Recycling of technical sulphur production waste

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Abstract. A method is proposed for producing composite solutions using sulphur, a waste product, as a structuring additive to composite solutions. It is found that the greatest increase in the strength of the composite solution occurs when sulphur is introduced 0.3 % by weight of cement. It is proved that the introduction of sulphur into the composite solution leads to more intensive hydration of cement and an increase in the density of cement stone.

1. Introduction

When processing high-sulphur hydrocarbon raw materials, production waste is formed – technical sulphur, which accumulates on its storage sites in the places of extraction and processing of oil raw materials. During the storage of sulphur, its dusting occurs, as well as microbiological oxidation with the formation of sulphuric acid, sublimation and weathering, oxidation under the influence of external factors, interaction with hydrocarbons with formation of sulphur-containing organic compounds.

Sulphur compounds occupy one of the first places among pollutants in terms of their negative impact on the environment. About 96 % of sulphur enters the atmosphere in the form of SO₂, the remaining amount is accounted for by sulphates, H₂S, CS₂, and other compounds. In addition to the negative environmental impact, elemental sulphur in the form of dust irritates the respiratory system, mucous membranes, and also causes eczema. The maximal permissible concentration (MPC) in the air is 0.07 mg/m³. Poisoning with sulphur derivatives can lead to irritation of the mucous membranes, respiratory tract, and integumentary tissues, which with prolonged exposure can lead to serious ailments: eye diseases, bronchitis, and eczema [1-4].

In addition, dangerous compounds such as sulphur dioxide occur in the air. When ingested, it has an irritating effect on the mucous membranes. In addition, upon contact with water, sulphur dioxide forms sulphuric and sulphurous acids, which negatively affect all adjacent areas.

Specific properties of sulphur compositions, including a low natural radioactive background and protective properties against electromagnetic and radioactive radiation, make it possible to use technical sulphur in the construction and road industry [5]. Concreting objects with sulphur concrete under water creates a reliable and long-lasting protective structure over the protected object [6-11].

One of the ways to solve this problem is to modify it with molten sulphur. Sulphur, when heated above 120°C, transforms from a crystalline state into polymer chains, which fill the pores of the cement stone, lead to its complete waterproofness and high corrosion resistance to solutions of salts and weak acids, and guarantee high performance of cements. To impregnate concrete products with sulphur, they
are usually immersed in a sulphurous melt, kept there for some time, and then cooled in air to normal temperature. According to another technology, sulphur is added into the concrete mixture at the kneading stage. The products that have gained the brand strength are heated and kept at a temperature of 140-150°C for 1.5 hours, after which they are cooled in air. The sulphur contained in the concrete melts and fills the pores and capillaries, preventing the migration of moisture and aggressive substances and reducing the surface of contact between concrete and the environment [12, 13].

Thus, a decrease in the porosity of a cement stone due to filling with grey voids and pores leads to an increase in the resistance of the concrete product to the destructive effects of the environment. Composite mortars are used in transport construction, prepared without steaming at ambient temperature and immediately pumped to anchor soils or for lining tunnels. Therefore, in this work, we studied the addition of sulphur to the composite solution under normal conditions.

The purpose of this work was to develop new grouting compositions modified with sulphur with improved technological properties.

2. Methods
The materials used in the present work are: cement grade 500, bentonite grade P2T2A (GOST 127.5-93) of the Zyryansk deposit, and liquid glass (GOST13078-81); water-cement ratio is 2:1.

Cement is the main component of the injection solution. Laser diffraction method according to ISO 13320-1: 2009 “Particle size analysis. Laser Diffraction Methods” is used to determine the size distribution of cement particles. It is established that the specific surface area is 450 cm²/g, the particle size is from 1 to 90 μm, as well as up to 88 % of the cement consist of particles less than 57 μm, and about 12 % have a size not exceeding 2 μm.

The composite solution contains bentonite. Bentonite clay in a composite solution increases its plasticity and toughness, and maintains resistance to delamination. The oxides included in the clay are the basis for hydraulic binders and have a chemical affinity for cement.

The composition of bentonite, established by semiquantitative X-ray phase analysis, includes montmorillonite (75-80 % by weight), quartz (15-17 %), kaolinite (1-2 %), and muscovite hydromica (1-2 %). The sorption capacity of bentonite is 113.3 mg · eq per 100 g.

To obtain a composite solution, a previously prepared 5 % bentonite suspension was mixed with cement with sulphur additives, in various concentrations from 0.09 % to 3 % to the mass of cement, and at the end of the process, water glass was added.

3. Results
The strength was determined on a Controls 50-C0050 / CAL50 hydraulic press (Italy) after 7, 14, and 28 days. The best results in terms of strength were shown by samples with the addition of sulphur: 0.18 %, 0.30 %, and 0.60 % by weight of cement (Fig. 1).

![Figure 1. Structure formation of the composite solution at different sulphur contents to the weight of cement: 1 – 0.3 %; 2 – 0.6 %; 3 – 0.18 %; 4 – 0.00 %.]
It was found that the addition of sulphur from 0.09 % to 0.9 % by weight of cement in all cases led to an increase in strength. Moreover, it should be noted that the greatest increase in strength occurred when 0.3 % of the cement weight was added, and the strength increased by 40 % relative to the control sample by 28 days of storage (Fig. 2).

Changes in the structure formation of composite solutions with various additives of sulphur can be explained by its dissolution in concentrated solutions of alkalis [11]. Since the preparation of composite solutions creates an alkaline medium with pH of 12.5, sulphur in this medium can dissolve and form homocains, in the presence of which the structure formation of the system is accelerated.

The structure formation of a nanodispersed system acquires exceptional importance in the initial period of cement hydration, since from the moment of combining the primary particles, first the coagulation occurs, and then the crystallization structure of the cement stone is formed.

Since the main strength of the cement-benton mortar is formed after seven days, the effect of sulphur additions on the rate of structure formation at the initial stage of the composite mortar formation was investigated. The rate of structure formation was determined by the dependence of the change in strength on time at different sulphur contents to the mass of the solution.

The analysis of the kinetics of curing without changing the strength of the binder compositions was carried out on a Rebindor-Gorazdovsky device – a conical plastometer, which makes it possible to assess the change in the plastic strength of the hardening mass over time.

During testing, for each stage of loading, graphs of the dependence of the clay-cement system strength on the storage time for various sulphur concentrations to the solution mass were built. On the obtained curves, linear sections were distinguished, reflecting the deformation of the solidifying sample of the solution at a constant rate, at a given strength value. For the selected linear sections, the deformation rate of the sample $\tan \alpha$ was determined, according to the formula:

$$\tan \alpha = \frac{\Delta P_i}{\Delta t_i},$$

where $\Delta P_i$ is the difference between the longitudinal deformations of the hardening sample at the end and the beginning of the deformation period at a constant rate at the $i$-th stage of loading, MPa; $\Delta t_i$ is the duration of the curing period of the sample at a constant rate at the $i$-th stage of loading, days.

Based on the obtained values, a dependence of the rate ($\tan \alpha$) of the strength gain of the composite solution on the storage time for different sulphur concentrations is plotted (Fig. 3). It can be seen from the figure that the rate of increase in the strength of the composite solution with the optimal addition of sulphur is the highest and is almost two times higher than the structuring of the system without the addition. Moreover, the highest rate of structure formation of the cured composite mixture occurs during the first seven days.
Figure 3. Kinetics of structure formation with sulphur content, wt%:
1 – 0.3%; 2 – without additives.

The acceleration of the structure formation of the composite system can be explained by the formation of nano-formations of sulphur arising from its partial dissolution in a strongly alkaline medium with pH = 13 and arising during the preparation of the composite solution.

Tests for frost resistance of a composite solution with an optimal concentration of sulphur were performed. Based on the obtained dependence of the maximum relative difference between the volume deformations of the cured composite solution and the standard sample on the freezing temperature, it was found that the frost resistance of the modified cured composite solution and the standard sample of the composite solution corresponds to the F100 brand.

4. Conclusion

The conducted studies prove that the addition of sulphur to cement leads to more intensive hydration of cement and an increase in the density of cement stone [12]. They allow us to recommend a composite solution for increasing strength in the construction and repairing the underground structures.

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