Modification of sulfur cake – a waste product from the production of sulfuric acid

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The demand for road construction materials is increasing every year due to the rapid development of construction worldwide and requires huge volumes of cement production, which causes environmental problems such as increasing levels of CO_2 emissions into the atmosphere. The shortage of road bitumen in Kazakhstan in 2022 amounted to about 300 thousand tons. In addition to the shortage of bitumen, there is the problem of improving the quality of bitumen used in road surfaces.

In 2018, the total annual global sulfur production amounted to 80 million tons, Kazakhstan with a volume of 3.5 million tons took 6th place. The Stepnogorsk sulfuric acid plant produces about 130-200 tons of sulfur cake per year and the issue of its disposal in order to obtain the target product is urgent. The use of modified sulfur cake to produce and improve the quality of sulfur concrete and sulfur bitumen allows us to solve the problem of recycling sulfuric acid production.

In the production of sulfuric acid, sulfur is first purified from ash and other impurities that deactivate the catalyst. Vapors of molten sulfur are passed through a filtration material - a mixture of perlite, carbonate and calcium hydroxide, which turns into sulfur cake with a sulfur content of 35-40 wt. %.

Sulfur cake belongs to class IV, the sulfur in it belongs to hazard class III and is characterized by the ability to spontaneously combust and is prohibited from being buried in industrial waste landfills, which leads to its accumulation [1]. Its accumulation and storage harm the environment and human life.

In recent years, sulfur-based compositions have been used as a binder in building materials. This is due to their rapid hardening, strength, resistance to aggressive environments and hydrophobicity [2]. The sulfur content in concrete makes it more durable, increases frost resistance and abrasion of products by 1.5 times.

Sulfur in its pure form, due to its fragility, is not used in the production of building materials, therefore it is chemically modified by introducing various additives in order to give it strength, oxidation resistance, adhesive and enveloping characteristics, stable structure, elasticity and biostability. Dicyclopentadiene, styrene, turpentine and furfural, which inhibit sulfur crystallization, have been proposed as modifiers [3]. All of them are high-boiling liquids or light solids, giving the binder plasticity. They undergo copolymerization with sulfur at 140°C, forming linear or cross-linked structures.

The purpose of the work is to chemically modify sulfur cake and produce sulfur concrete and sulfur bitumen based on it, used in road construction.

The elemental composition of sulfur cake from Stepnogorsk Sulfuric Acid Plant LLP is represented by sulfur (57.85%), oxygen (21.8%), silicon (2.13%), calcium (1.15%) and other elements such as Na, Mg, Al, Cl, Fe , Cu and Zn in small quantities. The results of X-ray phase analysis showed that it consists of 84.0% sulfur, 7.0% calcium sulfate ($CaSO_4$) and 4.8% gypsum ($CaSO_4 \cdot 2H_2O$). It also contains iron (II) disilicate ($Fe_2Si_2O_6$) in an amount of 4.2%. The content of organic compounds in sulfur cake is low, and the mineral components - gypsum and calcium sulfate - are contained in small quantities, which makes it possible to use it for the production of composite materials for construction purposes.

The process of modifying sulfur cake is carried out as follows: the sulfur cake is heated to a temperature of 150±5 °C, then a 1-5% polymer-binding modifier is introduced and the mixture is stirred for 30, 50 and 70 minutes. In this work, styrene, glycerin, oleic acid and acrylamide were used as polymer-forming modifying reagents.

When modifying sulfur cake with the addition of ready-made monomers, a polymerization reaction occurs with the formation of new crystalline structures. In the IR spectrum of the modified sulfur cake, the absorption band at 1150 cm^{-1} shows the S=O functional group, in the form of RSO_3H and RSO_3, which were formed as a result of the reaction of sulfur with oleic acid. A relatively low temperature leads to the destruction of polycyclic sulfur structures in the sulfur cake, which may indicate the occurrence of a copolymerization reaction, which leads to the formation of network or branched structures with side polysulfide branches. The absorption bands of the C-S bond correspond to 700-600 cm^{-1}, the S-S bond is observed in the region of 500-400 cm^{-1}, the frequency of the bending vibration of the polysulfide bond is observed in the region of 460 cm^{-1}.

At temperatures from 138 to 143°C, sulfur melts without the formation of harmful gases such as H_2S and SO_2. The addition of styrene led to polymerization with the formation of low molecular weight products of cyclic (five and six-membered rings) and linear structures with a sulfidity degree of 2 to 5, as well as the predominant formation of oligomers with a molecular weight of 400-2500. Absorption bands in the region of 690 cm^{-1} correspond to C-S bonds, the absorption frequency of 465 cm^{-1} indicates an S-S bond and bending vibration of the polysulfide bond.

The results of X-ray phase analysis of the modified samples showed that they consist of 85.8% and 87.1% synthesized sulfur. The samples contain almost the same amount of calcium sulfate ($CaSO_4$) at 7.8-7.9%. It should be noted that a new mineral compound was formed - $Ca_5(Si_6O_{16})(OH)_2$ clinozoisite (or clinotobermorite) in the modified sulfur cake in an amount of 5-6%.

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