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in cooperation with

CENTRE OF EXCELLENCE FOR INTEGRATIVE BIOETHICS

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EDITORS

Anita Štrkalj

Zoran Glavaš

Sanja Kalambura

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REUSE OF WASTE SULFUR AS A BINDING AGENT IN CONCRETE

Milica Vlahović*, Sanja Martinović*, Aleksandar Savić, Zoran Stević*****
Tatjana Volkov Husović****

[*] Institute of Chemistry, Technology and Metallurgy, Belgrade, Serbia
[**] University of Belgrade, Faculty of Civil Engineering, Belgrade, Serbia
[***] University of Belgrade, Technical Faculty in Bor, Belgrade, Serbia
[****] University of Belgrade, Faculty of Technology and Metallurgy, Belgrade, Serbia

corresponding author: Milica Vlahović,e-mail: mvlahovic@tmf.bg.ac.rs

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ABSTRACT

Mainly due to the strict global environmental regulations regarding the oil and gas refining processes, which limit the maximum quantity of sulfur in combustibles, the availability of waste sulfur has been considerably growing during the last decades and it is evident that there will be a continuous abundant supply of waste sulfur in the future. Finding new ways for waste sulfur consumption thus becomes very important. In this research, possibility of using waste sulfur as a binding agent in concrete was analyzed and the properties of the obtained sulfur polymer concrete in aggressive environments were examined using destructive and non-destructive testing methods. Compressive strength changes were insignificant. Ultrasonic measurements indicated significant homogeneity changes and slight internal degradation. Based on the obtained results, the material with satisfying quality for possible application in corrosive environment was produced.

Keywords: *waste sulfur, sulfur polymer concrete, destructive testing methods, non-destructive testing methods*

1. INTRODUCTION

During the last decades, environmental concerns have resulted in severe sulfur emission constraints that requires the active management of industrial sulfur. Therefore, the availability of sulfur has considerably grown worldwide, mostly owing to the oil and gas refining processes. Sources of sulfur are organic sulfur compounds in crude oil and hydrogen sulfide in sour natural gas. Organic sulfur compounds in crude oil are converted to hydrogen sulfide by a hydrogenation process [1]. Hydrogen sulfide from both crude oil and natural gas is converted to elemental sulfur by Claus process, summarized in Eq.(1):

$$3\ H_2S + 3/2\ O_2 \rightarrow 3/X\ S_x + 3\ H_2O + 620\ kJ \quad (1)$$

Claus process is schematically presented in figure 1.

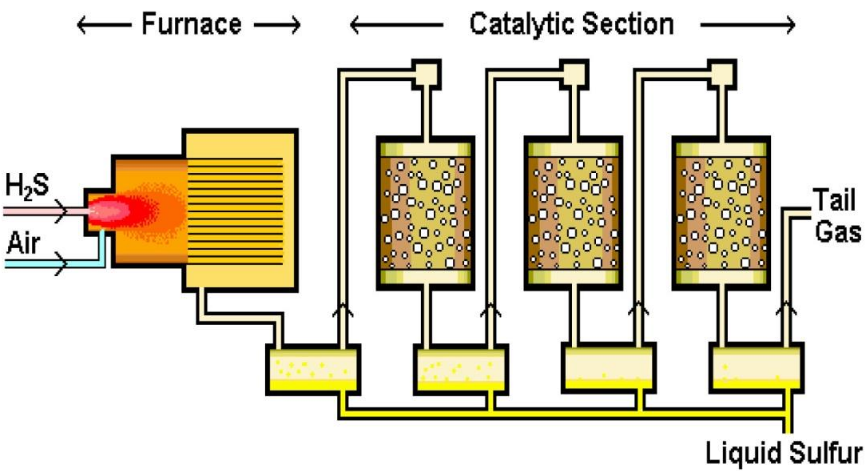


Figure 1. Scheme of Claus process [2]

Produced sulfur can be made into several forms. Piles and blocks of sulfur produced by Claus process are given in figure 2.

Figure 2. Piles [3] and blocks [4] of sulfur produced by Claus process

Waste sulfur from oil processing has been stored leading to more or less controlled disposal, while waste sulfur from ore processing, in the form of gaseous oxides, is usually converted into sulfuric acid and onwards used for artificial fertilizers. Sulfur demand has to increase drastically or thorough disposal practices must develop, otherwise, sulfur by-product will persist as a chemical waste problem. Modern industrial production still needs further development of technologies that would provide incorporating waste sulfur into useful products, thus removing it from the environment. Construction materials should always be considered as potential recipients of large amounts of wide range of waste that can be inertized by incorporating into usable and sustainable construction materials. Therefore, construction materials are preferred acceptors because of huge amounts of secondary sulfur. On the other hand, they have wide practical application [5].

Sulfur can completely substitute Portland cement to form new, stable, hard concrete product. Using sulfur as a binder is based on its physico-chemical characteristics: chemical passivity, hydrophobicity and excellent resistance to aggressive agents (mainly acids and salt solutions, but not bases) [6]. Unlike concrete with Portland cement, concrete made from sulfur needs heating during production, usually by the combustion of fossil fuels. In spite of heating, concrete made with sulfur releases far fewer greenhouse gas emissions compared with Portland cement concrete. By using sulfur as a binder, the emissions released in the calcination process during clinker production as well as the combustion emissions generated to supply heat to the calcination process are eliminated.

Consuming sulfur for the production of sulfur polymer concretes and mortars is a relatively new technology that has to be proven in practice. Recent experience shows that concrete produced with sulfur binder instead of cement and water has significant chemical and physico-mechanical advantages comparing with Portland cement concrete. Sulfur polymer concrete is environmentally friendly and cost-effective with relatively simple composition and manufacture, and interesting properties. Due to its mechanical strength, fast hardening, quick setting and corrosion resistance, it belongs to high performance materials suitable for numerous applications, especially those in which other materials fail.

Sulfur polymer concrete is a high performance environmentally sustainable and durable thermoplastic composite material made of mineral aggregates and modified sulfur as a replacement for cement and water in conventional Portland cement concrete at temperatures above the hardening point of sulfur (120 °C). Additionally, such material allows using large amounts of sulfur from worldwide oil refineries and metallurgical industry. This relatively new building material can possibly replace conventional Portland cement concrete in many branches of construction [7].

The possibility of using sulfur by-product as a binder for concrete production was investigated in this research. Mechanical strength, internal destruction and homogeneity of the obtained sulfur polymer concrete during acid and salt resistance testing was examined.

2. EXPERIMENTAL

2.1. Technological procedure of sulfur polymer concrete production

The initial materials for the production of sulfur polymer concrete were aggregate, sulfur and modified sulfur and filler.

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. Classical chemical analysis combined with AAS and AES 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 %).

Elemental sulfur, the basic component for a modified sulfur binder, as a granular shape with purity of 99.9 % originates from oil refining process by Claus's procedure in the Oil Refinery Pancevo, Serbia. Dicyclopentadiene (DCPD), cyclic hydrocarbon, was used for sulfur modification. The modification procedure consisted of mixing elemental melted sulfur and DCPD in the temperature range from 120 to 140 ºC and ambient pressure for 30 min, and then rapid cooling and solidification of the obtained sulfur polymer [8].

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, Serbia). Filler plays an important role because with sulfur it forms paste that coats and binds the aggregate particles. Talc, microsilica and fly ash fulfill these requirements and therefore are recommended for the sulfur polymer concrete production [1], while fine fractions of calcined alumina are used as fillers for refractory concretes [9]. Particles size of all used fillers was below 75 μm.

The applied manufacturing technological procedure for sulfur polymer concrete preparation is described in literature [10]. Preheated aggregate and filler (up to 160 ºC) 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 2 minutes of homogenization and mixing, the sulfur polymer concrete mixture was casted into molds preheated at 120 ºC 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. Sulfur polymer concrete hardens very rapidly (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 time. The samples were demolded after 3 h and then kept at room temperature for 24 h. For the purpose of this testing, prism-shaped samples with dimensions (4 x 4 x 16) cm were prepared.

2.2. Characterization of sulfur polymer concrete

Characterization of sulfur polymer concrete was realized before and during acid and salt resistance testing. The prepared prism-shaped samples were immersed in three solutions: 10 % HCl, 20 % H_2SO_4 and 3 % NaCl for 360 days.

The experimental program consisted in performing the following properties measurements on sulfur polymer concrete samples.

- *Compressive strength*

Compressive strength was conducted using the "Amsler" press (Germany) with maximum load of 200 kN, and method for testing the strength of concrete according to the standard [11].

- *Ultrasonic pulse velocity*

The measurement of ultrasonic pulse velocity was realized to monitor the internal material degradation and to discuss its homogeneity. It was performed using the equipment OYO model 5210 (Japan) according to the standard testing procedure (SRPS D. B8. 121.).

3. RESULTS AND DISCUSSION

3.1. Visual inspection

The appearance of sulfur polymer concrete samples after 12 months in acid and salt solutions is presented in figure 3. Obviously, there are no signs of destruction.

It is well known that Portland cement concrete is not resistant to acid and salt influence.

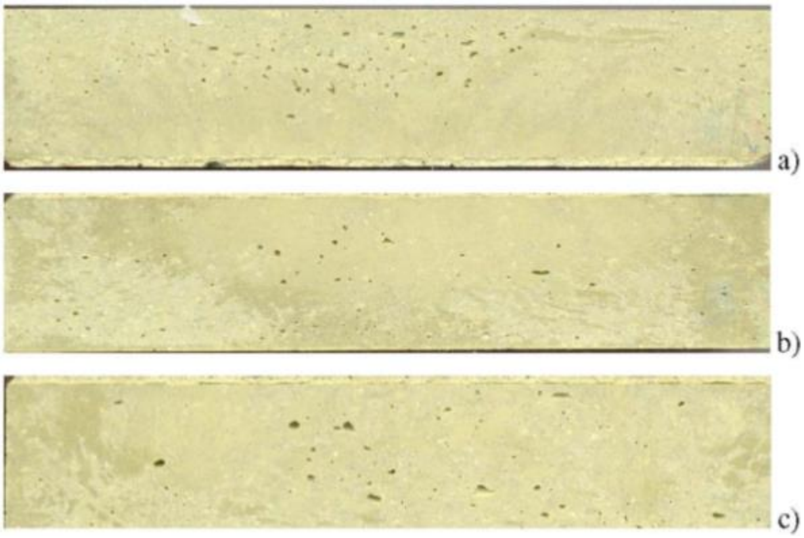


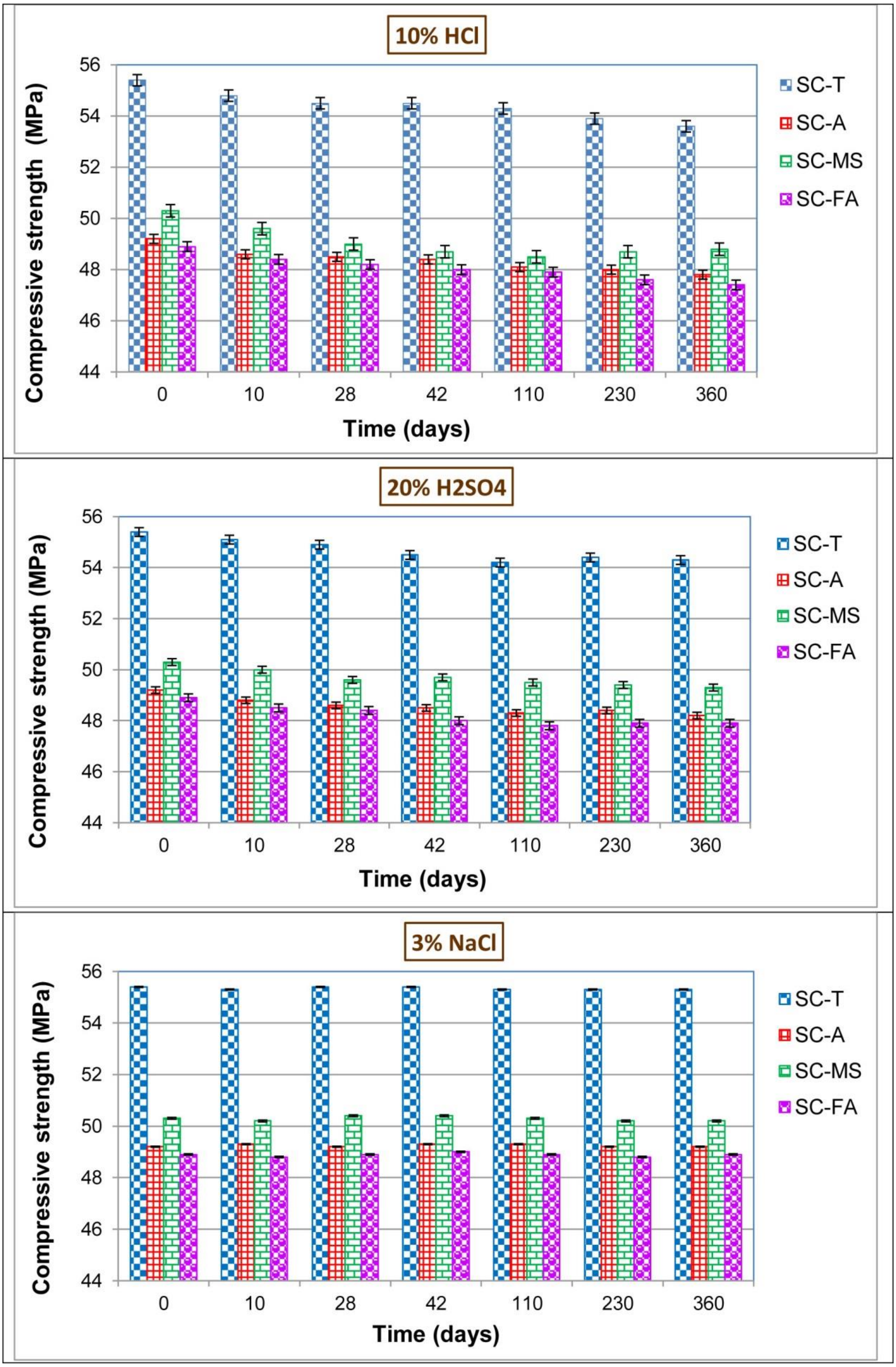
Figure 3. Surfaces of sulfur polymer concrete samples after one year:
a) with talc in 10 % HCl solution, b) with microsilica in 20 % H_2SO_4 solution,
c) with fly ash in 3 % NaCl solution

3.2. Compressive strength

The obtained results, given in figure 4, represent durability of sulfur polymer concrete samples depending on the filler type and solution expressed through compressive strength change as a function of immersion time.

According to these results, behavior of the sulfur polymer concrete samples with different fillers regarding compressive strength changes was quite uniform in three solutions. Generally, all sulfur polymer concrete samples after 360 days lost ~ 3 % of their strength in 10 % HCl, ~ 2 % in 20 % H_2SO_4 and negligibly in 3 % NaCl. It means that the type of filler did not exhibit significant influence on strength degradation [12].

Since mechanical strength is dependent on the defects in concrete microstructure, it can be assumed that the reason for mechanical strength degradation lies in increased porosity of the treated sulfur polymer concrete samples compared with the untreated samples. Porosity is related to the movement of chemical substances into and out of the material and consequently affects durability of concrete, as it is connected to deterioration processes driven by the transport properties of concrete. In sulfur polymer concrete, the majority of the matrix is composed of sulfur coated materials (aggregate and filler) and sulfur accumulated in the voids between particles.



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

Figure 4. Compressive strength of sulfur polymer concrete with different fillers in acid and salt solutions

3.3. Ultrasonic pulse velocity

The measured values of ultrasonic pulse velocities, both longitudinal (V_p) and transversal (V_s), in three directions (x, y, z) during the immersion time suggest that sulfur polymer concrete was very stable regarding internal degradation, as velocity decrease was negligible - less than 5 % at the end, which means that the porosity increase was not significant.

Based on differences between maximum and minimum values of ultrasonic pulse velocities in three directions (ΔV) during the immersion time, homogeneity of sulfur polymer concrete can be discussed. As an example, those differences for sulfur polymer concrete sample with alumina as filler in 10 % HCl are presented in figure 5.

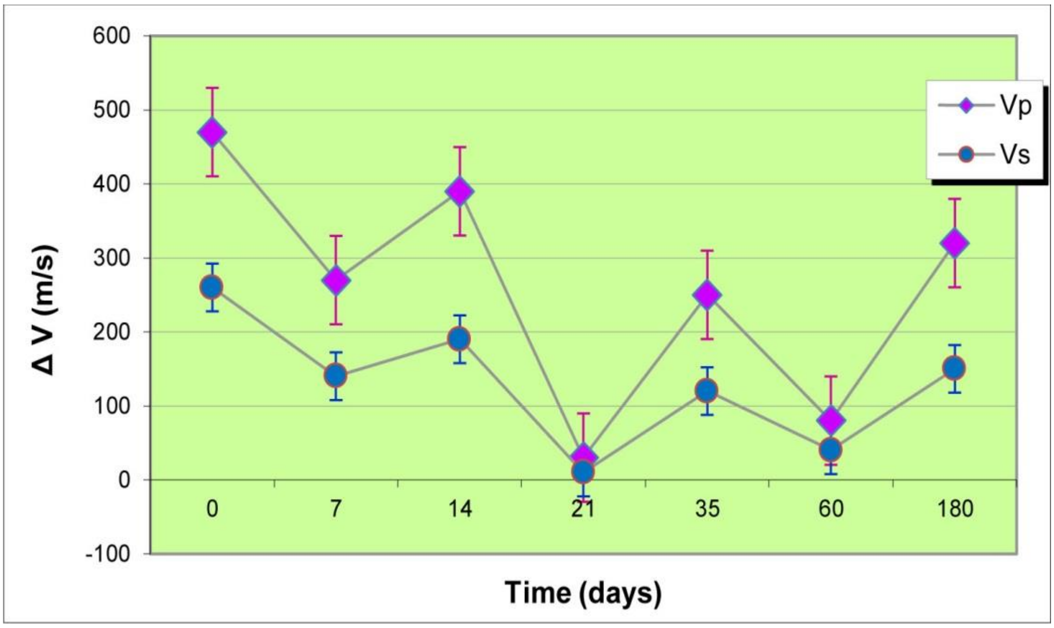


Figure 5. Differences between maximum and minimum values of ultrasonic pulse velocities in three directions for sulfur polymer concrete with alumina during immersion in 10 % HCl

Greater differences between maximum and minimum values of ultrasonic pulse velocities of the samples before the immersion compared to those after 180 days of immersion indicate that the material after acid treatment became more homogeneous. Since those differences for 21 days of immersion are negligible, the material can conditionally be considered as homogenous. For that period compressive strength was the highest (figure 4). All observed homogeneity changes are the result of material structure rearrangement caused by the acid influence.

4. CONCLUSION

In this study the possibility of using waste sulfur from oil refinery as a binding agent for concrete production was successfully proved. Technological procedure for obtaining sulfur polymer concrete was precisely given. Sulfur polymer concrete was produced of the secondary sulfur from oil refining process, sand as an aggregate, and various fillers. Modification of sulfur was performed by cyclic hydrocarbon, dicyclopentadiene. Behavior of produced sulfur polymer concrete during acid and salt resistance testing was investigated. The compressive strength did not change significantly. Ultrasonic measurements indicated significant homogeneity changes as a result of structure rearrangement provoked by acid influence but internal degradation was insignificant. It can be concluded that by adequate technological procedure and selection of the initial components, sulfur polymer concrete with satisfying mechanical strength and good resistance to acid and salt solutions was obtained. This in turn will make this material a good candidate for its use in construction industry and for other applications where high resistance to corrosive effect of the environment is required.

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