POBOLJŠANJE SVOJSTAVA BETONA DODATKOM LETEĆEG PEPELA IZ TERMOELEKTRANE ZA PRIMENU U GEOTERMALNIM SISTEMIMA

ENHANCING PROPERTIES OF CONCRETE BY ADDITION OF FLY ASH FROM A THERMAL POWER PLANT FOR APPLICATION IN GEOTHERMAL SYSTEMS

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Električnu energiju u Srbiji pretežno obezbeđuju termoelektrane. Svih jedanaest termoelektrana u Srbiji koriste ugalj, uglavnom lignit u procesu proizvodnje električne energije, čime se godišnje generiše oko 6 miliona tona letećeg pepela. Procenjena količina letećeg pepela iz termoelektrana akumulirana na deponijama u Srbiji prelazi 200 miliona tona. S druge strane, poslednjih decenija poštovanje principa ekološki održivog razvoja nametnuto je industrijama, a jedna od njih je i građevinska. Zahvaljujući prisustvu amorfnog SiO_2 i Al_2O_3, pepeo kao pucolanski materijal pogodan je za proizvodnju betona i maltera. Zbog toga se pravilnom upotrebom letećeg pepela mogu očekivati višestruki pozitivni efekti- smanjenje deponija i poboljšanje svojstava betona. Ideja ovog istraživanja je analiziranje mogućnosti recikliranja letećeg pepela iz termoelektrane tako što će delimično zameniti uobičajeni mineralni punioc- krečnjak u proizvodnji samozbijajućeg betona (SCC). Upoređena su svojstva konvencionalnog SCC sa krečnjakom i kompozicija sa različitim sadržajem pepela. S obzirom da je u slučaju dodatka letećeg pepela potrebno da budu zadovoljeni zahtevi za SCC, kao i da svojstva betona ostanu ista ili poboljšana, ova studija je pokazala da se sve dizajnirane smeše mogu koristiti za konstrukcijske primene.

Ključne reči: *samozbijajući beton (SCC); leteći pepeo; dizajn smeša; fizičko-mehanička svojstva; mikrostruktura*

Electric power in Serbia is predominantly provided by thermal power plants. All of eleven existing thermal power plants in Serbia use coal, mainly lignite in the electricity production process thus generating about 6 million tons of fly ash per year. The estimated amount of fly ash from thermal power plants accumulated in Serbian landfills exceeds 200 million tons. On the other hand, during the last decades, respecting the principles of ecologically sustainable development has been imposed on industries, and one of them is the construction industry. Due to the presence of amorphous SiO_2 and Al_2O_3, fly ash as pozzolanic material is convenient for the production of concrete and mortar. Consequently, multiple positive effects can be expected by the proper consumption of fly ash- reducing landfills and improving concrete properties. The idea of this study is to analyze the possibility of recycling fly ash from a thermal power plant by replacing a part of common mineral filler- limestone in the production of self-compacting concrete (SCC). Properties of conventional SCC with limestone and compositions with different fly ash content were compared. Considering that requirements for

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SCC should be satisfied and all properties remain or enhance in the case of fly ash addition, this study proved that all designed concretes can be used for structural applications.

Key words: *self-compacting concrete (SCC); fly ash; mixture design; physico-mechanical properties; microstructure*

1 Introduction

About 70 % of electric power in Serbia is generated in the existing 11 thermal power plants belonging to the Electric Power Industry of Serbia and they all use coal, mostly lignite, thus making them the largest lignite producers. In this electricity production, about 6 million tonnes of fly ash (FA) per year is obtained, which is stored in landfills covering an area around 1,800 ha. The total estimated amount of fly ash in Serbian landfills is over 200 million tonnes [1-3]. Fly ash is a fine, loose material that is being collected in the electro filters of the chimneys in thermal power plants with the particle size usually in the range of 1-150 µm.

The development of concrete additives mainly of polycarboxylate-type, led to spreading application of self-compacting concrete (SCC), considered as a revolutionary discovery in concrete technology. This concrete, owing to its own weight, fills the formwork, thus coats reinforcement bars and fulfills all available space, while achieving the highest compactness, important for hardened state properties and durability [4].

Fly ash, capable of reacting with calcium hydroxide at room temperature, due to the presence of SiO_2 and Al_2O_3 in the amorphous form, can be considered as pozzolanic material and therefore, it has been used for decades as an additive in commercial types of cement and for the production of concrete and mortar. Inhomogeneous composition is one of the disadvantages that reduce its use [5-9].

The use of fine FA particles in concrete leads to the effect of the aggregate fluidity, as well as to an increase in the solid to liquid ratio, at the same water/ cement factor; consequently, the risk of segregation and water extraction on the surface reduces.

Due to the spherical shape and glassy surface of the majority of FA particles, usually finer than the cement particles, the addition of 10 mass. % of FA in relation to the cement mass reduces the water requirement by 3-4 %.

The principles of sustainable development and ecology have been constantly and intensively promoted in all spheres. Hence, the consumption of FA will create multiple positive results, including the reduction of accumulated material at landfills and the improvement of concrete properties [5].

The idea in this study is to investigate the possibility of producing high-performance SCC using FA from Thermal Power Plant "Kolubara A", Serbia, without prior processing, for a partial replacement of mineral filler, limestone. It is presumed that small amounts of FA improve hardened SCC properties without serious deterioration of its fresh state properties. The properties of SCCs with different amounts of FA will be compared and accordingly the optimal composition will be recommended.

2 Experimental

2.1 Mixture design and samples preparation

The initial components used for SCC preparation were aggregate, cement, limestone, fly ash and superplasticizer.

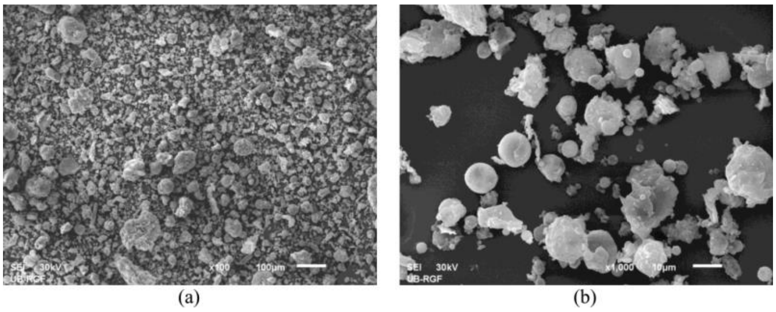
Natural aggregate, from the river Danube, mostly with rounded particles, was used in three fractions: I- fine (0-4 mm), II- coarse (4-8 mm), and III- coarse (8-16 mm). The contents of coarser grains (> 4 mm) in fractions I, II, and III were 1.96 %, 5.81 %, and 0 %, respectively. The contents of fine particles in fractions II and III were 1.84 % and 0.94 %, respectively. In fraction I the contents of fine particles, <0.063 mm and < 0.09 mm, were 0.59 % and 1.68 %, respectively.

A commercial type I Portland cement (*CEM I 42.5R, Lafarge, Serbia*) was used as a binder. Chemical composition of the cement was: 61.64 % CaO, 21.21 % SiO_2, 2.22 % MgO, 4.81 % Al_2O_3, 2.13 % Fe_2O_3, 1.11 % K_2O, 0.33 % Na_2O, 0.18 % TiO_2, and 6.37 % SO_3.

Natural limestone (*Granit Pescar, Ljig, Serbia*), with a medium size of 250 μm was used as mineral filler. According to chemical analysis, it consists of: 54.86 % CaO, 0.21 % SiO_2, 1.10 % MgO, 0.5 % Al_2O_3, 0.09 % Fe_2O_3, 0.05 % K_2O, 0.005 % MnO, 0.5 % P_2O_5, and SO_2 in traces (LOI 43.64 %).

Fly ash, from Thermal Power Plant "Kolubara A", Serbia, was used in its original form for partial replacement of limestone. According to chemical analysis, it consists of: 58.60 % SiO_2, 21.92% Al_2O_3, 6.12 % CaO, 5.97 % Fe_2O_3, 1.77 % MgO, 1.50 % K_2O, 0.37 % Na_2O, and 0.49 % TiO_2 (LOI 3.09 %). Density of FA in the loose and compacted state was 690 kg/m^3 and 910 kg/m^3, respectively. The specific gravity was 2190 kg/m^3.

Microstructure of FA was performed by SEM (scanning electron microscope), type JEOL JSM-5800 and the obtained microphotographs are given in Figure 1.



(a) (b)

Figure 1. SEM microphotographs of fly ash taken at magnification of:
a) 100 x, b) 1000 x

As seen in Figure 1, FA particles are generally spherical. Since only organic matter is lost during coal combustion, the inorganic residue remains in the ash. A large number of irregularly shaped particles is evidently present.

A polycarboxylate (Glenium Sky 690, *BASF Construction Chemicals, Italy*) additive was used as a superplasticizer that enables self-compacting capacity and improves the flowability of concrete.

The compositions of designed four SCC mixtures are shown in Table 1.

The reference SCC mixture E contains only limestone as filer. Other three SCC mixtures were made with partial replacement of FA in regard to the limestone amount: FA-10 with 10 mass. % of FA, FA-20 with 20 mass. % of FA and FA-50 with 50 mass. % of FA and with increased superplasticizer content neccessary to provide workability.

Table 1. Design of SCC mixtures

	E	*FA-10*	*FA-20*	*FA-50*
Coarse aggregate (8-16mm) (kg/m^3)	430	430	430	430
Coarse aggregate (4-8mm) (kg/m^3)	430	430	430	430
Fine aggregate (0-4mm) (kg/m^3)	840	840	840	840
Cement C (kg/m^3)	380	380	380	380
Water W (kg/m^3)	183	183	183	183
Limestone powder LP (kg/m^3)	220	198	176	110
Fly ash FA (kg/m^3)	0	22	44	110
Superplasticizer (kg/m^3)	7.6	7.6	7.6	11.4
Water- to- cement ratio W/C	0.482	0.482	0.482	0.482

Each SCC mixture was proportioned by weight. A laboratory concrete mixer with a capacity of 60 l, fixed drum, and paddles at the vertical axel was used. The aggregate was mixed for one minute in a mixer, then the filer and cement were added and mixed for 30 s. Afterwards, water with the superplasticizer was added and mixing continued until homogeneity (270 s). The preparation was realized at the ambient temperature (20-22 °C).

After preparation, rheological tests in fresh state of SCC were made.

Subsequently, casting was done. The specimens were removed from the molds after 24 h, and then cured in water until tests on hardened concrete were done. Each of the data obtained from testing corresponds to an average of at least three measurements.

2.2 Characterization of the SCC

The characterization of the **fresh state** of the produced SCC was performed by standard determination of density, entrained air content, flowability (Slump flow, Slump flow time (t_{500}), V-funnel time (t_v)), passing ability (L-box), and segregation resistance [10-14].

Investigations on the **hardened** SCC included: density, mechanical strength, static modulus of elasticity, water permeability, resistance against freezing in the presence of de-icing salt, and SEM analysis. Density was tested on prisms 12x12x36 cm up to the age of 180 days [15]; compressive strength on cubes at each age (3, 7, 14, 21, 28, 63, 90 and 180 days) [16]; three point bending (flexural strength) test on prisms 12x12x36 cm at the age of 28 days [17], static modulus of elasticity on cylinders with diameter of 15 cm and height of 30 cm, at the ages of 28 and 180 days [18]; water penetration at the older age of 63 days [19]; resistance against freezing in the presence of de-icing salt (3 % aqueous solution of NaCl) on special samples with the bottomless container on the top at the age of 28 days [20]. For the microstructure characterization, statistically representative samples of all mixtures were prepared and tested using the SEM (scanning electron microscope), type JEOL JSM-5800.

The SCC samples were kept in water for 180 days. They were periodically removed from water to perform measurements.

The performed qualitative analysis included comparison of the reference mixture E with the mixtures containing FA in terms of their porosity and structure.

3 Results and Discussion

3.1 Fresh SCC tests

The results of characteristic rheological tests on SCC are presented in Table 2.

According to the EFNARC, all SCC series with FA meet the requirements for the determined fresh state properties except the viscosity of FA-50. SCCs with FA exhibit lower workability than E, which is manifested in flowability and passing ability decrease as well as in segregation resistance increase. It can be concluded that the addition of FA in the higher proportion affects negatively the fluidity and workability of SCC.

Table 2. Fresh state properties of SCCs

	E	*FA-10*	*FA-20*	*FA-50*
Density (kg/m^3)	2397	2391	2370	2347
Entrained air content (%)	1.9	1.5	2.0	2.8
Slump flow (mm)	761.2	701.2	663.8	702.5
Slump flow time t_{500} (s)	2.62	5.71	10.91	11.32
V-funnel time t_v (s)	9.73	15.92	22.46	27.21
Passing ability L-box (H2/H1)	0.97	0.92	0.92	0.95
Seggregation factor (%)	3.5	3.0	2.0	1.7

t_{500} - time required for spreading; t_v - V-funnel time; H1 and H2-heights at the beginning and at the end of the horizontal part of L-box, respectively

3.2 Hardened SCC tests

Density

Density values of tested series up to the age of 180 days are in the range of 2350-2420 kg/m^3. Figure 2 shows the density change versus the logarithm of time.

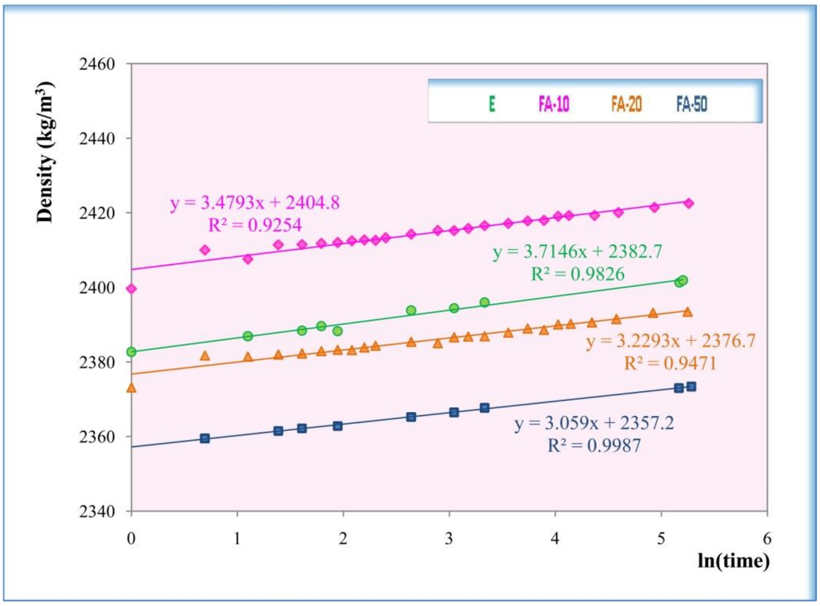


Figure 2. Density change of hardened SCCs versus time

As seen in Figure 2, at all ages, FA-50 exhibited the lowest density values, and FA-10 the highest. Unexpectedly, the density of FA-10 was higher than that of E, which is probably the result of measurung errors. Linear regression analysis gave equations with high values of correlation coefficients. Obviously, E has the greatest slope, and thus the fastest water absorption, which is in accordance with the fact that the FA addition improves the concrete structure resulting in lower water absorption [21]. Comparing only mixtures with FA, FA-10 has the greatest slope, followed by FA-20 and finally by FA-50.

Mechanical strength

The compressive strength is a basic property of hardened concrete and is often used as its quality indicator [22]. The obtained results of compressive strength are given in Figure 3.

As seen in Figure 3, the increase in FA amount leads to compressive strength decrease of SCCs at early ages and to strength increase at older ages. This is explained by the pozzolanic effect, which is more pronounced for larger FA quantities and older ages. 50 % of FA leads both to strength increase and decrease depending on age. This can be attributed to the negative effect of the mechanically weaker FA grains, especially coarser inhomogeneous, apart from the positive pozzolanic impact. However, LP-50 showed higher strength than E at all ages- from 4.3% at the age of 90 days to 16.5% at the age of 63 days. In this respect, a clear positive effect of using FA is evident. These results show that the addition of FA results in strength increase at all ages depending on its amount compared with the strength of E.

At the age of 28 days mixtures FA-10, FA-20, and FA-50 reached significantly higher strengths than E; precisely, higher for 11.3 %, 16.8 %, and 12.9 %, respectively. The 16.8 % increase for FA-20 in relation to E at 28 days of age is at the same time the largest difference among all data. This strength increment with the increasing FA content can be explained by the pozzolanic effect, which is more pronounced for larger FA quantities and at later ages.

Based on the analysis performed, a positive effect of the use of FA in SCCs is evident.

For concrete with FA, the rate of compression strength increment depends on a number of factors. Since FA, with the total content of oxides $SiO_2 + Al_2O_3 + Fe_2O_3$ over 80 % was used, the effect of a later increase in the concrete strength (but also a slower strength development at early ages) can be expected due to its pozzolanic reaction [23].

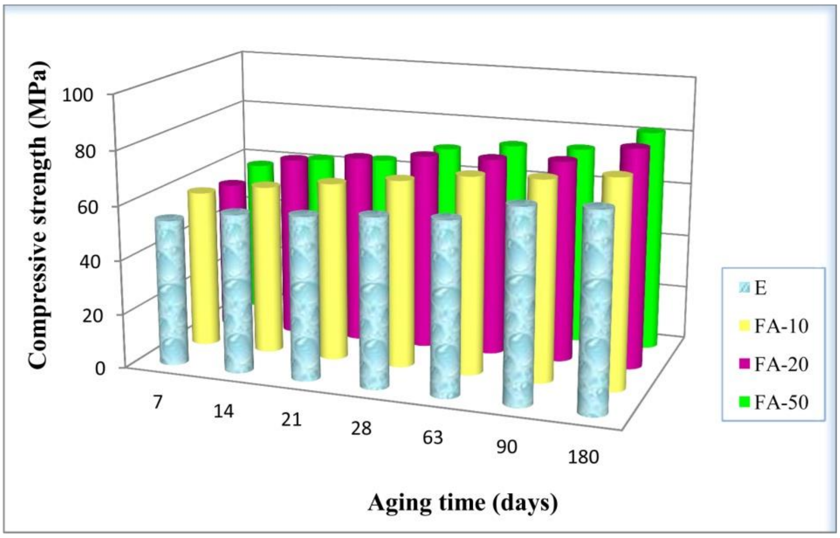


Figure 3. Compressive strength of SCC mixtures during time

Figure 4 shows the compressive strength increment of SCCs versus logarithm of time. A family of curves described by equations with high correlation coefficients was obtained by regression analysis.

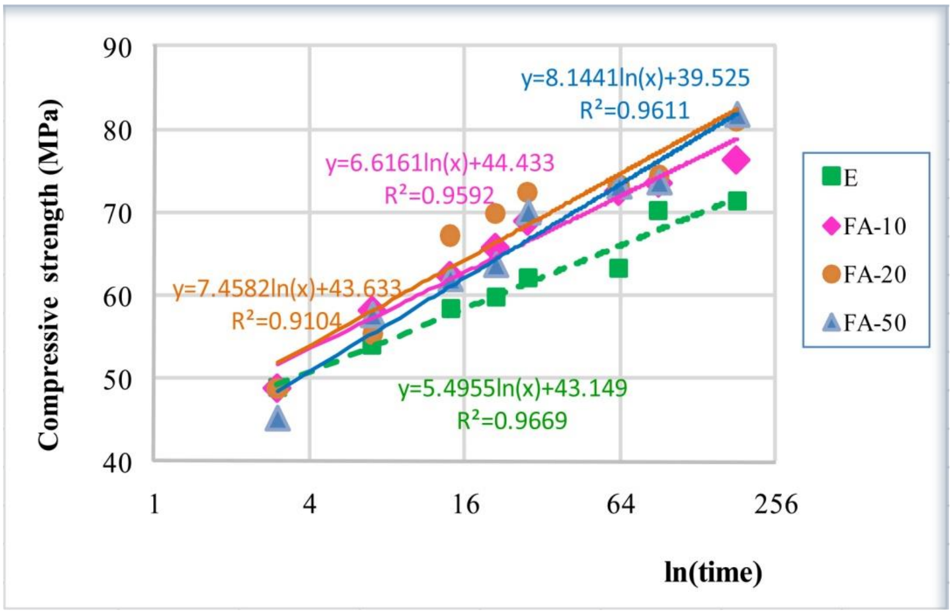


Figure 4. Compressive strength increment of SCC mixtures during the aging time

It can be observed that E represents the lower boundary of the curve family, while FA-20 the upper boundary line of the formed functional dependency family. The functional regressions derived for FA-10 and FA-50, from lower to higher, are between the two boundaries. In terms of the cement stone hardening, where the cement hydration and the pozzolanic reaction are involved, the rate of compressive strength increment, and thus the rates of the corresponding chemical reactions, can be interpreted by the slopes of the created lines. Namely, the slopes of all lines are positive- its lowest value is for E, which corresponds to the slowest rate of strength increment. A slope increment for SCCs containing FA is evident with FA content increase, which corresponds to the pozzolanic contribution to the strength enhancement. At some moment, due to the pozzolanic reaction, further significant strength increase for mixtures with FA, especially of FA-50, can be expected.

The flexural strength results for SCCs at the age of 28 days are given in Table 3.

As can be seen from Table 3, FA-10 had a 1 % lower flexural strength compared to E. FA-20 and FA-50, showed a slight flexural strength increase compared to E- 12 % and 3 %, respectively. Regarding flexural strength, the optimum FA content is 20 %.

Table 3. Flexural strength of SCC mixtures at the age of 28 days

	E	*FA-10*	*FA-20*	*FA-50*
Flexural strength f_{zs} [MPa]	10.3	10.2	11.5	10.6

Static elasticity modulus

The static elasticity modulus results for SCCs at the ages of 28 and 180 days are shown in Table 4.

Table 4. Static modulus of elasticity Es [GPa] of SCCs at the ages of 28 and 180 days

Age (days)	E	FA-10	FA-20	FA-50
28	34.1	35.6	35.7	37.3
180	38.5	35.6	41.9	39.4

FA-10, FA-20 and FA-50, at 28 days of age showed higher static elasticity modulus than E- 4.4 %, 4.5 % and 9.4 %, respectively. Similarly, at 180 days of age, FA-10, FA-20 and FA-50, showed higher values than E- 8.1 %, 8.8 % and 2.3 %, respectively. Based on these results, and the evident elasticity modulus drop for FA-50 at the age of 180 days, it can be concluded that lower FA content provides better elasticity at older ages.

Water permeability

Maximal and average depths of water penetration for each specimen of each mixture, as well as the average values for each mixture are given in Table 5.

Table 5. Depths h [mm] of the water penetration

	E		*FA-10*		*FA-20*		*FA-50*	
Specimen	Aver.	Max	Aver.	Max	Aver.	Max	Aver.	Max
1	8	16	10	15	9	14	11	15
2	9	16	9	17	10	15	10	17
3	11	17	9	16	11	17	9	15
Average value:	**9.3**	**16.3**	**9.3**	**16.0**	**10.0**	**15.3**	**10.0**	**15.7**

It is evident that all mixtures exhibited a similarly high level of water impermeability.

Resistance against freezing in the presence of de-icing salt

Mass loss for each mixture as well as damage depth after 25 cycles of simultaneous exposure to frost and 3 % aqueous solution of NaCl is presented in Table 6.

Table 6. Mass loss and damage depth for SCC mixtures

	Mass loss (mg/mm^2)	*Damage depth (mm)*
E	0.12	0.6
FA-10	0.09	0.4
FA-20	0.10	0.4
FA-50	0.10	0.5

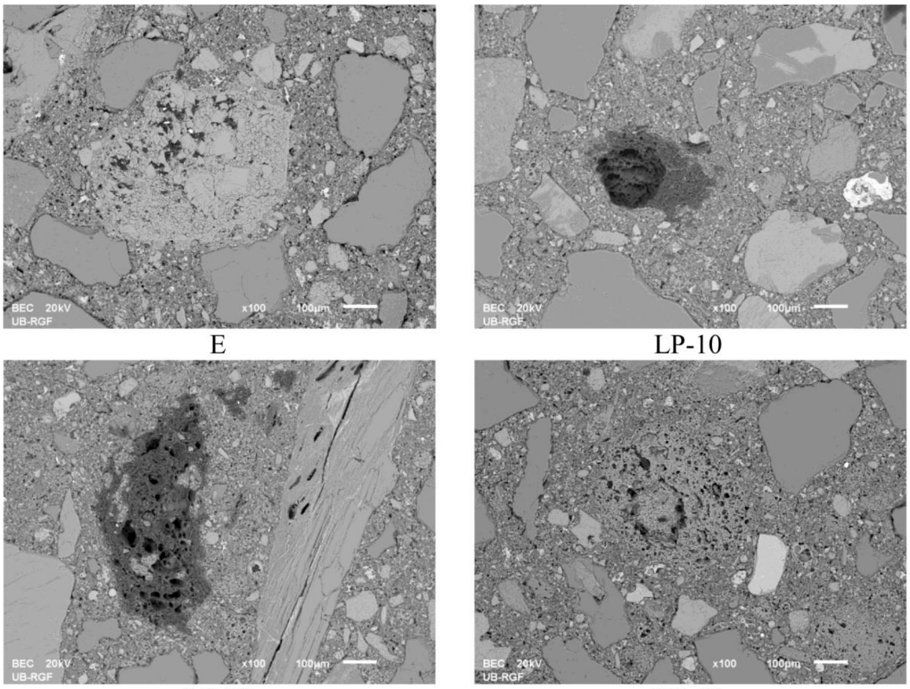
Frost resistance testing has shown some advantages concerning fly ash addition to SCC mixtures and also its contribution to improving durability in the salt environment.

The mixtures with FA after treatment underwent a certain mass loss, but lower than E. A similar effect is observed regarding the damage depth, with optimum effects for FA-10.

SEM analysis

Representative samples of all SCCs were prepared for the structure characterization by the use of SEM. Basicaly, the performed analysis had qualitative character.

Based on the SEM analysis, it can be observed that the homogeneity was achieved in all SCC mixtures, while the porosity was visually similar (Figure 5). Furthermore, although the contact of aggregate grains and the cement matrix is generally good, it should be noticed that this contact is better for certain grains (sandstone, limestone) than for others (quartzite), owing to the surface character and compactness of the aggregate grains themselves.



E LP-10

LP-20 LP-50

Figure 5. SEM microphotographs of SCC series

4 Conclusion

In compliance with the trends of promoting sustainable development in the field of construction, the possibility of using industrial byproduct- FA for partial substitution of the mineral filler-limestone in SCC was investigated. SCCs with the addition of FA were examined and compared with the reference mixture with limestone in order to optimize the properties and composition of these concretes.

All SCCs with FA met the standards concerning fresh state properties except the viscosity of FA-50.

Regarding hardened SCC properties, positive effect of FA is evident. Lower amounts of FA led to compressive strength increase, which was especially pronounced for FA-20 and at older ages. Flexural strength values were similar. The SCCs with FA exhibited better resistance against freezing in the presence of de-icing salt and higher values of static elasticity modulus than the reference mixture. All mixtures have similarly high impermeability and hence compactness, which was proved by SEM. Based on the SEM analysis, it can be concluded that homogeneity was achieved in all mixtures, while the porosity was visually similar. High degree of compactness of SCCs with FA is an an indicator of good durability.

This study showed that it is possible to obtain a high-performance SCC using FA and that its optimal content is 20 % with respect to the total filler mass.

It is of great importance for the construction industry and should be continued towards the practical application of the designed SCC mixtures. This application may include testing of structural elements (beams and columns) in laboratory conditions, as well as the design of construction systems in the field and their monitoring as part of full-scale feasibility studies.

Research can be widened to designing new mixtures with a higher proportion of FA as a mineral additive, which would raise the valorization of this industrial by-product in Serbia to a larger scale.

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