Science of Sintering, **52** (2020) 307-327

---

doi:https://doi.org/10.2298/SOS2003307S

UDK: 666.972; 666.952; 676.017.2

Valorization of Fly Ash from a Thermal Power Plant for Producing High-Performance Self-Compacting Concrete

Aleksandar Savić[1], Milica Vlahović[2*)], Sanja Martinović[2], Nataša Đorđević[3], Gordana Broćeta[4], Tatjana Volkov Husović[5]
[1]University of Belgrade, Faculty of Civil Engineering, King Alexander Blvd. 73, Belgrade, Serbia
[2]University of Belgrade, Institute of Chemistry, Technology and Metallurgy, Karnegijeva 4, Belgrade, Serbia
[3]Institute for Technology of Nuclear and Other Mineral Raw Materials, Franchet d'Esperey Blvd. 86, Belgrade, Serbia
[4]University of Banja Luka, Faculty of Architecture, Civil Engineering and Geodesy, Vojvode Stepe Stepanovica 77/3, Republic of Srpska
[5]University of Belgrade, Faculty of Technology and Metallurgy, Karnegijeva 4, Belgrade, Serbia

---

Abstract:
This study analyzes the feasibility of valorizing industrial by-product, fly ash from a thermal power plant as a partial replacement of mineral filler-limestone for the production of self-compacting concrete (SCC). Three types of SCC mixtures with different portions of fly ash and the reference mixture with limestone were designed. The synthesized SCCs in the fresh state were examined for density, entrained air content, flowability (Slump flow, Slump flow time (t500), V-funnel time (tv)), passing ability (L-box), and segregation resistance, while hardened state testing included: density, compressive and flexural strength, static modulus of elasticity, water permeability, resistance against freezing in the presence of de-icing salt, and SEM analysis. Taking into account the obtained results it can be concluded that the addition of fly ash has a positive impact on the concrete properties and that the optimal content of fly ash is 20 % with respect to the total filler mass.

Keywords: *Self-compacting concrete (SCC); Fly ash; Mixture design; Mechanical strength; Durability.*

---

1. Introduction

The development of the chemical industry, primarily polycarboxylate-type admixtures for concrete, enabled the wider application of self-compacting concrete (SCC). SCC is concrete that can, due to its own weight, without installing and vibrating means, completely fill the formwork, thus wrapping reinforcement bars and filling all spaces between them and in the formwork, at the same time with achieving the highest degree of compactness, which is important for its properties in hardened state and durability [1]. Generally, although distinctively different from the normally compacted concrete (NVC) in fresh state, SCC is characterized by quite similar properties as NVC in hardened state. SCC

[*)] **Corresponding author:** mvlahovic@tmf.bg.ac.rs

has been identified as a revolutionary discovery in concrete technology by most experts in the field [2].

At the same time, the approach to the implementation of the principles of sustainable development and ecology has been intensively promoted in the construction industry. Scientists are involved in investigating the properties of various wastes to manufacture new materials with the aim to reduce disposal problems and the production cost. Consequently, the use of fly ash represents one of the areas where multiple positive effects can be achieved, including the reduction of accumulated material at landfills and the improvement of concrete properties. Fly ash is defined as a fine, loose material that is collected in the electro filters of the chimneys in thermal power plants and whose quantities reach up to several tons per minute. The particle size of fly ash usually ranges from 1 to 150 µm [3-5].

The dominant sources for electric power in Serbia are thermal power plants. Based on available data from theElectric Power Industry of the Republic of Serbia, there are 11 thermal power plants in Serbia. All of them use coal, mainly lignite in the electricity production process and generate about 6 million tonnes of fly ash per year, which is stored in an old manner and covers an area of about 1,800 ha. It is estimated that landfills in Serbia contain over 200 million tonnes of fly ash from thermal power plants [6-8].

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 suitable for use in concrete and mortar [9-14]. Therefore, fly ash has been used for decades as an additive in commercial types of cement for the production of concrete and mortar.

The inhomogeneous composition of fly ash is one of the largest disadvantages that reduce its use [3].

In terms of the fineness (particle size) of mineral admixtures, a fraction below 0.125 mm is generally considered acceptable, with more than 70 % of the material preferably passing through a 0.063 mm mesh. Especially ground fillers have the advantage of being used in SCC because of their improved properties and continuous quality when producing concrete [15].

The use of fine fly ash particles in concrete leads to the effect of the aggregate fluidity, as well as to an increase in the solid to liquid volume 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 fly ash particles, provided that they are finer than the cement particles, which usually is the case, research has shown that the addition of 10 mass.% of fly ash in relation to the cement mass reduces the water requirement by 3-4 % [16].

In the case of partial replacement of sand, the fly ash content of about 8% in relation to the volume of sand improves both workability and slump, at the same water/ cement factor [16]. However, with a higher content of particles above 0.045 mm, as well as with an increase in the content of unburned coal particles (loss of ignition over 1 %), the need for water increases. According to some research, segregation resistance is the highest for SCC with 80 % of fly ash [15, 17].

The effect of partial replacement of fine aggregate (sand) with different mass percentages (10 %, 20 %, 30 %, 40 %, 50 %) of fly ash (class F) on the strength of the NVC was investigated in a study [18]. The compressive, flexural and tensile strength of those NVCs was higher than that of ordinary concrete at all ages, with this effect being more pronounced for older concrete ages. The highest values of compressive and tensile strength were achieved in concrete with 50 % of fly ash at all ages. The results of numerous studies indicate that fly ash slows down the hardening process and reduces the compressive strength of NVC at early ages [16].

A number of NVC studies have shown that the addition of fly ash to cement has a similar effect on the elasticity modulus of concrete as on strength. In general, the elasticity modulus of concrete with the addition of fly ash is lower at early ages and slightly higher at later ages [16].

In a study [19], it was reported that pozzolanic additives (fly ash and granulated blast furnace slag) gave the best results in terms of durability of SCC. A 10 to 50 μm thick region next to the coarse aggregate particles in concrete is known as the transition zone. The pozzolanic reaction decreases the thickness and porosity of the transition zone, thus strengthening the bond between the paste and the aggregate [20, 21]. Mechanical properties of structural materials are strongly dependent on microstructure of pores size and shape in a way that less porosity leads to higher material strength and stiffness [22].

However, based on water permeability tests, with the increasing mineral additives amount, the depth of penetration of water under pressure was also increasing. On the other hand, research [23] concluded that fly ash is suitable for use in SCC because it improves mechanical properties and potential durability.

Concerning the durability of concrete, the use of fly ash (classes C and F) leads to increased resistance to sulfates and potentially corrosive salts that can damage the reinforcement with cracks and spalling. The reaction of fly ash with calcium hydroxide released during cement hydration has been found to result in the formation of additional calcium aluminate silicate hydrates and is accompanied by a reduction in concrete permeability [3].

Based on the results of compressive and tensile strength tests, as well as the durability assessment (salt action on a concrete surface, carbonation and chloride resistance) of hardened SCCs in which 15 to 35 % of cement was replaced by fly ash, it was concluded that concrete with 35% of fly ash exhibited the optimal behavior [24].

The aim of this study is to investigate the possibilityof producing high-performance SCC using domestic fly ash, originated from Thermal Power Plant "Kolubara A", Serbia as a replacement for certain portions of mineral filler, limestone. It is intended to utilize fly ash in the so-called "as is" state, i.e. without any prior processing. The basic assumption is that small amounts of fly ash lead to the improvement of concrete properties in the hardened state without significant negative effects on the properties of SCC mixtures in the fresh state. The fresh, hardened and microstructural properties of SCC depending on the proportion of limestone replaced by fly ash will be compared. Based on the results obtained, the optimal amount of fly ash will be recommended.

2. Materials and Experimental Procedures

2.1 Materials

2.1.1 Aggregate

One type of aggregate of natural origin, taken from the river Danube in the region, with a predominance of rounded particles, suitable for concrete requiring high workability and fluency, was used in this study.

Thus, aggregate of various sizes, specifically, 0 to 4 mm (fraction I- fine), 4 to 8 mm (fraction II- coarse) and 8 to 16 mm (fraction III- coarse) was used.

The particle size distribution of the fractions and of the aggregate mixture determined by the standard method [25] is provided in Figure 1.

Figure 1.

The contents of coarse grains (> 4 mm) in fractions I, II, and III were 1.96 %, 5.81 %, and 0 %, respectively.

The contents of fine particles, determined according to the standard procedure [27], infractions 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.

The main physico-mechanical and chemical properties of used aggregate, determined according to the standards [28-32] are given in Table I.

Tab. I Physico-mechanical and chemical properties of used aggregate.

Property	**Size (mm)**		
	0-4	4-8	8-16
Real density of aggregate grains (kg/m^3)	2640	2641	2642
Bulk dry loose density (kg/m^3)	1667	1519	1493
Bulk dry compacted density (kg/m^3)	1788	1621	1599
Water absorption (%)	1.0	0.8	0.7
Total sulfur as SO_3(%)	0	0	0
Chloride ion(%)	0	0	0

The used aggregate meets the quality requirements defined by the standards [33, 34] for the use of concrete in civil engineering structures.

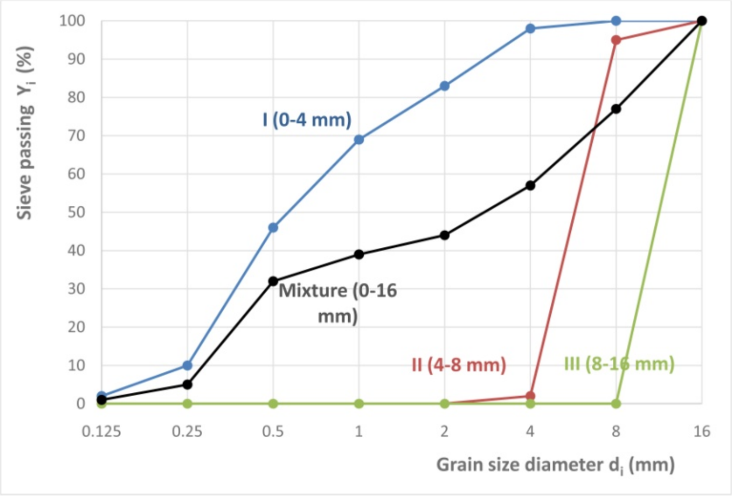


Fig. 1. Particle size distribution of aggregate [26].

2.1.2 Cement

A commercial type I Portland cement (*CEM I 42.5R*, *Lafarge*, *Serbia*) was used as a binder.

Analysis of the chemical composition of this cement was performed by the standardized procedure [35] and the results are shown in Table II.

Tab. II Chemical composition of cement.

Component/ Oxide	CaO	SiO_2	MgO	Al_2O_3	Fe_2O_3	K_2O	Na_2O	TiO_2	SO_3
Content (% mass)	61.64	21.21	2.22	4.81	2.13	1.11	0.33	0.18	6.37

The physico-mechanical properties of cement were determined by the standardized procedures [36-38]; the results are provided in Table III.

Tab. III Physico-mechanical properties of cement.

Property	Value
Sieve 0.09 mm residue (%)	0.5
True density (kg/m^3)	3040
Loose density (kg/m^3)	890
Specific area- Blaine (cm^2/g)	4240
Standard consistency (%)	27.8

2.1.3 Limestone

Natural limestone (*Granit Pescar, Ljig, Serbia*), which had a medium size of 250 μm was employed as mineral filler. The results of analysis of the chemical composition of this limestone, provided by the producer, are given in Table IV.

Tab. IV Chemical composition of limestone.

Component / Oxide	CaO	SiO_2	MgO	Al_2O_3	Fe_2O_3	K_2O	MnO	SO_2	P_2O_5	LOI
Content (% mass)	54.86	0.21	1.10	0.5	0.09	0.05	0.005	Traces	0.5	43.64

Physico-mechanical testing of limestone was performed using standard procedures [37,39-44] on natural stone- limestone, prior to grounding into limestone powder. The obtained physico-mechanical properties and shown in Table V.

Tab. V Physico-mechanical properties of limestone.

Property	Value
Density with pores and vacancies (kg/m^3)	2700
Density without pores and vacancies (kg/m^3)	2720
Porosity (%)	0.7
Water absorption (%)	0.12
Specific surface area (cm^2/g)	3800
Compressive strength in dry state (MPa)	143
Compressive strength in saturated state (MPa)	137
Flexural strength (MPa)	21
Abrasion resistance (cm^3/cm^2)	18/50
Frost resistance	Sound

2.1.4 Fly ash

Fly ash was used in its original form, without any prior processing, for partial replacement of limestone filer.

Fly ash, with accompanying results of chemical analysis (Table VI) and particle size distribution (Table VII) was provided from Thermal Power Plant "Kolubara A", Veliki Crljeni, Serbia.

Tab. VI Chemical composition of fly ash.

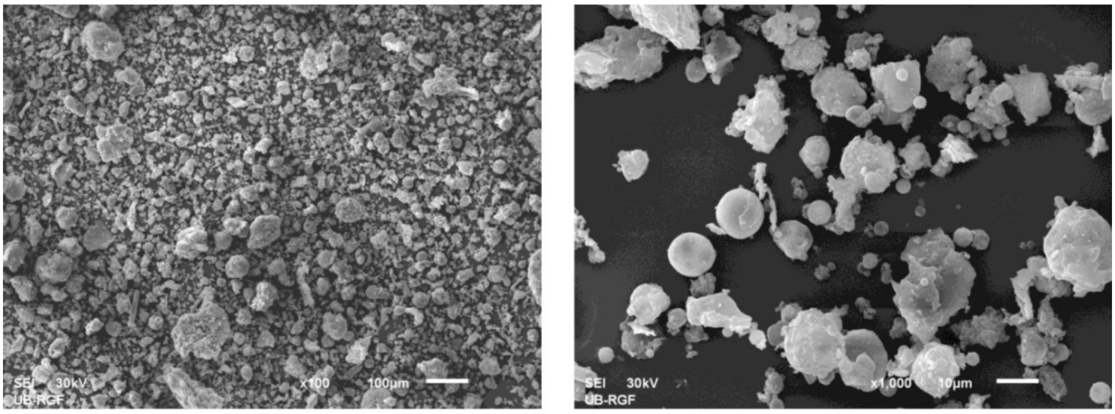
Component	**Content (% mass)**
Mineralogical composition	
SiO_2	58.60
Al_2O_3	21.92
CaO	6.12
Fe_2O_3	5.97
MgO	1.77
K_2O	1.50
Na_2O	0.37
TiO_2	0.49
Cations/Anions in traces	
Pb	0.017
Cd	0.0005
Zu	0.0092
Cu	0.01
Cr	0.014
Ni	0.013
Mn	0.036
PO_4^{3-}	0.053
SO_4^{2-}	<0.02
Cl^-	<0.035
LOI (% mass)	3.09

Tab. VII Particle size distribution of fly ash.

Size (mm)	**Sieve passing Y (%)**
0.9	100.0
0.63	98.6
0.4	97.3
0.3	95.6
0.2	90.9
0.1	68.6
0.075	63.6
0.063	51.0
0.037	38.0
0.01	12.0
0.001	0.0

Density of fly ash in the loose and compacted state was 690 kg/m^3 and 910 kg/m^3, respectively. The specific gravity, determined by pycnometer method, was 2190 kg/m^3.

Microstructure of fly ash was performed by SEM (scanning electron microscope), type JEOL JSM-5800 and the obtained microphotographs are given in Figure 2.



(a) (b)

Fig. 2. SEM microphotographs of fly ash taken at magnification of:
a) 100 x, b) 1000 x.

As seen in Figure 2, fly ash particles are generally spherical in shape. Since only organic matter is lost during coal combustion, the inorganic residue remains in the ash. According to given microphotographs, especially of higher magnification, a large number of irregularly shaped particles is evidently present. These particles include incombustible inorganic matter present in coal that during the combustion is partly transformed into a glassy, amorphous substance and various impurities (sand, clay, etc.).

2.1.5 Superplasticizer

A superplasticizer admixture based on polycarboxylate (Glenium Sky 690, *BASF Construction Chemicals, Italy*) was used for all tested concretes.

This admixture enables self-compacting capacity and improves flowability of concrete.

Physico-mechanical and chemical properties of superplasticizer, provided by the producer, are given in Table VIII.

Tab. VIII Physico-mechanical and chemical properties of superplasticizer.

Property	**Value**
Density at 20°C (kg/dm^3)	1.06
Viscosity at 20°C (mPa·s)	30-200
pH	5-8
Solid particles content (%)	26
Chloride ion content (%)	0.01
Alkali content (as Na_2O equivalent) (%)	0.26

2.2 Mixture design and manufacture of SCC

Four mixtures of SCC were designed for this investigation.
The compositions of four SCC mixtures are shown in Table IX.

Tab. IX Design of SCC mixtures.

Series/ Compound	**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
Powder component P=C+LP+FA	600	600	600	600
Water- to- cement ratio W/C	0.482	0.482	0.482	0.482

All mixtures had the same total aggregate content (1700 kg/m^3) with equal portions of aggregates fractions, the same cement content (380 kg/m^3), the same total mineral filer content (220 kg/m^3) and, consequently the same total powder component content (600 kg/m^3).

The E denotes the SCC having limestone as filer, which was used as reference series.

Three mixtures of SCC were made with different replacement percentages in mass of mineral filler- limestone by fly ash.

The FA-10 denotes the SCC with 10 % mass of fly ash in regard to the limestone amount.

The FA-20 denotes the SCC with 20 % mass of fly ash in regard to the limestone amount.

The FA-50 denotes the SCC with 50 % mass of fly ash in regard to the limestone amount and with increased content of superplasticizer required to provide workability for chosen content of limestone and fly ash.

All mixtures had water- to- cement ratio W/C set at 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 coarse and fine aggregates were mixed for one minute in a concrete mixer, then the filer and cement were added and mixed for 30 s. Afterwards, water with the super plasticizer admixture were added and mixing was 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 using cube and prism molds. The specimens were removed from these molds after 24 h, and then they were cured in water until tests on hardened concrete were done. Cube specimens (10 cm), prisms (12x12x36 cm), cylinders (diameter of 15 cm, height of 30 cm) and plates (50x50x8 cm) were prepared for further testing.

Each of the data obtained from testing corresponds to an average of at least three measurements.

2.3 Characterization of the SCC

Fresh state

The characterization of the fresh state of the produced SCC was performed by determination of the density, entrained air content, flow ability (Slump flow, Slump flow time

(t_{500}), V-funnel time (t_v)), passing ability (L-box), and segregation resistance according to the standard procedures [45-49].

Density and air content were determined following the standard procedures for fresh concrete [45, 46].

The Slump flow test was done according to the standard procedure [47] using the Abrams cone to assess the flowability, in other words the ability of SCC to deform under the action of its own weight without restriction. It also allows visual estimation of the segregation possibility of SCC.

Viscosity of SCC mixtures, as a flowability component, was estimated by measuring the flowing time $\mathbf{t_{500}}$ during the slump-flow test and the efflux time $\mathbf{t_v}$ during the V-funnel test which was realized according to the standard [48].

The L-box test determines the passing ability (PA) of SCC to flow through a narrow opening between bars without segregation or blockage.

Segregation resistance (SR) was determined according to the standard sieve segregation test [49].

Hardened state

Investigations on the hardened SCC included: density, compressive and flexural strength, static modulus of elasticity, water permeability, resistance against freezing in the presence of de-icing salt, and SEM analysis.

The SCC specimens were kept in water for 180 days. Periodically they were removed from water to perform measurements according to standardized procedures.

Density of the hardened concrete was recorded according to the standard [50] on three prisms 12x12x36 cm for every mixture, up to the age of 180 days.

Compressive strength was tested on five cube specimens at each age (3, 7, 14, 21, 28, 63, 90 and 180 days), according to the standard procedure [51].

Three point bending (flexural strength) test was performed on five prisms specimens 12x12x36 cm at the age of 28 days, according to the standard procedure [52].

Modulus of elasticity was tested on three cylinder specimens with diameter of 15 cm and height of 30 cm for each series, at the ages of 28 and 180 days, according to the standard [53].

According to the standard test procedure [54], but at the older age of 63 days, specimens were exposed to the water under pressure. After the treatment of specimens, maximal and average depths of water penetration were measured for each specimen.

Resistance of SCC mixtures against freezing in the presence of de-icing salt, 3 % aqueous solution of NaCl, was conducted according to the relevant standard [55]. The specimens at the age of 28 days were specially prepared with the bottomless container on the top of each specimen. This enabled constant presence of the salt at the concrete top surface.

For the microstructure characterization of the studied SCC series, statistically representative specimens of all mixtures were prepared and tested using the SEM (scanning electron microscope), type JEOL JSM-5800.

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

3. Results and Discussion

3.1 Fresh SCC tests

Characteristic rheological tests were performed on SCC according to the standard procedures. Each of the results presented in Table X corresponds to an average of three specimens.

Tab. X Fresh state properties of the self- compacting concretes.

Property	**Series**			
	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

As can be seen in Table X, there are no significant differences between density of the reference E mixture and those of SCC mixtures with fly ash. A slight density decrease with the raising content of fly ash is also noticed. This can be attributed to the higher density of limestone in comparison with the density of fly ash.

The content of entrained air did not significantly change for SCC mixtures with addition of lower percentage of fly ash (10 and 20 %) compared to the reference E mixture, but 50 % of fly ash led to air content increase.

It is obvious that the slump flow diameter of the reference mixture E is the highest, which indicates that the addition of fly ash lowers the flow ability of SCC mixtures. This can be attributed to the high content of unburned coal particles in used fly ash (loss of ignition value was 3.09 % mass) which required increased amount of water. A range of values for an adequate slump flow is 550 mm - 850 mm [15]. All mixtures under study were adjusted following the recommendations of EFNARC, because the slump test of SCC mixtures was in the range from 663.8 to 761.2 mm. Precisely, all mixtures belong to the class SF2 except the mixture E, which belongs to the class SF3. According to EFNARC, the class SF2 is suitable for many normal applications (e.g. walls, columns), while the class SF3 is used for vertical applications in very congested structures, structures with complex shapes, or for filling under formwork.

Regarding the slump flow time to reach a diameter of 500 mm (t_{500}), the lowest value is noticed for the reference E mixture. Also, it is observed that the incorporation of fly ash affects the slump flow time of the mixtures, proportionally to the percentage of replacement in a way that higher content of fly ash prolongs the slump flow time. This is especially pronounced when replacement of limestone by fly ash is 20 %. Such a behavior is due to the fact that a greater quantity of fine particles requires more water and consequently reduces viscosity/flow ability. These effects are expected since high levels of fly ash may produce a paste fraction which is so cohesive that it can be resistant to flow [15]. Also, the presence of unburnt particles contributes to the same effects. The value of t_{500} for the FA-50 mixture would have been surely substantially higher, if a quantity of super plasticizer hadn't been increased to improve the self-compacting capacity of that particular mixture.

The time in V-funnel should not exceed 25 s according to the qualifications of EFNARC. The V-funnel time for the SCC mixtures with fly ash exhibited significant differences compared with the reference mixture E. The values of V-funnel time fell in the range of 9.73-27.21 s, indicating that this property was not satisfied only for the mixture FA-50. It is evident that 50 % of added fly ash affects negatively the fluidity and therefore workability of SCC.

Based on the obtained values of slump flow time and V- funnel time, mixtures E, FA-10 and FA-20 belong to the viscosity class VS2/VF2 with slump flow time above 2 s and V-funnel time in the range of 9-25. The mixture FA-50 does not fulfill viscosity requirements for SCC and therefore cannot be categorized [15].

According to the defined criteria in this standard for the opening with three smooth steel bars of 12±0.2 mm in the L-box test, all series belong to the class PA2 (H2/H1> 0.8) since they have the blocking ratios in the range of 0.92-0.97. It can be concluded that the passing ability values for all tested SCC mixtures indicate that there was not any tendency of blockage and that sufficient resistance to segregation around congested reinforcement area was achieved. Generally, there are no significant changes in passing ability between the examined mixtures, indicating their similar behavior. Slight reduction of the passing ability of SCC with fly ash compared with the reference mixture E indicates their slight workability decline. Having in mind the same aggregate composition in all mixtures, the aggregate and the amount of paste, which was also constant for all mixtures, were the dominant factors, enabling excellent blocking ratio values of the studied SCC mixtures.

Segregation resistance (SR), expressed as a percentage of segregated particles, is important property of SCC since it greatly affects the in-situ properties of hardened concrete. The segregation factor of all tested SCC mixtures ranged from 1.5 to 3.5 %, thus classifying them to the segregation resistance class SR2 ≤ 15 % according to the recommendations of EFNARC. By comparing the segregation factor of the reference SCC mixture E with those of the mixtures containing fly ash, it is observed that with the increasing percentage of fly ash, the segregation factor decreases, which means that the segregation resistance improves.

3.2 Hardened SCC tests

Results of the tests conducted on hardened SCC are shown in Figures 3-8 and Tables XI-XIV.

3.2.1 Density

Due to the fact that the prisms were kept in water all the time, water was absorbed through the fine capillary network in the specimens, which resulted in the apparent increase of hardened concrete density.

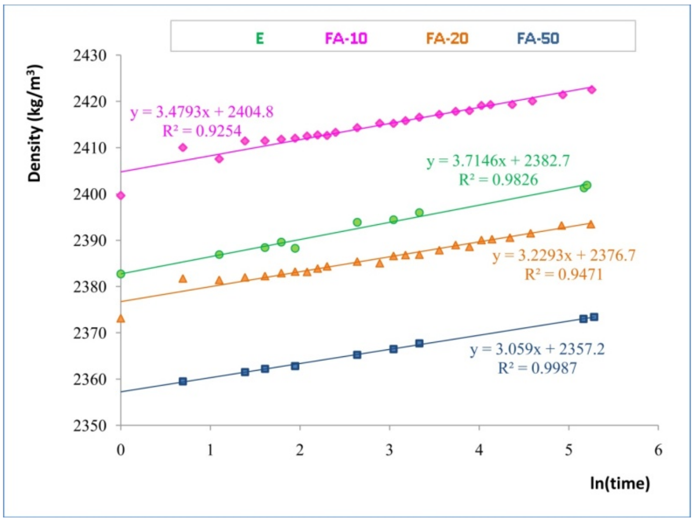


Fig. 3. Density change of sharpened SCCs cured in water as a function of time.

Density values of tested hardened SCC mixtures up to the age of 180 days are in the range of 2350-2420 kg/m^3.

Figure 3 shows the increasing trend of density change as a function of time, more precisely the logarithm of time for the examined SCCs. Correlations with high values of correlation coefficients were obtained by linear regression analysis.

The lowest values for the density of hardened concrete at all ages were obtained for the FA-50 mixture and the highest for the FA-10. Although not expected, the density of FA-10 mixture is higher than that of E. However, these values are not real but can be attributed to the experimental errors in determining the density. Namely, the volumes of all the specimens were considered to be the same and equal to the volume of the mold.

When the slope of the line obtained by the regression analysis method is taken as a parameter, it can be observed that the mixture E has the greatest slope, and thus the fastest water absorption of all tested mixtures. This is in accordance with the fact that the addition of fly ash improves the structure of the concrete and thus the water absorption is less, which corresponds to the attitude given in the literature [56]. Comparing only mixtures containing fly ash, FA-10 has the highest slope, followed by the FA-20 and finally the FA-50.

3.2.2 Compressive strength

The compressive strength of hardened concrete is a basic property of concrete and is often used as a good indicator of its quality [57].

The testing of compressive strength provided the results that can be seen in Figure 4.

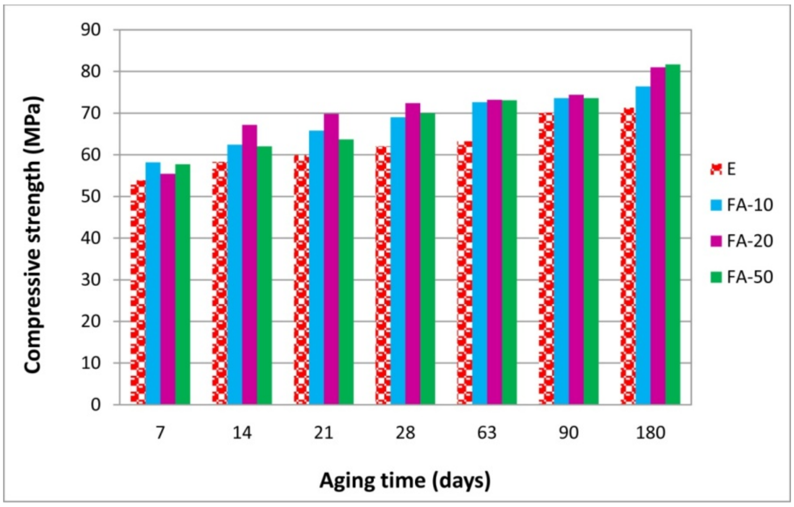


Fig. 4. Compressive strength of SCC mixtures during aging.

It can be observed that the increase in fly ash amount leads to compressive strength decrease at early concrete ages and to compressive strength increase at older concrete ages. The compressive strength enhancement with an increase in fly ash amount in relation to the total filler mass in the SCC mixture can be attributed to the pozzolanic effect, which is more pronounced when larger quantities of fly ash are applied and at older concrete ages. Increasing the fly ash content to 50 % in relation to the total filler mass leads to opposite effects, that is, to strength enhancement at some ages and to strength reduction at other ages. This can be explained by the fact that, in addition to the afore mentioned positive pozzolanic effect, there is also a negative influence of the presence of mechanically weaker fly ash grains (especially coarse grains of inhomogeneous composition).However, it should be pointed out that the SCC mixture LP-50 showed higher compressive 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 fly ash is evident.

These results show that the incorporation of fly ash in the self-compacting concrete causes an increase in compressive strength at all ages depending on the percentage of limestone that was replaced by fly ash compared with the compressive strength of the reference mixture E. This is in accordance with the results of a study conducted by Siddique in 2003 [18] where sand was partially replaced by fly ash.

At the age of 28 days mixtures FA-10, FA-20 and FA-50 reached significantly higher strengths compared with E; precisely, higher for 11.3 %, 16.8 % and 12.9 %, respectively. The strength increase of 16.8 % for FA-20 in relation to E at 28 days of age is at the same time the largest difference observed among all mixtures and for all ages.

Evidently, based on the analysis performed, a positive effect of the use of fly ash in SCC mixtures was observed.

For concrete with fly ash, the rate of compression strength increment depends on a number of factors. Since fly ash, with the total content of oxides $SiO_2 + Al_2O_3 + Fe_2O_3$ over 80 % (thus belonging to class F) was used, the effect of a later increase in the strength of concrete (but also a slower strength development at early ages) can be expected due to its pozzolanic reaction [58].

By comparing the obtained values with the theoretical ones from the relationship (Eq. 1) given by Sukumar et al. (2008) for early ages of SCC with large quantities of fly ash [59]:

$$f_{ct} = f_{c28} \cdot \frac{t}{4.2 + 0.85 \cdot t} \qquad (1)$$

where f_{ct} and $f_{c28}$are compressive strength values after *t days* and *28 days*, a good correlation was obtained.

Figure 5 shows the increment in compressive strength of SCC mixtures during the aging time, whereby the natural logarithm of time is shown on the abscissa. A family of curves, presenting correlation dependence in the form of logarithmic function, with high correlation coefficient, was obtained by regression analysis for each of the SCC mixtures.

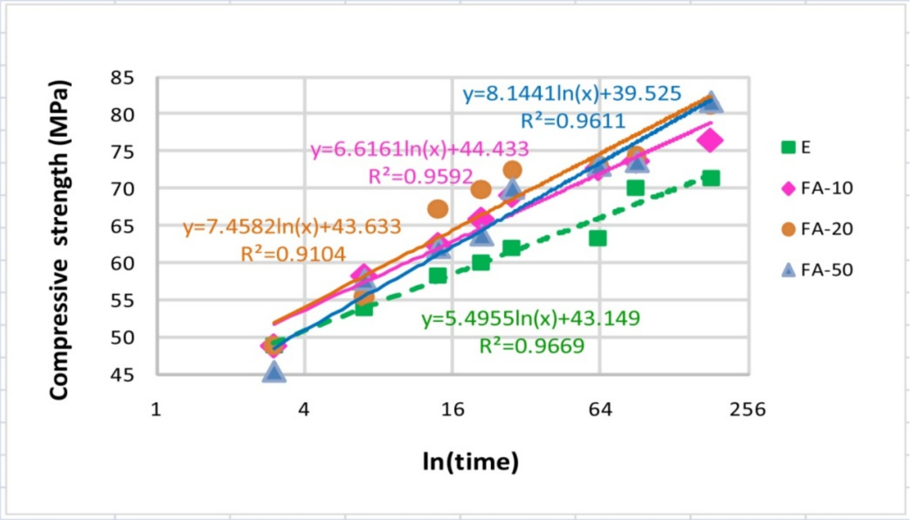


Fig. 5. Compressive strength increment of SCC mixtures during the aging time.

Regarding the relationship of compressive strength values of SCC mixtures at different ages, it can be generally observed that the reference mixture E represents the lower boundary of the curve family, while the FA-20 mixture presents the upper boundary line of the formed functional dependency family. The functional regressions derived for mixtures

FA-10 and FA-50, from lower to higher, are in the area of the diagram between the two mentioned boundaries.

If the compressive strength increment of the studied SCC mixtures is observed in terms of the cement stone hardening, where the chemical reactions of cement hydration and the pozzolanic reaction are involved, then the rate of strength increment, and thus the rates of the corresponding chemical reactions, can be interpreted by the slopes of the created lines. Namely, directions of all relationships compressive strength- time are increasing (lines go up from left to right), which means that the slopes are positive. The line of reference E mixture has the lowest slope value which corresponds to the slowest rate of strength increment.

The mixtures containing fly ash show an increment in slope with an increase in fly ash content, which corresponds to the contribution of the pozzolanic reaction to the compressive strength enhancement. According to the analysis applied, and based on the graphical representation, it can be expected that at some moment, due to the pozzolanic reaction, there will be a further significant increase in compressive strength of SCC mixtures with fly ash, and mostly for FA-50.

In spite of the certain presence of larger, partially burnt and unburned coal particles, this application of fly ash in its original, delivered state resulted in a positive effect on the compressive strength.

3.2.3 Flexural strength

The results of flexural strength tests for SCC mixtures at the age of 28 days are given in Table XI.

Tab. XI Flexural strength of SCC mixtures at the age of 28 days.

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

As can be seen, the FA-10 mixture had a 1 % lower flexural strength compared to E. Concretes with higher fly ash content, FA-20 and FA-50, showed a slight increase in flexural strength compared to E - 12 % and 3 %, respectively. Based on the above, it can be concluded that, regarding flexural strength, the optimum content of fly ash was 20 % of the total filler mass.

3.2.4 Static modulus of elasticity

The results of static elasticity modulus for SCC mixtures at the ages of 28 and 180 daysare shown in Table XII.

Tab. XII Static modulus of elasticity Es [GPa] of SCC mixtures 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	41.6	41.9	39.4

All SCC mixtures with fly ash, FA-10, FA-20 and FA-50, at 28 days of age showed higher values of static modulus of elasticity than the reference E mixture- 4.4 %, 4.5 % and

9.4 %, respectively. Similarly, at 180 days of age, all SCC mixtures with fly ash, FA-10, FA-20 and FA-50, showed higher values of static modulus of elasticity than the reference mixture E- 8.1 %, 8.8 % and 2.3 %, respectively. This is in agreement with the research on NVC published by Siddique [16, 18], according to which the addition of fly ash led to an increase in the value of static elasticity modulus.On the basis of the above disscussed results, and the evident elasticity modulus drop for the FA-50 mixture at the age of 180 days, it can be concluded that lower percentage of fly ash replacement provides better elasticity at older ages.

3.2.5 Water permeability test

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 XIII.

Tab. XIII Depths h [mm] of the water penetration.

Series	**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 can be stated that all SCC mixtures exhibited a similarly high level of water impermeability. This contradicts the statement that the depth of water penetration increases with the increasing fly ash content in self-compacting concrete [19], although there are studies that have reported results consistent with those shown here [23].

3.2.6 Resistance against freezing in the presence of de-icing salt

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

Tab. XIV Mass loss and damage depth for SCC mixtures.

SCC mixture	**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

Generally, 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 fly ash after treatment underwent a certain mass loss, but lower than the E mixture.

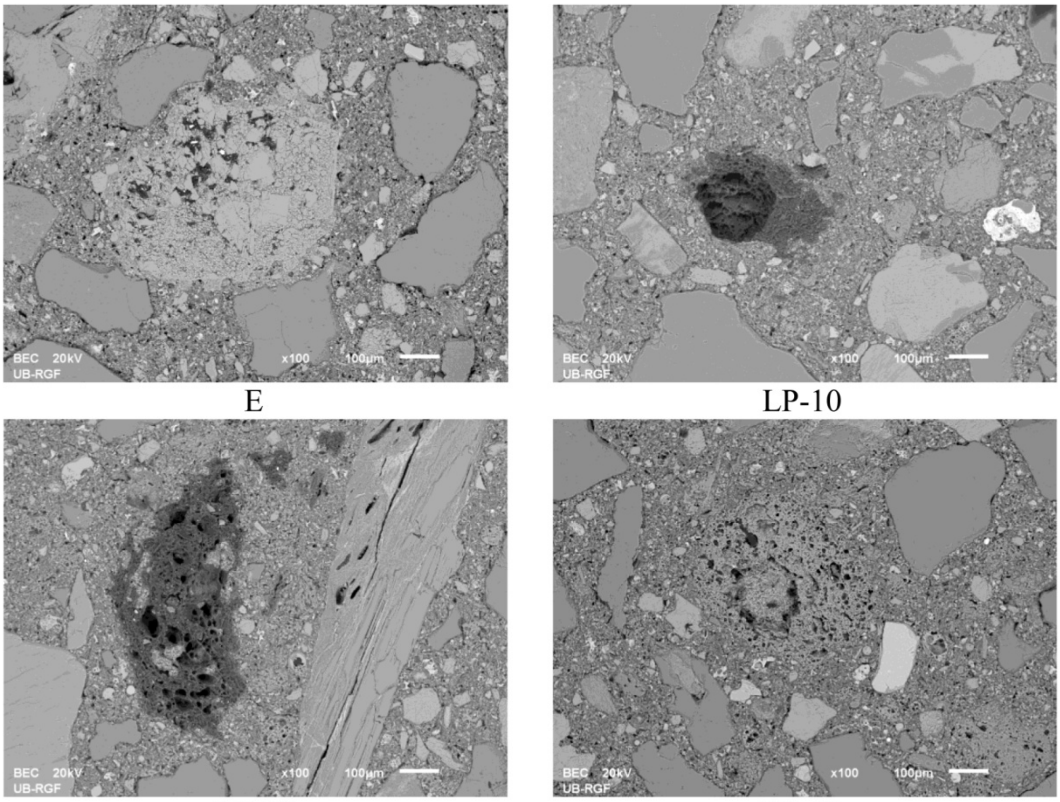
A similar effect is observed regarding the damage depth, with optimum effects for FA-10 concrete. The results obtained are in agreement with the research of Sidique et al. [24].

3.2.7 SEM analysis

Representative specimens of all SCC mixtures 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 6).

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

Fig. 6. SEM micrographs of SCC series.

The contact zone between the aggregate grains and the cement matrix, so-called interfacial transition zone (ITZ) is also characterized.

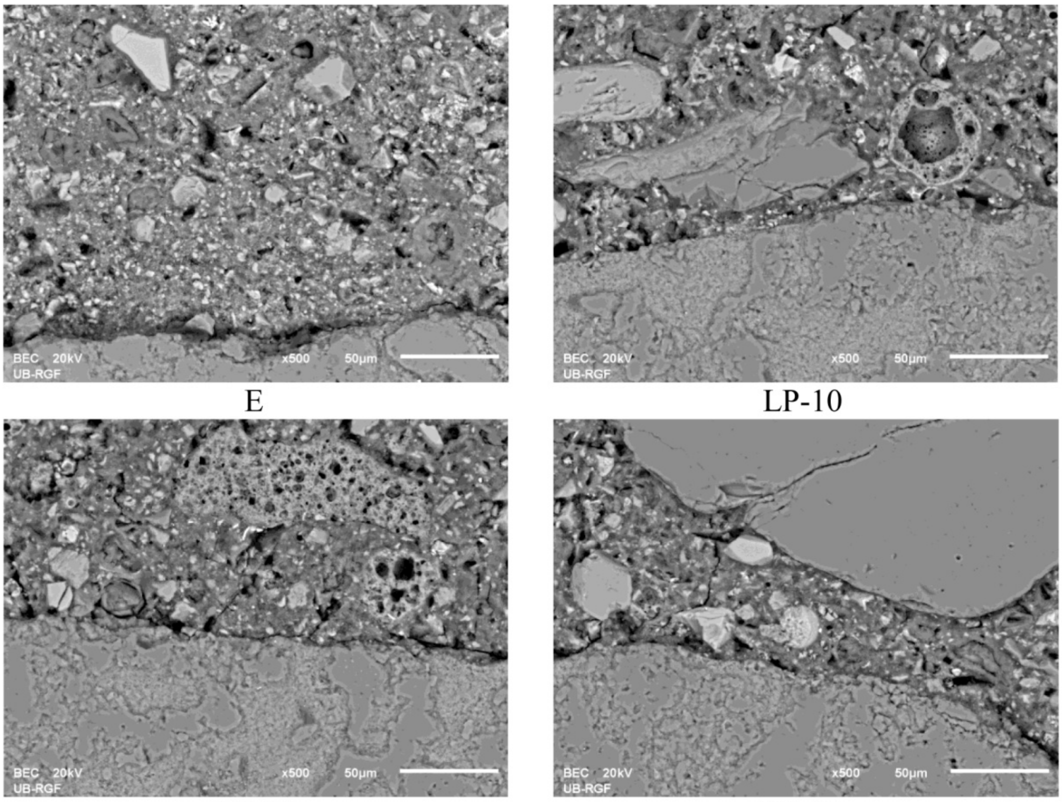
Representative interfacial transition zones of aggregate grains and cement matrices for all tested SCC mixtures are shown in Figure 7.

As can be seen from Figure 7, in all SCC series the interfacial transition zones are filled, which can be connected with the low water-to-cement ratio that led to the high compactness, as well as with the pozzolanic reaction that took place in the concrete matrix of SCC mixtures with fly ash.

Regarding the dimension of the interfacial transition zone between the aggregate grains and the matrix, it varies from 20 μm for smaller aggregate grains to 100 μm for coarser grains. It can also be observed that the representative interfacial transition zones at the contact with the coarse aggregate grain in SCC mixtures containing fly ash did not differ significantly from those in the reference mixture E, thus providing a high degree of compactness of all tested SCC series with fly ash.

Owing to the pozzolanic reaction in SCC series with fly ash the porosity and thickness of the interfacial transition zone are reduced which results in reinforcement of aggregate-matrix bond.

In addition, the smaller fly ash grains, which are characterized by a spherical shape, reacted with the matrix to a greater extent than the larger grains, irregular in shape and with more complex chemical composition.



E LP-10

LP-20 LP-50

Fig. 7. SEM microphotographs of representative interfacial transition zones between the aggregate grains and cement matrices for SCC mixtures.

4. Conclusion

In accordance with the contemporary trends of promoting sustainable development in the field of construction, the possibility of using industrial byproduct- fly ash for partial substitution of the mineral filler- limestone in SCC was investigated. SCC mixtures with the addition of fly ash were examined in the fresh and hardened state and compared with the reference mixture with limestone in order to optimize the properties and composition of these concretes.

Presented investigations of SCC mixtures with fly ash provide detailed insight into their behavior in terms of flowability and placeability of fresh concrete mixtures, passing ability (between reinforcement bars), segregation resistance, as well as physic-mechanical properties of hardened composite (compressive and flexural strength, elasticity modulus) and durability (water impermeability and simultaneous action of frost and de-icing salt).

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

Generally, it can be concluded that referring to hardened state properties of SCC mixtures, positive effect of fly ash is evident.Based on the compressive strength results, it is obvious that the addition of fly ash in the lower amounts leads to compressive strength rising, which is especially pronounced when the content of fly ash in the SCC mixture is 20 % of the total filler mass and at older ages. Similarly, the best flexural strength values are obtained for the same SCC mixture. The SCC mixtures with fly ash exhibited better resistance against freezing in the presence of de-icing salt and higher values of static elasticity modulus than the reference mixture. All investigated mixtures are of a similarly high degree of impermeability and hence compactness, which is proved by SEM analysis. Based on the SEM analysis, it can be concluded that homogeneity is achieved in all mixtures, while the porosity is visually similar. Furthermore, the dimensions of the interfacial transition zone at contact with the large aggregate grainsare not significantly different, that is, a high degree of compactness of all SCC mixtures with fly ash is accomplished which presents an indicator of high durability.

The results showed that it is possible to obtain a high-performance self-compacting concrete using fly ash and that the optimal content of fly ash is 20 % with respect to the total filler mass.

This research 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 fly ash originating from Thermal Power Plant "Kolubara A" as a mineral additive, which would raise the valorization of this industrial by-product in Serbia to a larger scale.

Acknowledgments

This work was financially supported by the Ministry of Education, Science and Technological Development of the Republic of Serbia (Grant Nos. 92166/3-19, 451-03-68/2020-14/200026, 451-03-68/2020-14/200023 and 451-03-68/2020-14/200135).

5. References

1. H. Okamura, Concr.Int., 19 (1997) 50.
2. J. A. Daczko, M. A. Kurtz, in: Proc.The Second International Symposium on Self-Compacting Concrete, Tokyo, Japan, 2001.
3. K. Wesche, Fly Ash in Concrete: Properties and performance (Rilem Report 7), Report of Technical Committee 67-FAB Use of Fly Ash in Buildings, Taylor & Francis e-Library, 2005.
4. [N. F. B. Pallan , K. A. Matori, M. Hashim , R. S. Azis, N. Zainuddin , N. F.B. Pallan, et al., Science of Sintering, 51 (2019) 377.
5. N. Mijatović, A. Terzić, L. Pezo, Lj. Miličić, A. Milosavljević, D. Živojinović, Science of Sintering, 51 (2019) 429.
6. D. Jevtić, D. Zakić, A. Savić, A. Radević,in: Proc. Scientific conference Planing, design, construction and building renewal, Novi Sad, Serbia, 2012.
7. D. Jevtić, J. Markićević, A. Savić,in: Proc. 6th International Conference "Science and Higher Education in Function of Sustainable Development" SED, Užice, Serbia, 2013.

8. D. Jevtić, A. Mitrović, A. Savić,in: Proc. 2nd International Symposium on Environmental and Material Flow Management, Zenica, Bosnia and Herzegovina, 2012.
9. D. Jevtić, A. Savić, A. Radević,in: Proc. XV YuCorr International Conference, Tara Mountain, Serbia, 2013.
10. D. Jevtić, D. Zakić, A. Savić, in: Proc. 14th International Conference "Research and Development in Mechanical Industry" RaDMI, Topola, Serbia, 2014.
11. D. Jevtić, D. Zakić, A. Savić, A. Radević, in Proc: III International Congress Engineering, Environment and Materials in Processing Industry, Jahorina Mountain, Bosnia and Herzegovina, 2013.
12. D. Jevtić, D. Zakić, A. Savić, A. Radević, Materials Protection, LV (2014) 39.
13. J. Bijeljić, N. Ristić, Z. Grdić, G. Topličić-Ćurčić, D. Đorđević, Science of Sintering, 52 (2020).
14. A. Terzić, L. Pezo, Lj. Miličić, N. Mijatović, Z. Radojević, D. Radulović, Lj. Andrić, Science of Sintering, 51 (2019) 39.
15. European Guidelines for Self-Compacting Concrete: Specification, Production and Use, European Project Group, 2005.
16. R. Siddique, Waste Materials and By-Products in Concrete, Springer-Verlag, Berlin, Heidelberg, Germany, 2008.
17. M. Liu, Constr. Build. Mater., 24 (2010) 1245.
18. R. Siddique, Cem. Concr. Res., 33 (2003) 539.
19. U. Mucteba, Y. Kemalettin, I. Metin,Constr. Build. Mater., 27 (2012) 263.
20. M. Kuroda, T. Watanabe, N. Terashi, Cem. Concr. Res., 30(2000) 253.
21. Y. L. Wong, L. Lam, C. S. Poon, F. P. Zhou, Cem. Concr. Res., 29(1999) 1905.
22. M. Higaeg, I. Balać, A. Grbović, M. Milovančević, M. Jelic, Science of Sintering, 51 (2019) 459.
23. G. Bermejo, M. Canovas, in: Proc. The 3rd FIB International Congress, 2010.
24. R. Siddique, Mater. Des., 32 (2011) 1501.
25. SRPS EN 933-1, Tests for geometrical properties of aggregates- Part 1: Determination of particle size distribution- Sieving method, 2013.
26. A. R. Savić, Investigation of the Properties of Fresh and Hardened Self-Compacting Concrete with Mineral Additions Based on Industrial By-Products, Doctoral dissertation, University Of Belgrade, Faculty Of Civil Engineering, 2015.
27. SRPS B.B8.036, Crushed aggregate- Determination of fine particles with the wet sieve analysis, 1982.
28. SRPS ISO 6783, Coarse aggregates for concrete- Determination of particle density and water absorption - Hydrostatic balance method, 1999.
29. SRPS ISO 7033, Fine and coarse aggregates for concrete- Determination of the particle mass-per-volume and water absorption-Pycnometer method, 1999.
30. SRPS ISO 6782, Aggregates for concrete- Determination of bulk density, 1999.
31. SRPS B.B8.044, Natural and crushed stone aggregate- Test for freezing resistance, 1982.
32. SRPS B.B8.042, Natural and crushed aggregate- Chemical analysis of aggregares for concretes and mortars, 1984.
33. SRPS B.B2.010, Aggregate for concrete- Technical requirements, 1986.
34. SRPS B.B2.009, Raw materials for production of aggregates for concrete- Technical requirements, 1986.
35. SRPS EN 196-2, Method of testing cement-Part 2: Chemical analysis of cement, 2015.
36. SRPS B.C8.023, Cements. Methods of testing cements- physical tests, 1982.
37. SRPS EN 196-6, Methods of testing cement- Part 6: Determination of fineness, 2019.

38. SRPS EN 196-3, Methods of testing cement- Part 3: Determination of setting times and soundness, 2017.
39. SRPS EN 1936, Natural stone test methods- Determination of real density and apparent density and of total and open porosity, 2009.
40. SRPS EN 13755, Natural stone test methods- Determination of water absorption at atmospheric pressure, 2009.
41. SRPS EN 1926, Natural stone test methods- Determination of uniaxial compressive strength, 2010.
42. SRPS EN 12372, Natural stone test methods - Determination of flexural strength under concentrated load, 2009.
43. SRPS EN 14157, Natural stone test methods - Determination of the abrasion resistance, 2017.
44. SRPS EN 12371, Natural stone test methods- Determination of frost resistance, 2014.
45. SRPS EN 12350-6, Testing fresh concrete- Part 6: Density, 2010.
46. SRPS EN 12350-7, Testing fresh concrete- Part 7: Air content- Pressure methods, 2010.
47. SRPS EN 206-1, Concrete- Part 1: Specification performance, production and conformity, 2011.
48. SRPS EN 12350-10, Testing fresh concrete- Part 10: Self-compacting concrete- L box test, 2012.
49. SRPS EN 12350-11, Testing fresh concrete- Part 11: Self-compacting concrete- Sieve segregation test, 2012.
50. SRPS EN 12390-7, Testing hardened concrete- Part 7: Density of hardened concrete, 2010.
51. SRPS EN 12390-3, Testing hardened concrete- Part 3: Compressive strength of test specimens, 2010.
52. SRPS ISO 4013, Concrete- Determination of flexural strength of test specimens, 2000.
53. ASTM C469/ C469M10, Standard Test Method for Static Modulus of Elasticity and Poisson's Ratio of Concrete in Compression, 2005.
54. SRPS U.M1.015, Concrete- Hardened concrete- Determination of the depth of penetration of water under pressure, 1998.
55. SRPS U.M1.055, Concrete- Method of test for resistance of concrete against freezing, 1984.
56. S. Assie, G. Escadeillas, G. Marchese, V. Waller, Mag. Concr. Res., 58 (2006) 1.
57. M. Muravljov, Osnovi teorije i tehnologije betona, Građevinska knjiga, Beograd, 2011.
58. ASTM C 618, Standard specification for coal fly ash and raw or calcined natural pozzolan for use in concrete, 2003.
59. B. Sukumar, K. Nagamani, R. Srinivasa,Constr. Build. Mater., 22 (2008) 1394.

Сажетак: *Ова студији анализира могућност валоризације индустријског нуспроизвода, летећег пепела из термоелектране за делимичну замену минералног пунила- кречњака у производњи самозбијајућег бетона (SCC). Дизајниране су три SCC мешавине са различитим уделима летећег пепела и референтна смеша са кречњаком. Испитана су следећа својства синтетисаних самозбијајућих бетона у свежем стању: густина, садржај ваздуха, течљивост, способност проласка и отпорност према сегрегацији, док је испитивање бетона у очврслом стању укључило: густину, чврстоћу на притисак и савијање, статички модул еластичности, водонепропусност, отпорност на дејство мраза и соли, као и SEM анализу. Узимајући у обзир добијене резултате, може се закључити да додавање летећег пепела има позитиван утицај на* *својства бетона и да је оптималан садржај летећег пепела 20 % у односу на укупну масу пунила.*

Кључне речи*: самозбијајући бетон (СЦЦ), летећи пепео, дизајн смеша, механичка чврстоћа, трајност.*