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USING TECHNICAL SULFUR AS A STRUCTURING ADDITIVE FOR MINERAL BINDERS BASED ON CALCIUM SULFATE

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Abstract. The article discusses physical and chemical characteristics of producing effective materials based on calcium sulfate dihydrate, the pretreated waste of man-made production being added at the stage of mixing the air binder. The high degree of consumption of exhaustible natural resources causes increased research activities in the field of application of industrial waste in construction. Using man-made waste, such as technical sulfur, as a modifier of the structure and properties of building materials is a significant step in solving environmental, resource, and economic problems. Industrial production of building materials today follows the principles of sustainable development and waste minimization by optimizing product formulations and reducing energy consumption required for their production. In addition, the improvement of quality and performance indicators of standardized products is relevant and sought-after. The need for efficient technologies for utilization of technical sulfur is due to large volumes of production and the environmental threat which accompanies the storage of its large volumes. Adding technical sulfur as a component of technological construction mixtures will create an alternative to the methods of utilization of this production waste. Physical and technical and physical and chemical properties of technical sulfur predetermine the possibility of its use, with certain additional treatment, as an effective modifier of the structure and properties of gypsum products. The results presented in the article prove the potential use of this production waste as an effective structure-forming additive, which has a positive effect on the physical and technical parameters of calcium sulfate-based materials.

Keywords: polymerization, man made sulphur, gypsum, structure formation, thermoplastic additive, surface working, waste product, properties improvement.

Introduction

Sulfur-containing building compositions are known to have a number of specific properties, such as inertness to aggressive effects, protective properties from electromagnetic and radioactive radiation, which allows evaluating these materials as quite promising (Bazhenov, 1983).
However, the widespread use of sulfur is complicated by the need for heat treatment of modified composites as a result of which an artificial stone material is formed from a molded and cooled mixture (Al-Hadithi et al., 1987).

This problem becomes relevant when using technical sulfur for the modification of gypsum systems since during heat treatment it is necessary to take into account the light dehydration of gypsum stone at relatively low heating temperatures. In addition, the degree of dehydration of a gypsum system significantly depends on the pressure of water vapor; when heated to 65 °C, the process of calcium sulfate dihydrate passing into calcium sulfate hemihydrate starts (Bazhenov, 1983; Al-Hadithi et al., 1987).

Heating the gypsum stone to a temperature of 107–115 °C is accompanied with a rapid water loss and ends with passing into calcium sulfate hemihydrate $CaSO_4$*O.5H_2O, known in two modifications: **α** and **β** (Steudel, 2003), **α** – modification of the hemihydrate is dehydrated at 200–210 °C, and **β** – hemihydrate at 170–180 °C, in the process of dehydration the crystal lattice is restructured (Bazhenov, 1983; Steudel, 2003). Based on the studies of D. S. Belyankin and L. G. Berg (Berg, 1969; Beliankin et al., 1952), at the temperature higher than 220 °C **α** – dehydrated hemihydrate becomes **α** – soluble anhydrite, and **β** – dehydrated hemihydrate at tempera-

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ture 320–360 °C in its turn passes into **β** – soluble anhydrite. Based on this, the dehydrated hemihydrate of **α** modification can exist in a small temperature range.

Based on the research of E. V. Korolev et al. (Korolev et al., 2011; Gedik & Lav, 2016; Proshin et al., 2002), it is possible to talk about the use of any commercial form of technical sulfur in order to improve the performance characteristics of a gypsum system, taking into account the peculiarities of heat treatment of the binder and thermoplastic additive. Under normal conditions, sulfur is inert. The required reactivity manifests itself during heating and melting. During reactions, sulfur acts as biradicals and initiates radical transformations. Polysulfide chains resulting from heating are much more reactive than relatively stable cyclic S8 sulfur molecules (Bazhenov, 1983; Steudel, 2003).

Elemental sulfur has a large number of different modifications, which is associated with an increased tendency of sulfur atoms to form ring or chain molecules, and the technical properties of sulfur are largely determined by the allotropic form (Bazhenov, 1983; Steudel, 2003; Sassi & Gupta, 2008; La Mer, & Kenyon, 1947).

The most stable allotropic modifications of solid sulfur are: rhombic sulfur, monoclinic sulfur, and polymeric sulfur. The study used rhombic sulfur, the melting point of which is 112.8 °C.

The allotropic composition of sulfur and its properties are decisive indicators in the process of structure formation during the heat treatment of modified gypsum products (Bazhenov, 1983). In addition, formulary and technological factors have a significant impact. These factors being varied, a building material with enhanced performance characteristics can be obtained (Proshin et al., 2002).

Materials that use technical sulfur, as a rule, have a composite structure characterized by the boundaries of the phases "sulfur – dispersed phase". Basing on this, the effectiveness of sulfur in preparing the compounds by mixing sulfur with a binder, fillers, and special additives depends on the uniform distribution of powdered sulfur in the volume of the composition (Korolev et al., 2011).

Using technical sulfur, it is necessary to take into account that this material has a number of disadvantages that have a negative impact in the manufacture of compositions based on it, such as increased hydrophobicity and inertness. These sulfur deficiencies do not allow its use as an active additive in the composition since adding powder sulfur without its pretreatment during the mixing process leads to sulfur clumping, mixture separation, which ultimately reduces operational properties of products. In addition to sulfur, opoka rock, phosphogypsum, etc. can be used as thermo-active additives, followed by thermal activation (Menkovskiy & Yavorsky, 1985; Ciak & Harasymiuk, 2013).

Such technologies are used in preparing sulfur-anhydrite binder (Chaudhuri & Paria, 2010), where the use of sulfur ash in the amount up to 30% and joint grinding with fluoroanhydrite is described to provide compositions similar in properties to low clinker composite Portland cement with a compressive strength of more than 35 MPa.

Also considerable interest is arising in producing composite technical sulfur-based materials (Gamara & Pablo, 1980; Ciak & Harasymiuk, 2013), such as sulfur concrete and products based on it, sulfur-containing solutions for rehabilitation and decorative works (Chaudhuri & Paria, 2010; Sumio, 2004; Tager, 2007).

Thus, analyzing the research on producing composite sulfur materials and taking into account the technological features of technical sulfur, it is possible to predict its positive effect on the structure and properties of the gypsum binder with additional surface treatment of the manmade waste for its uniform distribution in the composite volume.

1. Experimental program

1.1. Raw materials

The study used powdered sulfur corresponding to grade 9998 according to GOST 127.1-93, which is a waste product from the oil refining industry, in particular TANECO JSC, Nizhnekamsk, Republic of Tatarstan, Russian Federation. The studied raw material based on technical sulfur had not previously been used for structural modification of the gypsum system. The chemical composition is given in Table 1.

In order to reduce the hydrophobicity of technical sulfur, the surface was modified using the following components:

– organic solvent GOST 2768-84;

– distilled water GOST 6709-72.

As a material for making the samples, gypsum binder of G4 GOST 125-79 was used. To determine the physical and technical and physical and chemical characteristics of the industrial waste and to assess the degree of its influence on the structure and properties of the modified binder, a number of studies were conducted using modern equipment. Particle sizes were determined with a SALD-7500 laser analyzer, the properties and patterns of structure formation were studied by means of IR spectral analysis with IRAffinity-1 device, and the microstructure was studied using an AdMas-Fast scanning electron microscope at the Research Center of the Technical University VUT in Brno, Czech Republic.

Table 1. Characteristics and chemical composition of technical sulfur (Petrukhina, 2016)

No.	Characteristic	Unit	Value
1	Particle shape	–	Hemispherical
2	Bulk density	g/cm^3	1.3
3	Sulfur mass fraction	%	99.99
4	Ash mass fraction	%	0.005
5	Mass fraction of organic matter	%	0.005
7	Water mass fraction	%	0.01

Currently, there are discrepancies in the data on the solubility of sulfur. Therefore, despite the data provided in the quality certificate (Petrukhina, 2016), the properties of the initial material have to be analyzed to select a solvent and determine the mechanism of the effect of the additive (Menkovskiy & Yavorsky, 1985).

Taking into account the sulfur production technology, in order to select the optimization parameters and predicting the effect of the modified additive, a study was made of the characteristics of the powdered production waste, including determining the sizes of sulfur particles (Figure 1) after treatment.

The analysis of integral and differential distribution of technical sulfur particles in an aqueous medium showed that the effective particle diameter without treatment and adding additional components is 60–70 μm.

According to the results of infrared spectroscopy presented in (Figure 2), it can be concluded that there is soot in the initial material (the appearance of a peak in the frequency range 1600–1500 cm^{-1}), as well as acid residue SO_3^{2-} (absorption in the region 844.82 cm^{-1}) and SO_4^{2-} (absorption lines in the region 1120.64 cm^{-1} and 698 cm^{-1}). The presence of these impurities can be explained by the imperfection of the Claus process.

According to the above results and basing on studies (Gedik & Lav, 2016; Menkovskiy & Yavorsky, 1985), the optimal solvent for treating the surface of sulfur was an organic solvent, which has optimal characteristics of sulfur solubility (at 25 °C it is equal to 2.08 g/l) and the effect on gypsum systems (Berg, 1956; Fedotov, 1956; Polyasnkikh et al., 2018).

1.2. Experimental process

The process of modifying the powder of technical sulfur was carried out during the manufacture of sol-gel (Polyasnkikh et al., 2018; Kuntsevich & Petrenas, 1976; Rivkin & Aleksandrov, 1984) under laboratory conditions. A suspension of technical sulfur in an organic solvent was passed through a filter. The filtered, not dissolved sulfur was dried and, depending on the required amount, was added into the gypsum system, in the range from 2% to 10% of the weight of the binder in 2.5% increments; the water-binder ratio is equally 0.8. Technical sulfur was added in addition to the amount of gypsum binder.

To study the effect of a modified thermoplastic additive, samples of gypsum stone were made in the form of beams with dimensions of 40×40×160 mm, which gained strength under normal conditions for 2 days after stripping; then the samples were placed in a chamber drier at 120 °C (melting and polymerization point of sulfur) for 90 minutes (time required for uniform heating of standard beam samples). After taking the beams out of the chamber drier, they were cooled, and their linear dimensions, mass, density, compressive and flexural strength, and water resistance were measured.

In the manufacture of the modified compositions, after treating technical sulfur with an organic solvent, an increase in its wettability and an improvement in the uniformity of its distribution in the volume of the composite were seen.

In addition, treatment with solvent significantly affects the decrease of the melting point of technical sulfur by stretching the monoclinic lattice and dissolving part of the sulfur molecules (Bormotov et al., 2010; Mikhailov et al., 1989; Vernigorova et al., 2009).

The analysis of the obtained results of the physical and technical properties of the modified gypsum composition showed (Figure 3) that the optimal amount of technical sulfur is 7.5% by weight of the binder, by adding which

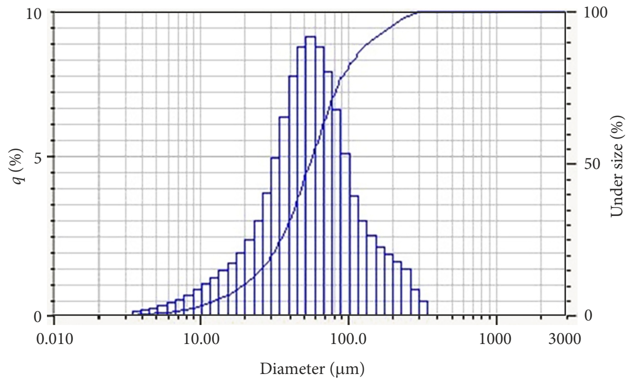

Figure 1. Distribution of particles of pretreated technical sulfur in water

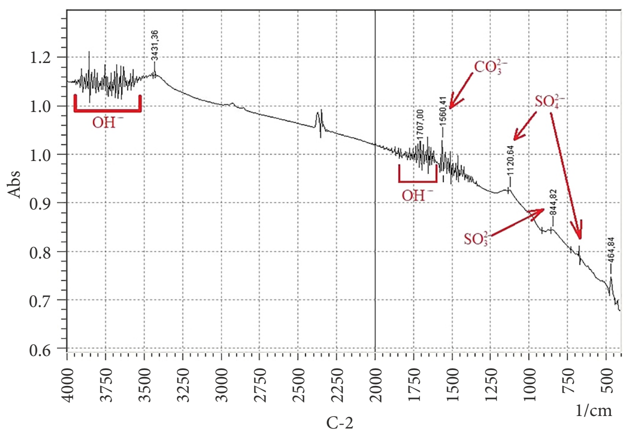

Figure 2. IR spectral analysis of raw technical sulfur

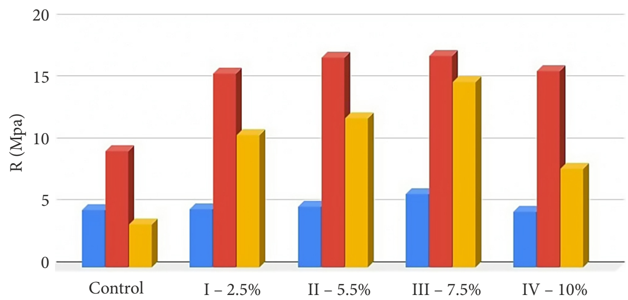

Figure 3. Physical and technical characteristics of gypsum composites after 28 days (blue – bending strength, red – compressive strength, yellow – strength in a water-saturated state)

in the composition the increase in compressive strength was 26%, bending strength 69.8%, the softening amounted was 0.88.

It is known that at the melting temperature 120–160 °C, there is a slight formation of polymeric sulfur. The growth of the mechanical characteristics of the modified composite is based on the structural change and the interfacial transition during the heat treatment process. Studies (Patent No. 3997355; Gemot, 1978; Rayne, 1951) state the dependence of the process of sulfur polymerization on the temperature and duration of heating, as well as the blend composition of impurities. Under the conditions of using sulfur as a thermoplastic additive in a gypsum stone, the given amount is quite sufficient to enhance the physical and mechanical characteristics of the composite material.

It should be noted that after treating technical sulfur with an organic solvent, its wettability increases, which significantly improves its uniform distribution in the volume of the composite.

In addition, treatment with solvent might affect the change in the melting point of technical sulfur by changing the lattice structure and dissolving part of the sulfur molecules (Panfilov, 2004; Gregor & Hackl, 1978).

The nature of the morphology change was determined by raster electron microscopy (Figure 4), the results of which show that adding technical sulfur leads to a change in the conditions of structure formation, which ultimately manifest themselves in the formation of a large number of amorphous new formations compacting the structure and enhancing the modified physical and mechanical characteristics of the modified samples.

Using differential scanning calorimetry, the processes were studied that characterize the heating of the modified samples (Figure 5).

According to the results of differential thermal analysis, it can be concluded that the endothermic peak is shifted due to the stepwise dissociation of calcium sulfate in the range of 190–230 °C. An exothermic peak was found in the region of 300–400 °C, caused by sulfur burnout (with the formation of SO_2 and SO_3), which is accompanied with a significant loss of mass. In the region of 780–800 °C, there is an endothermic effect associated with

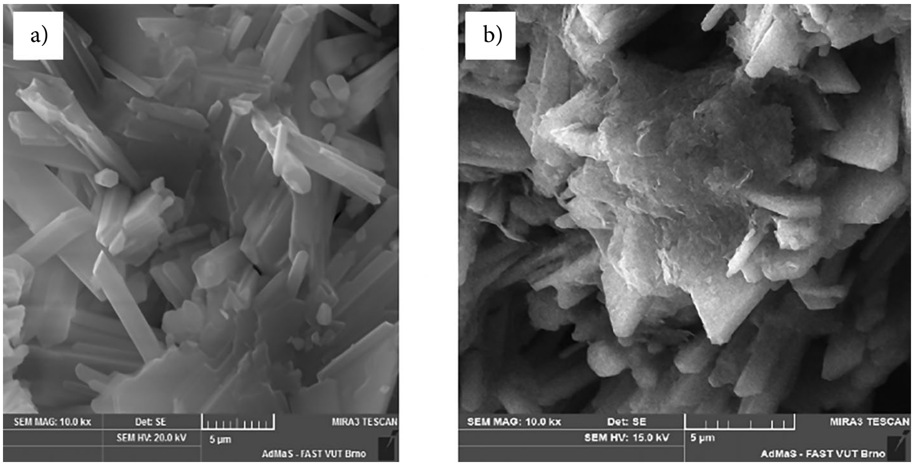

Figure 4. Microstructure study: the check sample (a), the sample with 7.5% of modified technical sulfur (b)

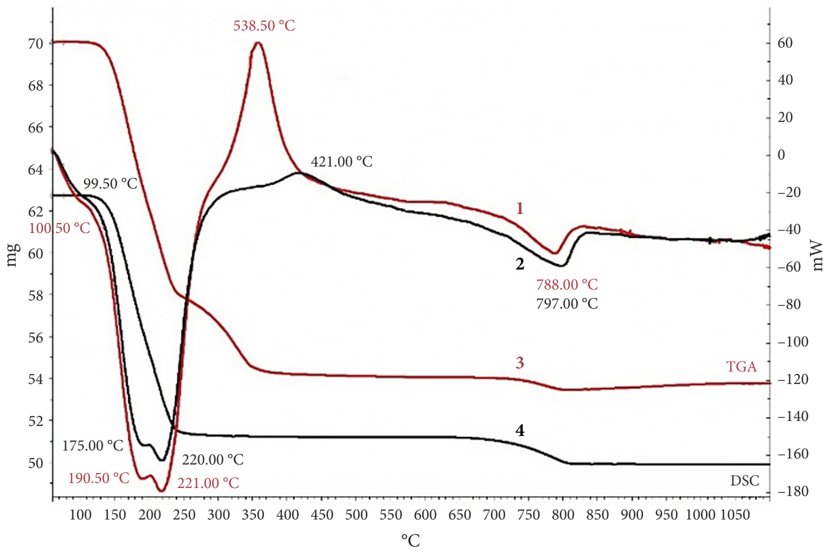

Figure 5. Differential scanning calorimetry spectra: the check sample (2, 4), the sample with 7.5% of modified technical sulfur (1, 3)

the decomposition of calcium carbonate. A comparative analysis of DSC spectra suggests the appearance of new formations, as well as a change in the nature of hydration of the sulphate-based binder.

To identify the nature of the effect of the treated technical sulfur on the process of structure formation, IR spectral analysis of the check and modified samples was conducted (Figure 6, Table 2).

Analysis of the IR spectra shows that significant shifts of the absorption lines correspond to the SO_4^{2-} and OH^- groups, a significant value of the shift of the absorption bands suggests a considerable effect of the treated technical sulfur on the structure formation pattern, which leads to changes in hydration conditions.

To determine the allotropic state of sulfur in the modified state, spectral analysis was performed on a DRON-7 X-ray diffractometer (Figure 7).

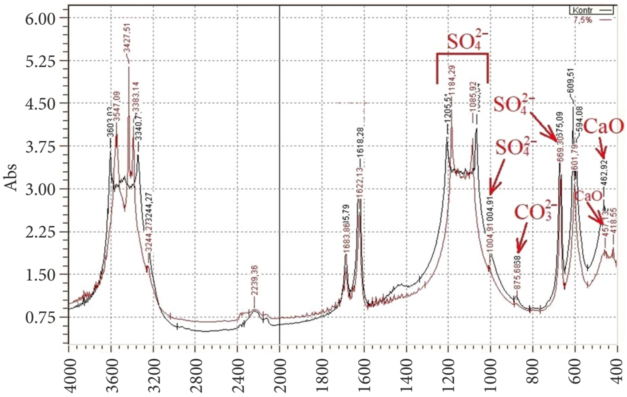

Figure 6. IR spectra of the check (black) and modified sample (red), 7.5% of technical sulfur being added

Table 2. Comparison of wave numbers of the check and modified samples

Ion	Wave numbers cm^{-1}, the check sample	Wave numbers cm^{-1}, the modified sample
CaO	462.92	457.13
SO_4^{2-}	675.09;1066.64; 1205.54	669.30;10085.92; 1184.29
CO_3^{2-}	875.68	875.68
OH^-	1618.28;1685.79	1622.13; 1683.86

The obtained X-ray patterns of the check and modified compositions show the presence of sulfur, type A16, in the structure (distinctive reflection bands d_α = 3.84; 3.44; 3.32; 3.21). The interpretation of the X-ray spectra is hampered by the presence of sulfate-containing components in the modified matrix.

Conclusions

The conducted studies have shown the possibility of using technical sulfur as a structuring additive to calcium sulfate-based binders. It was found that pretreatment allows to increase the workability of the powdered production waste, positively affecting the wettability, the uniformity of its distribution in the volume of the gypsum composite and melting point.

Adding the optimal amount of the treated modifier followed by heating the samples led to an increase in physical and technical characteristics, such as compressive and bending strength (by 26% and 69.8%, respectively). The softening coefficient was 0.88, which classifies the obtained material as waterproof.

Analysis of the microstructure, IR, DTA, and X-ray diffraction spectra showed the presence of polymerized sulfur in the modified composition, which affects the conditions of hydration of the modified compositions and the nature of structure formation.

The suggested additive based on processed technical sulfur has a practical application potential, i.e. the possibility of its use for modifying compositions based on gypsum binders.

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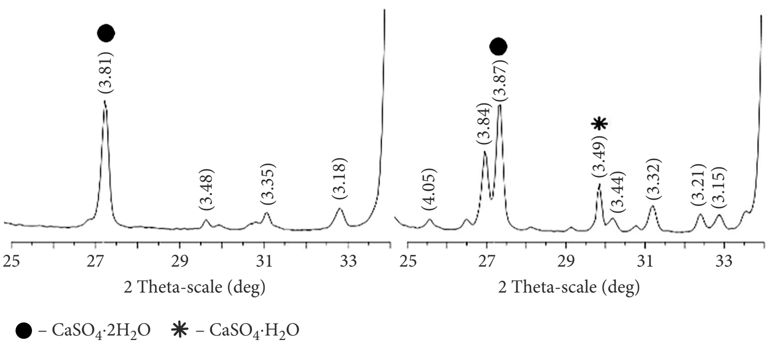

Figure 7. Comparison of the results of X-ray phase analysis of the check and modified compositions

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