Development of low-waste technology for the processing of sulphur into polysulphides and materials based on them

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Abstract. The interaction of sulphur with silicate and aluminium chloride was studied, the regularities of inorganic polysulfide formation, its structure and properties were established. The materials obtained on their basis have high physicomехanical properties, which are due to the chemical interaction of sulphur with aluminium, fixed on the surface of the silica-containing material, as well as with oxygen and silicon of the silica itself through the donor-acceptor mechanism with the formation of polysulphides. The results of IR spectroscopy, X-ray, electron-paramagnetic analysis, and quantum-chemical calculations are presented. Modification of silicate with aluminium chloride contributes to an increase in the active centres of the surface of silicate, the disclosure of sulphur rings. The use of electrophilic activator (aluminium chloride) contributes to the binding of sulphur with the formation of polysulphides and the question of the formation of toxic sulphur compounds.

1. Introduction
The need to reduce sulphur emissions into the environment, the increase in the production of regenerated sulphur from combustible gases, oil, metallurgical waste gases, is becoming an increasingly important factor in finding the effective use of sulphur in the production of various innovative products.

The range of modern sulphides, polysulphides and materials based on low molecular weight crystalline and polymeric sulphur is significant, diverse in quality and purpose. The literature describes in detail the technological regimes and properties of the materials obtained [1-2]. But most works do not consider the interaction mechanisms of components in the system as well as data on chemical processes. Environmental aspects are also not given due attention.

However, it is known that the heating of sulphur to the melting point is always accompanied by the formation of sulphur dioxide.

All known technologies for the processing of sulphur into inorganic sulphides and polysulphides are accompanied by the release of sulphur dioxide, which hinders their widespread use and as a result, prevents its effective utilization. To eliminate or minimize gas formation in technologies for the sulphur raw material processing, it is necessary to carry out the process through an intermediate stage of obtaining polysulphides, which, when interacting with other components of the system, will not form harmful emissions. Thus, the study of the environmental aspect of the technology of inorganic sulphides is an urgent task.
2. Experimental part

The following components were used as a feedstock: sulphur - waste of the Nizhnekamsk refinery with the content of the main substance of 99.98 wt %. (State Standard 127-93; Aluminum chloride · (Standard 3759-75); silica-bearing rock of the Dobrinsky deposit in the Saratov region, containing, mass %: opalkristobalite - 78 ± 7, zeolite - 7 ± 2, montmorillonite - 5.

Silica-containing raw material pre-ground in a ball mill (particle size not more than 0.5 mm) was modified with aluminium chloride in a drying chamber at a temperature of 200 °C.

The compositions were examined by the following methods: IR spectroscopy (Bruker Vector 22 FT-IR spectrometer), X-ray diffraction (DRON-3 diffractometer with monochromatic Cu Kα radiation), EPR spectroscopy (RE-1306 radio spectrometer), X-ray fluorescence analysis.

Studies using electron paramagnetic resonance were carried out at frequencies of 9100 and 9370 MHz at 77 and 300 K, respectively. A ruby single crystal with Cr3 + was used as an internal standard. The spectra were recorded in three ranges of the sweep of the external magnetic field.

Micrographs of the samples were obtained using a transmission-type EMMA-4 electron microscope-microanalyzer, magnified 250 times.

The quantum chemical calculations presented in this paper were obtained using the Gaussian 98 (B3LYP, PM3) and Priroda (DFT) application programs. To calculate the radical decomposition reactions and to study the structure of the biradical transition state, we used the unrestricted Hartree-Fock method, in which the highest, occupied, and lowest free molecular orbitals were mixed at the beginning of the calculations. The method is labour-intensive, but it gives accurate results.

In the study of sulphur interaction with modified amorphous silica, the structure of transition states and reaction barriers was evaluated. For this, relaxed scanning of geometrical parameters of molecules was used. Then, to confirm the existence of the calculated transition state in the process under study, descents were made along the path of the reaction to the reagents and products.

3. Results and discussions

All known sulphide technologies are based on the preliminary melting of inert sulphur under normal conditions with the formation of active Sₙ biradicals [3-5]. However, in addition to thermal activation, other methods could be used, for example, opening a sulphur ring under the action of electrophilic activators, which include chlorides of iron, aluminium, titanium, silicon and zinc.

In our opinion, use of electrophilic agents would make it possible to intensify the process of obtaining inorganic sulphides and reduce harmful gas evolution in the production of composite materials based on them. In addition, these chlorides have an effect on the filler, changing its surface properties, and ensuring the chemical interaction of the components to produce sulphides. The processing of sulphur raw materials through an intermediate stage of sulphide production will reduce the toxicity of production and will increase the strength of the synthesized materials. The chemical interaction between the components will ensure good adhesion between the matrix and the filler and prevent the binder from splitting. We consider that an opal-crystallite rock with a high specific surface was used as a filler. The use of aluminium chloride (electrophilic agent) would allow to activate both silica-containing material and sulphur, contributing to the chemical interaction of the components and the production of silicon polysulphides and sulphur-based composite materials with their high physicomechanical properties.

Modification of silica-containing compound surface with aluminium chloride was carried out in the temperature range of 200-500° C. Then, the modified material and molten sulphur, taken in predetermined ratios, were mixed until homogeneous for 40 minutes at the temperature of 150-160° C.

It is obvious that aluminium having vacant d-orbitals is able to form interatomic bonds with non-metallic interlayers (Si-O-Al, Si-O-Al-S), which is confirmed by the results of IR spectroscopy of the samples obtained (figure 1).

When aluminium silicate is modified by aluminium chloride, a triplet is observed in the range of 2850-2950 cm⁻¹, which indicates the appearance of new chemical bonds in the system and the formation of active centres with an increase in temperature to 400-500° C.
Figure 1. IR spectra of aluminium chloride (1), silicate (2), samples of silicate modified with 5% AlCl₃, at different heat treatment temperatures: (3) - 200° C; (4) - 500° C; and a sulphuric composition based on silicate with 5% AlCl₃ (500 ° C) (5).

New absorption bands 468, 332, 88 cm⁻¹ typical for Al-S bond appear on the IR-spectra of the interaction product of sulphur with aluminium chloride (figure 2).

It proves the formation of aluminium sulphide in the interaction of sulphur with aluminium chloride. As the results of X-ray phase studies showed, the degree of sulphur sample crystallinity with the addition of aluminium chloride is 61%, and without the addition the degree is 69%. A decrease in the crystallinity of the sample using modified silicate indicates partial expenditure of crystalline sulphur on the formation of a covalent bond with aluminium, silicon and oxygen of the filler and the formation of X-ray amorphous compounds.

Studies of silicate samples by electron paramagnetic resonance (EPR) were also conducted. The maximum content of radicals is registered in a sample of silicate with aluminium chloride (figure 3). With the introduction of sulphur, the concentration of active centres decreases to "traces", which also indicates a possible chemical interaction in the system.

Chromatographic studies have established that when the composition of sulphur and aluminium chloride is heated in the temperature range of 150-160° C, air and water are in the gas phase. Since the
release of sulphur dioxide is not observed, it can be concluded that the chemical bonding of free sulphur and the formation of aluminium polysulfide is fast.

![Graph](image)

**Figure 3.** Silicate EPR: 1 - dried at T=500° C; 2 - modified (AlCl₃ ~ 10%); 3 - modified (AlCl₃ ~ 5% + S ~ 50%).

Studies on the EMMA-4 microscope-microanalyzer showed that the formation of a homogeneous, dense, non-porous material structure is typical for samples of optimal composition.

Thus, it can be assumed that the high physicomechanical properties of the obtained samples are due to the chemical interaction of sulphur with aluminium, fixed on the surface of the silica-containing material, as well as with oxygen and silicon of the silica itself through the donor-acceptor mechanism with the formation of silicon polysulfide. The sorption properties of silicate are reduced, and the water absorption of the samples does not exceed 5%.

Samples of optimal composition prepared according to the proposed recipe have a high coefficient of resistance to HCl, H₂SO₄, CaCl₂, NaCl, MgSO₄ solutions, high impact strength (52 MPa), frost resistance (240 cycles) and density (1.790 g / cm³).

The work considers stable silicate and flexible, melt-elastic sulphur structures. The combination of flexible and rigid segments in macromolecules creates difficulties in recognizing the mechanisms of formation of stable and durable materials based on them.

The creation of quantum-chemical models of the products obtained, along with practical research, will contribute to an understanding of the mechanism of their formation and, as a consequence, the development of materials with given physical and mechanical characteristics [6-7].

In work with the help of quantum chemical programs, the system “silica - aluminum chloride - sulfur” was modelled in stages.

The mechanism of interaction in the system has been studied. The process of chlorides chemisorption on the surface of silicon dioxide and the sulfur activation were considered. Cluster models of silica active centers and the 3z.bas basis were chosen.

Attaching of diatomic sulfur to the silicate-modified aluminum silicate surface is exothermic (table 1) and nonactivated. The reaction of addition of triplet sulfur is thermodynamically stable. The Al-S bond formed by a single sulfur atom is the strongest.

Further, with an increase in sulfur atoms in the chain, it decreases (from 70.30 to 43 kJ/mol) and stabilizes, and the bond length increases to 250.9 pm. When sulfur interacts with aluminum chloride, no weakening of the bond in the sulfur chain is observed. Weak bonds of sulfur with aluminum cause a redistribution of the electron density and hardening of bonds within the sulfur chain.

The activating effect of aluminum chloride on the weakening of bonds in the S₄, S₈ cycle is illustrated in figure 4. The bonds closest to aluminum S-S are extended from 216.0 to 216.8 pm and from 209.7 to 231.4 pm in cycles S₄, S₈. The S-S energy (213.4 pm) of coupling in the S₈ cycle decreases by 27.59 kJ/mol, and in the S₄ cycle - by 10 kJ/mol.
Table 1. Energy assessment of sulphur addition by various mechanisms.

| Sulphur addition mechanism          | Monoatomic sulphur | Diatomic sulphur |
|-------------------------------------|--------------------|-----------------|
|                                     | ΔH (298K) kJ/mol   | Eakt, kJ/mol    | ΔH (298K) kJ/mol | Eakt, kJ/mol |
|                                     |                    | M=1             | M=3             | M=1          | M=3          |
| Oxygen atom injection               | -126.78            | 67.32           | 8.36            | 149.06       | 133.76       | 166.91       |
| OH substitution                     | 106.86             | 120.16          | 24.46           | 261.33       | 147.55       | 267.06       |
| Joining to aluminium               | -70.38             | No              | -86.86          | No           | No           | No           |

Thus, our assumption about the possibility of chemical interaction between sulphur and silicate modified with aluminium chloride is confirmed by the results of quantum chemical calculations. Modification of silicate with aluminium chloride contributes to an increase in the active centres of the surface of silicate, the disclosure of sulphur rings. Breaking the sulphur ring, breaking up bonds in the sulphur chain with prolonged heating and stirring will lead to the formation of stable short S-S bonds for oxygen and silicon, the formation of silicon polysulphides and the creation of a dense structure. Since sulphur is chemically bound in the developed technology, the formation of sulphur dioxide is practically excluded, and the technology can be considered low-waste.

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