IOP Conf. Series: Materials Science and Engineering **775** (2020) 012128 doi:10.1088/1757-899X/775/1/012128

Basis of use of dispersed carbon-containing modifiers for production of construction materials with given properties

S S Yusupova [1], M A Myzernaya [2], A A Khairullina [2] and A V Kartygin [1]

[1] Belgorod V.G. Shukhov State Technology University, Branch in Novorossiysk, 75, Myskhakskoe highway, Novorossiysk, 353919, Russia
[2] East Kazakhstan D. Serikbayev State Technical University, 69, Protozanov str., Ust-Kamenogorsk, 070004, Kazakhstan

E-mail: Svetlana- svetli4na@mail.ru

Abstract. The mineralogical composition and structure of shungite rocks of East Kazakhstan is investigated. The possibility of obtaining a dispersed modifier from shungite for the production of various building materials is studied. The structure of dispersed carbon-containing modifiers obtained in the process of «dry» and «wet» grinding of shungite is investigated. The possibility of modifying cement compositions with a carbon-containing modifier is studied. Due to the adsorption-bound water the modifier under examination ensures a sufficiently intensive process of hydration and structure formation of hardening cement stone. It predetermines the structure and physical and mechanical properties of the cement stone. The effect of dispersed carbon-containing modifiers on the structure formation and adhesion of bitumen to mineral materials is shown.

1. Introduction

Many researchers in Russia and Kazakhstan have dealt with issues of use of dispersed mineral modifiers in building materials [1, 2].

According to projected estimates of the development of the black shale region of East Kazakhstan, gold sulfide deposits contain about 530 million tons of shungite.

The total prognosis resources of this most valuable raw material are at least hundreds of times greater than the reserves of the only well-studied and exploited Zazhoginsky deposit (Russia, Karelia). This allows talking about the possibility of forming a new mineral resource base of scarce carbon raw materials for Russia, Kazakhstan and Central Asia [3, 4].

The methodology of research data included the consistent implementation of interrelated modules. First, the study of the structural and textural characteristics of shungite rocks of East Kazakhstan Bakyrchik field in order to obtain carbon-containing modifiers for the production of building material was performed. Second, the study of the process of structure formation of cement and bitumen compositions prepared using the shungite modifier. Then the determination of its influence on the structural and physic-mechanical characteristics of the materials under study was performed.

2. Methodology and results of researches

In carrying out the work modern research methods were used.

The mineral composition of shungite rocks was studied in transmitted and reflected light in thin rock sections and polished sections. Sample preparation for scanning electron microscopy was carried out in the sector of sample preparation in the laboratory of the engineering profile «Irgetas». For this purpose, a high-precision Minitom disc cutting machine manufactured by «Struers» (Denmark) was used. Grinding of samples was carried out on a grinding-and-polishing machine with a device for automatic grinding and polishing of samples. Removal of abrasive particles was carried out using an ultrasonic bath.

The study of the topography, microstructure of the sample surface and building profiles of the distribution of elements along a given line (50 samples) was carried out using a JSM-6390LV scanning electron microscope manufactured by «JEOL Ltd» (Japan). The qualitative and quantitative elemental microanalysis in a point area and building the distribution of elements in a selected area was carried out with the INCA Energy Penta FET X3 energy dispersive microanalysis system from «OXFORD Instruments Analytical Limited» (UK). The following parameters were observed: accelerating voltage is up to 30 kV; resolution is up to 3 nm; instrument magnification is up to x300 000; defined elements are from B to U; detector energy resolution is 137 eV.

The chemical composition was studied according to the results of research on a JSM-6390 LV scanning electron microscope and X'Pert PRO X-ray diffractometer.

Quantitative elemental analysis was performed using an ICP-MS Agilent 7500 cx inductively coupled plasma mass spectrometer manufactured by «Agilent Technologies» (USA). The minimum detectable concentration of elements was taken: in liquid object is up to 10^{-9} g/dm^3; in solids is up to 1 ppb.

The study of the phase composition of the materials under study was carried out on a D8 ADANCE X-ray diffractometer manufactured by BRUKER. When processing the peaks of X-ray diffractograms and searching for the corresponding phases in the databases, the universal program DIFFRAC was used.

The main physical and chemical properties of the materials under study are determined by their structure. To do this, studies were carried out using a JEM-2100 transmission scanning electron microscope. The dispersion of materials was determined by the specific surface area on the instrument PSH-10A with an accuracy of ± 1 cm^2/g. In the PSH-10A device, measurements and calculations of gas permeability, specific surface area and average mass size of powder particles are performed under the control of a processor operating according to a specially created program.

Studies have shown that the structure of shungite is characterized by a uniform distribution of polar highly dispersed (0.1–10 μm) crystalline silicate particles in a non-polar carbon matrix of spherical, hollow, multilayer fullerene-like carbon globules in size of 10–20 nm (Figure 1).

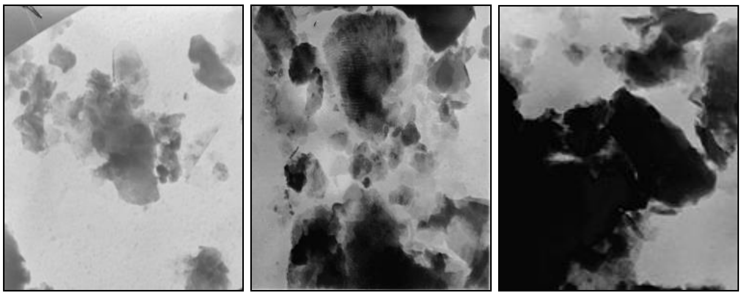


Figure 1. Figure with short caption electron microscopic images of three morphological phases (photos by A.I. Mizerny).

Using diffractometry, it was established that shungite substance can be interpreted as large globules or crystallites of shungite substance (Figure 2) and smaller isolations. These smaller isolations are fullerene-like particles (Figure 3), tubular-shaped separations (nanotubes) often occur, belonging to carbon nano-forms (Figure 4).

IOP Conf. Series: Materials Science and Engineering **775** (2020) 012128 doi:10.1088/1757-899X/775/1/012128

As can be seen, this feature of the internal structure of shungite carbon suggests that shungite in an ultra-dispersed state will be able to combine well and work with mineral and organic binders.

The structure of shungite carbon with its high internal energy potential characterizes it as a material with high impact strength, resistance to aggressive media, adsorption activity, bactericidal properties, etc. This implies high physic-mechanical properties and durability of building composite materials, produced from shungite.

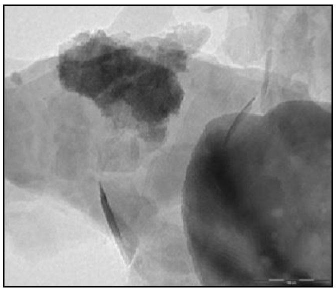


Figure 2. Microphotograph of large globules of carbonaceous matter of shungite.

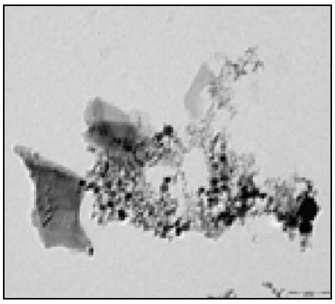


Figure 3. Distribution of polar highly dispersed (0.1–10 μm) crystalline silicate particles.

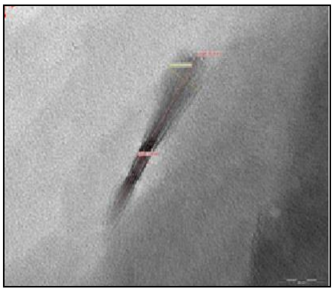


Figure 4. Tubular form segregations

In view of the above prerequisites, the effect of grinding parameters on the granulometry of the modifier obtained by grinding in a vibratory grinder was studied [5].

To obtain the shungite modifier, the shungite was previously crushed on a laboratory jaw crusher before obtaining fractions of 0.63−1.25 mm. Then, on a two-chamber vibratory grinder of periodic action of «VIBROMASH UK» LLP, designed by Kovshyk A.V. in abrasion and shock loading modes.

The analysis of the dependence of the increase in specific surface area (S_{sp}) of shungite powder on the duration of grinding using the PKS-10a instrument showed that an intensive increase in S_{sp} occurs in the interval from 10 to 60 minutes of grinding in a vibratory grinder. After that the growth kinetics of S_{sp} decreases (Figure 5).

In order to confirm the presence of nano-sized particles in the carbon-containing modifier and to determine the shape of their surface, electron microscopic studies were performed on a JEM 2100 JEOL (Japan) JET transmission electron microscope.

IOP Conf. Series: Materials Science and Engineering **775** (2020) 012128 doi:10.1088/1757-899X/775/1/012128

The average particle size of shungite powder after grinding was from 10 to 250 nm. Based on the studies, it was established that the initial shungite particles after grinding in a vibratory grinder are quite homogeneous and have a flaky and spherical shape (fullerene-like formations). There are fragments in the form of elongated tubular formations (nanotubes). The diameter of the tubes is tens of nanometers; the length varies up to 200 to 700 nanometers as can be seen from Figure 6.

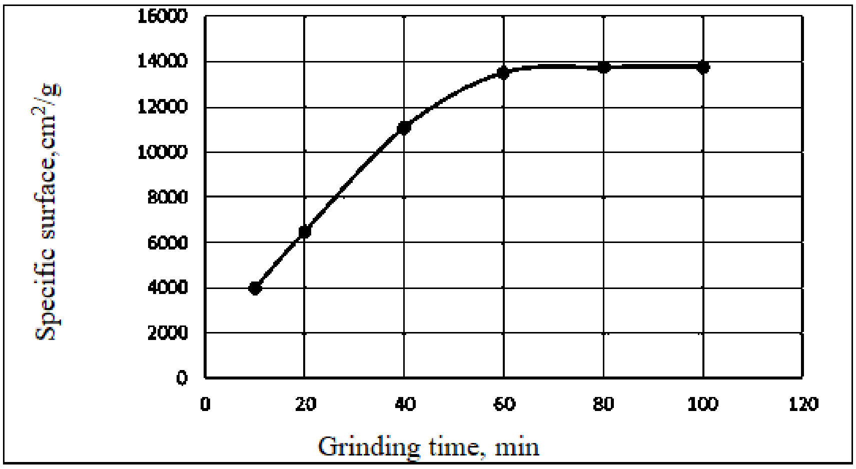


Figure 5. Increase dependence of the specific surface area of shungite filler on grinding time.

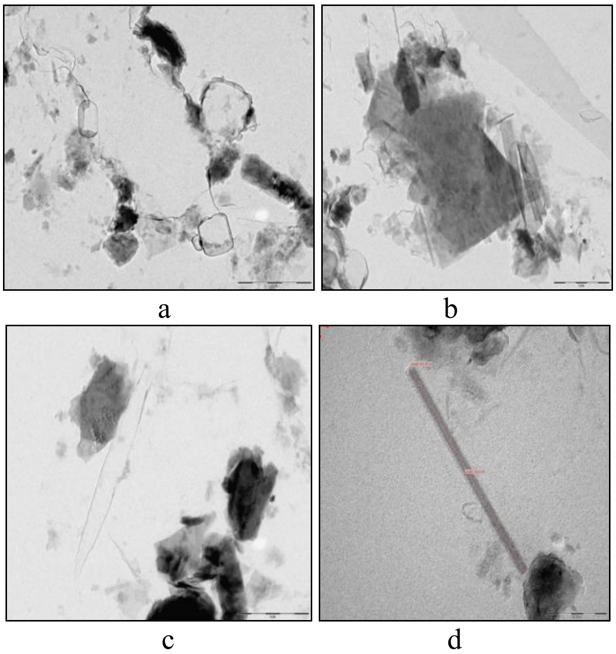


Figure 6. Micro-photographs of shungite after grinding: a – rounded isomorphic particles of shungite carbon; b – serrated, tabular particles of shungite rocks; c – acute-angled fragments of carbonaceous matter and alumino-silicates; d – hollow nanoscale tubular formations.

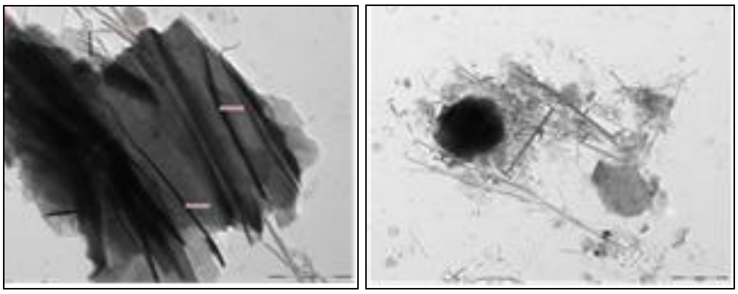
As further studies have shown, the process of mechanical activation by grinding associated with changes in the particle size distribution, specific surface area, shape and surface micro-topography of shungite particles (serrated particles, tubes and round formations) had a positive effect on their interaction with cement, bitumen and varnish-and-paints materials.

The studies on shungite grinding in the «wet» grinding mode revealed the facilitation of dispersion. This one is well explained by the effect of adsorption decrease in the strength of materials (Rebinder effect).

By the method of «wet» grinding of shungite, a multifunctional product was obtained in the form of a colloidal solution. To obtain the above specified product shungite was crushed in a vibratory grinder with the addition of distilled water. After grinding (activation), the resulting black aqueous solution of shungite (suspension) was filtered through a No. 008 sieve in order to separate the colloidal solution containing carbon nanoparticles in the range of 0.005%−0.02%.

After filtering the resulting suspension, the liquid component — the active colloidal solution — was used as a mixing fluid and also as a modifier of plasticizers for cement mixtures. A solid residue of shungite was used as filler in cement composites. The structure of the colloidal solution and the solid residue was studied using an electron microscope PEM JEM-2100.

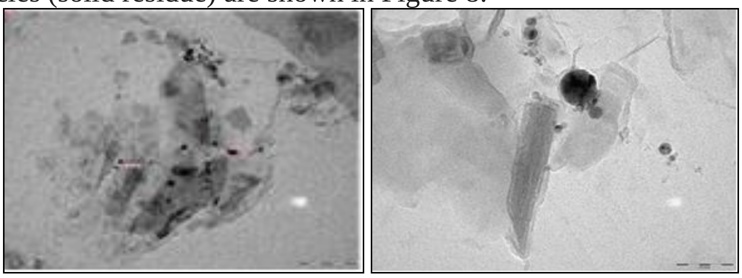
The method of sample preparation for the study of a colloidal solution on a transmission electron microscope consisted of the following steps. From the liquid component of the suspension − a colloidal solution prepared on the basis of shungite powder, − a sample was taken in an amount of 1 ml with a pipette and placed on a copper mesh and dried at a temperature 120−150 C. The dried sample was treated with 96% alcohol and dried at room temperature 23−25 C. Micrographs of the dried residue of a colloidal solution are shown in Figure 7.



a b

Figure 7. Microphotographs of the dried residue of a colloidal solution: a – series of tubular and acute-angled particles of shungite carbon; b – rounded, (fullerene-like) and tube-shaped (nanotubes?) formations.

The solid residue of shungite after filtration (hydrolyzed shungite powder) was placed on a carbon mesh sprayed with carbon, dried at room temperature. Electron microscopic images of the shungite modifier nano-particles (solid residue) are shown in Figure 8.



a b

Figure 8. Micrographs of the solid residue of the shungite modifier: a – acute angular nano-sized fragments of carbon substance; b – hollow nano-sized tubes and fullerene-like formations.

As further studies have shown, it is the presence of shungite nano-particles (tubes, fibers) that contribute to increasing the plasticity and strength of the binder composites due to the increased reinforcing capacity of the latter [6, 7].

The analysis of the results of testing concrete from equally moving concrete mixtures shows an increase in strength by 26%, frost-resistance by 17% for concrete samples manufactured using the shungite modifier. At the same time a compact structure of cement stone is noted. That is, the modifier under study, due to the adsorption-bound water, ensures a rather intensive flow of hydration processes and the structure formation of hardening cement stone. That predetermines the structure and physical and mechanical properties of the cement stone [8, 9].

It was also established that shungite carbon enhances the mechanism of action of plasticizing additives of the ligno-sulfonate technical group, superplasticizer based on Na salt naphthalene sulfonic acid and formaldehyde C-3 in the system “cement-water”. Shungite powder enhances the effect of plasticizer C-3 almost by 50%.

The paper substantiates the possibility of using materials based on nano-dispersed carbon-containing materials to impart special properties to building materials. For this purpose, studies have been carried out on the modification of the following materials: bitumen for asphalt concrete, mineral powder for asphalt concrete and vanish-and-paints materials.

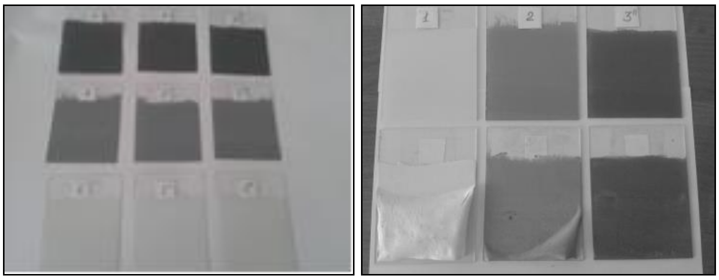
Analysis of the research indicates the role of shungite powder as a structuring additive for bitumen; this component allows bitumen being evenly distributed on mineral grains with thinner structured layers. And this generally reduces the porosity of the mineral asphalt concrete mix and increases its durability. At the same time, the amount of the modifier is in the range of 1–3% ensures good adhesion of bitumen to mineral materials. This amount of the shungite powder must have a specific surface of 13500 cm^2/g.

Modification of bitumen with shungite powder containing nano-particles allows a slight decrease in penetration values. It is significantly increasing the adhesive properties of bitumens and the softening temperature. Therefore, shungite powder can be classified as a structuring and adhesive additive.

The addition of shungite modifier to limestone mineral powder for asphalt concrete in the amount of up to 15% leads to an increase in durability during operation in various temperature ranges. It is especially important for the northern regions of the country. Prototypes of asphalt concrete with modified mineral powder had high water resistance and frost resistance. In the aggregate, the best indicators of the properties of hot asphalt concrete were recorded when modifying the mineral powder with shungite powder in an amount of 15%.

In order to confirm the assumption about the effect of the dispersed shungite modifier on the properties of paints and vanishes, some properties of shungite powder were studied that characterize its potential possibilities of using it as a pigment for paints and varnishes [10].

Resistance of a paint coating to static effect of water of the developed structures of paints and varnishes. The standard regulates the enamel resistance to water for at least 10 hours. As a result of tests of paints based on white enamel PF-115 and the addition of a pigment-shungite powder for the resistance of coatings to the static effects of water obtained the following results (Figure 9). After the colored glass plates had been into distilled water for 30 days, the adhesion of the paint film to the surface of the glass plate was completely violated in control sample No. 1 (white enamel PF-115) .



a b

Figure 9. Tests on the resistance of the coating to the static effects of water: a – before the test; b – after 30 days.

This can be explained as follows. When water is applied to the paint film, it swells and, as a result, its length, width and thickness increase. But since the film of paint coating is fixed on the surface of the substrate (glass plate), only its thickness increases. Water molecules, penetrating into the body of the film, "spread" the film-forming macromolecules. At the same time, its adhesion deteriorates and film breaks off from the substrate.

Sample No. 2 (white enamel PF-115 with the addition of 20% shungite powder) partial peeling of the paint film appeared after 26 days of testing. The paint film of sample No. 3 (white enamel PF-115 with the addition of 40% shungite powder) showed good adhesion to the glass surface. Therefore, the particles of shungite powder reduce the swelling of the film in water, i.e. contribute to creating a protective coating.

To study the anticorrosive properties of paints and varnishes with shungite pigment powder, steel rods were prepared with the above compositions based on white P-115 white enamel (Figure 10).

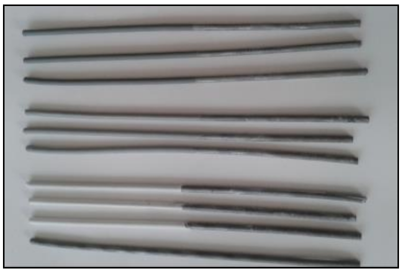


Figure 10. Steel rods before testing.

The painted steel rods (three series) were placed in distilled water, in a 3% solution of NaOH and left in the open air. One sample of the rod, not painted, was placed in distilled water. The condition of the surface of the paint film was monitored for 3 months. The test results are shown in Figure 11.

Figure 11. Test results of steel rods in various environments..

Studies have shown that shungite powder provides corrosion protection for steel rods.

The work also considered methods for determining the chemical resistance of paint coatings used to protect mortar and concrete when exposed to corrosive media. For this purpose, a visual method was used, which allows assessing the resistance of the coating to the effects of a chemical reagent on it (3% aqueous solution of alkali NaOH, 3% aqueous solution of HCl, etc.) based on signs of changes in appearance paint coating (wrinkling, bubbling, peeling, etc.), as well as the condition of the building material under the coating was monitored.

3. Conclusion

The following conclusions have been made.

Shungite carbon of Bakyrchik deposit is a material with high impact strength, resistance to aggressive media, adsorption activity, etc., which provides high physical and mechanical properties and durability of shungite-based composite building materials.

Testing of concrete made from concrete mixtures with equal mobility by means of a shungite-based modified plasticizer shows an increase in strength by 26%, frost resistance by 17%.

Shungite powder enhances the effect of a plasticizer of technical lignosulfonate group, a superplasticizer based on Na salt of naphthalenesulfonic acid and formaldehyde C-3 for cement concretes by almost 50%.

The results of conducted research unequivocally showed the possibility of using shungite powder as a bitumen modifier. Dispersed contained in shungite can reduce penetration value and significantly increase adhesion properties.

Shungite powder can be classified as a bitumen modifier which improves structure formation and adhesion of bitumen to mineral materials.

It has been established that as a result of using shungite powder as a mineral powder modifier, asphalt concrete has the best water resistance and long-term water saturation characteristics, which provides a higher corrosion resistance of asphalt-concrete coating in comparison with a traditional limestone powder.

The possibility of using the shungite powder as a pigment and filler in varnish and paint materials has been studied. The effect on improving of anticorrosion properties of varnish and paint materials has been shown. The test results showed the possibility of using the developed formulations of paints and varnishes for mortar and concrete. Studies have shown that shungite is well dispersed in varnishes and drying oil to form highly stable dispersions and provides black color of painted materials, excellent appearance of coatings, and color stability to the action of ultraviolet radiation. This direction of using shungite is promising and requires special development.

References

[1] Mizernaya M A and Bortsov V D 2008 *Polyfunctional nanomaterials and nanotechnology* **2** 32–35
[2] Kazankapova M K and Bekzhanova A Zh 2012 IX *International Correspondence Scientific and Practical Conference* 120–129
[3] Golubev E A and Glebashev S G 2006 *Vestnik of the Institute of Geology of the Komi Science Centre UB RAS* **4** 4–7
[4] Glebashev S G , Ignatiev S V and Kovyazin A N 1989 *Soviet geology* **1** 33–42
[5] Misernaya M A , Khayrullina A A 2013 *Bulletin of EKSTU, Computational Technologies, CIT SB RAS* 127-131
[6] Korolev E V, Bazhenov Yu M and Beregovoi V L 2006 Building materials **8** 2–4
[7] Voitovich V L 2006 *Stroyprofil* **6 (52)** 43-45
[8] Tolmachev S N and Belichenko E A 2014 *Nanotechnologies in construction* **6(5)** 13-29
[9] Kaprielov S S 1995 *Concrete and reinforced concrete* **6** 16–20
[10] Mizernaya M A , Khayrullina A A and Salimbaeva Z N 2017 *Science and World* **10 (50)** 40–42