DRUŠTVO ZA ISPITIVANJE I ISTRAŽIVANJE MATERIJALA I KONSTRUKCIJA SRBIJE

SOCIETY FOR MATERIALS AND STRUCTURES TESTING OF SERBIA

MEĐUNARODNI SIMPOZIJUM

O ISTRAŽIVANJIMA I PRIMENI SAVREMENIH DOSTIGNUĆA U GRAĐEVINARSTVU U OBLASTI MATERIJALA I KONSTRUKCIJA

INTERNATIONAL SYMPOSIUM

ON RESEARCHING AND APPLICATION OF CONTEMPORARY ACHIEVEMENTS IN CIVIL ENGINEERING IN THE FIELD OF MATERIALS AND STRUCTURES

ZBORNIK RADOVA
PROCEEDINGS

XXVII Kongres - Vršac, 18-20. oktobar 2017.
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CIP- Каталогизација у публикацији
Народна библиотека Србије

624/628(082)
69(082)
666.7/.9(082)

МЕЂУНАРОДНИ симпозијум о истраживањима и примени савремених достигнућа у грађевинарству у области материјала и конструкција (2017 ; Вршац)
Zbornik radova = Proceedings / Međunarodni simpozijum o istraživanjima i primeni savremenih dostignuća u građevinarstvu u oblasti materijala i konstrukcija, [u okviru] XXVII kongres[a Društva za ispitivanje i istraživanje materijala i konstrukcija (DIMK) Srbije] - Vrsac, 18-20. oktobar 2017. = International Symposium on Researching and Application of Contemporary Achievements in Civil Engineering in the Field of Materials and Structures, [within] XXVII Congress [of Society for Materials and Structures Testing of Serbia] - Vrsac, October 18-20, 2017. ; [editor Dragica Jevtić, Radomir Folić]. - Beograd : Društvo za ispitivanje i istraživanje materijala i konstrukcija Srbije, 2017 (Beograd : Razvojno istraživački centar grafičkog inženjerstva TMF). - 563 str. : ilustr. ; 30 cm

Radovi na srp. i engl. jeziku. - Tiraž 100. - Napomene uz radove. - Bibliografija uz većinu radova. - Summaries.

ISBN 978-86-87615-08-3

1. Друштво за испитивање и истраживање материјала и конструкција Србије (Београд). Конгрес (27 ; 2017 ; Вршац)

а) Грађевински материјали - Зборници

b) Грађевинске конструкције - Зборници

c) Грађевински објекти - Зборници

COBISS.SR-ID 247427852

Izdavač: **Društvo za ispitivanje i istraživanje materijala i konstrukcija Srbije**
Beograd, Kneza Miloša 9/I

Editor: **Prof. dr Dragica Jevtić, dipl.inž.tehn.**
Građevinski fakultet Univerziteta u Beogradu, Beograd
Emeritus prof. dr Radomir Folić, dipl.inž.građ.
Fakultet tehničkih nauka, Novi Sad

Štampa: Razvojno istraživački centar grafičkog inženjerstva, Karnegijeva 4, Beograd

Tiraž: 100 primeraka

"Simpozijum o istraživanjima i primeni savremenih dostignuća u građevinarstvu u oblasti materijala i konstrukcija", koji je upriličen u okviru **XXVII Kongresa Društva za ispitivanje i istraživanje materijala i konstrukcija (DIMK) Srbije**, Vršac 18.-20. oktobra 2017. godine, održan je u saradnji sa **Institutom za ispitivanje materijala IMS Beograd**, a pod pokroviteljstvom **MINISTARSTVA PROSVETE, NAUKE I TEHNOLOŠKOG RAZVOJA REPUBLIKE SRBIJE.**

Vršac, oktobar 2017. godine

XXVII KONGRES I MEĐUNARODNI SIMPOZIJUM O ISTRAŽIVANJIMA I PRIMENI SAVREMENIH DOSTIGNUĆA U GRAĐEVINARSTVU U OBLASTI MATERIJALA I KONSTRUKCIJA

Dragica Jevtić [1], Mihovil Logar[2], Aleksandar Savić [3]

INVESTIGATION OF THE SELF-COMPACTING CONCRETE WITH FLY ASH FROM THE MICROSTRUCTURAL ASPECT

Summary: *Characterization of concrete with the aid of Scanning Electron Microscope (SEM) is a useful segment of the correlation analysis between formed structure and the physical and mechanical properties of these composites. Use of fly ash in our construction industry is a modern theme, due to the ecological impact and also, due to the positive effects in physical and mechanical properties of the composites with fly ash. Results of investigation of Self-Compacting Concrete – SCC with mineral addition of fly ash with accent on their microstructure are presented in the paper. Analyzed components of the microstructure included: porosity, interface transition zone (ITZ), quality of cement matrix and the other relevant properties. Results of these investigations showed improvement of the microstructure of SCC with fly ash, due to pozzolanic reaction of fly ash.*
Key words in English: *composites, SEM, pozzolanic activity, physical and mechanical properties*

ISTRAŽIVANJE SAMOUGRAĐUJUĆEG BETONA SA LETEĆIM PEPELOM SA ASPEKTA MIKROSTRUKTURE

Rezime na srpskom jeziku: *Karakterizacija betona pomoću skenirajućeg elektronskog mikroskopa (SEM) predstavlja koristan segment analize veze između formirane strukture i fizičko-mehaničkih svojstava ovih kompozita. Upotreba letećeg pepela u domaćem graditeljstvu aktuelna je tema zbog ekološkog impakta sa jedne i zbog pozitivnih efekata u smislu fizičko-mehaničkih svojstava cementnih kompozita koji ga sadrže, sa druge strane. U radu su prikazani rezultati ispitivanja samougrađujućih betona (Self-Compacting Concrete - SCC) sa mineralnim dodatkom letećeg pepela sa naglaskom na njihovoj mikrostrukturi. Analizirane komponente mikrostrukture SCC uključile su: poroznost, prelaznu zonu, kvalitet cementne matrice i ostala relevantna svojstva. Rezultati ovih ispitivanja pokazali su poboljšanje mikrostrukture SCC betona sa letećim pepelom zahvaljujući pucolanskoj reakciji letećeg pepela.*
Ključne reči na srpskom jeziku: *kompoziti, SEM uređaj, pucolanska aktivnost, fizičko-mehanička svojstva*

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1. INTRODUCTION

The contemporary science stands on a generally accepted point of view, that the physical and mechanical properties of concrete can be linked to its structure. Overall premise is, that the porous concretes have poorer physical and mechanical characteristics than the compact. However, due to the large number of parameters, regarding the correlation between the structure and the physical and mechanical characteristics of the concrete mix, this problem is generally considered too complex to be investigated and formulated in a shape of a reliable correlation.

The development of microscopic devices and various sensors has enabled better understanding of the microstructure of concrete with high magnifications. Analysis by scanning electron microscope, in the majority of cases, is reduced to the observation of porosity, the characterization of the transition zone at the contact of the aggregate and the paste, and sometimes other valuable qualitative and quantitative indicators of the concrete's microstructure. During the tests on Self-Compacting Concrete – SCC (concrete that will, without mechanical compaction, fill all the formwork parts and spaces between the bars of reinforcement, ultimately producing compact concrete of higher durability [1]), a Scanning Electron Microscope (SEM) was used, equipped with modern energy-dispersive spectrometer (EDS).

In the present research, basic aspects of the microstructure have included the following parameters:

• Formation and distribution of hydration products [2];
• Visual assessment of the cement paste homogeneity;
• Arrangement of the pores and porosity of the transition zone;
• Interfacial Transition Zone (ITZ) characterization (the dimensions of the transition zone, the layers, minerals in the zone - CSH (calcium silicate hydrate), CH (calcium hydroxide), potential presence of recognizable AFT (ettringite) and AFM (monosulfate);
• Dispersion of the mineral addition grains, and the manner in which they reacted with CH;
• The character of contact grain mineral admixture and the cement matrix (whether there is a contact zone of the contact or out).

Besides the results of EDS analysis, which can be considered quantitative, other test results in the case of these tests are qualitative.

2. MATERIALS AND MIXTURES

Natural river aggregate (separated in three standard fractions) originated from Danube river, Belgrade region. Sieve passing analysis of this aggregate was tested according to [3] and presented in the Figure 1. Modulus of fineness of the fine aggregate (0/4 mm) was 2,92 and satisfied conditions defined in the standard [4] (limit values 2.3-3.6). Moduli of fineness of second (4/8 mm) and third (8/16 mm) fraction were 6,04 and 6,99 respectively. Content of fine particles in the first fraction was 0.59% for particles smaller than 0.063 mm, and 1,68% for particles smaller than 0.09 mm. In the coarse aggregate this content was close to zero. Based on the previous tests, mixture consisted of

31.8% of the fine aggregate, and 32.5% of both second and third fraction of the coarse aggregate.

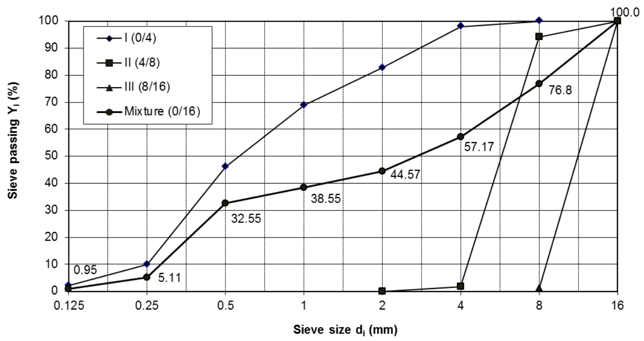

Figure 1. Particle size distribution curves of the used fractions of aggregate (together with the curve of the mixture)

Portland cement of the type CEM I was used, declared as PC 42.5, produced by Lafarge, Beočin. Specific surface of the cement, according to Blaine, was 4240 cm^2/g, while its density was 3040 kg/m^3.

Basic filler component for all of the mixtures was limestone filler produced by "Granit Peščar" Ljig, with average particle diameter of 250 µm. Specific surface of limestone filler was 3800 cm^2/g, while its density was 2720 kg/m^3. Chemical content of this filler together with chemical content of fly ash are presented in Table 1. Fly ash used in this study was obtained at the Thermal Power Plant Kolubara, and was used 'as received', i.e. without any kind of chemical or mechanical activation.

Table 1. Chemical composition of the used mineral fillers (%)

Parameter	SiO_2	Al_2O_3	CaO	Fe_2O_3	MgO	K_2O	Na_2O	TiO_2	LOI
Limestone filler	0.21	0.50	54.86	0.09	1.10	0.05	<0.005	<0.005	43.64
Fly ash	58.60	21.92	6.12	5.97	1.77	1.50	0.37	0.49	3.09

The greatest differences in chemical content were, as expected, in higher content of SiO_2, Al_2O_3 and Fe_2O_3, and lower content of CaO in the fly ash than in the limestone filler. The loss on ignition was substantially higher in the limestone filler, due to the CO_2 extraction during ignition phase.

Water from city water supply system was used for concrete mixtures. Temperature of water was measured before each mixing and it ranged between 19°C and 22°C. Superplasticizer Glenium Sky 690, produced by BASF Italia (density 1060 kg/m^3) was dosed in amount of 2% in all mixtures, except the SCC LP50 (3%).

Final compositions of SCC mixtures were set using the modified "step by step" method, where parameters are defined through several phases. This method was originally developed on the Tokio University [5]. Besides the reference SCC E, mixtures with fly ash (10%, 20% and 50% of limestone filler mass replaced with fly ash, designated as SCC LP10, SCC LP20 and SCC LP50, respectively) were made. These SCC mixtures are further analyzed and discussed in the paper. The final compositions are shown in table 2.

Table 2. Composition of the studied SCC mixtures (kg/m^3)

Mixture	SCC E	SCC LP10	SCC LP20	SCC LP50
Water W	183	183	183	183
Cement C	380	380	380	380
Limestone filler KB	220	198	176	110
Fly ash LP	0	22	44	110
Sand (0/4mm)	840	840	840	840
Coarse aggregate (4/8mm)	430	430	430	430
Coarse aggregate (8/16mm)	430	430	430	430
Superplasticizer	7.6	7.6	7.6	11.4

3. RESULTS AND DISCUSSION

Study of fresh and hardened series of SCC were performed, followed by the SEM characterization of representative samples of mixtures with and without fly ash. Research of all of the properties except SEM analysis were done in the Laboratory for materials, Institute for the materials and structures, Faculty of Civil Engineering, University of Belgrade. The analysis with the aid of SEM was performed at the SEM-EDS Laboratory, Faculty of Mining and Geology, University of Belgrade.

3.1 Fresh and hardened properties of SCC mixtures

Following properties were studied on the SCC mixtures in fresh state: density, temperature of the fresh concrete, entrained air content, slump-flow, periods t_{500} and t_V, as well as the heights ratio in the L-box. Following properties were studied in the hardened state, at 28 days: compressive strength, adhesion (pull-off method), ultrasonic pulse velocity, dynamic modulus of elasticity. The results of these tests are presented in Table 3. Generally, use of fly ash showed to be reducing the density, noticeably to slightly, reducing slump flow and passing ability (periods t_{500} and t_V and L-box), while mechanical properties at the age of 28 days improved, with the exclusion of adhesion of LP50.

Table 3. Properties of the studied SCC mixtures

Property	SCC E	SCC LP10	SCC LP20	SCC LP50
Fresh concrete density (kg/m^3)	2397	2391	2370	2347
Temperature (°C)	20.6	23.9	20.3	22.0
Entrained air (%)	1.9	1.5	2.0	2.8
Slump - flow test (cm)	76.12	70.12	66.38	70.25
t_{500} (s)	2.62	5.71	10.91	11.32
t_v (s)	9.73	15.92	22.46	27.21
L-box (H1/H2)	0.97	0.92	0.92	0.95
Compressive strength, 28d (MPa)	62.0	69.0	72.4	70.0
Adhesion, 28d (MPa)	5.77	6.09	6.52	5.37
Ultrasonic pulse velocity, 28d (km/s)	4.657	4.682	4.720	4.669
Dynamic modulus of elasticity, 28d (GPa)	43.4	45.6	45.5	43.9

3.2 SEM characterization of SCC with fly ash

Microstructural analysis of SCC samples was carried out by SEM. Three representative samples of SCC were prepared. Besides the reference sample (SCC E), two samples of SCC LP50 were also selected. One of them was prepared by polishing and the second one was not, in order to avoid the damage that polishing can induce at its surface.

Samples for SEM analysis were cleaned immediately before testing, from dust particles, fibers, paper, untied or loosely bound particles in a sample, greasy parts, finger prints and the like, using petroleum ether. After that, the samples were held several minutes in an ultrasonic cleaning bath, and then dried under the lamp. Samples were then prepared, before the test, by steaming a thin layer (15-25 nm) of carbon (polished samples) or gold (broken sample).

As a first step, a characterization of aggregate was conducted (quartzite, limestone, sandstone, amphibole, quartz etc.), detection of mineral addition grains (limestone filler and fly ash) and the cement matrix, with the aid of the appropriate EDS analyzes (Figure 2). Further analysis included characterization of the interface transition zone of aggregate and cement matrix. Generally speaking, ITZ of aggregate and cement matrix could be characterized as very good (although the operation of compacting was omitted when the concrete was placed), but it should be noted that the contact with the certain aggregate types was better (sandstone, limestone) than with others (quartzite). This effect can be attributed do the nature of surface and compactness of aggregate itself. The dimensions of the ITZ were very small, reaching not more than 5 μm, testifying of the dense concrete structure.

The fly ash particles and their pozzolanic reaction was studied in the next phase. Figure 3 shows the contact between the coarser fly ash particle and the matrix, in the SCC made with 50% mass replacement of limestone filler with fly ash.

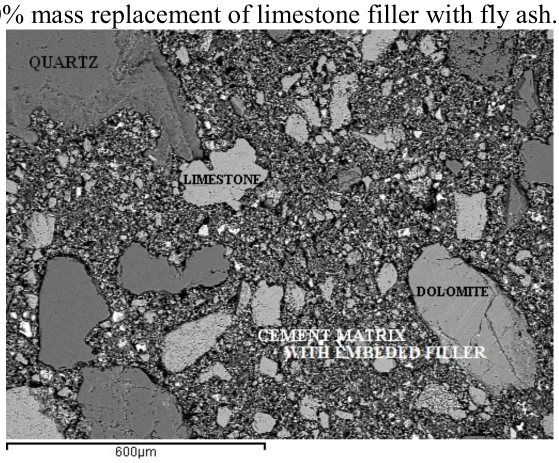

Figure 2. Characterization of the aggregate in the matrix of SCC E

In Fig. 4 some ash spheres partially covered with reaction product are arrowed. This figure might be suggesting that the precipitation of the reaction products forms, in a short period of time, a layer on still unreacted spheres, which would inhibit its activation.

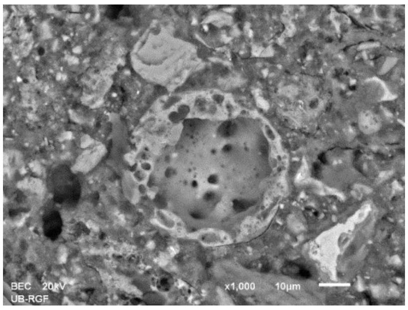

Figure 3. Contact between the coarser fly ash particle and the matrix in SCC LP50

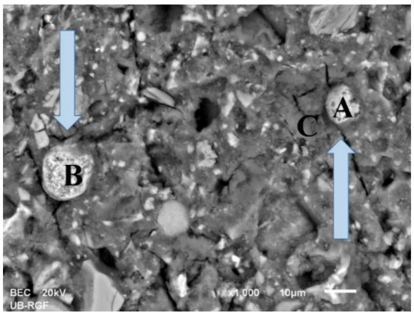

Figure 4. Presence of the partially reacted fly ash particles in SCC LP50

Together with the unreacted spheres (point A and B), there exists the amorphous aluminosilicate gel (points C). From the EDS analysis (see Table 4), an averaged compositional ratio of Si/Al = 4.4 has been deduced for that gel. The presence of only a few unreacted or not totally consumed spheres is indicating a high degree of pozzolanic reaction [6].

Table 4. EDS analysis on specific points of the samples

Point	Na	Mg	Al	Si	S	K	Ca	Ti	Mn	Fe	O	Total
A	0.70	6.67	15.93	2.97	0.00	0.00	30.31	0.23	0.00	6.11	37.07	100.00
B	0.00	5.77	8.76	8.36	0.43	0.00	28.13	0.45	0.29	10.12	37.70	100.00
C	0.76	6.25	5.03	22.35	0.97	0.33	18.55	0.26	0.60	0.90	43.99	100.00

Mapping based on the elements Si, Al, Fe, Ca, S (qualitative analysis) was used on several spots in the samples, firstly, as a supporting method in the identification of dispersion of hydrated fly ash grains, since, fly ash is characterized by the presence of large amounts of aluminum (the alumina from clay of Kolubara origin). Secondly, the degree of dispersion of the limestone filler (map Ca) was also estimated in the matrix. Of course, both dispersions are a result of mixing process. Figure 5 presents a complementary relation of Ca and Al at the site of coarse grains of fly ash (the central zone of the observed sample).

The final part of the characterization of SCC with fly ash included characterization of the pore structure in the samples, through analytical image analysis. Image analysis, based on images with magnification of 500 and 1000 was performed, in order to obtain data regarding the quantity of different pore sizes, both in reference SCC E and in SCC LP50. The results of this analysis are displayed in the Figure 6, as a graph of pore sizes versus the percentage of the area on the images that the pores of specified size class occupy. The graph presents porosity percentage as an average value (av) obtained on the basis of five images for each sample. Additionally, cumulative (cumul) porosity percentages are plotted (as lines) for both concrete mixtures.

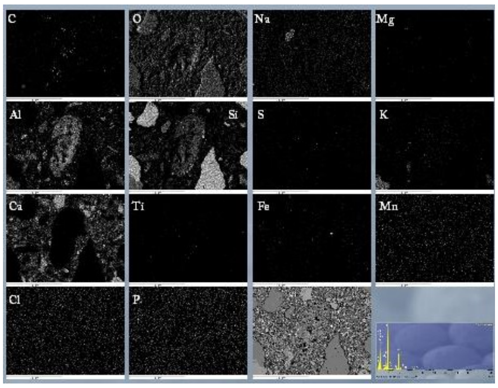

Figure 5. Results of mapping on the sample obtained from the SCC LP50

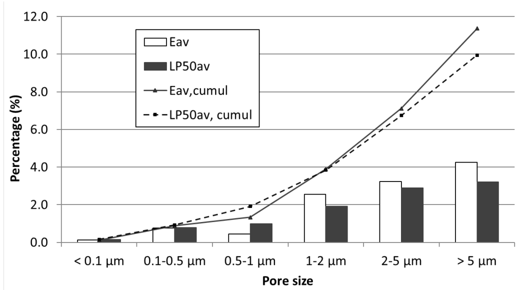

Figure 6. Pore structure analysis of SCC E and SCC LP50

It was found that percentage of the porosity increases with the size of the pores, although pores of 0.1-0.5 µm and pores of 0.5-1.0 µm occur to be similarly represented in the analyzed images. Also, the effect of fly ash use was found to decrease the amount of pores of all sizes. This can be explained by the pozzolanic reaction with products that tend to fill the existing pores. The exception of this effect is found in the pores range of 0.5-1.0 µm, and this effect is still to be additionally examined. Nevertheless, the cumulative porosity shows porosity of 11.36% in the case of SCC E, against the porosity of 9.95% in the case of SCC LP50 (12.5% difference).

4. CONCLUSION

Based on the presented research, incorporation of up to 50% of fly ash from TPP Kolubara, as a partial mass replacement of limestone filler, leads to decrease in filling and passing ability of Self-Compacting Concrete, but increases segregation resistance. Also, the most important properties of hardened concrete are improved, depending on the amount of the fly ash used. The SEM analysis was used to characterize the structure of the concretes. The analysis showed that the contact with the certain aggregate types was better (sandstone, limestone) than with others (quartzite), due do the nature of surface and compactness of aggregate. The rare occurrence of the unreacted fly ash particles in the SEM images indicated a high degree of pozzolanic reaction. Results of these investigations showed improvement of the microstructure of SCC with fly ash, due to the pozzolanic reaction of fly ash (12.5% reduction of porosity based on the image analysis). The SEM analysis remains one of the useful instruments for description of the processes and correlations in the cement composites, such as Self-Compacting Concrete. Image analysis, as a complementary tool, is expected to improve further, and become more reliable source for analyzing SEM images. Nevertheless, the stochastic character of the studied phenomena both increases the number of the samples needed for this study and reduces the reliability of the related conclusion, and the investigator has to have that in mind at all times.

5. ACKNOWLEDGEMENT

The work reported in this paper is a part of the investigation within the research project TR 36017 "Utilization of by-products and recycled waste materials in concrete composites in the scope of sustainable construction development in Serbia: investigation and environmental assessment of possible applications", supported by the Ministry of Education, Science and Technological Development, Republic of Serbia. This support is gratefully acknowledged.

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