Jumaat, I. I. Bashar: The development of compressive strength of ground granulated blast furnace slag-palm oil fuel ash-fly ash based geopolymer mortar. *Materials and Design*, **2014**, vol 56, p.p. 833-841.
[4] S. Thokchom1, D. Dutta, S. Ghosh: Effect of Incorporating Silica Fume in Fly Ash Geopolymers. *International Journal of Civil and Environmental Engineering*, **2011**, vol. 5, № 12.
[5] S. Pachamuthu, P. Thangaraju: Utjecaj pepela iz papirnog mulja na geopolimerni beton s letećim pepelom. *Journal Gradevinar*, **2017**, vol. 69, № 9, p.p. 851-859.
[6] P. Nath, P. K. Sarker, Vijaya B Rangan: Early age properties of low-calcium fly ash geopolymer concrete suitable for ambient curing. *Procedia Engineering*, **2015**, vol. 125, p.p. 601- 607.

[7] F.N. Okoye, J. Durgaprasad, N.B. Singh: Effect of silica fume on the mechanical properties of fly ash based-geopolymer concrete, *Ceramics International*, 2015.
[8] N. Marjanović, M.Komljenović, Z.Baščarević, V.Nikolić, R.Petrović: Physical–mechanical and microstructural properties of alkali-activated fly ash–blast furnace slag blends. *Ceramics international*, **2014,** vol. 41, № 1, Part B, p.p. 1421-1435.
[9] SRPS B.C1.018:2015 Non-metallic mineral raws - Pozzolanic materials - Constituents for cement production - Classification, technical conditions and test methods.
[10] SRPS ISO 6274:1998 Concrete - Sieve analysis of aggregates.
[11] SRPS EN 1015-6:2008/A1:2008 Methods of test for mortar for masonry - Part 6: Determination of bulk density of fresh mortar.
[12] SRPS EN 13395-1:2010 Products and systems for the protection and repair of concrete structures - Test methods - Determination of workability - Part 1: Test for flow of thixotropic mortar.
[13] SRPS EN 196-1:2018 Methods of testing cement - Part 1: Determination of strength
[14] ASTM:C618-12a Standard Specification for Coal Fly Ash and Raw or Calcined Natural Pozzolan for Use in Concrete.
[15] SRPS EN 197-1:2013 Cement - Part 1: Composition, specifications and conformity criteria for common cements.

УТИЦАЈ НУСПРОДУКАТА НА КАРАКТЕРИСТИКЕ ГЕОПОЛИМЕРНИХ МАЛТЕРСКИХ МЕШАВИНА

Резиме: *У овом раду су испитиване физичко-механичке карактеристике геополимерних малтерских мешавина на бази електрофилтерског пепела са додатком отпадних алуминосиликатних материјала попут црвеног муља, пепела из биомасе, силикатне прашине и отпадних керамичких плочица. Четири мешавине справљене су са истим процентуално масеним односом електрофилтерског пепела и других везивних материјала 90:10, док је једна мешавина справљена само са електрофилтерским пепелом. Количина других материјала потребних за справљање геополименрих малтера попут количине и вртсе агрегата, алуминосиликатних активатора и воде била је константна. Све мешавине су неговане у истим лабораторијским условима и то на температури од 95ºC у трајању од 24 часа, а затим су до времена испитивања неговани на температури од 22ºC. Циљ овог истраживања био је утврђивање како исти водо/везивни и везивно/агрегатни фактор утиче на физичко-механичке карактеристике геополимерних малтерских мешавина справљених од различитих отпадних материјала.*

Кључне речи: *Геополимерни малтер, електрофилтерски пепео, нуспроизводи, физичко механичке карактеристике*