Reactivity of dispersed schungite to bitumen

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Abstract. Some aspects of the use of schungite mineral powder to obtain effective compositions based on bitumen are considered in this paper. The high reactivity of dispersed schungite to bitumen is shown. The studies are performed by studying the water extracts from suspensions, as well as the state of the surface of the powders and the concentration of active surface centers using the indicator method of fixing the distribution of adsorption sites (DAS) in the spectrophotometric version. Based on the analysis of the results obtained it is concluded that the molecules of organic substances contained in bitumen can actively interact with the surface of schungite. At the interface between the binder and schungite the processes take place that are accompanied by the formation of a strong adsorption layer which is necessary for the formation of a high-quality and durable composite. The presented studies of asphalt binders confirm the conclusions and show that asphalt concrete pavements using shungite mineral powder will be able to work in a wider temperature range both for high summer and low winter temperatures.

1. Introduction

The amazing properties of schungite have long been known. This is a Precambrian rock, which is a transitional stage from anthracite to graphite [1]. This rock formation experienced its rebirth when fullerene was discovered. It was found that the water-soluble part of schungite contains up to 1% of fullerenes. This predetermined increased interest and thorough research of the possibility of its use presented in various spheres of human life: from high technology, medicine, etc., to construction and agriculture.

Shungite is a carbon-containing composite consisting of amorphous carbon, actively entering into redox reactions, silica, as well as aluminum oxides, iron, cobalt, vanadium, titanium and others [2]. Moreover, it was established [3-5] that fullerenes (C60) are well soluble in aromatic substances and solvents such as carbon disulfide, whereas in polar solvents they are poorly soluble. The content of aromatic hydrocarbons can reach 8% according to modern concepts [6] in bitumens.

Considering the significant use of road bitumen in the construction and repair of highways, the use of shungite mineral powder and the development on its basis of new technologies for building high-quality and durable asphalt concrete pavements is an actual subject [7-9].

2. Materials and methods

The object of research in the work was the schungite of the Karelian deposite which is the largest not only in Russia but also in the world. The possibility of obtaining a mineral powder for road construction with enhanced consumer properties from it is not only scientific, but also of practical interest. As a base
mineral powder, limestone from the Yelets deposit was used. The properties of shungite rock are as follows: the average density is 2630 kg/m³, porosity is 3.7%, water absorption is 6.9%. Limestone average density is 2490 kg/m³, porosity is 23%, water absorption is 45.8%.

The chemical composition of shungite and limestone rocks is shown in table 1.

Table 1. Chemical composition of mineral powders

| Powder name | SiO₂  | Al₂O₃ | Fe₂O₃ | Fe₃O₄ |
|-------------|-------|-------|-------|-------|
| schungite   | 45.5  | 2.3   | 1.9   | 1.0   |
| limestone   | 2.1   | 0.1   | 1.2   | 0.8   |

The raw rock was ground in a mill to obtain mineral powders. Grinding of shungite was performed for comparison on 2 types of mills. Ball mill and vertical mill were used. It should be noted that the dynamics of the behavior of the material during grinding was not changed. The grinding time was 1-4 hours in increments of 1 hour. The dispersion of the final filler was evaluated using a MICROSIZER 201C laser particle size analyzer.

The complex of studies was carried out by studying water extracts from suspensions on a pH meter I500 instrument to assess the state and comparative analysis of the surface properties of mineral powders. Also, the state of the surface of the powders and the concentration of active surface sites were studied using the indicator method of fixing the distribution of the adsorption sites (DAS) in the spectrophotometric version [10]. This method makes it possible to characterize the presence of active sites of a certain type in terms of the acidity of pKa and evaluate their quantitative content.

Table 2. Physical and mechanical properties of the binder

| The name of indicators | State Standard 33133 | Actual results BND 70/100 bitumen |
|------------------------|----------------------|----------------------------------|
| 1                      | 2                    | 3                                |
| Needle penetration depth 0.1 mm, | >71-100 | 72 |
| at 25°C                | 21                   | 23                               |
| at 0°C                 |                      |                                  |
| Extensibility, cm,    | >62                  | 75                               |
| at 25°C                | 3.7                  | 3.7                              |
| at 0°C                 |                      |                                  |
| Softening temperature, °C | > 47               | 49                               |
| Britteness temperature, °C | > - 18         | -19                              |
| Dynamic viscosity, Pa·s, at 60°C, Condition 1 | - | 298.5 |
| Change in dynamic viscosity after shear, Pa·s, at 60°C, Condition 2 | - | 12.97 |
| RTFOT after aging tests |                      |                                  |
| Mass change of the sample after aging, % | > 0.6             | 0.4                              |
| Change of softening temperature, °C, after aging | > 7           | 6.2                              |
| Dynamic viscosity after aging, Pa·s, at 60°C, Condition 1 | - | 807.11 |
| Change in dynamic viscosity after shear, after aging Pa·s, at 60°C, Condition 2 | - | 24.72 |
3. Results
The raw rock is crushed in the process of preparing the mineral powder. At this stage of technological redistribution, the potential of the mineral is maximally revealed and the active sites located on its surface are exposed.

In accordance with the generally accepted model of interaction of bitumen with mineral materials, the contacts formed by bitumen and the main rocks - limestone, dolomite, etc. are the most durable and irreversible. Therefore, one of the main parameters that allow investigating the surface of construction materials and at the initial stage predicting the intensity of the processes of interaction of mineral raw materials with an astringent is its ability to exhibit acid-base properties. During the study, it was found that limestone, as expected, exhibits alkaline characteristics and refers to the main rocks, schungite tends to show acidic properties, Figure 1.

\[
\begin{array}{ccc}
\text{shungite} & \text{pH} & \text{limestone} \\
5.48 & 7.0 & 11.44
\end{array}
\]

**Figure 1.** PH values of the studied mineral powders

As it can be seen, the pH of filler of the limestone is almost 2 times higher than that for shungite powder. It is possible to assume that shungite filler due to its acidic properties when in contact with bitumen will be inert. However, modern studies indicate that the surface of acidic mineral materials is not inert with respect to the components of bitumen [14, 15].

Shungite was formed from organic sediments [1]. These organic sediments covered on top with new layers were gradually compacted, dehydrated and plunged into the depths of the earth. Under the influence of compression and high temperature was the process of metamorphization. As a result, amorphous carbon sprayed in the mineral matrix was formed in the form of globules characteristic of shungite. Such processes could not but affect the state of the surface of the mineral and the concentration of active surface sites. The results obtained on the basis of the indicator method of fixing the distribution of the adsorption sites (DAS) are presented in Figure 2.

**Figure 2.** Content of active adsorption sites on the surface of mineral materials
As it can be seen, the total number of active sites on the surface of schungite is several times greater than this value for limestone. At the same time, the greatest difference is observed in the range of the main Bronsted sites (pKa 7–13) and Lewis acid sites (pKa> 13).

It is worth noting the following paradox, when studying various fillers (sand, granite, slags) using the DAS method, limestone was positioned as an active material characterized by a high content of adsorption sites. However, a comparative analysis of the distribution of active sites on the surface of schungite made it necessary to look differently at the reactivity of the previously studied powders.

Comparing the data obtained with the scale of distribution of adsorption sites on the surface of solids and possible schemes of interaction with bitumen components [14], it was concluded that the molecules of organic substances contained in the binder can actively interact with the surface of shungite.

For example, at the Bronsted acid sites, which are surface hydrosilic groups (pKa 0–7), hydrogen bonds can form with the participation of a surface hydrogen atom exhibiting electron-acceptor properties. Bitumens also contain nitrogenous bases and compounds, including hydroxyl, carbonyl, ester, and other groups, which are formed during the oxidation of oil residues, which are Bronsted bases and will interact with Bronsted acid sites on the surface.

A part of asphaltenes and resins are aromatic polycyclic structures, including heterocycles with nitrogen and sulfur, having π-bonds and atoms with lone electron pairs. They can be electron donors and interact with electron-acceptor Lewis acid sites (pKa> 13). The complex compounds of phenols and nitrogenous bases contained in the composition of resinous substances of bitumen are also capable of forming donor-acceptor bonds with Lewis acid sites (pKa> 13) of the surface.

Acids will be able to interact with the main Brensted sites (pKa 7-13). Moreover, aromatic acids are stronger than aliphatic ones, and the presence of two substituents, for example — COOH and —OH, in naphthenic and aromatic rings, which are observed in the composition of bitumen, increase the acidity and adsorption capacity of these compounds.

Anions of organic acids of bitumen will also interact with cations of heavy and alkaline-earth metals with the formation of chemical compounds.

The nature of the interaction of bitumen and mineral filler is also significantly influenced by the dispersion of the latter. The high level of the dispersion of the filler leads to increased interaction with bitumen. It results in a highly structured binary system. As it is noted earlier, the work considered a different time interval for grinding the schungite mineral 0.315 mm into mineral powder, corresponding to [11]. The results of the dependence of the fineness of grinding on the grinding time are presented in Figure 3.

As it can be seen, the distribution line of shungite particles after grinding the powder for 4 hours (line 4) is superimposed on line 1, corresponding to 1 hour of grinding. When grinding rocks for 2 and 3, a similar pattern is observed. In general, the graphs are identical with a slight deviation in the range up to 100 microns. Thus, it is possible to conclude that, regardless of the time of grinding, the content of fine fractions does not increase. This was not observed during the grinding of limestone - the main and granite - sour rock. On the basis of the data obtained for the optimal time for grinding the mineral powder was chosen as 1 h. Dispersed schungite was examined for compliance with the requirements for mineral powder, table 3.
Table 3. Indicators of the properties of the investigated fillers

| Name of an indicator | Mineral powder | State Standard requirements |
|----------------------|----------------|-----------------------------|
|                      | shungite       | limestone                   |
| Grain composition, % by weight: |                |                             |
| smaller than 1.25 mm  | 100            | 100                         |
| <0.315 mm             | 90             | 92                          |
| <0.071 mm             | 80             | 77                          |
| Porosity, %           | 37             | 28                          |
| Bitumen indicator, g  | 48             | 68                          |
| Humidity, % by weight | 0.55           | 0.74                        |
| Swelling of samples from a mixture of powder with bitumen, % | 1.67 | 1.15 |
|                      |                |                             |

As it can be seen, the filler meets the requirements of the standard. However, the porosity of this material is on average 30% higher than the porosity of the limestone filler and the specific surface area with the same particle size distribution is 60-70% more which allows concluding that the system of micropores of the studied material is more developed.

For the formation of a high-quality and durable composite for construction purposes, it is necessary that at the interface between the binder and mineral materials the processes take place, accompanied by the formation of a strong adsorption layer. The determination of the ability of the fillers to adsorb and hold bitumen on their surface was based on the method of adsorption-desorption of bitumen from benzene solutions by the surface of the fillers Figure 4.
Figure 4. Indicators of adsorption-desorption of bitumen on the surface of mineral powders:

As it can be seen on Figure 4, shungite has a higher adsorption activity with respect to bitumen. Such activity of the filler is obviously associated with a highly developed system of pores and a significant number of active sites on the surface, capable of adsorbing almost all organic compounds contained in bitumen. Acid and main Bronsted and acid Lewis sites make the greatest contribution to this interaction.

Thus, at a concentration of bitumen in a benzene solution of 12 kg/m$^3$, the value of its adsorption by the surface of shungite is $2.9 \times 10^{-3}$ kg$_{bit}$/kg$_{por}$, and the surface of limestone is $2.1 \times 10^{-3}$ kg$_{bit}$/kg$_{por}$. The study of bitumen desorption showed that part of the binder exfoliate from the surface. This suggests that the extremely saturated adsorption layer of bitumen on the surface of the fillers consists of firmly, chemically, and reversibly, physically bound bitumen. Thus, after desorption, $1.8 \times 10^{-3}$ kg$_{bit}$/kg$_{por}$ remained on the surface of shungite, and $1.4 \times 10^{-3}$ kg$_{bit}$/kg$_{por}$ on the surface of limestone.

For a preliminary assessment of the health of the mineral shungite powder and prediction of the properties of road composites based on it studies of asphalt binder (AB) were carried out.

There is a theory [15, 16], according to which the most important characteristics of AB include the optimal content of bitumen and its strength with such content. It should be noted that the strength indicators are associated with the size and surface activity of the mineral powders used, as well as with the grain size. However, there is another point of view [17] according to which only the total contact area of the mineral core particles with each other (according to which bitumen that is most structured by surface can be used) is the main factor determining the strength and other properties of AB. Such an area depends on the modulus of the surface of the mineral material used and the porosity of the mineral core.

In this paper AB samples were made by the standard method. Preliminary for each composition the optimum content of bitumen was determined. So for samples of shungite, it was 16%, for limestone 19%.

Data on the study of asphalt binders are presented in table 4.
Table 4. Physical and mechanical properties of asphalt binders

| Name of the indicator                                      | Mineral powder |            |
|------------------------------------------------------------|----------------|------------|
|                                                            | shungite       | limestone  |
| Compressive strength, MPa:                                 |                |            |
| at 0 °C                                                     | 10.9           | 14.7       |
| at 20 °C                                                    | 4.3            | 2.5        |
| at 50 °C                                                    | 3.9            | 2.1        |
| at 60 °C                                                    | 3.7            | 1.8        |
| Water resistance of samples from a mixture of powder with   | 0.93           | 0.86       |
| bitumen, %                                                  |                |            |
| Long-term water resistance of samples from a mixture of    | 0.89           | 0.76       |
| powder with bitumen, %                                      |                |            |

4. Conclusion
The obtained results confirmed the existing theories [15, 17, 18]. High AB strength properties correspond to shungite filler, which is characterized by a greater true specific surface area and the presence of active surface centers. This suggests that asphalt coatings using such mineral powder will be able to work in a wider temperature range both at high summer temperatures and at low winter temperatures.

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