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Production of Sulfur Composite Materials from Sulfur Containing Waste for Construction Applications.

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ABSTRACT

Production of high-quality sulfur composite materials with high performance. The physicochemical analysis and quantum chemical studies established that high physical and mechanical properties of the developed materials resulted from a chemical interaction between the components, which favored the formation of a compact homogeneous structure of the material.

Keywords: sulfur composite materials, sulfur concrete, aluminum chloride, physical and chemical parameters.

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INTRODUCTION

Sulfur composite materials with quartz sand as a filler are well known in present-day materials science and widely used. Since quartz sand is thermodynamically stable and has low reactivity the interaction between the filler and binder is force-induced in these systems. From a physical and chemical point of view the interface between silicon dioxide and sulfur is the area where such complex processes as adsorption, dissolution and growth of new phases occur. In this area silicon dioxide and sulfur form the bond to transfer strain between constituents of the composite material. This bond is necessary to transfer strain through the interface, that's why the state of the latter defines the mechanical properties of composite materials in many ways. Usage of active silica gel with high specific surface area and reactivity as a filler governs the possibility of chemical interaction between sulfur and silica gel with formation of silicon sulfides. We think that it will help to produce from them sulfur composite materials with high physical and mechanical properties [1-10].

It is known that there is a way to change surface properties, specifically for silica and silicates, by treating them with chlorides and organic derivatives of some elements. Production of silicon dioxide derivatives by this method is based on reactivity of surface hydroxyl groups and respective chlorine substances. Thus, when $AlCl_3$ reacts with silica gel at a high concentration of OH-groups it, together with polysilicic acid, forms supramolecular oxychloride $(SiO_2)_xO(AlCl_2)_2$, and at a low concentration – $(SiO_2)_xOAlCl_2$. Therewith, on the surface of silica gel the active sites with vacant d-orbitals form. Sulfur's electron configuration is $3s^23p^43d^0$. The presence of lone pairs defines its activating ability under the influence of electrophiles including $AlCl_3$. The polysulfide radicals resulting from sulfur ring opening may interact with the active surface of modified silica gel through a donor-acceptor mechanism using vacant d-orbitals in the surface and sulfur lone pairs [11-13].

MATERIALS AND RESEARCH METHODS

The specimens of sulfur composite material were made using aluminum chloride in two stages. At first, the silica gel was modified with aluminum chloride by mixing the reagents at elevated temperatures (200-500 °C), and then the modified silica gel was added to the sulfur melt.

It was determined whether compressive strength of the sulfur composite specimens depended on the content of aluminum chloride at various temperatures of preliminary heat treatment, on the time of modification with aluminum chloride. The structure and properties of sulfur composite materials were studied with the current practices: Fourier transform infrared spectroscopy, X-ray diffraction analysis, electron paramagnetic resonance, quantum chemical studies.

RESULTS

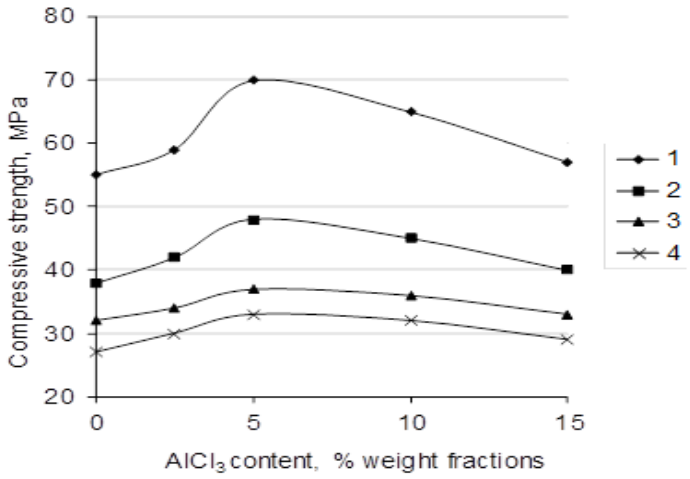

Figure 1: Relationship between compressive strength of the sulfur composite specimens and content of aluminum chloride at different temperatures of preliminary heat treatment: 1 – 500 °C; 2 – 400 °C; 3 – 300 °C; 4 – 200 °C. The binder/filler ratio is 1:1.

Figure 1 shows that the relationship between strength of the specimens and amount of $AlCl_3$ modifier is of extreme nature. The specimens had optimum compressive strength when they were precalcined at 500 °C and when their aluminum chloride content was equal to 3-5 % weight fractions. Strength of the composite material was 70 MPa.

As the silica gel modification temperature lowered to 200 °C strength of the specimens decreased twice. Increase in aluminum chloride content to 5-8% at temperature 200-400 °C made an insignificant contribution to strength. Higher modification temperature (higher than 500 °C) did not improve mechanical properties of the composite material qualitatively. It appears to be related to the sintered silica gel and changed crystal structure.

Apparently, the aluminum chloride did not modify the silica gel at low temperatures or did not modify it fully, and a sufficient amount of electrophilic sulfur activation centers were not formed in the surface of the silica gel. Content of aluminum chloride 3-5% weight fractions and modification temperature 500 °C are optimum conditions for activation of silica gel surface, and it significantly increases strength of the composite material with a given binder/filler ratio.

It was observed that a higher filler content (ratio 1:1.5) resulted in lower strength of the sulfur composite (Figure 2), which was mainly related to an insufficient amount of binder. Maximum strength of the specimens did not exceed 42 MPa. With increasing amount of the bulky modifier strength of the specimens decreased continuously at any preliminary heat treatment temperature.

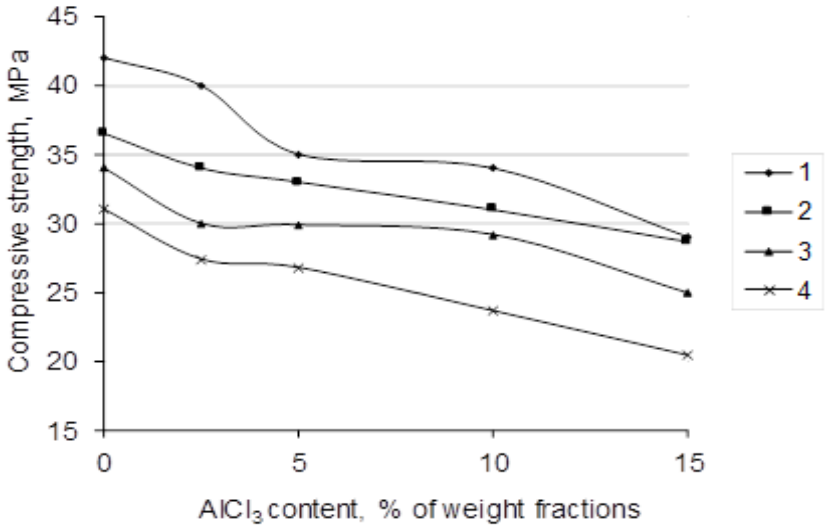

Figure 2: Relationship between compressive strength of the sulfur composite samples and content of aluminum chloride at different temperatures of preliminary heat treatment: 1 – 500 °C; 2 – 400 °C; 3 – 300 °C; 4 – 200 °C. The binder/filler ratio is 1:1.5.

From Figures 1 and 2 it follows that the specimens have maximum strength with a binder/filler ratio of 1:1, and maximum strength is equal to 70 MPa.

Figure 3 shows the relationship between strength of the composite materials and time of modification with aluminum chloride. At modification temperature 400-500 °C strength of the composite materials steadily increased and stabilized within 30 minutes. Thus, optimum modification time at 500 °C is 30 minutes.

At a binder/filler ratio of 1:1.5 the relationship between strength and modification time is similar in nature to that shown in Figure 3. Optimum modification time is 30 minutes (500 °C).

Table 1 shows the physical and mechanical test results of the specimens made at the optimum conditions from the content of aluminum chloride in the composite material.

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As seen from the table, the specimens made by the proposed formula at an optimum ratio of the ingredients have high resistance index in HCl, H_2SO_4, $CaCl_2$, NaCl, $MgSO_4$ solutions, high impact resistance (52 MPa), cold resistance (240 cycles) and density (1.790 g/cm^3).

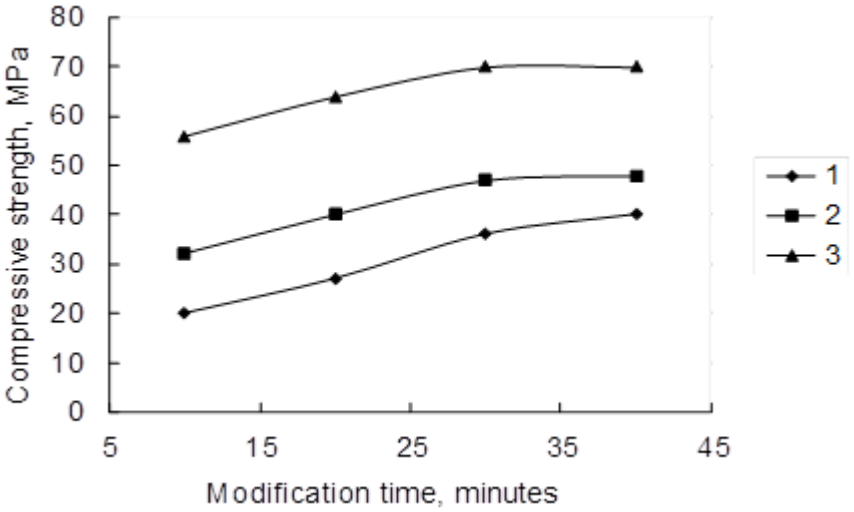

Figure 3: Relationship between compressive strength and modification time at different temperatures: 1 – 300 °C; 2 – 400 °C; 3 – 500 °C. The binder/filler ratio is 1:1.

Table 1 – Physical, mechanical and performance values of sulfur composite material

Binder/filler ratio, weight fractions	Modification temperature, T °C	Density of specimens, g/cm^3	Cold resistance, cycles	Water absorption, % weight fractions	Impact resistance, MPa	Resistance index				
						5% HCl	5% H_2SO_4	5% $CaCl_2$	5% NaCl	5% $MgSO_4$
1:1	400	1.786	230	2.80	36	0.967	0.952	0.965	0.979	0.965
1:1.5	400	1.660	190	3.98	25	0.932	0.922	0.930	0.935	0.931
1:1	500	1.790	240	2.32	52	0.972	0.963	0.969	0.983	0.968
1:1.5	500	1.730	200	3.58	27	0.936	0.927	0.934	0.938	0.935

At a firm contact between modified silica gel, filler and sulfur, i.e. after their heating and pressing, new chemical bonds may form and phase interaction forces may occur to provide optimum structure formation at the microscale and macroscale level.

In the structure of such substance the metal atoms (with the empty d-level) are known to bond with the nonmetallic layers by chemical bonds which form the bridges like M-S-M or M-O-M. It is apparent that in our system aluminum with vacant d-orbitals can also form similar bonds (Si-O-Al, Si-O-Al-S).

The physicochemical studies were carried out to reveal the reasons for improving the physical and mechanical properties of the composite materials with optimum formulation as a result of possible chemical interaction with formation of silicon sulfides.

After the silica gel was modified with aluminum chloride the triplet was observed in the area 2850-2950 cm^{-1} in the IR spectrum suggesting that in the system new chemical bonds and active sites formed at temperature rise to 400-500 °C.

At a firm contact between the modified silica gel and sulfur after heating and hot pressing the chemical bonds formed between the touching bodies. Apparently, in the structure of this substance, with the nonmetallic layers by the chemical bonds the metal particles formed the bridges like M-S-M or M-O-M, thereby increasing the strength of the composite material.

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The X-ray diffraction studies showed that the crystallinity of the sulfur specimens with aluminum chloride was 61%, and without aluminum chloride – 69% (Figure 4).

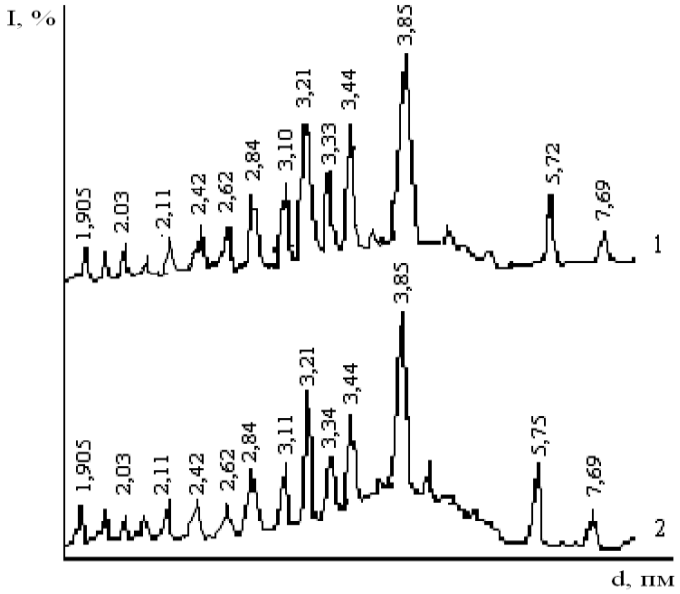

Figure 4: X-ray diffraction analysis of the sulfur composite specimens with (2) and without (1) aluminum chloride.

Lower crystallinity of the specimen with the modified silica gel indicates that a part of crystalline sulfur went to form a covalent bond with aluminum, silicon and oxygen of the filler and create X-ray amorphous compounds.

The silica gel samples were studied by electron paramagnetic resonance (EPR) as shown in Figure 5. The electron hole centers detected by EPR were the crystal structure defects of the subjects studied. In a general way, the electron hole centers can be presented as electron configurations of the clusters of atoms which are connected to the defective areas of atomic structure which trapped an electron or hole. The EPR spectrum for paramagnetic centers, in this case for electron hole centers, was represented as a single line with g-factor ≈ 2.00. The shape, width and position of the line in the scale of magnetic field (H=3300 Gs, g ≈ 2.036) corresponded to those for paramagnetic centers such as “free radical” formed due to broken chemical bonds.

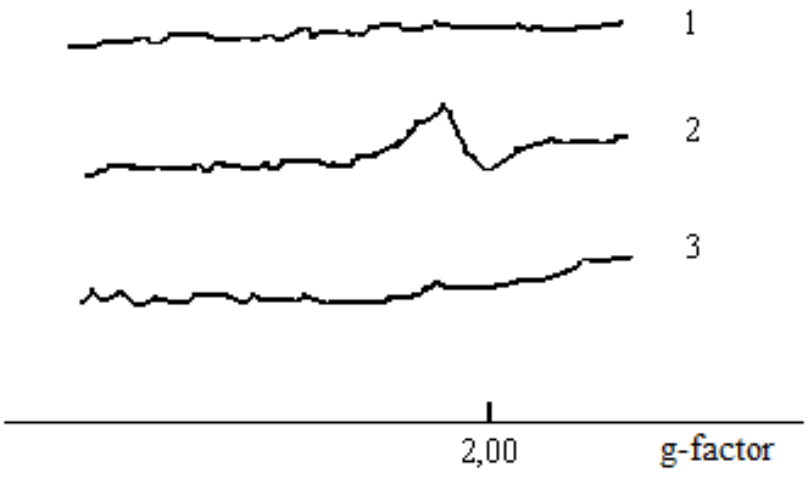

Figure 5: EPR of silica gel: 1 – dried at T=500 °C; 2 – modified ($AlCl_3$ ~ 10%); 3 – modified ($AlCl_3$ ~ 5% + S ~ 50%).

ISSN: 0975-8585

Table 2 shows a number of electron hole centers (in conventional units) in the test samples of the original and modified silica gels. Maximum number of electron hole centers (19 conventional units) was detected in sample no. 2, in other samples (no. 1, no. 3, no. 4) a concentration of electronic hole centers lowered to “the trace amounts of electronic hole centers”.

Table 2 – EPR definitions of silica gel containing materials

no	Test sample	Number of electron hole centers (conventional units)
1	Silica gel dried at T = 500 °C	Trace amounts
2	Modified silica gel ($AlCl_3$~10%)	19
3	Modified silica gel ($AlCl_3$~5%+S~50%)	Trace amounts
4	Synthetic amorphous silica gel	Trace amounts

As the silica gel was chemically modified with aluminum chloride it resulted in the intended change of its surface. The vacant d-orbitals of the resulted silica gel-aluminum chloride system were electron hole centers of the surface. Modification with aluminum chloride ($AlCl_3$~5%) gave higher number of electron hole centers – 19 conventional units (Table 2). Thus, we obtained the material with catalytic properties. The presence of sulfur lone pairs defined its activating ability under the influence of the electrophiles of the modified silica gel surface. The polysulfide radicals resulting from sulfur ring opening interacted with the active surface of the modified silica gel by a donor-acceptor mechanism. It dramatically reduced the number of electron hole centers on the silica gel surface (Table 2) – inhibition of the active sites Si–$AlCl_2$.

From the results of the physicochemical studies it can be assumed that the reason for high physical and mechanical properties of the obtained specimens is a chemical interaction between sulfur and aluminum attached to the surface of silica gel, and also between sulfur and oxygen, silicon of the silica gel itself using the donor-acceptor mechanism.

The microscopic analysis showed that for the specimens of optimum composition it was common to form a compact homogeneous nonporous structure (Figure 6-8).

When the sulfur specimens were obtained the homogeneous crystals were formed in the filler surface in the process of sulfur cooling, their size was much smaller than in the volume of free sulfur. At the optimum filling degree almost all the sulfur became more homogeneous and finely crystalline (Figure 6), which explained a significant strength improvement.

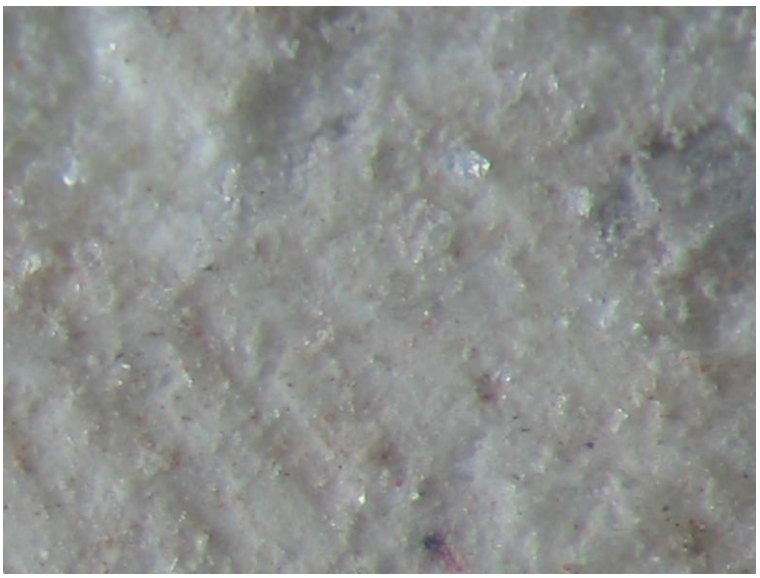

Figure 6: Micrograph of the surface of sulfur composite material based on silica gel modified with aluminum chloride (5% weight fractions) at 500 °C (x32). The binder/filler ratio is 1:1.

ISSN: 0975-8585

In the micrographs of the specimens with binder/filler ratio 1:1.5 (Figure 7-8) it was observed that the specimen had an inhomogeneous structure with the pores, voids and even cracks which are the reason of low physical and mechanical properties.

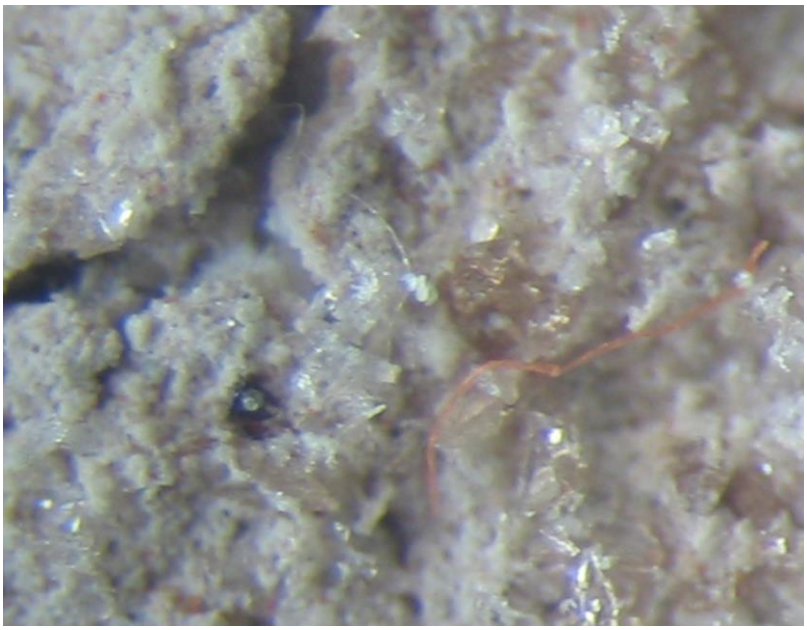

Figure 7. Micrograph of the surface of sulfur composite material based on silica gel non-modified with aluminum chloride (x32). The binder/filler ratio is 1:1.5.

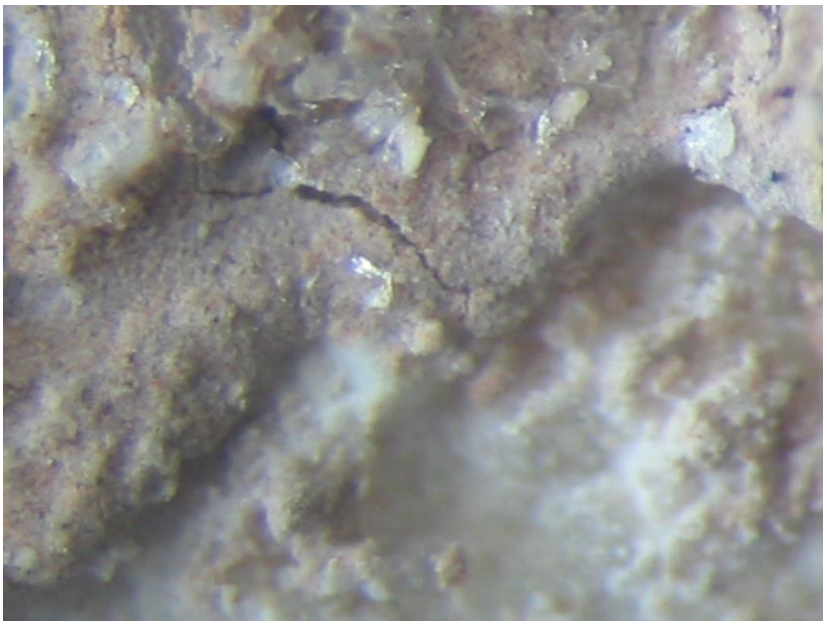

Figure 8. Micrograph of the surface of sulfur composite material based on silica gel modified with aluminum chloride (10% weight fractions) at 500 °C (x32). The binder/filler ratio is 1:1.5.

In order to provide deeper insight into the mechanisms of the system processes and confirm the formation of new chemical bonds S–S, Si–O–S, Si–O–Al, Si–O–Al–S the quantum chemical studies were performed.

The important prerequisite for successful quantum chemical studies is a correct choice of calculation method, primarily, way of electron correlation measurement and the used basis set. Different quantum chemical methods were first tested for accurate transfer of energy behavior with the broken bonds in different molecules. The second test was to define the transfer accuracy for a geometrical structure.

ISSN: 0975-8585

It was evaluated if sulfur could be combined with the silica gel modified with aluminum chloride by the donor-acceptor mechanism using vacant d-orbitals in the system “silica gel-aluminum chloride” and lone pairs of sulfur biradical.

The resulting relative energy curve at S-Al bond compression in the range 500-230 pm was monotonic, it was proved by the absence of characteristic points on the potential energy surface and a barrier of the combination reaction between sulfur and modified silica gel.

It can serve as a proof of the legitimacy of ΔH(S–Al) calculation for the reaction by the equation:

$$\Delta H(S–Al) = \Delta H^0_{f\,(Si\text{-}Al\text{-}S)} – (\Delta H^0_{f\,(S)} + \Delta H^0_{f\,(Si\text{-}Al)}),$$

where $\Delta H^0_{f\,(S)}$ and $\Delta H^0_{f\,(Si\text{-}Al)}$ are enthalpies of formation of parent compounds of S biradical and silicon-aluminum chloride system (model of modified silica gel surface) respectively, $\Delta H^0_{f\,(Si\text{-}Al\text{-}S)}$ is the enthalpy of formation of a product of combination reaction between sulfur and modified silica gel surface. The heat of the reaction was 70.38 kJ/mol. Sulfur was added to aluminum using the donor-acceptor mechanism. The products of these reactions formed strong valence bonds between sulfur and oxygen atom and silicon atom which governed the formation of stable sulfides and high-quality sulfur composite materials derived from them.

The results are presented for model calculations of interaction between S_5 oligomer acting as an electron donor at the expense of terminal sulfur atoms and two $AlCl_2$ fragments (Figure 9). Both terminal sulfur atoms of this molecule formed donor-acceptor bonds with $AlCl_2$ fragments. Formation of such adsorption complex featured the negative enthalpy change (-114.3 kJ/mol).

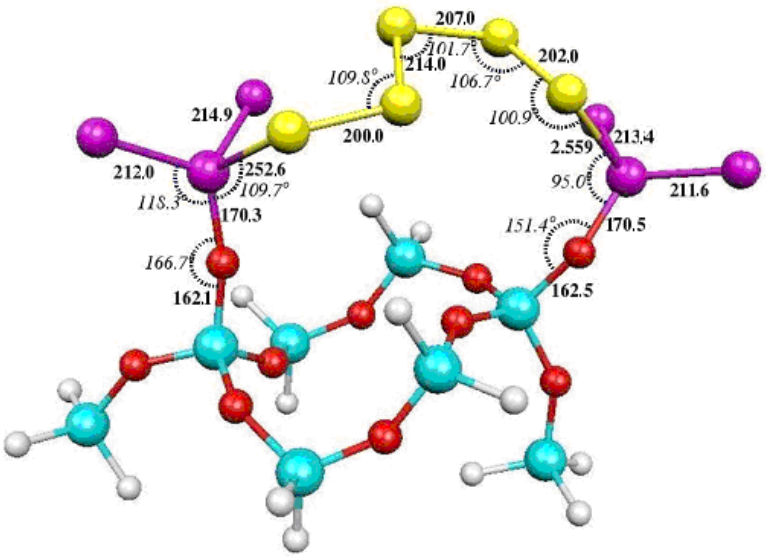

Figure 9. Structure and geometry of S_5 molecule adsorbed on two $AlCl_2$ fragments of model silica gel cluster.

Thus, the idea about the possibility of chemical interaction between sulfur and silica gel modified with aluminum chloride is supported by the results of the quantum chemical studies. As the heat treated mixture cools down the active sites of aluminum chloride will form weak donor-acceptor bonds with the unreacted sulfur. It will encourage its binding and uniform distribution in the filler.

CONCLUSION

Thus, we considered and confirmed the possibility of using the electrophilic sulfur activator – aluminum chloride to obtain high-quality sulfur composite materials. The physicochemical analysis and quantum chemical studies established that high physical and mechanical properties of the developed materials are the result of more intensive sulfur ring opening, formation of active sulfur radicals and chemical interaction between the components. It favors the formation of a compact homogeneous structure of the material. The work results address the environmental disposal problem for waste sulfur from petrochemical plants.

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