Quantum chemical simulation for calculation of processes of sulfur composite materials

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Abstract. Sulfide composite materials are becoming more widespread as they have a number of advantages such as strength, density, water resistance, and resistance to aggressive environments due to a chemical interaction between components. To ensure this, amorphous silica and silicon tetrachloride activator are used (in our opinion) to encourage electrophilic opening of sulfur molecules and formation of reactive sulfur radicals in order to increase the probability of chemical interaction between components in a system. The paper provides the quantum chemical calculations to demonstrate the interaction mechanism for components in a system.

1. Introduction The known sulfur materials feature only mechanical mixing of sulfur and mineral components. In our opinion, chemical bonding of components with the formation of sulfides will have a positive influence on the strength properties of materials, and environmental and health industrial safety. In that respect, it is reasonable to use amorphous silica as a mineral component, which has extended specific surface area and a large number of active sites on the surface. However, additional activation is required to ensure a chemical interaction between components due to a high energy barrier. A Lewis acid can be used as an activator. It attaches to the surface of amorphous silica (atomic layer deposition), thus increasing the activity of a mineral component. Today, there is a lot of information about atomic layer deposition in academic literature. The principles of atomic layer deposition technique based on Aleskovsky matrix hypothesis were described by V.B. Aleskovsky and S.I. Koltzov [1, 2]. The fundamental idea behind atomic layer deposition technique lies in a gradual growth of monolayers of structural units with a given chemical composition and structure on the surface of solid phase matrix due to chemical reactions between functional groups of a solid body and added reagents as far as possible from equilibrium [1-3].

Atomic layer deposition technique makes it possible to synthetize nanostructures with various chemical compositions on the surface of solid phase matrix, and to perform atom-by-atom chemical assembly of surface nano-, micro-, and macrostructures by repeatable alternation of chemical reaction following a set program [4, 5]. It should be noted that atomic layer deposition technique ensures the formation of nanolayers on the surface of solid substrate within the accuracy of one monomolecular layer. And the thickness of nanolayer is defined not by reagent omission time but by a number of atomic layer deposition cycles that includes a set of certain chemical reactions. Therefore, there are elements of self-organization that are observed during formation of the first and next monomolecular layers in the process of atomic layer deposition.
The theoretical approaches and, in particular, quantum chemical methods become more significant when addressing critical challenges in the field of synthesis of new composites. The results of theoretical studies on inorganic compound structure and reactivity often complement data of experimental studies, simplify their interpretation, and make it possible to get important information.

For this paper, quantum chemistry methods were used to study the structures of reagents, geometry of systems, reaction mechanisms. A reaction mechanism is a sequence of unit steps that add to conversion of initial reagents to products. A structure and energy of reagents and reaction products, as well as transient state that separates them should be known for each unit step. Today’s quantum chemical study methods for electronic structure and geometry of molecules, which are implemented in software such as Gaussian and Priroda, make it possible to conduct a simulation experiment and obtain data about the structure and energy of transient states, as well as the structure and geometry of reagents and reaction products. These software products can calculate a reaction path - lowest energy line that connects reagents and products and goes through a transient state [3].

The calculations were performed using Priroda application software (basis1.bas). The unrestricted Hartree-Fock method was often used to estimate radical decomposition reactions and study the structure of biradical transit state. It involved mixing of the highest occupied and lowest unoccupied molecular orbitals at the start of calculations. So, the Priroda can be used for qualitative evaluation of molecule geometry and energies. For studies of polyatomic systems, the Priroda software is more preferable as the calculations do not take a lot of computing time.

2. Body text
We know from the earlier papers that a direct interaction between sulfur and silica is impossible due to a very high activation energy for this reaction. Aluminum chloride can be used as an activator [6-8]. Our paper proposed that an activator of sulfur and amorphous silica surface should be used, and it would be silicon tetrachloride SiCl4.

We assumed that fragments of an electrophilic activator of silicon tetrachloride, which are attached to the surface of opal-cristobalite rock, would act as a bridge that connects opal-cristobalite rock and sulfur, and, therefore, ensure a chemical interaction between binder and filler, and high physical and mechanical properties.

The possible mechanism of polysulfide formation is shown in Figure 1.

![Figure 1. Mechanism of polysulfide formation with silicon tetrachloride activator](image)

The quantum chemical calculations showed that the activation energy for addition of sulfur to amorphous silica decreased by 103.8 kJ/mol with silicon tetrachloride activator.

As a result, sulfide composite materials are formed, and they have high strength, density, water resistance, and resistance to aggressive environments.

3. Conclusions
Therefore, the theoretical quantum chemical methods confirmed that silicon tetrachloride activator decreased the consumption of energy for formation of sulfide composite materials with high physical mechanical and performance properties. These materials can be used for flagstones, curbstones, and poured composite floors resistant to aggressive environments for chemical plants.

References
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