Durability of Concrete with Man-made Thermoplastic Sulfur Additive

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Abstract. In the article, the data on sulfur surface modification and its influence on the properties of common cement mix and concrete are discussed as well as durability and corrosive resistance of modified compositions. The composite components, conditions of mixtures making, and required temperature treatment were established in the laboratory testing. The potentiometric model was used to assess the interaction between the corrosive environment and the modified composites, a corrosive agent being used as a sulfate environment. This model takes into account the change in reaction potentials and is used as an index of the solvolysis reaction between the sulfate solution and constituents of the modified cement matrix. This modelling determined two main characteristics used to predict the durability of building material. These are the depth of corrosive agent in the material structure and the amount of solved calcium hydroxide. The established data show the potential usefulness of the modified additive based on man-made sulfur as an additive for cement composites. The modified additive can be used for materials with a high performance and durability in an aggressive environment. The increasing of corrosive resistance might be explained by the structure changing and by the properties of the formed crystalline hydrates.

1. Introduction

Today, sulfur compounds in terms of their negative environmental impact are one of the leaders among pollutants. More than 90% of sulfur enter the atmosphere in the form of SO₂ from the exhaust gases from the combustion of hydrocarbons; the remaining amount falls to the share of sulfates and other compounds [1, 2]. In addition to the negative impact on the environment, elemental sulfur in the form of dust has significant anthropogenic harm, irritating the skin and respiratory organs of a person [1, 3].

Global sulfur production is almost completely a by-product of oil and gas processing, as well as non-ferrous metallurgy. Sulfur-containing wastes are collected in dumps and stored, as a rule, in open landfills. The production, storage, and transportation of large volumes of industrial sulfur are associated with high current and capital spendings and pose a serious environmental problem for the population of nearby cities. One of the possible ways of utilizing sulfur-containing wastes is the development of sulfur concretes with a relatively simple component composition and production.
technology, which are able to exhibit unique operational properties [4, 5]. This feature is due to the specific properties of industrial sulfur, such as: inertness to alkalis and acids, low natural radioactive background, and protective properties from electromagnetic and radioactive radiation [6, 7]. The use of this waste product when modifying gypsum and cement matrices by impregnation led to products with high corrosion resistance and mechanical strength [7, 8].

Since 1975, the USA and Canada have been conducting research and actively introducing the use of industrial sulfur in road construction, as well as using sulfur melt to create products to produce sulfur concrete [9]. Several methods for introducing industrial sulfur have been developed in road construction: a) adding sulfur into bitumen, followed by mixing the sulfur-bitumen binder with other components of the asphalt mix and b) adding sulfur into asphalt concrete at the stage of mixing its components [9].

There is a process for the production of sulfur concrete, based on "hot" technology, when all mixed components are heated to 140-150 °C.

There is also a direction presented in studies [10, 11], which is the impregnation of concrete in sulfur melt. Impregnation in this case is carried out under atmospheric pressure at a temperature of 146 °C for 10 to 24 hours; as a result, while cooling in surface pores, crystallization of sulfur occurs.

It should be noted that all of the above methods of using industrial sulfur for the modification of mineral compositions have very significant drawbacks such as: increased energy costs, the need for complete industrial re-equipment, economic inexpediency, and increased complexity of the process.

The analysis of previous experience in modifying mineral compositions with industrial sulfur and evaluating the physicotechnical characteristics of the additive made it possible to determine the degree of influence of the thermoplastic additive (hereinafter TSD) on the performance properties of cement concrete, including assessing the effect of the additive on the rate of sulfate corrosion. In the study, modified industrial sulfur was used as a thermoplastic additive, represented by polymorphic allotropes formed under heat treatment conditions: crystalline (cyclooctaser), active allotropic compounds, and polymer sulfur. At the same time, some researchers isolate up to seven different polymorphic sulfur allotropes [12, 13]. As studies [14] show, the percentage ratio of these forms directly depends on the temperature and cooling rate of the melt in the manufacture of products.

J. Stark [15] established that the main criteria affecting the corrosion resistance of concrete obtained on the basis of a hydraulic binder are the packing density of crystalline hydrates of the cement matrix, as well as the main characteristics of the pore space of the concrete, which is a capillary-porous structure.

Sulfate corrosion was chosen as the main aggressive component affecting artificial stone with a hydraulic binder since during this process new formations appear and their volume increases, which leads to the appearance of internal stresses, gradually leading to the destruction of the composite.

Sulfate-containing solutions are the main sources of sulfate corrosion as they are present in sufficient quantities in natural or waste water. The regular impact of such an aggressive environment on concrete structures leads to the formation of ettringite crystals in the pore space of concrete, and as a result, increases internal stresses [15].

The formation of complex salt occurs according to the reaction:

\[3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot n\text{H}_2\text{O} + 3\text{CaSO}_4 + (31-n)\text{H}_2\text{O} \rightarrow 3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 31\text{H}_2\text{O}\]

In the pores of set cement, trisulfate hydrosulfoaluminate is formed, and in this connection, the set cement expands 2–4 times [15].

This article presents the results of a study of the physicotechnical and physicochemical properties of compositions modified with industrial sulfur and the parameters of the pore space as well as the simulation results of the effect of aggressive sulfate medium on the developed compositions.
2. Experimental program

Raw materials

In order to experimentally study the effect of thermoplastic sulfur additive on the performance of products based on hydraulic binder, a two-stage series of experiments and a detailed study using modern methods of physicochemical and physicotechnical analysis were carried out.

To conduct the research on corrosion resistance, cubic samples were made with geometric dimensions of 20x20x20 mm. In the process of preparing the mixture, the cement of CEM I 32.5H of Topkinsky cement plant was used as well as fractionated sand, in accordance with the requirements of Russian State Standard 8736-2014 with the fineness modulus Mk=0.7. The choice of the sand fraction is determined by the requirements for reactive powder concrete and research in this direction [16-19].

TSD was added at the stage of mixing the main components with the subsequent introduction of mixing water. Subsequently, the mixture was molded into metal molds and removed after 2 days, followed by heat treatment.

Physico-technical properties of the material were determined according to Russian State Standard 10180-2012 «Concretes. Methods for determining the strength of control samples».

To study the degree of corrosion resistance, samples of the modified composition were tested by the potentiometric method described in the study [20].

Portland cement. To assess the influence of thermoplastic additives on the physicotechnical and physicochemical properties of artificial stone, Portland cement of CEM I 32.5H, Topkinsky cement plant, was used. The main properties of Portland cement are shown in Tables 1 and 2.

| Chemical composition of cement, weight, % |
| --- |
| CaO | SiO₂ | Al₂O₃ | Fe₂O₃ | SO₃ | MgO | Other |
| 65.73 | 21.66 | 5.16 | 4.42 | 1.56 | 1.12 | 0.35 |

| Mineral composition of cement |
| --- |
| C₃S | C₂S | C₃A | C₄AF | Other |
| 61.00 | 19.00 | 4.00 | 15.00 | 1.00 |

Properties of Portland cement: Specific surface, m²/kg - 380; Normal density of cement paste, % - 25.5; Start/end of setting, min. - 165/215;

Sand: technical specifications of the filler correspond to Russian State Standard 8736-2014 and are presented in Table 1.

| Technical specifications of filler |
| --- |
| Fraction, mm/particle size module (State Standard 8736-2014) | Moisture content, not more than, % | Content of dusty clay particles, not more than, % | Clay content in lumps, not more than, % | Content of organic impurities | Content of contaminants | Bulk density, kg/m³ |
| 0-1.25/0.7 | 0.3 | 5 | 0.5 | no | no | 1500-1600 |
**Industrial sulfur.** For the study, industrial sulfur of grade 9998 was used, which corresponds to Russian State Standard 127.1-93. The specifications and chemical composition are presented in Table 2.

| Name          | Particle shape | Bulk density | Mass fraction of sulphur | Mass fraction of ash | Mass fraction of organic substances | Mass fraction of water |
|---------------|----------------|--------------|--------------------------|----------------------|-------------------------------------|-----------------------|
| Unit          | -              | g/cm³        | %                        | %                    | %                                   | %                     |
| Specifications| Hemispherical  | 1.3          | 99.99                    | 0.005                | 0.005                               | 0.01                  |

### 2.1. The process of experiment

Before adding directly into the mixture, industrial sulfur was treated with a laboratory dissolver. The processing conditions were 1500 rpm, the ratio of organic solvent being 1:3.

The study of the effect of thermoplastic additives was carried out on sample cubes with dimensions of 20x20x20 mm. After stripping, in order to develop strength, the samples were kept under normal conditions and then placed in an oven at a temperature of 180 °C (sulfur obtained from the melt at this temperature contains three allotropic forms of sulfur in certain amounts for 60 minutes (time required for uniform heating [22]). After the heat treatment, the samples were cooled under normal conditions, and their linear dimensions, mass, density and compressive strength, and corrosion resistance were measured.

Samples based on Portland cement of the control composition without additives and with additives of 2, 5, 7 and 10% of industrial sulfur by weight of the binder were made from paste of normal density. The samples were kept in the mold for 48 hours in humid conditions, then the stripping formwork was carried out, and the samples were subjected to heat treatment according to the following scheme: isothermal exposure at 180 °C for 1 hour, then 2 hours cooling to 35-40 °C.

To determine the changes in the structure of the samples based on the modified cement-sand composition, a complex of studies was carried out at different stages of strength development of an artificial stone using scanning electron microscopy and multipurpose X-ray microfocus CT system for 3D metrology and analysis.

The state and characteristics of the pore structure of the samples were determined using X-ray computed tomography, which is a method for studying the internal structure of an object by repeated X-ray radiation in various directions, followed by processing the obtained data by mathematical methods and algorithms. As a result of the computational processes, a three-dimensional image is formed [23, 24].

X-ray tomography was used in this study to determine the nature of the changes in the pore structure of the artificial stone and assess the effect of the sulfate medium. The measurements were made with the GEPheonixVtomexM300 instrument at the AdMaS research center in Brno, Czech Republic.

The establishment of structural and physico-chemical changes, in its turn, was carried out when shooting the microstructure with TESCANMIRA3 XMU used to obtain high-resolution and ultra-high resolution microstructure images as well.

For faster determination of the corrosion resistance of the samples, the potentiometric method was used, which allows simulating in laboratory conditions the effect of a sulfate medium on objects based on mineral matrix.
In order to recreate the conditions of exposure to an aggressive environment, a uniform solution of sodium sulfate was prepared.

The following initial components were used to create an aggressive sulfate environment:
- distilled water according to State Standard 6709-72;
- Glauber's salt according to State Standard 4171-76.

Hydrolysis of the salt proceeds according to the scheme “strong base - strong acid”:

\[
Na_2SO_4 \times 10H_2O + 2HCl = 2NaOH + H_2SO_4 + 9H_2O
\]

In the process of testing the samples, the cubes were placed in laboratory glass vessels, in which they were kept for 7, 14, 28 days.

This technique is based on the dependence of the rate of release of calcium hydroxide from samples on the exposure time in an aggressive environment. The amount of calcium hydroxide was calculated according to the results of titrimetric analysis and the results of measuring the hydrogen index (pH).

3. Analysis of results

In order to determine changes in the morphology of crystalline hydrates under the influence of an aggressive sulfate medium on the samples and the control composition modified by a thermoplastic additive, a microstructure study was carried out. A comparative analysis showed (Fig. 1) that the dense packing of crystalline hydrates and the formation of a significant amount of an amorphous phase slows down the reaction of the interaction of the components with aggressive sulfate agents. At the same time, in the control composition, the formation of ettringite is observed, which contributes to the rapid leaping of reactive components.

![Figure 1](image1.png)  
**Figure 1.** The microstructure of the samples (28 days) after testing for corrosion resistance with 10,000-fold magnification: (a) control sample, (b) modified sample

The presented analysis of the microstructure is confirmed by the data of physical and technical tests of the samples for compressive strength before and after testing for sulfate corrosion resistance (Fig. 2). Based on the results of the experiment, we obtained a diagram reflecting the degree of sulfate corrosion in the control and modified samples, which shows a significant slowing down of the leaching of portlandite from the structure of set cement. In this case, the optimal content of the additive is 7% by weight of the binder in comparison with the control composition.
Figure 2. Strength of cement compositions after exposure to aggressive conditions for 28 days in 1N of the solution Na₂SO₄

Using computed tomography, studies were performed of the characteristics of the pore space of the sample cubes, modified and control compositions after testing for corrosion resistance. This method, taking into account the sensitivity of the equipment, constructs an image by means of transverse lines and sections (Fig. 3), allowing the opportunity to estimate the value of the air content taking into account the distance factors. The obtained values on the plane were compared with control distances in three-dimensional space (Fig. 4).

![Figure 2](image)

**Figure 3.** Scale of equivalent indicators, pore space diameter in mm³

The color gradation (Fig. 3) demonstrates equivalent parameters in pore diameter in millimeters, allowing one to estimate the size and volume of pores, microcracks, and regions in which the soluble components of the artificial stone were actively washed out.

![Figure 3](image)
**Figure 4.** Cross sections of a 3D model of samples (28 days) after testing for corrosion resistance: (a) control sample, (b) modified sample

**Figure 5.** 3D model of the segmented phase of the spatial distribution of the pore space in the samples (28 days) after testing for corrosion resistance: (a) control sample, (b) modified sample

The results of three-dimensional visualization of the structure of the control and modified composition presented in Fig. 6 confirm the efficiency and positive effect of the thermoplastic additive on the resistance of the modified samples to sulfate corrosion. Processing the obtained three-dimensional data allows us to carry out a quantitative analysis of the characteristics of the structure after exposure to an aggressive sulfate medium (Table 5), demonstrating change in the volume of the pore space after exposure to sulfate corrosion in the modified and control samples.

**Table 5.** Pore Space Parameters

| Sample     | Material volume, mm$^3$ | Air volume, mm$^3$ | Porosity value, % |
|------------|-------------------------|-------------------|-------------------|
| Control    | 4104.30                 | 361.16            | 8.8               |
| 7% TSD     | 4514.45                 | 181.44            | 4                 |

**4. Conclusion**

This study shows the potential use of thermoplastic sulfur additive when it is introduced into a cement-sand mortar as an active component, leading to a change in the structure and properties of the final modified composite. A change in the morphology of crystalline hydrates during heat treatment and melting of the additive in the material allows creating the conditions for an increased content of the amorphous phase. The morphological parameters of the obtained structure made it possible to confirm in laboratory conditions the increased corrosion resistance of the modified compounds, which is manifested in the delayed leaching of reactive and readily soluble portlandite. This allows predicting the increased corrosion resistance of the modified composition in comparison with the control samples.
The conducted studies confirm the effectiveness of technological solutions for the use of industrial sulfur to modify artificial stone material. In addition, these results demonstrate the positive effect of thermoplastic sulfur additives on the technical and operational properties of fine-grained concrete.

Acknowledgment

The work was carried out at the financial support by Kalashnikov Izhevsk State Technical University within the framework of the grant no GAF/20-67-22.

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