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Possibilities of Biomass Wood Ash Usage in Geopolymer Mixtures

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Abstract: This paper presents the results of testing the physical and mechanical properties and durability of geopolymer mixtures. Fly ash was used as the basic binder, while its replacement was performed with wood biomass ash.The initial and final setting time were tested on the geopolymer paste, while flow value and bulk density were tested on the fresh mortar. Compressive and flexural strength and sulfate and freeze-thaw resistance were tested on hardened geopolymer mortar. Based on the most optimal results of mortar testing, the composition of concrete was determined, and slump, bulk density, compressive and flexural strength, penetration of water under pressure and sulfate and freeze-thaw resistance were tested. According to the results of compressive strength tests of geopolymer materials and concrete exposed to sulfate solution attack, the mixtures prepared with the addition of 20% wood biomass ash showed better sulfate resistance than the mixtures prepared only with fly ash.

Keywords: biomass wood ash; durability; fly ash; fresh and hardened properties; geopolymer

1 INTRODUCTION

It is known that various industrial by-products can be used as admixtures to the basic binder in the preparation of traditional building composites. However, in practice, they are not used so often, so lately, attention has been shifted to the economic viability of environmental materials. It can be said that in the last decade, the field of ecological construction materials has been marked by geopolymers. The ecological and economic advantages of geopolymers could be seen through the reduction of pollution, the implementation of waste materials, as well as through the final product cost [1].

In order to make high-performance geopolymers, the influence of different types of binders and curing regimes on physical and microstructural characteristics has been studied so far. Yet, the largest number of tests was conducted on the samples of geopolymer paste, while much less attention was paid to the testing of geopolymer mortars and concrete [1].

Rajamma et al. [2] tested the characteristics of geopolymer mortars made on the basis of high calcium ash wood biomass and metakaolin, while as alkaline activators NaOH and Na_2SiO_3 were used. The authors concluded that with increasing metakaolin content, the compressive strength of the mortar increases. Abdulkareem et al. [3] examined the effect of replacing fly ash with wood biomass ash in the percentage of 10 to 30% by weight at a replacement step of 10%. According to the test results, a correlation can be established between the strength and the ash content of wood biomass. Namely, due to the increase in the ash content of wood biomass in the binder, the compressive strength decreases. In their research, Cheah et al. [4] tested geopolymers made with paper processing ash, wood biomass ash and granulated blast furnace slag using alkaline activators NaOH and Na_2SiO_3. The samples were cured in ambient conditions until the time of testing, and the highest achieved compressive strength was 49.61 MPa. In their other research Cheah et al. [5] tested geopolymers based on fly ash, the content of which was 50, 60, 70 and 100% with high calcium ash wood biomass. The compressive strength of geopolymer mortar samples prepared in this way ranged between 6 and 18 MPa.

It is well known that exposing structures to aggressive external action may compromise their durability properties. In relation to that, it is necessary to conduct many long-lasting laboratory researches in order to predict the material behaviour in different field conditions [6]. Freeze-thaw resistance is often related to the critical saturation point and the amount and content of pores in the composite. Reaching the point of critical saturation and exposing the samples to freezing and thawing cycles leads to the changing of water into ice and the onset of internal stress, which results in the emergence of cracks and destruction of the material. [7]. The increase of the number of freeze-thaw cycles increases the destructive effect [8]. Until now, only several authors researched the impact of freeze-thaw cycles on geopolymers. Slavik et al. [9] investigated the effect of kaolin replacement by slag using standard EN 14617-5. The number of freeze-thaw cycles of mortar samples was 50, and all tested samples proved to be resistant to the cyclic effects of freezing and thawing. Sun and Wu [10] tested geopolymer mortars made on the basis of the class "F" fly ash which were cured at a temperature of 75 °C until the time of testing. The test was performed using the ASTM C666 standard, and the samples of cement mortar were used as reference samples. After 90, 210 and 300 cycles of testing, geopolymer mortars showed better resistance to cyclic action of frost and de-icing salts than cement reference samples. Digirmenci [11] researched the variation in compressive strength and mass loss of geopolymer mortars made with fly ash, granular slag and zeolite due to exposure of samples to freezing and thawing cycles. Cube-shaped specimens having sides of 50 mm were used for the test, and they were cured under ambient conditions until the time of the test. The compressive strength of mortars exposed to freeze-thaw cycles was lower than that of the reference samples of the same composition which were not exposed to freeze-thaw cycles. Exceptions to this test were mortar samples made with granulated blast furnace slag. Fu et al. [8] researched the resistance of geopolymer concrete made of slag to freezing and thawing cycles. The authors concluded that after 300 freezing cycles there was no significant change in mass, and the freezing resistance coefficient was about 90%. Zhao et al. [12] examined geopolymer concretes in which the fly ash was replaced by the slag in the percentage of 10, 30 and 50% by weight. The test was performed using the ASTM C666 standard, and physical changes were observed on the tested concrete after only 5 cycles of freezing and thawing.

Sulfate resistance is of great importance for structural elements exposed to sulphate corrosion [13]. However, despite the exceptional importance of this effect, only a few authors have studied the sulfate resistance of geopolymers. Bakharev [14] researched the sulphate resistance of the geopolymer paste. Samples were exposed to 5% sulphate solution for 30, 60, 90, 120 and 150 days from the start of the study. All tested samples proved to be resistant to sulfate attack. Ismail et al. [15] researched microstructural changes on the geopolymer pastes made with different water/binder ratio (0.4, 0.5 and 0.6). The tested mixtures were made with the fly ash and slag at the ratio of 1:1. The samples were immersed in a 5% sulfate solution of $MgSO_4$ and Na_2SO_4. Authors concluded that a lower water/binder ratio achieved a better geopolymer resistance. Komljenović et al. [16] and Bijeljić et al. [17] investigated sulphate resistance of geopolymer mortar by using testing report CEN/TR 15697. All series of geopolymer mortars after dipping into the sulphate solution continued to harden, and the coefficients of compressive strength resistance were higher than 1. Only a few authors examined the sulphate resistance of geopolymer concrete. However, despite the small number of studies, the authors Bakharev et al. [18], Chindaprasirt and Chalee [19] and Wallah and Rangan [20] conclude that geopolymer concretes have good sulfate resistance.

The main objective of this research is to examine the possibility of using biomass wood ash as a substitute for the production of geopolymer paste, mortar and concrete based on coal fly ash, as well as the effect of its addition on the properties in fresh and hardened state.

2 EXPERIMENTAL RESEARCH

2.1 Alkali Activators Used in the Experiment

Sodium hydroxide (SH) and sodium silicate (SS) manufactured by the local producers were used as alkali solutions. The SH was prepared by dissolving NaOH flakes (purity of 98%) in water to 10M solution 24 hours prior to mixing. The SS activator was of the following characteristics: module (Ms = SiO_2/Na_2O) 2.2; content SiO_2 - 26.70%, Na_2O - 13.30% and H_2O - 60%). Liquid SS and SH were mixed in a mass ratio 100:18.52 (i.e. $Na_2SiO_3/NaOH$ = 5.40). Such ratio caused the creation of a single activator with a content of 10% Na_2O in respect to the mass of the solid binder. This decreased the module of M_S (SiO_2/Na_2O) in SS to the value of 1.5.

2.2 Binder Materials Used in the Experiment

The fly ash in this study was a by-product obtained from a coal-fired power plant in Serbia. The used bottom biomass wood ash originates from the local biomass power plant. Ash is produced after the burning of collected driftwood waste materials of biofuel. The used binders were sieved through a 90 μm sieve. The specific gravity of fly ash was 2.26 g/cm^3, while the specific gravity of biomass wood ash was 2.68 g/cm^3. The chemical composition of binders used in tests is given in Tab. 1, while in Fig. 1 their SEM and photograph are displayed.

Table 1 Chemical composition of used fly ash and biomass wood ash [21]

Parameter	Fly ash / %	Biomass wood ash / %
SiO_2	51.68	4.45
Fe_2O_3	11.58	5.32
Al_2O_3	20.16	1.85
CaO	7.43	48.83
MgO	2.41	6.62
SO_3	2.02	2.11
P_2O_5	0.12	2.45
TiO_2	1.04	0.11
Na_2O	0.88	0.46
K_2O	1.04	10.42
LOI	2.57	12.24

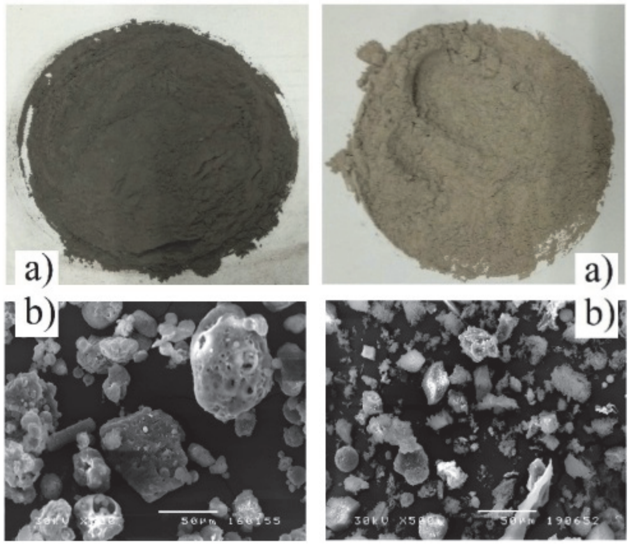

Figure 1 Photo (up) and SEM (down) display of used fly ash (a) and biomass wood ash (b)

In order to compare the pozzolanic activity of the biomass wood ash with fly ash in mortar mixtures, three different mix proportions were designed in accordance with EN 450-1. Mix proportions of tested mortar were listed in Tab. 2. In the test mixtures (FA-AI and BWA-AI), 25% of the mass of cement used in the reference mixture named "E-AI" was replaced by fly ash and the biomass wood ash respectively.

Table 2 Mix proportion of mortar for testing Activity index

Mixture	Cement /g	Water /g	Fly ash /g	Biomass wood ash / g	Standard sand / g
E-AI	450	225	-	-	1350
FA-AI	337.5	225	112.5	-	1350
BWA-AI	337.5	225	-	112.5	1350

The activity index was investigated by testing the compressive strength of samples at the ages of 28 and 90 days. The activity index was calculated as the ratio of the compressive strength of test mixture samples and the compressive strength of reference mix samples, when tested at the same age.

It is well known that pozzolanic activity and activity index are intended for cement and addition materials i.e. their suitability for use as type II addition material in concrete. According to previous research [1], higher pozzolanic activity and activity index is a good indicator that tested material can be used as a binder material in a geopolymer mixtures.

2.3 Additive and Water Used in the Experiment

Standard tap water was used during the paste, mortar and concrete production in all geopolymer mixtures. For the purpose of achieving better consistency, super plasticizer Sika ViscoCrete 5380 was used. Used superplasticizer was a chemical admixture based on the technology of polycarboxylates.

2.4 Aggregate Used in the Experiment

An aggregate from the South Morava river, Serbia, was used as a small fraction aggregate (0/4 mm). As a large aggregate (fractions 4/8 and 8/16 mm) the aggregate obtained by crushing the igneous rock gabbro from the quarry "Rakovdol", Serbia was used.

2.5 Mix Design

In order to investigate the effects of using biomass wood ash to replace fly ash on properties of paste (P), mortar (M) and concrete (C) different geopolymer mixtures were designed.

Based on our previous experimental research [1, 16], the mixture "0M" was designed as a reference one. The binder/aggregate ratio was 1:3, while the ratio of water/binder was 0.43.

To keep uniform consistency of tested geopolymer mortar, where flow value is lower than 140 mm, and according to standard EN 13395-1, superplasticizer was added. In general, by increasing the quantity of wood biomass ash in geopolymer mixtures the need for superplasticizer is reduced.

Six paste mixtures were marked as "0P", "5P", "10P", "15P", "20P" and "25P", while six mortar ones were marked as "0M", "5M", "10M", "15M", "20M" and "25M". In mentioned mixtures, biomass wood ash was used to replace fly ash at 0%, 5%, 10%, 15%, 20 % and 25% by weight, respectively.

Table 3 Mix proportion of geopolymer paste

Mixture	0P	5P	10P	15P	20P	25P
Fly ash / g	450	427.5	405	382.5	360	337.5
Biomass wood ash / g	0	22.5	45	67.5	90	112.5
Water / g	20	20	20	20	20	20
NaOH (10M) / g	56.16	56.16	56.16	56.16	56.16	56.16
Na_2SiO_3 / g	303.23	303.23	303.23	303.23	303.23	303.23
Superplast / %	2	0.8	0.6	-	-	-
w/*b*	0.43	0.42	0.42	0.41	0.41	0.41

The mix proportions of geopolymer paste are given in Tab. 3, while mix proportions of geopolymer mortar are given in Tab. 4. The moulds with samples of geopolymer were after demoulding, and until the testing, wrapped in a plastic foil to prevent moisture loss.

Also, two mixtures were made as geopolymer concrete. The composition of geopolymer concrete mixtures was determined on the basis of physical-mechanical and durability properties of mortar. Namely, the testing of mortar proved that the most optimal test results were obtained by 20% percentage-mass replacement of fly ash with wood biomass ash.

Table 4 Mix proportion of geopolymer mortar

Mixture	0M	5M	10M	15M	20M	25M
Fine aggregate /g	1350	1350	1350	1350	1350	1350
Fly ash / g	450	427.5	405	382.5	360	337.5
Biomass wood ash / g	0	22.5	45	67.5	90	112.5
Water / g	20	20	20	20	20	20
NaOH (10M) / g	56.16	56.16	56.16	56.16	56.16	56.16
Na_2SiO_3 / g	303.23	303.23	303.23	303.23	303.23	303.23
Superplast / %	2	0.8	0.6	-	-	-
w/*b*	0.43	0.42	0.42	0.41	0.41	0.41

Percentage-mass content of wood biomass ash is in relation to total mass of binders (0% and 20%). Also, the percentage content of wood biomass ash in binder material was used to mark the sample concrete series: "0C" and "20C". Also, in order to prevent moisture loss, concrete samples were cured in the same way as mortar samples. Mix proportions of geopolymer concrete mixtures for 1 m^3 of concrete are given in Tab. 5.

Table 5 Mix proportion of geopolymer concrete mixtures

Mixture		0C	20C
Fine aggregate 0/4 mm / kg		618	618
Coarse aggregate	4/8 mm / kg	356	356
	8/16 mm / kg	572	572
Fly ash / kg		400	320
Biomass wood ash / kg		-	80
NaOH (10M) / kg		50	50
Na_2SiO_3 / kg		270	270
Superplasticizer (SP) / kg		-	-
w/*b*		0,37	0,37

2.6 Type of Tests

Initial and final setting time of geopolymer paste were tested according to standard EN 196-3.

The following tests were conducted on geopolymer mortar: workability of mortar in fresh state was tested according to standard EN 13395-1 intended for testing the flow of thixotropic mortars. The measuring of geopolymer mortar workability was conducted by using test for flow of thixotropic mortars. A conical mould, of a base diameter 100 mm, was used for testing the workability. According to the standard, a mould was placed in the middle of the flow table and filled full with mortar. After that, the mould was removed and flow table was raised and dropped 15 times in 15 seconds. After raise-drop process, fresh mortar changed its shape to a "circular plate" and diameter was measured in two perpendicular directions. Bulk density was determined by using a cylindrical bowl of 1 l capacity and internal diameter of about 125 mm. After filling, vibration method was used for compaction in this examination. When testing the mortar in the hardened state, the mechanical characteristics were first examined at the age of 2, 7, 28, 56 and 90 days according to standard EN 196-1. The flexural strength test was performed on three prism-shaped specimens measuring 4 × 4 × 16 cm. The compressive strength test was performed on the halves of the mortar prisms after the flexural strength test. Durability testing of geopolymer mortar was performed on prism-shaped samples measuring 4 × 4 × 16 cm. After reaching the age of 28 days, the freeze and thaw resistance test according to the standard EN 14617-5 was performed.

Three samples of each series were exposed to alternating cycles of freezing and thawing, while the other three samples of the same shape and composition served as reference samples. One cycle consisted of four hours of saturation of the samples in water with a temperature of 20 ± 5 °C and four hours of freezing in an air chamber with a temperature of −20 ± 5 °C. The total number of cycles was 25. In order to get a better picture of the durability of geopolymer mortar, an examination of external sulfate resistance was performed. The test was performed using Technical report CEN/TR 15697. After reaching the age of 28 days, three samples of each mortar series were immersed in 5% Na_2SO_4 solution, while the other three samples of the same shape and composition served as reference samples. The sulphate solution was changed every 30 days, so that the pH was maintained in the range of 8 ± 0.5. After 180 days from the beginning of the test, the measurement of flexural strength and compressive strength of the tested samples was performed and compared with the values of strength measured on reference samples of the same composition. According to the used standard and testing report, the tested mortar samples are considered resistant to freeze-thaw cycles and external sulfate action if the ratio of compressive strength of tested and reference samples of the same composition is higher than 75% and 80%, respectively (resistance coefficient higher than 0.75 and 0.80, respectively).

On the fresh concrete, the consistency was measured according to provisions of the standard EN12350-2, while bulk density was measured according to standard EN 12350-6. Also, as on the hardened mortar, mechanical and durability properties were measured on the concrete specimens. Flexural strengths of geopolymer concretes were measured according to standard EN 12390-5 by applying two point forces at the thirds of the span. The test was performed on three prism shaped specimens, having dimensions 10 × 10 × 40 cm at the age of 90 days. The compressive strength test was conducted according to standard EN 12390-3 on cube shaped specimens having sides of 15 cm at the age of 2, 7, 28 and 90 days. The depth of penetration of water under pressure in hardened concrete was performed according to EN 12390-8 and was measured on the cube shaped specimens having sides of 15 cm. After reaching the age of 28 days, the samples were exposed to water under a pressure of 500 ± 50 kPa for 72 ± 2 h. After the test, the samples were halved and the depth of maximum water penetration was measured. Determination of freeze and thaw resistance was performed according to standard SRPS U.M1. 206 cube shaped specimens having sides of 10 cm. After reaching the age of 28 days, three samples of each series were exposed to alternating cyclic effects of freezing and thawing, while the other three samples of the same shape and composition served as reference samples. One test cycle consisted of freezing the samples for 4 hours at −20 ± 2 °C and thawing the samples in water for 4 hours at 20 ± 3 °C. The total number of freeze and thaw cycles was 200 (M-200). Reference samples of concrete of the same shape and composition were cured in ambient conditions until the time of testing, wrapped in plastic foil. Concrete cube shaped specimens having sides of 10 cm were used to test the sulfate resistance of concrete. The sulfate resistance of geopolymer concrete was tested by using the performance of technical report CEN/TR 15697. After achieving the age of 28 days the samples of concrete were completely immersed in Na_2SO_4 solution of 5% for 90 and 180 days. Three samples of each mixture were exposed to the sulfate solution, while the other three samples of concrete of the same composition served as reference samples. Reference samples were cured in ambient conditions until the time of testing. According to the used testing report, the tested samples are considered resistant to external sulfate action if the ratio of compressive strength of tested and reference samples of the same composition is higher than 80%.

3 RESULTS AND DISCUSSION

3.1 Testing of Pozzolanic Activity and Activity Index

The results of pozzolanic activity tests are presented in Tab. 6. According to the test results, the fly ash binder has the pozzolanic activity class 10. The tests of mechanical characteristics of mortar made with wood biomass ash satisfy the requirements for class 5. Pozzolanic class can be related to material reactivity, so a higher pozzolanic class might be an indicator of a higher material reactivity.

Table 6 The pozzolanic activity of fly ash and biomass wood ash

By product	Flexural strength σ_f / MPa	Compressive strength σ_c / MPa	Class	Requirements SRPS B.C1.018:2015
FA	3.04	10.38	**10**	Class 5: σ_f = 2 MPa, σ_c = 5 MPa Class 10: σ_f = 3 MPa, σ_c = 10 MPa Class 15: σ_f = 4 MPa, σ_c = 15 MPa
BWA	2.1	5.39	**5**	

* σ_f - Flexural strength, σ_c - Compressive strength

The results of activity index of fly ash and wood biomass ash are presented in Tab. 7. The test results indicated that wood biomass ash has a lower activity index in respect of the fly ash. Both materials fully meet the criteria according to SRPS EN 450-1 standard. The higher activity index of fly ash might be connected with the higher pozzolanic activity and also to the higher particle fineness of fly ash than of wood biomass ash.

According to the characteristics of powder materials, it can be concluded that fly ash and biomass wood ash can be used as binder materials in geopolymer mixtures.

Table 7 The activity index of fly ash and biomass wood ash [21]

Mix code	Compressive strength / MPa		Activity index / %	Requirements EN 450-1 / %
	28 days	90 days		
E-AI	53.8	57.6	-	90 days - 85
FA-AI	51.6	57.2	28 days - 95.9 90 days - 99.3	
BWA-AI	45.4	49.6	28 days - 84.4 90 days - 86.1	

3.2 Testing on the Geopolymer Paste

Test results of geopolymer paste are given in Tab. 8. The initial setting time of tested geopolymer mixtures varies from 330 to 750 min whereas the final setting time varies from 440 to 1230 min. The test results showed that the percentage by mass of wood biomass ash plays an important role in the length of geopolymer setting time. Mixtures made with wood biomass ash experience shorter setting time compared to the reference geopolymer paste made only with fly ash as a binder. The initial and final setting time decreases by increasing the percentage-mass content of wood biomass ash. This can be related to CaO content in the chemical composition of the binder. Generally, the mentioned compound of CaO found in wood biomass ash is more than six times higher than the content in fly ash.

Table 8 Results of testing on the geopolymer paste

Properties/ Mixture	0P	5P	10P	15P	20P	25P
Initial setting time / min	750	470	420	380	360	330
Final setting time / min	1230	1050	805	510	460	440

3.3 Testing of Geopolymer Mortar

Workability and bulk density: The test results of workability and bulk density are provided in Tab. 9. The workability testing results indicated that with the increase of biomass wood ash contents, increases the flow value, i.e. fluidity of mortar mixture. All tested mortar mixtures have stiff consistence except the mixture marked as "25M" which is on the border. The lowest flow value has the mortar made with only fly ash as a binder (122 mm), while the highest value was measured on the mixture made with 25% of biomass wood ash (141 mm). The reason lies in the fact that fly ash has more particles finer than 0.1 mm, so it requires a higher amount of water for grain moistening which directly affects the workability of mortar.

Table 9 Characteristics of mortar in fresh state

Mixture	0M	5M	10M	15M	20M	25M
Flow Value / mm	122	125	130	133	133	141
Bulk density / kg/m^3	2170	2170	2175	2175	2175	2180

Bulk density of fresh mortar slowly increases with the increase of the share of wood biomass ash. The mixture with 25% of biomass wood ash has the highest value of bulk density and it amounts to 2180 kg/m^3, while the mixture made with fly ash only as a binder has the lowest value of bulk density and it amounts to 2170 kg/m^3. Small difference in bulk density of mortar mixtures occurs because of the small difference in the specific gravities of fly ash and biomass wood ash which are 2240 kg/m^3 and 2320 kg/m^3, respectively.

Flexural and compressive strength: The flexural and compressive strength testing results of the geopolymer mortar made with addition of wood biomass ash are provided in Fig. 2. According to the test results of the mortar at the age of 2 and 7days, it can be concluded that the addition of wood biomass ash has a positive effect on flexural strength. Also, at mentioned ages, all mortar mixtures made with addition of wood biomass ash, achieved higher strengths than the reference geopolymer mortar marked as "0M" which was made with only fly ash as a binder material. At the age of mortar of 28 days, it is observed that the mixture marked as "20M" has the highest flexural value (7.56 MPa) which is more than 20% higher than the flexural strength measured on the reference mixture marked as "0M". The trend of the increase of strength by age was observable in almost all mixtures, but at the ages of 28 to 90 days it is negligibly small in comparison to the increase of strength in early ages.

According to the test results of compressive strength of the mortar at early ages, it can also be concluded that the addition of wood biomass ash has a positive impact on compressive strength. At the age of 7 days, all mortar mixtures made with wood biomass ash achieved higher compressive strength than the reference geopolymer mortar marked as "0M". The highest compressive strength was measured on the mixture named "10M" (24.91 MPa) which is around 60% higher than the reference mortar marked as "0M". At the age of 28 days, the highest compressive strength was measured on the mixture marked as "20M" was 50.38 MPa, while at the age of 90 days, it was 52,03 MPa. Mentioned values were around 17% and 3% higher than the compressive strength of the mixtures "0M" that is made with only fly ash as a binder, respectively.

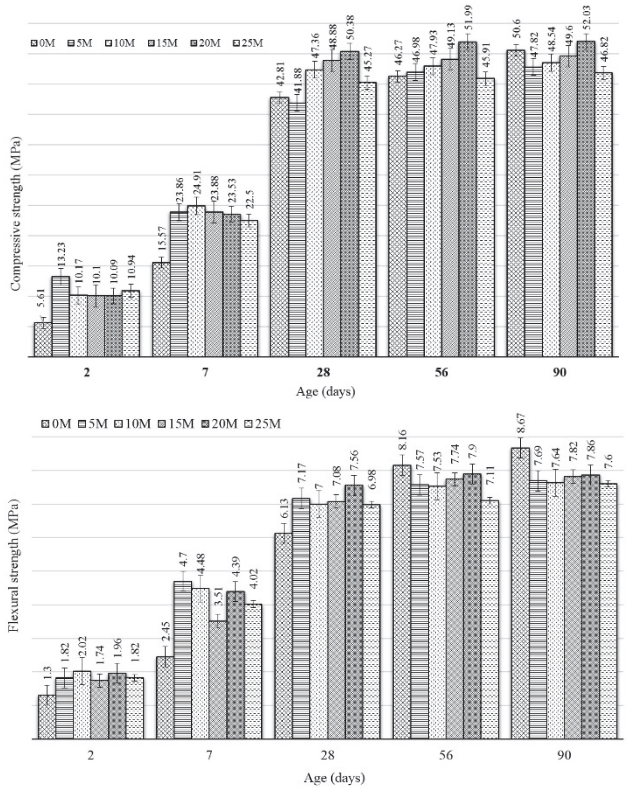

Figure 2 Compressive strength of geopolymer mortar mixtures (up) and Flexural strength of geopolymer mortar mixtures (down)

Sulfate resistance: The sulfate resistance testing results of the geopolymer mortar made with addition of wood biomass ash are provided in Tab. 10. Geopolymers sulfate resistance (CS SR) was determined by comparison of compressive strength of reference mortar samples at the age of 180 days (Ref. S.) and compressive strength of samples immersed in 5% Na_2SO_4 solution after 180 days (Treat. S.). The test results of geopolymer mortar indicate very good sulfate resistance under the implemented test requirements. The lowest sulfate resistance coefficient in terms of compressive strength was measured on the mixtures named "15M" and "10M" and it was 0.99 and 1, respectively. The highest sulfate resistance coefficient was measured on the mixture marked as "20M" and it was 1.12. The last mentioned value is by around 9% higher than the sulfate resistance coefficient of the etalon geopolymer mortar mixure marked as "0M". Physical changes on the tested samples were not observable. It can be concluded that all geopolymer mortar mixtures meet the basic requirements in the term of sulfate resistance under the given test conditions.

Table 10 Sulfate and freeze and thaw resistance of geopolymer mortar in hardened state

Mixture	Days	0M	5M	10M	15M	20M	25M
Sulfate resistance / MPa	Ref. S. σ	51.81 ± 1.3	48.14 ± 1.25	49.16 ± 1.2	50.11 ± 1.15	46.92 ± 1.25	47.14 ± 1.4
	Treat. S. σ	53.21 ± 1.1	51.84 ± 1.4	49.39 ± 0.9	49.54 ± 1.5	52.43 ± 1.1	52.50 ± 1.5
	SR Coef.	1.03	1.08	1.00	0.99	1.12	1.11
Freeze and thaw resistance / MPa	Ref. S. σ	45.27 ± 1.1	45.88 ± 1.5	47.13 ± 1.7	51.02 ± 2.0	52.12 ± 1.9	46.20 ± 1.3
	Treat. S. σ	46.46 ± 1.1	45.83 ± 1.4	44.98 ± 0.9	48.95 ± 1.5	50.18 ± 1.1	44.01 ± 1.5
	FTR Coef.	1.03	1	0.95	0.96	0.96	0.95

* Ref. S - Reference samples (samples of the same composition which were not exposed to durability tests), Treat. S - Treated samples, σ - Standard deviation, SR Coef. - Compressive strength sulfate resistance, FTR Coef. - Compressive strength freeze and thaw resistance

Freeze and thaw: The freeze and thaw testing results of the geopolymer mortar made with addition of wood biomass ash are provided in Tab. 10. The compressive strength resistance coefficients - FTR Coef. were calculated for the tested mortar mixtures and present the ratio of samples treated to 25 freeze - thaw cycles (Treat. S.) and reference sample at the age of 28 + 25 days (Ref. S.). The highest compressive strength freeze - thaw resistance coefficient was measured on mixtures marked as "5M" and it was 1. Mentioned value is 9 % higher than etalon "0M". The lowest value (0.95) is higher than 0.75 for all tested specimens. So, it can be concluded that the tested specimens of geopolymer mortars are frost resistant for 25 cycles of treating.

3.4 Testing of Geopolymer Concrete

The test results of fresh geopolymer concrete properties are given in Tab. 11. The table provides mean values of the obtained test results. Slump test results of mixtures marked as "0C" and "20C" and according to standard SRPS EN 206 belong to the class S3 and in the range from 100 to 150 mm, which has been the main goal when designing geopolymer concrete mixtures. Bulk densities of fresh geopolymer concretes practically do not change. The small difference in the bulk density occurs because of the small difference in the specific gravity of fly ash and biomass wood ash which is only 80 kg/m^3.

Table 11 Characteristics of concrete in fresh state

Mixture	Slump test / mm	Bulk density / kg/m^3
0C	110	2335
20C	130	2340

3.4 Properties of Hardened Concrete

Test results of compressive strength of geopolymer mixtures at the age of 2, 7, 28 and 90 days are provided in Fig. 3. Each value presented is the average of three measurements.

The results indicate that early compressive strengths of geopolymer concretes are low. At the age of 28 and 90 days mixture marked as "0C", made only with fly ash as a binder, had higher compressive strength value than the mixture marked as "20C" made with 20% biomass wood ash and 80% of fly ash. Compressive strength values of reference "0C" at earlier mentioned ages were 47.23 MPa and 49.49 MPa. The geopolymer concrete mixture made with 20% of biomass wood ash at the same ages had a compressive strength that is by 15.6% i.e. 5.1% lower in respect to the reference geopolymer mixture marked as "0C".

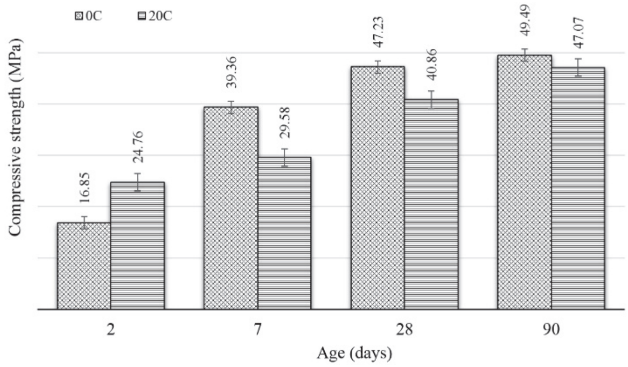

Figure 3 Compressive strength of geopolymer concrete mixtures

Fig. 4 presents the mathematical functions obtained by the statistical processing of data of mean compressive strength values of concrete of different ages. Logarithmic functions were used to process the results, and the obtained correlation coefficients ranged from 0.85 for the "0C" mixture to 0.98 for the "20C" mixture. High correlation coefficients indicate a good approximation of the function of change in compressive strength due to increasing age of geopolymer concrete.

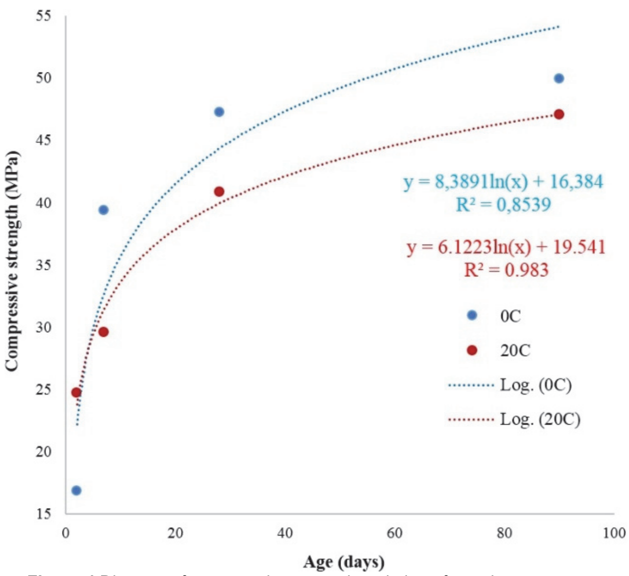

Figure 4 Diagram of compressive strength variation of geoplymer concrete samples in the function of time

The flexural strength test results (Tab. 12) of the geopolymer concrete mixtures are the mean value of three measurements. The results indicated that at the age of 90 days the etalon mixture marked as "0C" had lower flexural strength than the mixture marked as "20C" (5.11 MPa and 5.69 MPa, respectively). The biomass wood ash in mixtures increased the flexural strength of concrete by 11.4%. The values obtained by testing could be explained by the fact that the concrete mixture in which the fly ash was partially replaced by wood biomass ash had more homogenous structure which contributed to establish a better adhesion between the mortar and aggregate, which had a positive effect on the flexural strength of the geopolymer concrete.

Table 12 Characteristics of geopolymer concrete in hardened state

Mixture			0C	20C
Flexural strength / MPa	Days	90	5.11	5.69
Depth of penetration of water under pressure mm ± σ	Criteria V-I 50 mm V-II 30 mm V-III 20 mm		15 ± 1.5 **(V-III)**	16 ± 1.5 **(V-III)**
Sulfate resistance / MPa Criteria CEN/TR15697:2014 > 0.8	Ref. S. at 28 + 90 days σ		55.50 ± 1.6	49.85 ± 1.3
	Treat. S. at 28 + 90 days σ		54.12 ± 1.2	49.21 ± 1.5
	SR Coef. at 28 + 90 days		**0.98**	**0.99**
	Ref. S. at 28 + 180 days σ		55.79 ± 1.25	50.05 ± 1.25
	Treat. S. at 28+180 days σ		55.14 ± 1.95	51.99 ± 1.65
	SR Coef. at 28 + 180 days		**0.99**	**1.04**
Freeze and thaw resistance MPa Criteria SRPS U.M1.206-P > 75% M-100: Class XF1 M-200: Class XF3	Ref. S. σ		56.98 ± 1.45	-
	Treat. S. σ		43.85 ± 1.45	Breaking after 30 cycles
	FTR Coef.		77% **(M-200)**	-

* Ref. S - Reference samples (samples of the same composition which were not exposed to durability tests), Treat. S - Treated samples, σ - Standard deviation,SR Coef. - Compressive strength sulfate resistance, FTR Coef. - Compressive strength freeze and thaw resistance

Depth of penetration of water under pressure is mostly a reliable piece of data for creating an image of the durability of tested concrete. The results of testing of penetration of water under pressure (Tab. 12) indicate that the replacement of a part of fly ash with wood biomass ash to a smaller degree affected the depth of penetration of water under pressure. Both tested concrete mixtures showed good resistance to water under pressure, and depth of penetration of water under pressure (Fig. 5) was 15 mm for the concrete mixture marked as "0C" and 16 mm for the mixture marked as "20C". In general, both mixtures meet the requirements for the highest class of water tightness "V-III" according to SRPS U.M1.206.

Replacement of fly ash with wood biomass ash in the percentage-mass amount of 20% in the binder had a smaller effect on the value of the coefficient of external sulfate resistance (Tab. 12). Namely, after 3 months (90 days) from the immersion of specimens in a 5% solution of Na_2SO_4 measured coefficients of external sulfate resistance marked as "0C" and "20C" were 0.98 and 0.99, respectively. After 6 months (180 days) from the exposure of samples to the action of sulphate solution it was noticed that the resistance coefficients on the sulphate action were higher than the coefficients obtained at the previous measuring and they were 0.99 and 1.04, respectively. Under these test conditions, no physical changes were observed in the tested samples (Fig. 6).

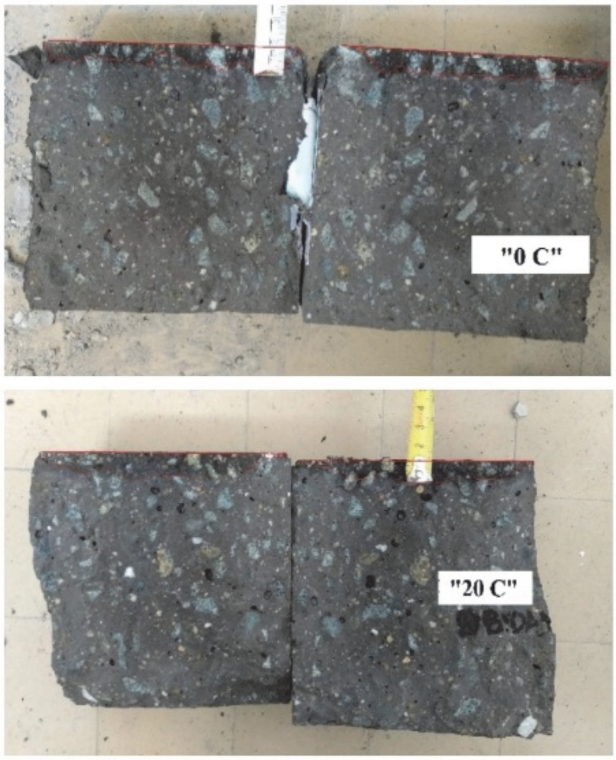

Figure 5 Appearance of the geopolymer concrete samples after testing of penetration of water under pressure: up - "0C", down - "20C"

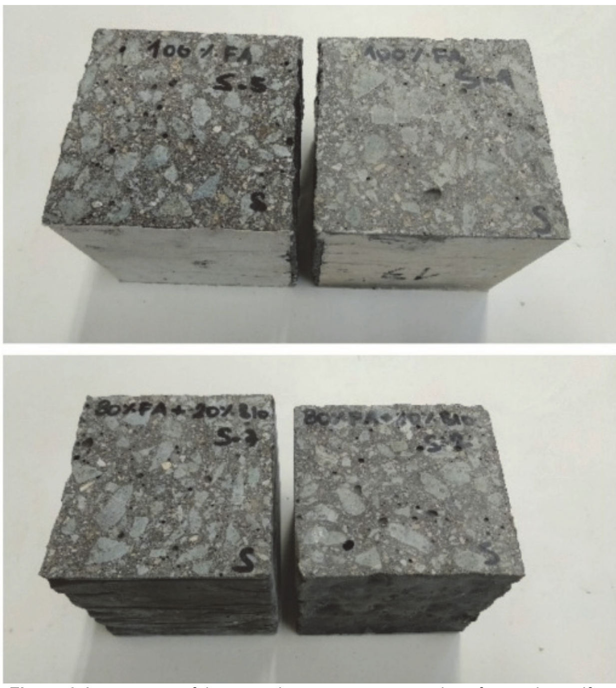

Figure 6 Appearance of the geopolymer concrete samples after testing sulfate resistance after 180 days of immersion in 5% Na_2SO_4 solution: up - "0C", down - "20C"

It can be concluded that all concrete mixtures tested for the sulphate effects due to immersion of samples in sulphate solution meet the basic criteria in terms of physical and mechanical characteristics which classifies them as sulphate resistant under these test conditions. It is assumed that the increase in the resistance coefficient when measured at 3 and 6 months from the immersion of geopolymer concrete samples in sulfate solution is due to strong bonds between the geopolymer binder and the alkaline solution maintained stable. The tested concrete mixtures did not react to the external action of sulfate under such test conditions.

The freeze and thaw test results of the geopolymer concrete mixtures are also given in Tab. 12. Each value presented is the average of three measurements. The results indicated that the replacement of fly ash with wood biomass ash caused the reduced resistance of concrete marked as "20 C" to the cyclic action of freezing. Namely, the testing of the mentioned mixture was interrupted after 30 cycles of freezing and thawing (Fig. 7).

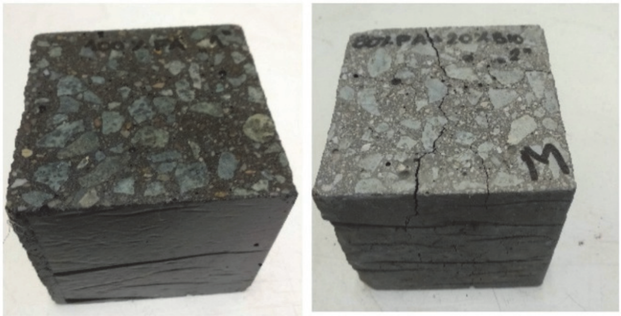

Figure 7 Appearance of the geopolymer concrete samples after testing freeze-thaw resistance of geopolymer concrete: left - "0C", right - "20C"

On that occasion, there were physical changes that are cracks in the transit zone. Therefore, it can be concluded that the mentioned mixture is not resistant to frost under these test conditions. A possible reason of this occurrence could be a higher porosity and unfavourable pore structure of geopolymer concrete mixtures with biomass wood ash. Only samples of geopolymer standard concrete marked as "0C" are considered resistant to frost. The decrease in compressive strength of the specimens exposed to the freezing and thawing cycles in relation to the reference specimens of the same composition which were cured in ambient conditions until the time of testing was 13.13 MPa. The test results obtained in this way cannot be fully related to the tests of other authors [22] who conclude that geopolymer concrete made with fly ash only has a resistance to frost for up to 40 cycles.

4 CONCLUSIONS

In this paper, a study of the effect of biomass wood ash as a co-binder material on physical, mechanical and durability properties of geopolymer paste, mortar and concrete was carried out based on fly ash. Six mixtures each, paste and mortar, were designed by adding biomass wood ash in the amount of up to 25%, of the total binder in order to improve geopolymer properties. According to physical-mechanical and durability properties of mortar investigation was continued in order to improve properties of geopolymer concrete mixtures.

The results can be summarized as follows:

Biomass wood ash and fly ash has satisfactory pozzolanic activity and activity index.

According to test results of flexural and compressive strength of geopolymer mortar it can be concluded that a trend of increasing strength is observed over time but it is negligibly smaller in comparison to the increase of strength at early ages up to 28 days. Also, results indicated that more than 90% of geopolymer mortar strength was achieved already after 56 days and it can be also concluded that polymerization is almost fully achieved at that age.

All geopolymer mortars satisfy basic requirements of freezing-thawing resistance after 25 cycles but this property is the highest in a mixture made only with fly ash as a binder.

All geopolymer mortar mixtures meet the basic requirements in the term of sulfate resistance under the given test conditions.

Based on the obtained mean values of compressive strength of geopolymer concrete, it can be concluded that the strength of concrete increases with the increasing degree of polymerization, which gradually develops over time.

The increase of geopolymer concrete compressive strength between the age of 56 and 90 days is negligible for the concrete made only with fly ash as a binder, while it is not negligible for the mixture made with wood biomass ash and fly ash.

Biomass wood ash does not have any impact on the concrete resistance to the effect of water under pressure which may be due to the content of gel pores inside the concrete matrix.

The concrete in which fly ash was replaced by wood biomass ash proved not to be resistant to the effects of freezing and thawing cycles, which may be a consequence of weaker bonds between geopolymer paste and coarse aggregate, but also the achieved reaction products.

The tested concrete mixtures showed good resistance to the action of sulfates, and the geopolymer binder and alkaline solution, after the exposure to the sulfate solution, continued to harden and retain their internal bonds stable without reacting to external influences.

Future research should be focused on the research of the influence of pore structure on freezing and thawing cycles as well as the development of computer software that could predict the characteristics of geopolymers depending on the characteristics of raw materials.

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