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Production and investigation of properties of sulfide composite materials based on technogenic sulfur waste with titanium chloride as an activator.

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ABSTRACT

The modification with titanium chloride contributes to the increase in active sites of silica-containing compounds and opening of sulfur rings. As an activator, titanium chloride helps to make resistant and durable high-performance sulfur composite materials.
Keywords: sulfides, titanium chloride, opal-crystobalite rock, sulfur composite materials, quantum chemical calculations

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INTRODUCTION

In the composite materials technology it is reasonable to use sulfur due to its chemical properties, electronic structure and high physical chemical properties of the resulting materials. Let us consider the methods for stimulating the formation of sulfur composite materials. Sulfur's electron configuration ($3s^2 3p^4 3d^0$), the presence of lone pairs and vacant 3d orbitals define its activating ability under the influence of electrophiles (E^+):

$$S_8 + E^{(+)} \rightarrow E - S_7 - S^{(+)}$$

The resulting polysulfide chains have higher reactivity than relatively stable cyclic S_8 molecules. For this reason, the above-mentioned reagent types can serve as catalysts for elemental sulfur reactions [1-3].

The electrophilic attack of S_8 molecules can be illustrated by their interaction with Lewis acids ($AlCl_3$, $AlBr_3$, AlI_3, $FeCl_3$, $SbCl_3$, SbF_5):

$$S_8 + AlCl_3 \rightarrow S^{(+)} - S - S_6 - S \rightarrow AlCl_3^{(-)}$$

It was found that aluminum chloride was an activator for sulfur ring opening [4-6]. No studies were made of $TiCl_4$ as an electrophile. It is an omission as $TiCl_4$ is waste from organic chemical processes.

Combination reactions, metathesis reactions and reactions where chlorine atom is displaced by other atoms or radicals are typical for titanium tetrachloride. With alkali metal chlorides titanium tetrachloride forms complexes containing $[TiCl_6]^{-2}$ ion which decompose into chlorides when heated.

SUBJECTS AND METHODS OF STUDY

The literature has no information about using titanium chloride as an activating reagent in sulfur composite materials. It was suggested that if cheap and available (waste from organic chemical processes) titanium chloride was used as an electrophile it would stimulate the interaction of the components in the sulfur containing system and provide high performance and mechanical properties of the resulting materials.

The paper uses the method for obtaining silica derivatives which is based on the reactivity between surface hydroxyl groups and chlorine substances. Therewith, on the surface of silica the active sites with vacant d-orbitals form [5, 7-8].

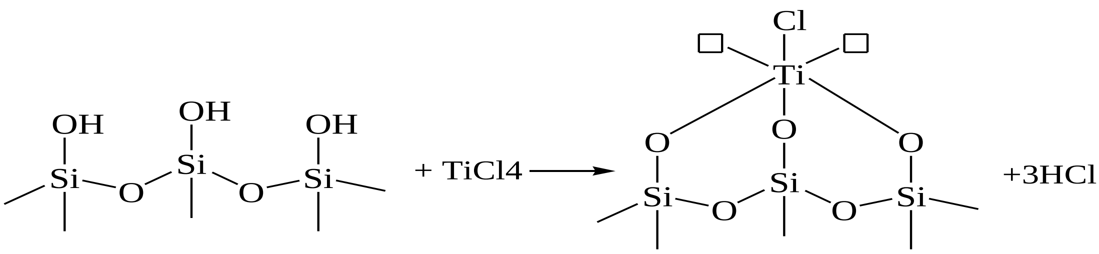

Figure 1: Diagram for interaction between silica gel and titanium tetrachloride

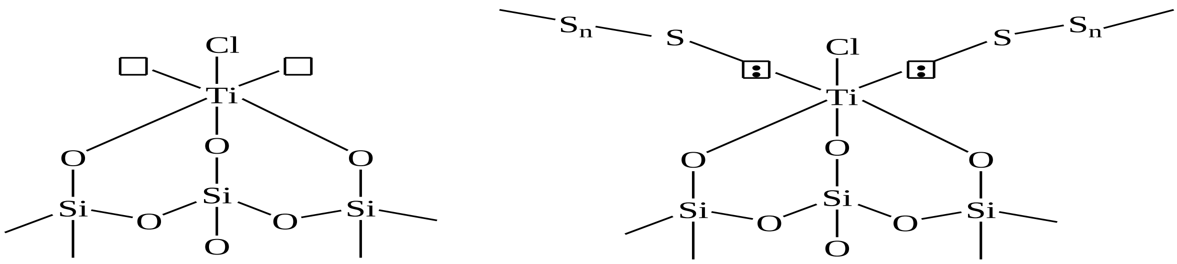

Figure 2: Diagram for addition of sulfur to surface of modified silica gel

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Sulfur's electron configuration is $3s^2 3p^4 3d^0$. The presence of lone pairs defines its activating ability under the influence of electrophiles. The available titanium tetrachloride was used as an electrophile.

EXPERIMENTAL RESULTS AND DISCUSSION

The possibility of modifying the surface of silica gel with $TiCl_4$ was studied. The results of IR-spectroscopic studies are shown in Figure 3.

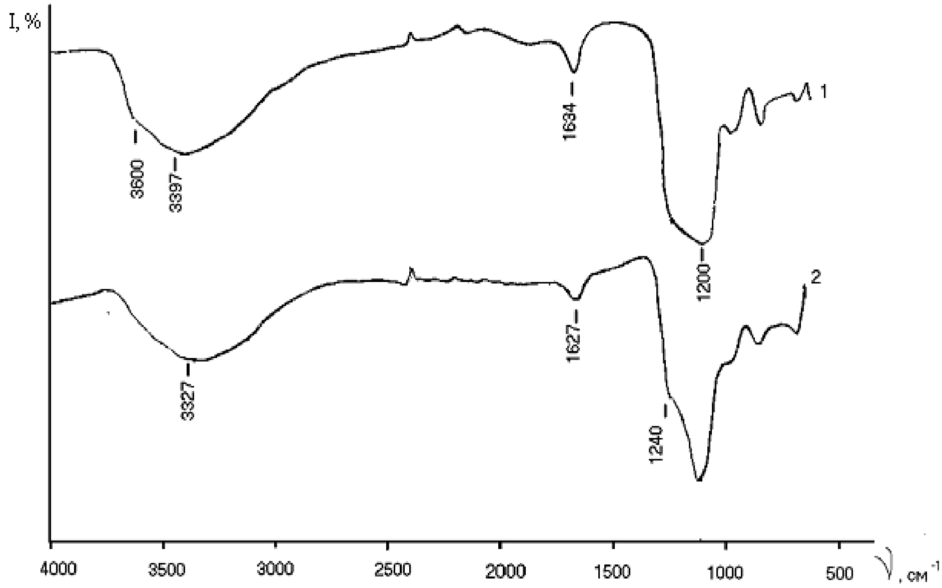

Figure 3: Infrared spectra of initial silica gel (1) and specimen treated with $TiCl_4$ (2)

Figure 3 shows the infrared spectra of the initial silica gel and synthesized specimen treated with titanium chloride. As seen in Figure 3, the absorption bands typical for hydroxyl groups of adsorbed water (3600, 1240 cm^{-1}) and absorption bands for bending vibrations of OH groups (1600-1650 cm^{-1}) are observed to decrease and disappear in the spectrum of $TiCl_4$-treated silica gel (Figure 3 (2)) [3].

The X-ray fluorescence analysis of $TiCl_4$-modified silica gel showed that the specimen had 8.3% of titanium. Figure 4 shows the results of X-ray phase analysis for the initial silica gel and the silica gel modified with $TiCl_4$. As seen in Figure 4, the amorphous ring decreases and the reflections of the crystalline phase appear, indicating that a certain amount of metals (in this particular case it is Ti^{4+}) penetrated the gel structure.

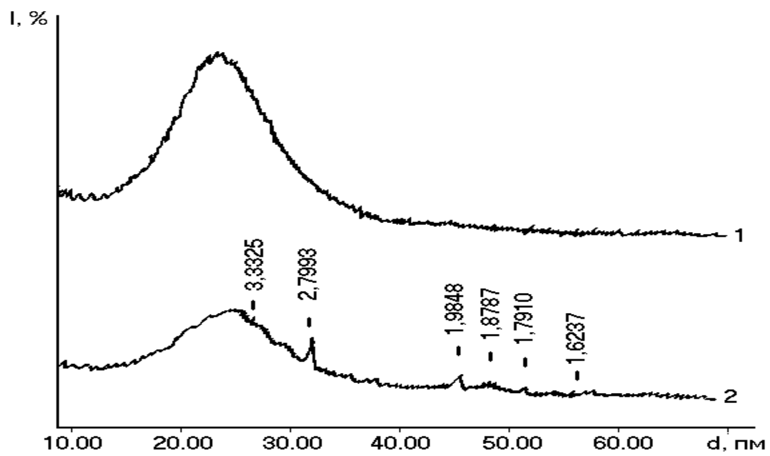

Figure 4: XRD patterns of initial silica gel (1) and $TiCl_4$-modified silica gel (2): 1) initial silica gel; 2) silica gel treated with $TiCl_4$

It can therefore be said that treatment of silica gel with titanium tetrachloride results in chemical interaction. With that, up to 8-9 wt% of metal is attached to the surface of silica gel.

As the structural units of opal cristobalite rock are similar to those of silica gel (cristobalite) $TiCl_4$ will act as the same active surface modifier as for silica gel. Opal cristobalite rock (OCR) is the available and cheap material to produce composites with high physical and mechanical properties.

The quantum chemical calculations were made using Priroda software to analyze the sulfur interaction by this mechanism.

The calculations were made for addition of singlet and triplet S_2 molecule to the model fragments of modified OCR. Addition to the smaller model runs activationless as a result of a strain of smaller cycles and presence of the redundant bond Ti-Si. The calculated process explains the activating behavior of Ti-Cl group in OCR by the activationless formation of the complexes 5 and 6 of coordinated titanium followed by displacement of the resulting intermediates [7].

Sulfur is added to titanium using the donor-acceptor mechanism.

Consideration was also given to the possibility of adding of sulfur biradical S_4 to the fragments of modified OCR. For singlet sulfur the reaction is endothermic in nature (ΔH of the reactions = 167.2 kJ/mol) (Figure 5), S_2-S_3 bond lengthens from 224.0 to 292 pm. In case of triplet sulfur S_2-S_3 bond is broken.

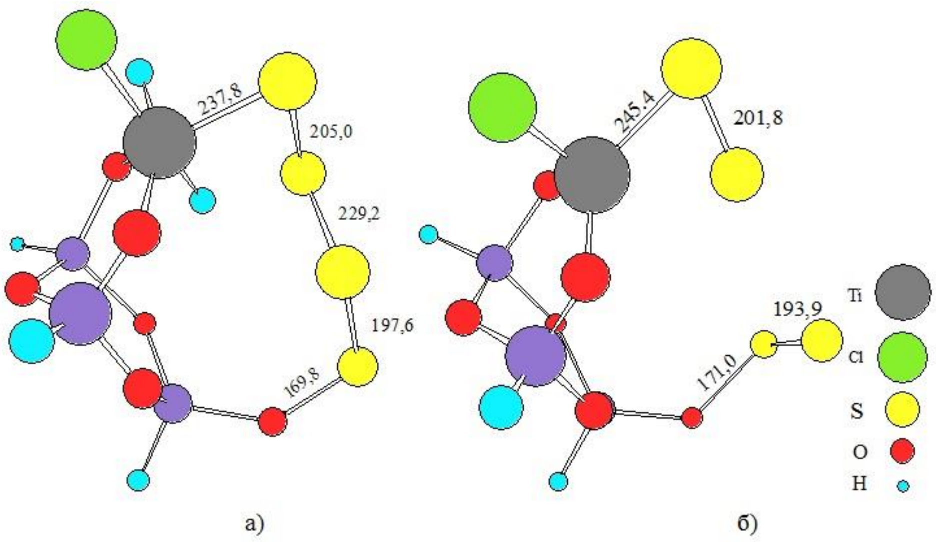

Figure 5: Product of interaction in sulfur – opal-cristobalite rock – titanium tetrachloride system: a) S_4 (M=1); б) S_4 (M=3)

Based on the results of the studies the procedure of producing sulfur composite materials from OCR was suggested. The specimens of sulfur composite materials are prepared by mixing original components at high temperature with $TiCl_4$ additive varying from 1 to 4%. Before preparation the filler is ground (maximum particle size is 0.5 mm) and sifted.

The calculation for TiCl4 hydrolysis mechanism made using DFT PBE method in L11 basis by Priroda software showed that it started with the activationless formation of aqua complex [$TiCl_4(H_2O)_2$], and HCl removal took place inside the aqua complex as a separate stage with energy of process activation significantly lower than HCl removal from $TiCl_3$(OH). The calculated process is a model of OCR modification mechanism [2].

Therefore, the OCR modification with titanium chloride contributes to the increase in active sites of silica gel surface and opening of sulfur rings. The reason for compact and strong structure is the stable short S-S bonds in oxygen and silicon resulted from prolonged heating and mixing.

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The most critical property of sulfur composite materials defining the quality of the formed structure is the durability which depends on physical and mechanical features of the components and strength of psysicochemical and chemical interaction in the phase interface under otherwise equal conditions. The more titanium chloride will be chemisorbed on the rock surface the more effectively the components will interact in the system. This effect depends directly on the content of the active silica – cristobalite – in the rock. The silica containing rock (zeolite opoka-like marl) from the Tatarsko-Shatrashanskoe field with low cristobalite content (28%) was chosen initially.

With lower filler content the strength decreases insignificantly, probably, as a result of excessive sulfur binder which makes pressing more difficult. The excessive filler amount also causes the loss of strength and increase in water absorption due to coating of the filler grains with the binder, it gives spongy specimens. The specimens with optimum composition have low water absorption 2-4% in accordance of the concrete-related requirements. As the OCR amount increases in the sulfur composite material the positive effect of $TiCl_4$ additive becomes more obvious.

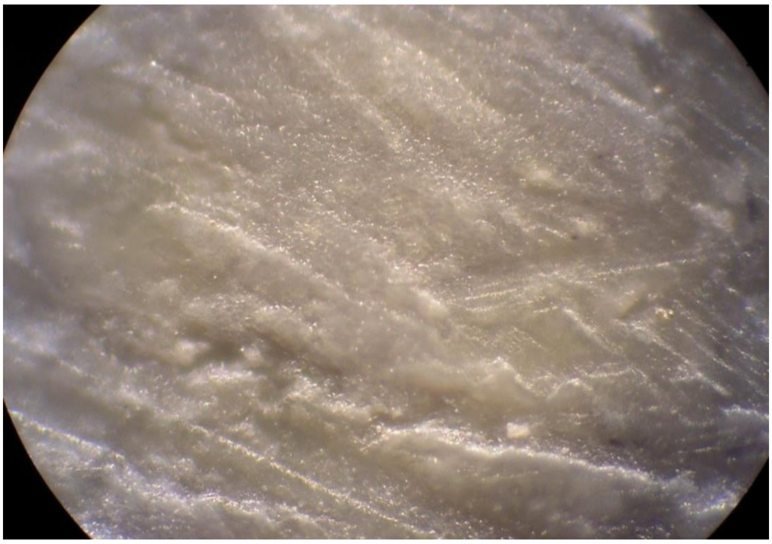

Figure 6: Micrograph of specimen with optimum composition

The resulting specimens have homogeneous structure, no cleavages and cracks, and have sufficiently high strength and water absorption. The developed composites can be used to produce a number of building materials: paving slabs, paving blocks, road construction materials, etc.

The micrograph of the specimen with optimum composition (Figure 6) shows a compact, non-porous structure which provides high specimen strength, density and water absorption while the specimen without any titanium chloride has an irregular and porous structure (Figure 7).

Thus, we considered and confirmed the possibility of activating sulfur and silica containing rocks with titanium chloride to produce inorganic sulfides and high-quality sulfur materials from them.

The technology for producing various inorganic sulfides and sulfur composite materials from them with high performance, physical and mechanical properties was developed. The compositions and technology for inorganic sulfides and sulfur composite materials were improved.

Figure 7: Micrograph of specimen of sulfur composite material not modified with titanium chloride

CONCLUSION

The resulting materials can be used for industrial, farm, storage structures which have higher requirements for corrosion resistance, frost and weather resistance, imperviousness during their operation. The following sulfur composite materials are most promising:

- road surface components (panels, paving slabs, paving blocks, curbs, guardrails);
- structures subjected to salt attack (floors, overflow launders, foundations);
- utilities (collector rings, sewage pipes, sewage facilities);
- lining blocks and other structures.
- Cost advantages of introducing sulfur composite technology result from the following:
- low cost of sulfur binder (price of sulfur is several times lower than price of silicate cement) and mineral fillers for which technogenic waste can be used;
- availability of sources of necessary raw materials;
- low production engineering costs.

REFERENCES

[1] Voronkova M.G., Vyasankin N.S., Deryagina E.N., “Reakchia seri s organicheckimi soedineniami [Sulfur reaction with organic bonds]”, Nauka, Novosibirsk. 368 p., 1979.
[2] Ysupova A.A., et al “Titanium Tetrachloride as Electrofilic Activator in Technology of Inorganic Polysulfides”, Journal of Quantum Chemistry, V. 111, Issue 11, pp. 2575-2578, 2011.
[3] Tsuboi T., Sakka T., Ogata Y. H., “Structure of prepared and amealed porous silicon surfaces stadied by nuclear magnetic resonance spectroscopy”, J. Electrochem. Soc., V. 146, No 1. pp. 372-375, 1999.
[4] Akhmetova R. T., Medvedeva G,Ahmetov T., Mejevich J., F. Gabbasov, “Surface-modified silica and sulfide containing composite materials on its base”, 20 International Congress of Chemical and Process Engineering CHISA 2012, Prague, Czech Repulic, 2012.
[5] Aleskovskiy V.B., “Napravlenie sintez tverdih veshestv [Directed synthesis of solid matters]”, Moscow, 255p, 1987.
[6] Yusupova A.A., Akhmetova R.Th., Treshchev A.A., Shafigullin L.N., Lakhno A.V., Bobrishev A.A., Sulfur composite technology from oil refinery waste, International Journal of Applied Engineering Research, Volume 11, No 5, pp 3057-3061, 2016
[7] Yusupova A.A., Baraeva L.R., Akhmetova R.T., “Design of patterns that form in synthesis of sulfide composites modified with silica”, Butlerov communications, V.26, Issue 12, pp. 60-64, 2011.
[8] Ridero Emerson S., Gushikem, “Yoshitaka Cobalt (2+) tetrasulfophthalocyanine complex adsorbdeon a silicogel surface chemical modified with 3-N propylpyridinium chloride”, Electroanalysis, Issue 11, No 17, pp. 1280-1284, 1999.