Highly effective composite materials based on waste of technogenic sulfur

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Abstract. The materials developed on the basis of technogenic sulfur of silicate and chloride zinc of akivator can be used as road materials (tiles, paving stones) for arranging the territory or inner rooms of enterprises for the machine-building complex in areas with aggressive media. X-ray, rheological and quantum chemical studies have shown that when sulfur interacts with zinc chloride, a system of strong thermodynamically stable compounds is formed, causing the formation of an effective material.

1. Introduction
Technological processes of the machine-building complex widely use a different spectrum of aggressive media. Meanwhile, even such effects as air saturated with moisture can relatively quickly - in 10-15 years - to lead the whole building in an emergency condition. Many structural elements of buildings - foundations for acid pumps, some sections of floors, etc. - need of repair or restoration annually, and sometimes more often. The application in the conditions of an aggressive environment is possible not for every material.

At the same time, a large number of sulfur-containing composite materials are known which are distinguished by a number of positive properties: high chemical resistance in corrosive environments with operating parameters, high mechanical strength, low cost and availability of materials [1-3].

2. Body text
The possibility of obtaining sulfur concrete on the basis of sulfuric acid was investigated in this work. The development of technologies for utilization of sulfuric technogenic waste and their processing into sulfuric composite materials is a highly topical task, because it allows obtaining efficient composite materials and solving environmental problems of modern production, which currently has high environmental safety requirements.

Zinc chloride was used as an activator of sulfur and silicate component of the composition. Its electronic structure, in particular, the presence of vacant p- and d-orbitals, will allow activating the initial components [4].

To obtain a sulfur concrete on the basis of sulfur and sulfur waste, the following components were used as the starting components: sulfur (S) - waste from the Nizhnekamsk refinery with a basic
substance content of 99.98% by mass. (GOST 127-93); zinc chloride ZnCl$_2$ (GOST 4529-78); sulfur waste of a metallurgical enterprise (sulfur cake) (chemical composition, wt. %: elemental sulfur (S) - 50-58%, aluminum oxide (Al$_2$O$_3$) 1.5-3.0%, ferrous sulfate (FeSO$_4$, Fe$_2$(SO$_4$)$_3$) - 4.5-15%, calcium oxide (CaO) - 0.3-0.5% silicon oxide (SiO$_2$) - 12-25% magnesium oxide (MgO) - 0.1-0.2%, water (H$_2$O) - 0.36%).

For testing samples of compositions of metallurgical production were made on the basis of sulfur and sulfur waste. The obtained samples were sent for physico-mechanical tests for sulfur concrete.

The compositions were also investigated by the methods of physicochemical analysis. X-ray diffraction studies were carried out on a DRON-3 diffractometer (Cu Ka-radiation).

As the results of X-ray analysis (Fig. 1) showed, the sulfur cake consists of a crystalline phase, represented by rhombic sulfur, thauzite Ca$_3$Si(OH)$_6$CO$_3$SO$_4$(H$_2$O)$_{42}$, aqueous ferrous sulfates - rhombic glaze and remarite, quartz SiO$_2$ and calcium sulfate CaSO$_4$.

According to emission spectral chemical analysis, the composition of the cake is represented mainly by the following compounds, wt. %: Sulfur - 50; C, 0.76; Ca 0.5; Al, 3.0; Mg - 0.2; Mo - 28.0; Fe $\geq$ 15; Si - 12.0; Co - 1.6; Ti is 0.1; Na - 0.2; K - 0.2.

Since this waste contains a crystalline rhombic sulfur and, at the same time, mineral components - calcite and sulphates - in an amount close to the technological one (mass-to-sulfur: filler ratio is 1:1) are assumed that it is possible to obtain composite materials from it for construction purposes. To compensate for the lack of the sulfur component, pure sulfur in the amount of 10 and 20% of the mass was added to the initial composition. At the same time, the particles of the mineral component were completely enveloped by the sulfur melt, the alignment of the shape of the samples was observed, which acquired a more dense structure.

It is known that the viscosity of a sulfur melt can significantly decrease with the introduction of some electrophilic additives, such as chlorides of aluminum, iron, titanium and zinc. Getting into the sulfuric melt, they interact with sulfur, promoting the shift of the electron density in the sulfur ring, lower the sulfur-sulfur bond energy and intensify the opening of the sulfuric molecule with the formation of a large number of short radicals. The viscosity decreases sharply from 0.025 to 0.003 Pa s [5, 6].

For a detailed analysis of the products of the interaction of sulfur with a zinc chloride activator, X-ray phase analysis was used. On the radiograph, the appearance of zinc sulfide crystalline zinc sulfide (ZnS) cubic syngony and zinc oxysulfate (Zn$_2$O (SO$_4$)$_3$) monoclinic syngony, which is a product of zinc sulfide oxidation, is observed. Also recorded are the reflections corresponding to the cyclocere $S_{12}$ of the orthorhombic modification, formed, apparently, as a result of the "stitching" of a huge number of short-chain radicals. This indicates some polymerization of short-chain radicals with the
formation of polymeric sulfur, which will positively affect the performance properties of the sulfide material [7-10].

In addition, x-ray phase analysis was made by calculating the quantitative ratio of phases of zinc sulfide 8%, 11% of the product of the oxidation of oxysulfate zinc, 11% of cyclosieris $S_{12}$, the unreacted zinc chloride was 2.1%. Considering the amount of injected $\text{ZnCl}_2$ (25%), almost all of its amount reacted with sulfur to form zinc sulphide $\text{ZnS}$. The resulting sulfide has a cubic syngony and refers to sphalerite found in nature. Thus, when sulfur interacts with zinc chloride, a system of strong thermodynamically stable compounds is formed.

Quantum-chemical studies using the "Prirodna" program confirmed the activating effect of zinc chloride. The activation energy of opening octasers using zinc chloride is reduced by 30 kJ/mol relative to the opening of cyclooctasers without an additive (Fig. 2). This fact proves the activating effect of the additive on the sulfur component, leading to the opening of cyclic sulfur molecules at lower temperatures, which ultimately leads to a reduction in process costs.

The $S_8$ molecule is very symmetrical and flexible. In the process of thermal disclosure of this molecule, the formation of various spatial rearrangements is possible. With the addition of $\text{ZnCl}_2$, the process of disclosing the sulfur molecule is much easier in two stages.

Zinc chloride significantly reduces the viscosity of the sulfur melt in a wide temperature range, it has a positive effect on the wetting and impregnating properties of the latter.

![Figure 2. Disclosure cyclooctane by thermal activation (on the left) and in the presence of the activator of zinc chloride (on the right)](image)

To improve the water-resistant properties, prevent the dissolution of sulphides existing in concrete and the subsequent destruction of the material, the obtained samples were dipped into the sulfur melt for a few seconds, removed from the melt and allowed to cool. The protective layer of hydrophobic sulfur formed on the surface reliably protected the obtained products from dissolution. The obtained samples were tested for mechanical and operational properties - compressive strength (30-35 MPa),
water absorption (not more than 1%), density (2.15-2.80 g/cm³), resistance to aggressive media (0.85-0.97).

On the basis of the data obtained, a schematic flowchart of the technology of sulfuric composite materials from sulfur cake was proposed.

3. Conclusions
The developed materials can be used as road materials (tiles, pavers) for arranging the territory or interior of enterprises of the machine-building complex in areas with aggressive media.

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