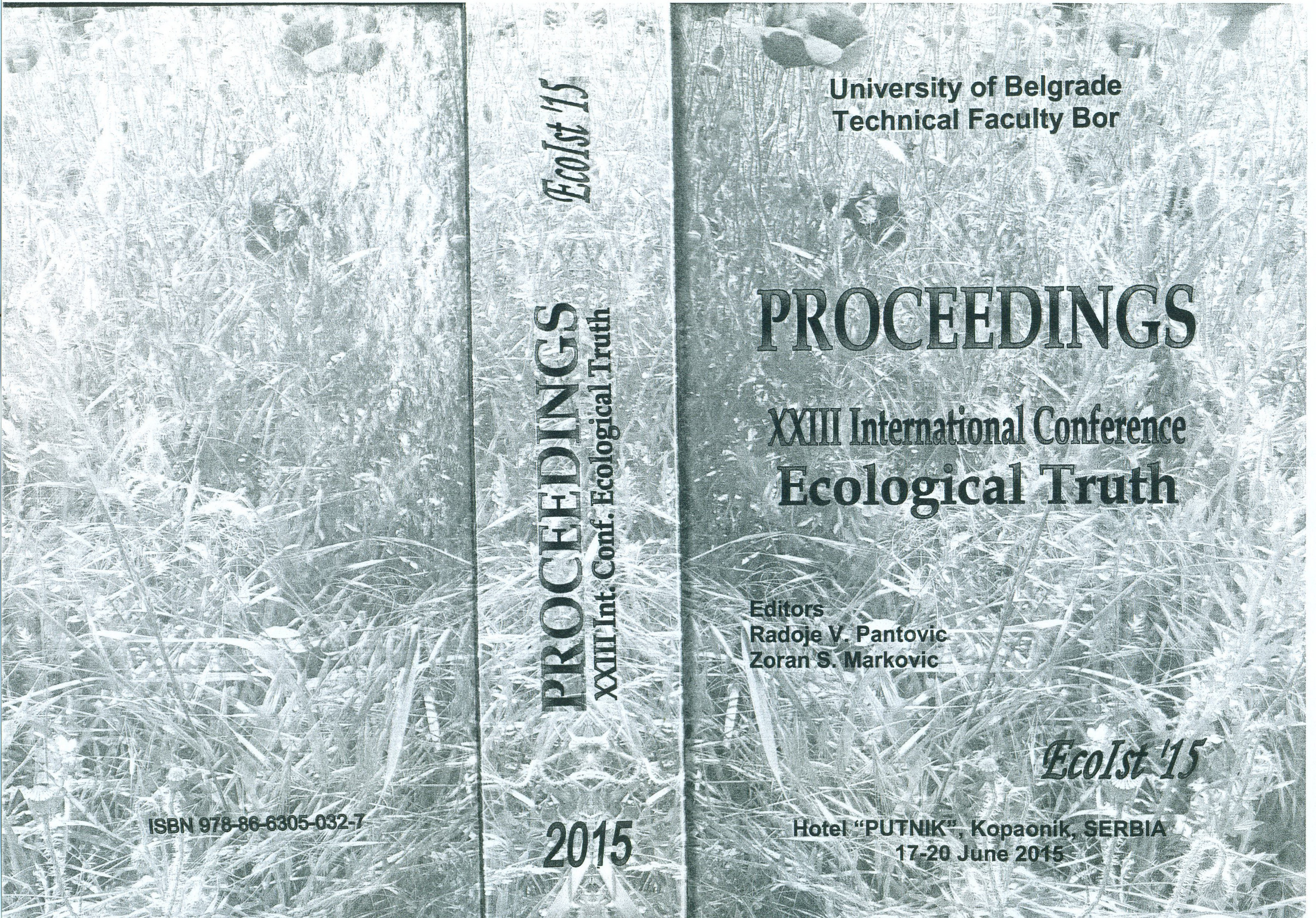

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Ecological Truth

Editors
Radoje V. Pantovic
Zoran S. Markovic

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VALORIZATION OF SECONDARY SULFUR FROM OIL REFINING PROCESS FOR SULFUR CONCRETE PRODUCTION

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ABSTRACT

Modification ofconventional building materials is commonly realized using differentwaste materials. In this research, the use of secondarysulfur as binding agent in concrete was analyzed. Sulfur concrete is a thermoplastic composite made of mineral aggregate and filler, with sulfur as a binder at temperature above the hardening point of sulfur. This relatively new building material can possibly replace conventional Portland cement concrete in many branches of construction. Also, in this research, sulfur concrete properties were examined, as well as its quality in the presence of the induced destruction agent.Destructive and nondestructive methods were applied and the material properties correlated withthe structure.

Key words: secondary sulfur, sulfur concrete, Portland cement concrete, destructive methods, nondestructive methods.

INTRODUCTION

Sulfur is an element that was being removed from the atmosphere by slow natural processes during eons. In these processes, sulfur was bound to metals giving ores. The other natural cycle of sulfur removal, by binding to organic materials through food chains, led to its storage in crude oil. The modern development of industrial society over the last 200 years, the so-called technological revolution, has in fact reversed those natural processes towards restoring sulfur to the environment by exploitation of minerals and crude oil.

Sulfur is the 16th most abundant element in nature. It is found in the earth's crust, in the ocean and even in meteorites. Sulfur occurs naturally all over the world and it is the most prolific where sulfur-rich oil and gas is processed and refined. Canada is the biggest exporter and China is the biggest importer of sulfur [1].

In the last decades, the availability of sulfur has considerably grown mainly due to the current environmental restrictions regarding the petroleum and gas refining processes, which limit the maximum quantity of sulfur present at combustibles. Sulfur

from oil processing was stored leading to more or less controlled disposal. Extremely large quantities of sulfur are thus obtained as a by-product of these processes.

Based on literature review and other reliable sources, it is evident that there will be a continuous abundant supply of sulfur in the future due to strict global environmental regulations [2]. The report from the World Business Council for Sustainable Development report, Cement Industry Energy and CO_2 Performance "Getting the Numbers Right" [3], clearly indicates that global production of sulfur will continue to increase, thus assuring its continued availability.

Therefore, the development of new applications for sulfur becomes fundamental.

Building materials come into the focus of interest at the time when waste, industrial or municipal, is becoming increasingly important as a potential raw material. Probable cause for that is the base of building materials- cement which contains numerous waste materials originating from the ingredients or the fuel used for its production. On the one side, the primary application area of building materials has been constantly expanding, but beside these materials, the alternative materials are also taking their place. Modification of conventional building materials is commonly realized using some of the secondary raw materials from various industrial processes. Generally, building materials and their products are important recipients of waste as long as they can provide complete immobilization without degradation of their basic properties.

In this research, possibility of using secondary sulfur as an alternative component of concrete was analized. Waste sulfur is often neglected despite the large amount of globally produced secondary sulfur which possibly exceeds the amount of ash to whom a great importance is given. Therefore, it was necessary to consider alternative ways of sulfur and sulfuric acid valorization in the real process (large scale). In this case, the solutions can be found in application of these types of secondary sulfur for fertilizers production, immobilization of waste materials by conversion into insoluble compounds, and as in the production of building materials.

Production and end use of sulfur is schematically presented in Figure 1.

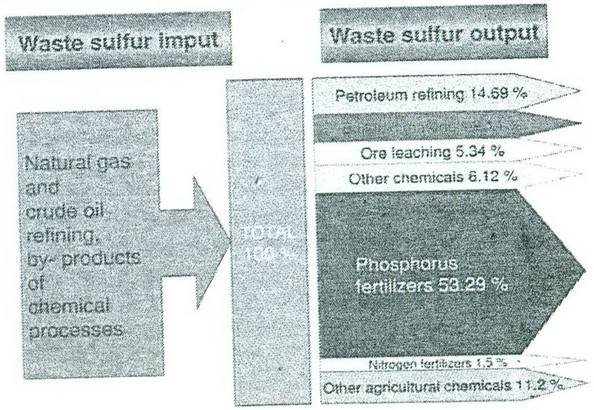


Figure 1. Production and end use of sulfur.

Building materials certainly represent media that should be examined as potential acceptors for large quantities of wastes from various sources.The fact is that wide range of hazardous waste can be inerted by their incorporating into usable building materials.

During the 1960s, there was a remarkable investment in environmental protection against discharge of sulfur into the atmosphere, thus making sulfur a surplus commodity on the market, particularly in the United States and Canada. This was a crucial point, that made the interest for usage of sulfur as a structural binder to grow further, and initiated extensive research programs which became very active in the 1970s and focusing on various properties of the material, including durability [2].

Construction materials such as sulfur concrete and sulfur modified asphalt continue to receive more attention since they are environmentally friendly and cost-effective. Beginning in the 1970s, successful projects in which sulfur concrete has been used as a construction material have been carried out in different levels. Most of these took place mainly in North America. Few and mainly research or test pilot projects have been carried out in Europe, with only Denmark conducting commercial or industrial activities on sulfur concrete.

On the other side, Portland cement may be partially or completely substituted with other binders such as modified heated sulfur to form a stable, hard concrete product. Unlike concrete made from Portland cement (which can be cold mixed), concrete made with modified heated sulfur needs to be heated during production. Although modified sulfur, together with aggregates, needs to be hot mixed (~135°C) when making sulfur concrete, with heat likely obtained from the combustion of fossil fuels, this process uses less energy than conventional cold concrete mixing processes because it avoids the energy needed to heat limestone to 1450°C to manufacture Portland cement. Furthermore, concrete made with modified heated sulfur releases far fewer GHG emissions than concrete made with Portland cement. Modified heated sulfur avoids the process emissions released in the calcination process of clinker production as well as the combustion emissions typically generated to supply heat to the calcination process [1].

It is, therefore, not surprising that such environmental demands and the surplus sulfur draw more attention for the use of sulfur concrete as a construction material. Research activities on sulfur concrete as a construction material are currently reported to be going on in Spain, Italy, and The Netherlands, while interest on medium scale industrial uses of sulfur concrete plans are underway in Poland. In South East Asia, preliminary reports are indicating a growing interest in the use of sulfur concrete as a result of the increase of surplus sulfur from refinery industry. Similar reports come from the Middle East (Saudi Arabia), South America (Chile) and Africa (South Africa), where attempts to use sulfur concrete were reported earlier, or are in progress [2].

Sulfur concrete and mortar are thermoplastic materials made of mineral aggregate and filler, with sulfur as a binder (instead of cement and water) at temperature above the hardening point of sulfur (120 °C). The proportion of aggregate, filler and binder for the preparation of concrete and mortar mixture may vary depending on the application.

Sulfur implementation for concrete production has started with using unmodified sulfur as a binder. However, despite excellent mechanical properties after

preparation, samples exhibited low stability, so spalling and failure occurred after a short period. Namely, exposure of such material to repeated cycles of freezing and defrosting in terms of high humidity or immersion into water caused its degradation and failure. This can be explained by sulfur transformation that is occurring during the preparation of sulfur concrete with unmodified sulfur. On cooling of casted liquid mixture, sulfur crystallizes as monoclinic S_β at 114 °C with volume contraction of7%. Below 95.5 °C, it transforms completely into rhombic S_α within 20 h. Since S_α is more dense than S_β high stresses and micro-cracking within the material are induced. This exposes the material to moisture penetration and it fails prematurely.The development of modified sulfur binder contributed to better endurance of sulfur concrete, which focused its application for roads construction and repairing and as a building material. Sulfur itself tends to polymerize to a large extent while chemical modification increases this tendency or prolongs the time required for the polymerization. Except the prevention of sulfur transformation from monoclinic to orthorhombic form, the degree of sulfur polymerization is increased and long chains are created due to modification.Modified sulfur has much lower thermal expansion coefficient compared with unmodified one, therefore shrinkage and residual stresses upon cooling are lower. The polymer prevents the growth of macro- sulfur crystals. Long-term durability of modified sulfur concrete lies in the stability of microcrystalline sulfur [4].

The use of sulfur to produce sulfur concrete and mortar is a relatively new technology that has to be proven in practice. The fact is that these materials are already in use, but refining their application quality is still certainly needed.Sulfur concrete has a relatively simple composition and manufacture, and very interesting characteristics and properties. The recent research programs on sulfur concrete have been continuing to study different properties related to the material performance, most of which are reported to be excellent. Its extremely high corrosion resistance, mechanical strength and fast hardening, make it a high performance material suitable for several applications, especially the ones in which other materials, fail [2]. Furthermore, sulfur concrete can be used for solidification and encapsulation of different waste materials (fly ash, cement kiln dust, phosphogypsum, mercury) into a sulfur-polymer matrix, thus obtaining the sustainable development of construction and industrial sectors and for corrosion protection of reinforcing steel and concrete[1]. Sulfur concrete should also find widespread application in chemical and fertilizer replacement for materials in acid and salt environments as well as in metallurgical operations since they fail in acid and salt environments. Sulfur concrete coated fertilizers were developed to provide better impact strength and controlled- release properties compared to sulfur- coated fertilizers.

In the presented research, the use of secondary sulfur as binding agent in concrete for wide application possibilities was analysed. The starting point was the fact that sulfur is known as a binder and that it can quite possibly be used as a binding agent in building materials. The initial studies were directed towards modification of sulfur for the application in sulfur concrete. Using sulfur to obtain modified sulfur binder is based on its physico-chemical characteristics. According to our terminology, modified sulfur binder considers a mixture of elemental sulfur and modified sulfur- sulfur polymer. Contemporary experience all over the world shows that concrete and mortar with modified sulfur binder instead of cement and water have significant chemical and physico- mechanical advantages comparing with Portland cement- based concrete and mortar [1,5].

The next step in this research was the analysis of technology ie. process of sulfur concrete obtaining in order to optimize the technological parameters for producing high- quality material. This was followed by the researches related to the examination of sulfur concrete properties, as well as testing the new material quality during the exploitation, which was more important. The fact is that the influence of various environmental factors causes a certain degree of destruction and therefore degradation of the basic properties of all materials, so the investigation of the newly obtained material- sulfur concrete was directed towards the analysis of its behavior in the presence of the induced destruction agent.

There are two key elements during the application of this methodology. The first one is a selection of the induced destruction agent, while the other one is a selection of methods, that means methodologies for monitoring and quantifying changes that occur under the influence of the certain agent.

In the scope of this research, hydrochloric acid, sulfuric acid, and sodium chloride were used as induced destruction agents. At the same time these experiments were screening experiments. Based on their results, the induced destruction agent, filler and treatment time for further investigationwere chosen.

In examining the materials properties, as well as in selecting methods for quantifying their changes, classical aspect was not applied. The idea was to implement a number of destructive and nondestructive methods and correlate the material properties with the structure. The structure of the obtained material was analyzed by the methodology of quantification of visual information whereby the images obtained by optical and scanning electron microscopes were used. It means that properties of the material structure were analyzed by different resolutions. The ultrasonic method, which offers defining the homogenity changes of the samples during the treatment time was also applied.

EXPERIMENTAL

Technological procedure for sulfur concrete production

Materials

The initial materials for technological procedure of sulfur concreteobtaining were aggregate, modified sulfur binder and filler.

- Aggregate

Sand with maximum grains size of 2 mm, obtained by sieving of locally available classical building mixture of sand and gravel, was used as an aggregate. Chemical analysis indicated that the aggregate mainly consisted of oxides of silica (89.98%), aluminium (3.61%), calcium (0.84%), iron (0.62%), potassium (0.59%), sodium (0.57%), and magnesium (0.19%).

- Sulfur

Sulfur, the basic component for a modified sulfur binder, originates from oil refining process by Claus's procedure in the Oil Refinery Pancevo, and its purity is 99.9%. Dicyclopentadiene (DCPD), cyclic hydrocarbon, was used for sulfur modification. The procedure performed according to the literature [6]consisted of mixing DCPD and melted sulfur in the temperature range from 120 to 140 °C and ambient pressure for 30 min, and then rapid cooling and solidification of the obtained sulfur polymer.

- Fillers

Fillers used in this production were: talc (technical quality, China), alumina (Almatis, Germany), microsilica (Sika, Switzerland) and fly ash (Power Plant "Nikola Tesla- A", Obrenovac).

The choice of filler is important because it forms with sulfur paste that coats and binds the aggregate particles. Talc, microsilica and fly ash are fillers that fulfill these requirements and therefore are recommended for the sulfur concrete production [7]. Fine fractions of calcined alumina are used as fillers for refractory concretes [8].

Common characteristic of all selected fillers is their particles size below 75 μm.

Samples preparation

Sulfur concretewas prepared according to the manufacturing technological procedure described in literature [4]. Preheated aggregate and filler (up to 160 °C) were stirred for about 15 min in a mixer, then melted sulfur and modified sulfur were mixed into homogenized dry mixture of aggregate and filler at sulfur melting temperature, 132-141°C. Preheating is desirable to avoid solidification of the molten sulfur by contact with aggregate at a low temperature and to reduce the mixing time. The heated aggregate and filler were then properly mixed with the molten modified sulfur until a homogenous viscous mixture was obtained. After homogenization and mixing that lasted for 2 minutes, the sulfur concrete mixture was casted into molds preheated at 120°C and vibrated for 10 seconds. Any extra material was removed to get a well-finish at top surface and left inside the molds at room temperature for hardening. A very important characteristic of sulfur concrete is rapid hardening (from 15 minutes to several hours, depending on size and shape of the sample), which allows removal from the mold and curing in a relatively short period of time (only 24 h at room temperature). Prism samples with dimensions (4 x 4 x 16) cm were prepared. After 3 h of hardening at room temperature, samples were demolded and kept at room temperature of 20°C for 24 h. Mechanical properties measurements were made after 72 h.

A schematic representation of the mixing process for sulfur concretepreparation is shown in Figure 2.

Characterization of sulfur concrete

The experimental program consisted in performing the following tests on concrete samples.

Acid and Salt Resistance

For sulfur concrete resistance and durability testing the standard testing method [4] was used. The prismatic samples with dimensions of 40 x 40 x 160 mm were immersed in three various aggressive environments: 10 % HCl solution, 20 % H_2SO_4 solution and 3 % NaCl solution.

The destruction of the material during 360 days of immersion was observed by determining variations of mechanical strength and apparent porosity with time.

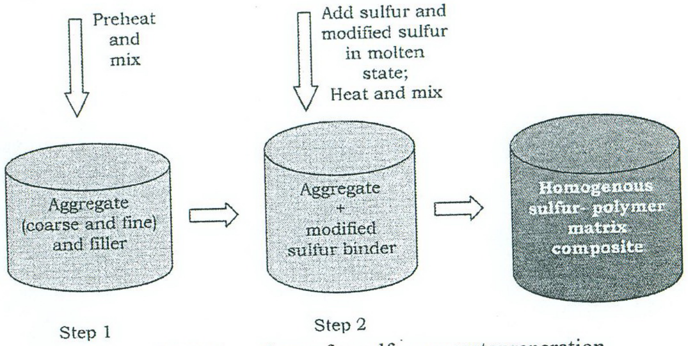


Figure 2. Mixing scheme for sulfur concretepreparation.

- Mechanical Strength Testing

Mechanical strength of the concrete samples before and after immersion tests was conducted using the "Amsler" press with maximum load of 200 kN, and method for testing the strength of concrete according to the standard [9].

- *Apparent Porosity Testing*

Apparent porosity of the samples before and after immersion tests was determined using boiling water saturation technique [10]. The samples were boiled for 5 h and then cooled for 19 h to a final temperature of 20-25 °C.

- *Image analysis*

The image analysis technique was used for surface destruction monitoring. It was performed using Image Pro Plus Program.

- *Ultrasonic pulse velocity testing*

The measurement of the ultrasonic velocity was used to monitor the internal material degradation with increasing the time of acid treatment. It was performed using the equipment OYO model 5210 according to the standard testing procedure (SRPS D. B8. 121.).

- *SEM analysis*

In order to inspect morphological changes in the inner structure of sulfur concrete, SEM microphotographs were provided using scanning electron microscopeJEOL JSM 5800.

RESULTS AND DISCUSSION

Referent Sulfur Concrete Samples Properties

Physico-mechanical properties of referent sulfur concrete samples, given in Table 1, were determined after removing from the mold and curing at room temperature for 72 h.

Table 1. Physico-mechanical properties of referent sulfur concrete samples after 72 h of curing at room temperature

Sample	Bulk density (g/cm^3)	Mechanical strength (MPa)		Apparent porosity (%)
		Compressive	Flexural	
SC-T	2.33	55.4	8.3	3.14
SC-A	2.34	49.2	8.4	1.38
SC-MS	2.31	50.3	7.2	3.21
SC-FA	2.25	48.9	7.8	4.93

SC-T = sulfur concrete with talc, SC-A = sulfur concrete with alumina,
SC-MS = sulfur concrete with microsilica, SC-FA = sulfur concrete with fly ash

It can be noticed that mechanical properties of all referent samples of sulfur concrete are mutually similar which can be connected with approximately the same values of their bulk densities.

By comparing properties of prepared sulfur concretewith literature [11], it can be concluded that, regarding mechanical strength, the samples with various fillers have completely satisfying quality.

Mutual differences in mechanical strength and apparent porosity valuesof sulfur concretesamples probably originate from the physical and chemical properties of applied fillers, since the other components were the same.

Durability Testing Results

Sulfur concrete samples in acid and salt environments after 12 months did not show any deterioration and their appearance is shown in Figure 3. For comparison, surfaces of Portland cement concrete samples after 2 months in the same environments are presented in Figure 6.

Figure 3. Surfaces of sulfur concrete:
a) with talc in 10 % HCl;
b) with microsilica in 20 % H_2SO_4;
c) with fly ash in 3 % NaCl.

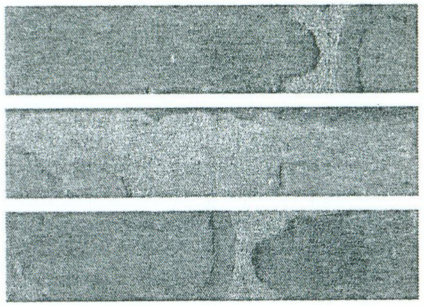


Figure 4. Surfaces of Portland cement concrete:
a) in 10 % HCl; b) in 20 % H_2SO_4;
c) in 3 % NaCl.

a) Compressive strength change of sulfur concrete under acid and salt influence

The obtained results, given in the following diagrams in Figure 5, represent durability of sulfur concrete samples depending on the type of filler and aggressive agent expressed through compressive strength change as a function of time.

The results showed that behavior of the sulfur concrete samples with different fillers regarding compressive strength changes was quite uniform in the investigated aggressive environments. Generally, all sulfur concrete samples after 360 days lost ~ 3 % of their strength in 10 % solution of HCl, and ~ 2 % in 20 % solution of H_2SO_4. Compressive strength loss after 360 days in 3 % solution of NaCl was negligible for all samples of sulfur concrete. It can be concluded that the type of filler did not exhibit significant influence on strength degradation [12].

In all three cases of chemical attack, found compressive strength loss of the treated sulfur concrete samples can be explained by increased porosity because mechanical strength is dependent on the defects in composite microstructure. Porosity is related to the movement of chemical substances into and out of the material and consequently affects durability of concrete, as porosity is connected to many deterioration processes driven by the transport properties of concrete. In sulfur concrete, the majority of the matrix is composed of sulfur coated materials (aggregate and filler) and sulfur accumulated in the voids between particles.

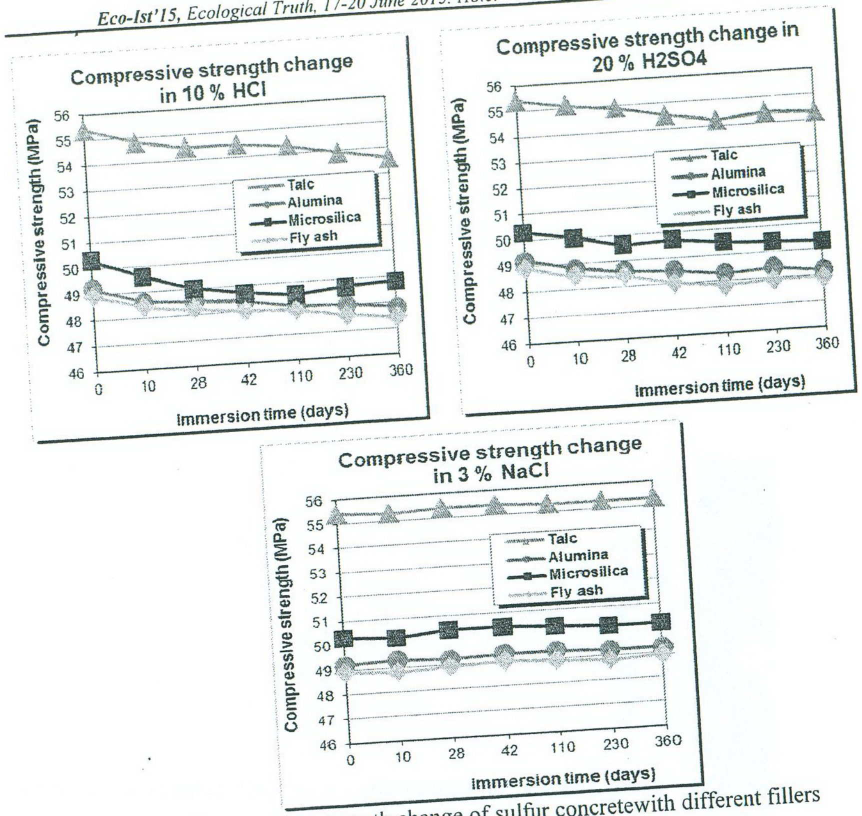


Figure 5. Compressive strength change of sulfur concretewith different fillers in three aggressive environments

During the acid attack, dissolving of basic and amphoteric oxides caused increase in porosity. Acid penetration and therefore corrosion was limited to the surface and open pores that were not coated by sulfur, which in turn resulted in slight porosity increase and slight compressive strength reduction.

During the salt attack, increased porosity is probably a result of a partial detachment between sulfur, aggregate and filler owing to sodium chloride crystals growth. Since sodium chloride penetration is only limited to the outer surface of the sulfur concrete [7], porosity increase was very slight and hence compressive strength loss was practically insignificant.

b) Apparent porosity change of sulfur concrete under acid and salt influence

The obtained results, given in the following diagrams in Figure 6, represent durability of sulfur concrete samples depending on the type of filler and aggressive agent expressed through apparent porosity change as a function of time.

As it was expected, all samples of sulfur concrete exhibited increase of apparent porosity after a year of treatment in the aggressive environments.

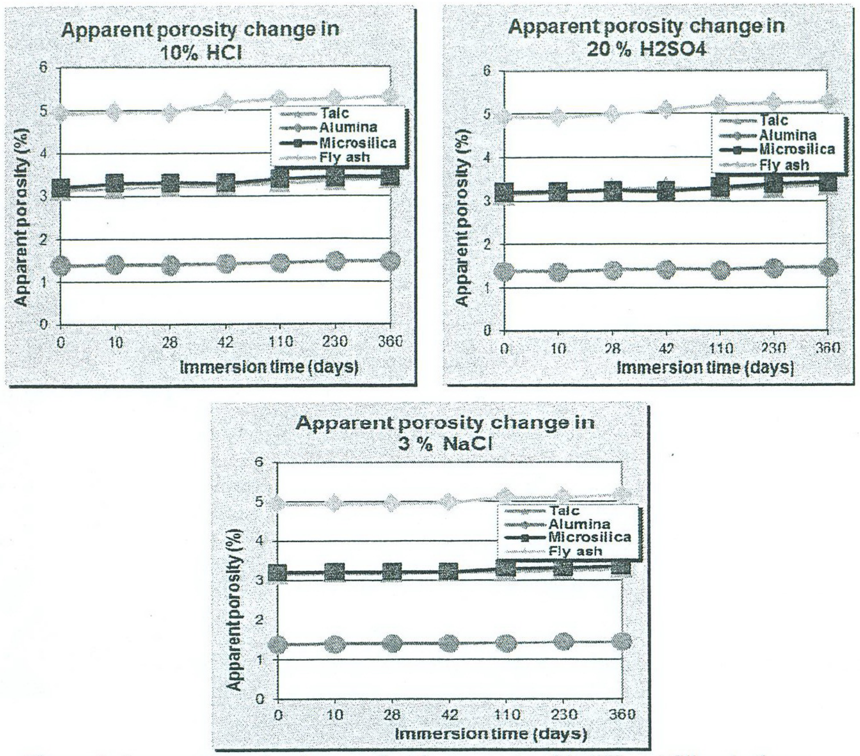


Figure 6. Apparent porosity change of sulfur concrete with different fillers in three aggressive environments

It is obvious that the apparent porosity values were the highest for all samples after a year of immersion in HCl, a bit lower for the samples treated in H_2SO_4, and significantly lower for the samples from NaCl.

The samples treated in HCl underwent the greatest apparent porosity increase of 7.3- 8.3 %, depending on filler. Apparent porosity increase of 6.5- 7.2 % was after treatment in H_2SO_4. In both acids, the samples with talc exhibited the highest apparent porosity changes, unlike those with alumina whose changes were the lowest. The difference between those ending values was ~1 % in HCl, and ~ 0.7 % in H_2SO_4. Apparent porosity increase of only ~ 4.5 % happened for the samples treated in NaCl. Since mutual differences of these changes among the samples were negligible, only 0.3 % between the highest and the lowest values, it can be considered that they were not caused by the type of filler.

Based on the obtained results, it can be concluded that apparent porosity increasement tendency of sulfur concrete samples with different fillers is in accordance with compressive strength loss due to contact with the aggressive agents.

Based onhe presented results, the highest mechanical strength loss and apparent porosity increasement were after treatment with hydrochloric acid. Sulfur concrete sampleswith alumina as filler exhibited great mechanical strength loss in hydrochloric acid accompanied by the lowest apparent porosity increasement.

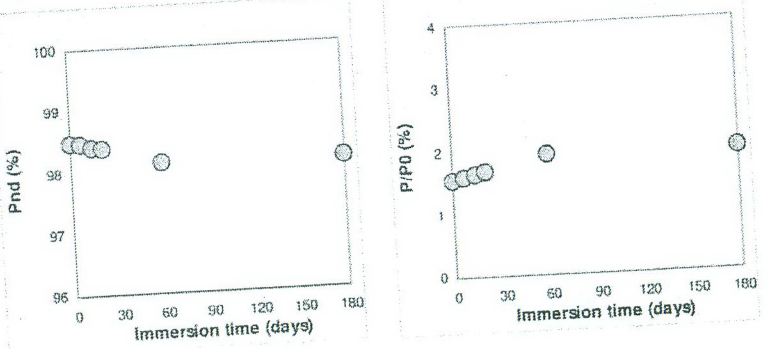
According to that finding, further investigation was realized on sulfur concrete samples with alumina in hydrochloric acid.Since these samples showed accordance between mechanical strength loss and apparent porosity increasement after only 21 days, treatment time was shortened to 180 days.

Image analysis

The image analysis technique was applied for surface destruction monitoring during durability testing.As addition to the classical porosity test in this research the porosity changes due to chemical influence were followed by the microscopic image analysis. In this case, the samples were analyzed with the minimum resolution in order to characterize only primary interactions between material and the induced stress agents.

Macro image analysis was realized with taking into account the total surface of the samples in order to monitor damage distribution at the surface. For the materials used in engineering, it is very important to analyze the whole sample surface, not only its part, as it is difficult to determine which part is representative for predicting the sample behavior. The level of surface destruction is defined as a ratio of damaged surface area (P) to original surface area before the acid resistance testing (P_0) [13-15].

Diagrams presenting non-damaged surface area (P_{nd}) and surface destruction level (P/P_0) of sulfur concrete samples with alumina in 10 % HCl are given in Figure 7 [16].



a)

b)

Figure 7. a) Non-damaged surface area of sulfur concrete with alumina in 10% HCl versus immersiontime; b) Surface destruction level of sulfur concrete with alumina in 10% HCl versus immersion time

Certain damage was present on sulfur concrete samples with alumina before the testing in 10 % HCl. Surface destruction level before the testing was 1.5 % and it slightly increased during the immersion time, the value of 1.9 % was reached after 180 days.

Detected surface changes of sulfur concrete samples can be connected with apparent porosity increase results previously presented. Acid penetration is limited to the surface and open pores that were not coated by sulfur, which in turn resulted in slight porosity increase. For the period of 180 days, apparent porosity enhanced from 1.38% to 1.46% (Figure 6). This is in accordance with slight surface destruction increase.

3.4 Ultrasonic pulse velocity

The measurement of the ultrasonic pulse velocities, both longitudinal (V_p) and transversal (V_s), was used to monitor the internal material degradation with increasing the time of acid treatment.

The results of ultrasonic pulse velocity changesin three directions (x, y, z) during the testing time are given in Figure 8.Presented results suggest that the material was very stable during testing, as velocity degradation was not significant- it was less than 5% at the end of the testing which means that the porosity increase is not significant. These results indicate that the samples exhibited excellent resistance to acid influence.

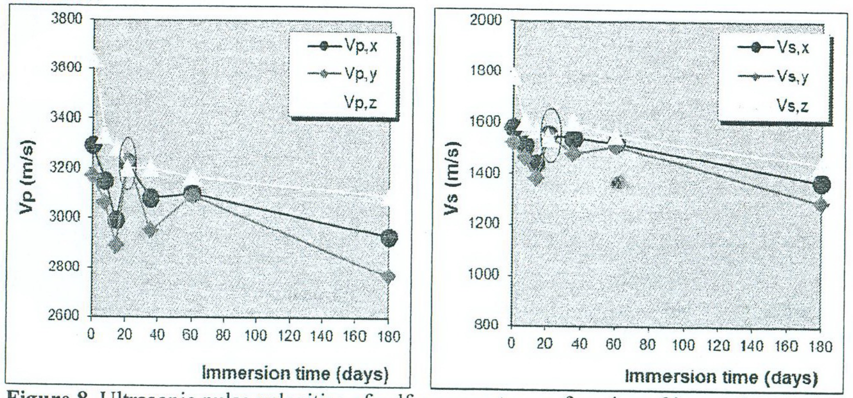


Figure 8. Ultrasonic pulse velocities of sulfur concrete as a function of immersion time

Furthermore, homogeneity of the material can be disscused based on mutual differnences in values of ultrasonic pulse velocities in three directions.

Differences between maximum and minimum values of ultrasonic pulse velocities are presented in Figure 9.

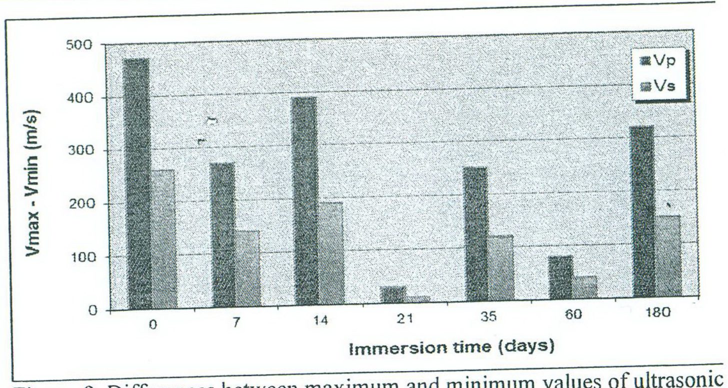


Figure 9. Differences between maximum and minimum values of ultrasonic pulse velocities

Bigger differences between the highest and the lowest values of ultrasonic pulse velocities of untreated samples compared to those treated for 180 days indicate that material after acid treatment became more homogeneous. Since those differences for the treatment period of 21 days are negligible, the material can conditionally be considered as homogenous. For that treatment period compressive strength was the highest. All observed homogeneity changes are the result of material structure rearrangement caused by the influence of acid.

SEM analysis

Bearing in mind that the testing of materials is related to the definition and quantification of the structure and homogeneity of the material, further investigation of the structure with increased resolution, in this case using a scanning electron microscope, was a logical step.For comparison, structural differences between sulfur concrete and Portland cement concrete samples, both treated for 21 days are given in Figure 10.

The analysis of SEM- pictures of sulfur concrete and Portland cement concrete shows two different material changes provoked by the influence of the induced destruction agent.In the case of sulfur concrete, binder phase (sulfur) rearranged and conditionally homogenized the structure. As a result of the treatment, secondary bonding of the aggregate, which additionally homogenized the material, was noticed. It can be concluded that introducing an external disturbance leads to a new quality of the material in terms of its exploitation. Obviously, chemical activation of sulfur concrete, precisely sulfur as a binder, resulted in structural changes of the material. Unlike sulfur concrete, the initial structure of Portland cement concrete was completely degraded, whereby the binder phase was destroyed due to the chemical agent influence. The presented image analysis proves that for both materials changes in the structure on micro scale exist and they are result of interactions with the induced destruction agent, which lead to different scenarios of concretes life circles.

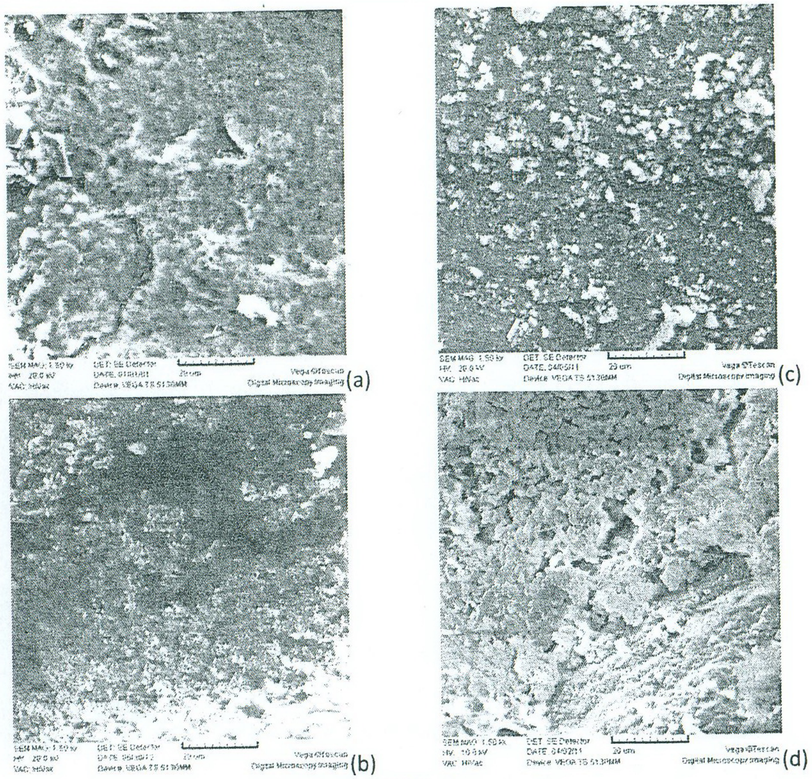


Figure 10. SEM- pictures of:
(a) sulfur concrete untreated, (b) sulfur concrete treated for 21 days,
(c) Portland cement concrete untreated, (d) Portland cement concrete treated for 21 days

CONCLUSION

In this research technological procedure for obtaining sulfur concrete was clearly defined. Sulfur concrete was produced of the secondary sulfur from the oil refining process, sand as an aggregate, and various fillers. Modification of sulfur was performed by cyclic hydrocarbon, dicyclopentadiene. Behavior of produced sulfur concrete in three aggressive environmentsas function of time was investigated.Mechanical testing results showed that sulfur concrete had possessed satisfactory properties and kept them after six months of treatment by the induced destruction agent.Image analysis signified negligible surface changes which are in accordance with slight porosity increase during the treatment.Ultrasonic examination indicated significant homogenity changes during the treatment.Scanning electron microscopy proved a rearrangement of the structure during the treatment which was manifested as enhanced homogeneity.It can be concluded that by adequate technological procedure and selection of the initial components, sulfur concrete with satisfying mechanical strength and good resistance to aggressive solutions was obtained. The obtained results can be used for finding new possibilities of sulfur concrete applying when high resistance to corrosive effect of the environment is required.

REFERENCES

1. Milica M. Vlahović, Predrag B. Jovanić, Sanja P. Martinović, Tamara Đ. Boljanac and Tatjana D. Volkov Husović, Influence of Chemical Stress on Sulfur-Polymer Composite Structure, Chapter 10 in New Developments in Sulfur-Polymer Composites Research, Editors: Stephan Laske and Andreas Witschnigg, Publisher: Nova Science Publishers, Inc., New York, USA, Pages: 257-278, 2013.
2. Gracia, V; Vàzquez, E; Cramona, S. Utilization of by-produced sulfur for the manufacture of unmodified sulfur concrete, International RILEM Conference on the Use of Recycled Materials in Buildings and Structures, Barcelona, Spain, 2004; 1054-1063.
3. World Business Council for Sustainable Development report, Cement Industry Energy and CO_2 Performance, Getting the Numbers Right, 2009.
4. Vlahovic, M., Martinovic, S., Boljanac, T., Jovanic, P. &VolkovHusovic, T. (2011). Durability of sulfur concrete in various aggressive environments,Constr. Build.Mater.,25, 3926.
5. Vlahović, M. &Jovanić, P. (2012). In Microscopy Book Series- Number 5: Current microscopy contributions to advances in science and technology; Editor, Méndez-Vilas, A.;Formatex Research Center, Spain, 2, 1171.
6. Đorđević, N., Boljanac, T., Vidojković, V., Vlahović, M., Branković, A. &Martinović, S. (2010). Modification of secondary sulfur from oil refining process by dicyclopentadiene and application of obtained modified sulfur, Patent 53412.
7. Mohamed, A.M.O.&El Gamal, M. M. (2010). Sulfur concrete for the construction industry- A sustainable development approach. J. Ross Publishing: U.S.
8. Banerjee, S. (1998). Monolithic refractories. Westerville: The American Ceramic Society, Singapore: World Scientific Publishing Co. Pte. Ltd.
9. Methods of testing cement- Part 1: Determination of strength (2008). Serbian standard SRPS EN 196-1, 2008.
10. Standard Test Method for Density, Absorption, and Voids in Hardened Concrete. (2006). ASTM C, 642-06.
11. ACI Committee 548, Guide for Mixing and Placing Sulfur Concrete in Construction, Report 548.2R-93, (American Concrete Institute), Farmington Hills, Mi (1993).
12. Vlahović, M., Boljanac, T., Branković, A., Vidojković, V., Martinović, S. &Đorđević, N. (2010). The influence of filler type on the corrosion stability of the sulfur concrete, Hemijskaindustrija.,64, 129-137.

13. Milica Vlahović, Maja Savić, Sanja Martinović, Tamara Boljanac, Tatjana Volkov-Husović, Use of image analysis for durability testing of sulfur concrete and Portland cement concrete, Materials and Design, 34 (2012) 346-354.
14. MilicaVlahović, PredragJovanić, Sanja Martinović, Tamara Boljanac, Tatjana Volkov-Husović, Quantitative evaluation of sulfur-polymer matrix composite quality, Composites Part B: Engineering, 44 (1) (2013) 458-466.
15. Milica M. Vlahovic, Sanja P. Martinovic, Predrag B. Jovanic, Tamara Đ. Boljanac and Tatjana D. VolkovHusovic, Image Analysis Technique for Evaluating Damage Evolution and Predicting Mechanical Strength of Concrete Structures under Corrosion Conditions, Chapter 7 in Advances in Image Analysis Research, Editor: Roger M. Echon, Nova Science Publishers, Inc., New York, USA, 147- 170, 2014.
16. Milica M. Vlahović, Predrag B. Jovanić, Sanja P. Martinović, and Tatjana D. Volkov Husović, Behavior of sulfur- polymer matrix composites with different fillers under acid and salt influence, Chapter 9 in Polymer-Matrix Composites: Types, Applications and Performance, Series: Polymer Science and Technology, Editor: Rakesh Kumar, Publisher: Nova Science Publishers, Inc., New York, USA, 215-240, 2014.