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The structure and composition of natural carbonaceous fullerene containing mineral shungite

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ABSTRACT

The composition and structural properties of amorphous, uncrystallized, fulleren analogous (fullerene content 0.01–0.0001% (w/w)) carbon containing natural mineral – shungite, from Zazhoginskoe deposit in Karelia (Russian Federation) are studied. There are submitted data about the nanostructure, obtained with the using of scanning electron microscopy, composition and physical chemical properties of this mineral. Also are demonstrated prospects of using shungite, possessing high absorption, catalytic and bactericidal activity, as an absorbent in water-treatment, water purification, and other industries.

Key words: shungite, nanostructure, fullerens, water treatment, water putrification

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1. INTRODUCTION

Shungite – the mineral of new generation of natural mineral sorbents (NMS), intermediate form between the amorphous carbon and the graphite crystal containing carbon (30% (w/w)), silica (45% (w/w), and silicate mica (about 20% (w/w)). Schungite carbon is a fossilized organic material of sea bottom Precambrian sediments of high level of carbonization containing the fullerene-like regular structures (0.0001–0.001% (w/w)).

Shungite got its name in 1887 after the village of Shunga in Karelia (Russian Federation), located on the shore of Onezhskoe Lake, where is located the only one mineral Zazhoginsky deposit of shungites on the territoty of the Russian Federation. The total shungite researves of Zazhoginsky deposit amount to approximately 35 million tons of shungite. The plant production capacity for the mining and processing of shungites makes up 200 thousand tons of shungite per year.

Initially shungite was used, mainly as a filler and substitute of the carbon coal coke (fuel) in blast furnace production of high-silicon cast iron, in ferroalloys melting, in the production of non-stick heat-resistant paints and coatings, and as a filler in rubber production. Subsequently there were discovered other new valuable properties of shungite – absorptional, bactericidal, catalytic, reduction-oxidation properties, as well as the ability of sungite minerals to screen off electromagnetic and radio radiations. These properties have made the use of shungite in various branches of science, industry and technology, for creating on its basis a variety of new nanotechnological materials with nano-molecular structure. On the basis of shuntite have been created new conductive paints, fillers for plastic materials, rubber and carbon black substitutes, composite materials, concrete, bricks, stuccoing plasters, asphalts, as well as materials having bactericidal activity, and materials shilding off the radio and electromagnetic radiation.

Absorptional, catalytic, and reduction-oxydation properties of shungite favored its use in water treatment and water purification technologies, i.g. in treatment of sewage waters from many organic and inorganic substances (heavy metals, ammonia, organochlorine compounds, petroleum products, pesticides, phenols, surfactants, etc.). Moreover, shungite has a strongly marked biological activity and bactericidal properties.

A wide range of properties of shungite and the unique structure of this natural fullerene containing mineral defines the search for new areas of industrial application of this mineral in science and technology that contributes to a deeper study of the shungite structure with using the modern analytical methods. This paper deals with investigatuon of the structural properties of shungite and its composition.

2. MATERIAL AND METHODS

2.1. Material

The study was performed with samples of shungite obtained from Zazhoginsky deposit (Karelia, Russia). Samples were taken and analysed in solid samples according to National standard of the Russian Federal Agency of Technical Regulation and Metrology. Samples were put into 100 cm^3 hermetically sealed glass tubes after being washed in dist. H_2O and dried in crucible furnace, and homogenized in homogenizer by mechanical grinding. For the decomposition of the shungate samples a system of microwave decomposition was used. Other methods of samples processing were waching with dist. H_2O, drying, and homogenization on cross beater mill Retsch SK100 (“Retsch Co.”, Germany) and Pulverisette 16 (“Fritsch GMBH”, Germany).

2.2. Analytical methods

The analytical methods were accredited by the Institute of Geology of Ore Deposits. Petrography, Mineralogy, and Geochemistry (Russian Academy of Sciences). Samples were treated by various methods as ICP-OES, GC, SEM and TEM.

2.3. Gas-chromatography

Gas-chromatography (GC) was performed at Main Testing Centre of Drinking Water (Moscow, the Russian Federation) on *Kristall 4000 LUX M* using *Chromaton AW-DMCS* and *Inerton-DMCS* columns (stationary phases 5% SE-30 and 5% OV-17), equipped with flame ionization detector (FID) and using helium (He) as a carrier gas.

2.4. Inductively coupled plasma optical emission spectrometry (ICP-OES)

The mineral composition of shungite was studied by inductively coupled plasma optical emission spectrometry (ICP-OES) on Agilent ICP 710-OES (Agilent Technologies, USA) spectrometer, equiped witth plasma atomizer (under argon stream), MegaPixel CCD detector, and 40 MHz free-running, air-cooled RF generator, and Computer-optimized echelle system: the spectral range at 167–785 nm; plasma gas: 0–22.5 l/min in 1.5 l/min; power output: 700–1500 W in 50 W increments.

2.5. Gas-chromatography

The total amount of carbon (C_{total}) in sungtate was measured according to the ISO 29541 standard using elemental analyzer CHS-580 (“Eltra GmbH”, Germany), equipped with electric furnace and IR-detector by combustion of 200 mg of solid homogenized sample in a stream of oxygen at the temperature 1500 ^{0}C.

2.6. Scan and transmission electrom microscopy

The structural studies were carried out with using scan electrom (SEM) and transmission electrom microscopy (TEM) on SEM JSM 35 CF (JEOL Ltd., Corea) device, equiped with SE detector, thermomolecular pump, and tungsten electron gun (Harpin type W filament, DC heating); working pressure: 10^{-4} Pa (10^{-6} Torr); magnification: 300.000, resolution: 3.0 nm, accelerating voltage: 1–30 kV; sample size: 60–130 mm.

3. RESULTS AND DISCUSSION

3.1. Structural properties and composition of shungite

According to the last structural studies shungite is a metastable allotropic form of carbon with high level of carbonization (carbon metamorhism), being on prior to graphite stage of coalification [1]. In addition to the carbon the shungite, obtained from Zazhoginsky deposit in Karelia (Russian Federation) contains SiO_2 (57.0% (w/w)), TiO_2 (0.2% (w/w)), Al_2O_3 (4.0% (w/w)), FeO (0.6% (w/w)), Fe_2O_3 (1.49% (w/w)), MgO (1.2% (w/w)), MnO (0.15% (w/w)), K_2O (1.5% (w/w)), S (1.2% (w/w)) (Table 1). The product obtained after the thermal firing of shungite (shungizit) at 1200–1400 ^{0}C contains in small amounts V (0.015% (w/w)), B (0.004% (w/w)), Ni (0.0085% (w/w)), Mo (0.0031% (w/w), Cu (0.0037% (w/w), Zn (0.0067% (w/w)), Co (0.00014% (w/w)) As (0.00035% (w/w)), Cr (0.72% (w/w), Zn (0.0076% (w/w)) and other elements (Table 2).

Table 1: The chemical composition of shungites from Zazhoginsky deposit (Karelia, Russian Federation), in % (w/w).

№	Chemical component	Content, % (w/w)
1	C	30.0
2	SiO_2	57.0
3	TiO_2	0.2
4	Al_2O_3	4,0
5	FeO	0.6
6	Fe_2O_3	1.49
7	MgO	1.2
8	MnO	0.15
9	CaO	0.3
10	Na_2O	0.2
11	K_2O	1.5
12	S	1.2
13	H_2O	1.7

Table 2: The chemical composition of shungit after heat treatment at 1200–1400 ^{0}C

№	Chemical component	Content, % (w/w)
1	C	26.25
2	SiO_2	3.45
3	TiO_2	0.24
4	Al_2O_3	3.05
5	FeO	0.32
6	Fe_2O_3	1.01
7	MgO	0.56
8	MnO	0.12
9	CaO	0.12
10	Na_2O	0.36
11	K_2O	1.23
12	S	0.37
14	P_2O_3	0.03
15	Ba	0.32
16	B	0.004
17	V	0.015
18	Co	0.00014
19	Cu	0.0037
20	Mo	0.0031
21	As	0.00035
22	Ni	0.0085
23	Pb	0.0225
24	Sr	0.001
26	Cr	0.0072
26	Zn	0.0067
27	H_2O	0.78
28	Calcination (burning) losses	32.78

Physical and chemical properties of shungite have been sufficiently studied [2]. Density of shungite 2.1–2.4 g/cm^3; porosity – up to 5%; the compressive strength – 1000–1200 kgf/cm^2; conductivity coefficient – 1500 SI/m; thermal conductivity coefficient – 3.8 W/m·K, the adsorption capacity up to 20 m^2/g.

Shungites differ in composition of mineral matrix (aluminosilicate, siliceous, carbonate), and the amount of carbon in schungite samples. Shungite minerals with silicate mineral basis are divided into low-carbon (5% (w/w) C), medium-carbon (5–25% (w/w) C), and high-carbon schungites (25–80% (w/w) C) [3]. The sum (C + Si) in shungites of Zazhoginsky deposit (Karelia, Russian Federation) is varried within 83–88% (w/w) (Fig. 1).

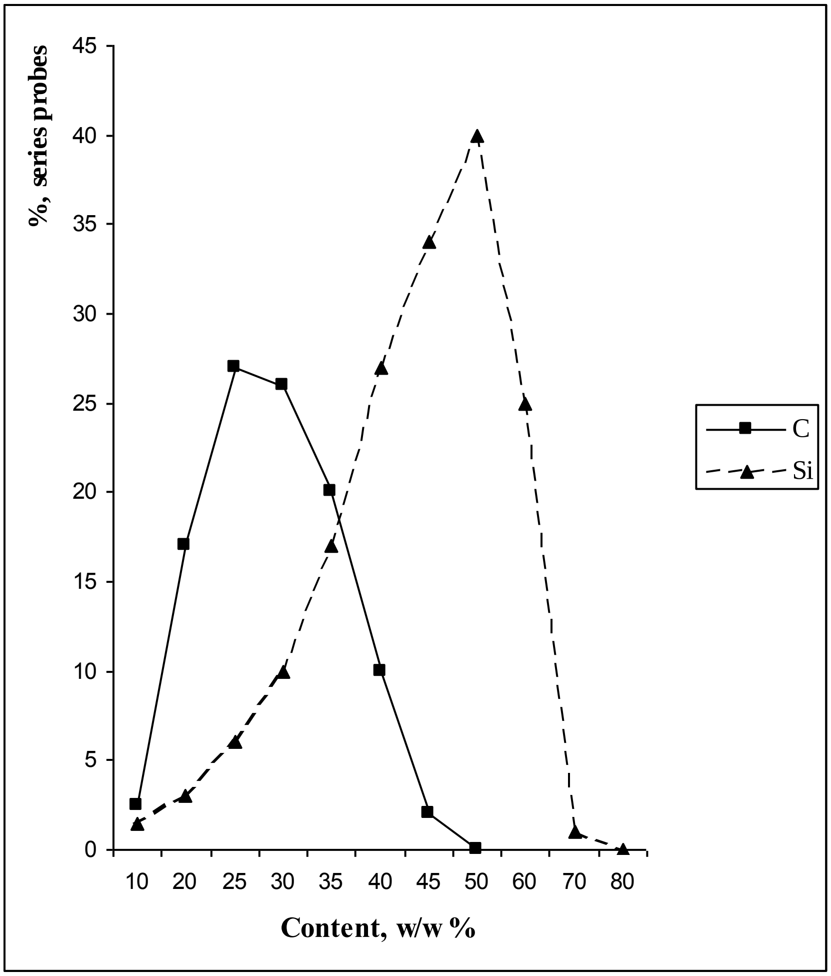

Figure 1: The distribution (% (w/w)) of carbon (C) (solid line) and silicon (Si) (dotted line) in shungate samples from Zazhoginsky deposit (Karelia, Russian Federation) according to atomic emission spectrometry (AES).

The crystals of crushed, fine ground shungite possess strong bipolar properties. This results in a high adhesion, and the ability of shungite to mix with almost all organic and inorganic substances. Besides, shungite has a broad spectrum of bacterecidal properties; the mineral is adsorptive active against some bacterial cells, phages, and pathogenic saprophytes [4].

The unique properties of shungit are defined by nanostructure and composition of its constituent elements. Schungite carbon is equally distributed in the silicate framework of fine dispersed quartz crystals having the size of 1–10 μm [5], as confirmed by studying of ultra-thin sections of shungite by transmission electron microscopy (TEM) in absorbed and backscattered electrons (Fig. 2).

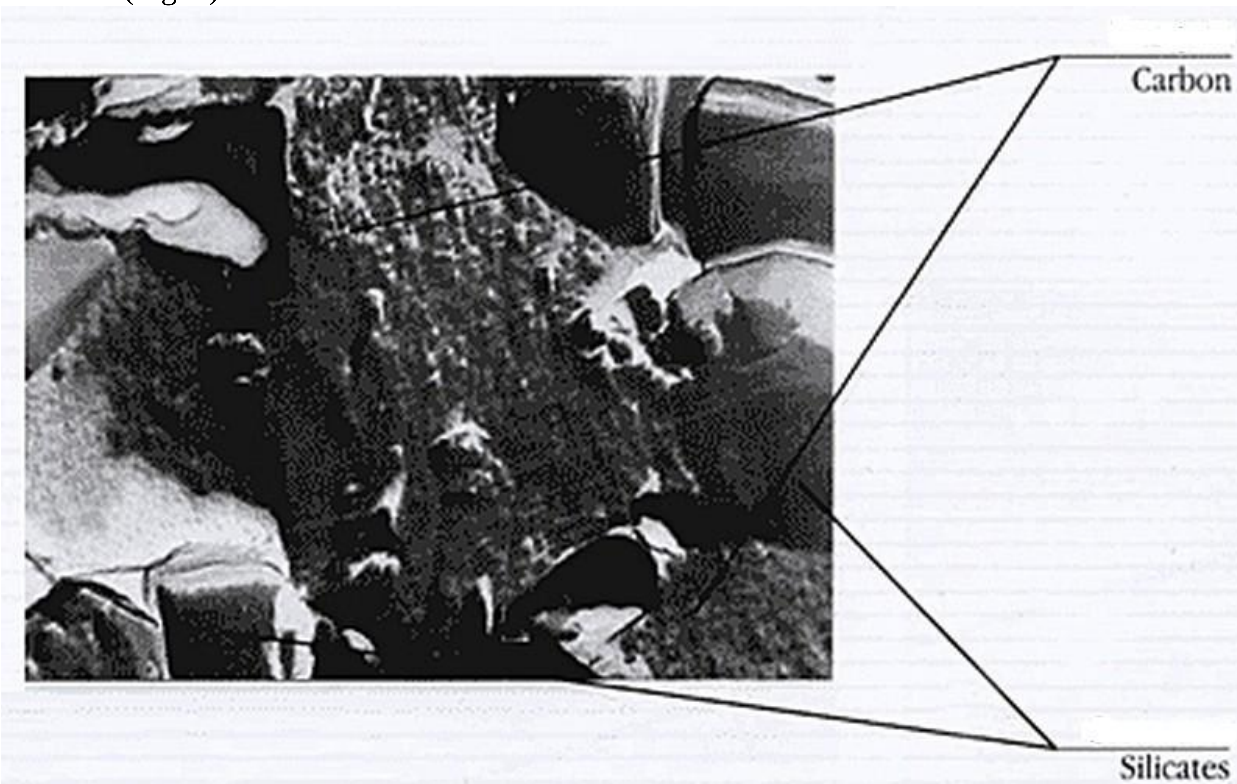

Figure 2: Structure of schungite rock in transmission electron microscope (TEM). Scanning area 100 × 100 mm., resolution 0.5 nm, magnification 300.000 times. The arrows show the silicate framework of fine dispersed quartz with the size 1–10 μm, and uniformly distributed carbon.

The carbonaceous material of shungite is the product of a high degree of carbonization of hydrocarbons. Its elemental composition (%, w/w): C – 98.6–99.6; H – 0.15–0.5; (H + O) – 0.15–0.9. With virtually constant elemental composition of shungite carbonaceous matter is observed variability in its structure – both molecular and supramolecular, as well as surface, and porous structure. X-ray studies showed that the molecular structure of schungite carbon is represented by a solid uncristallized carbon, which components may be in a state close as to graphite and carbon black and glassy carbon as well, i.e. the maximally disordered [6]. Carbonaceous matter of shungite having a strongly marked structural anisotropy shows a significant increase in the diamagnetism at low temperatures that is characteristic for fullerites.

The basis of shungite carbon compose the hollow carbon fullerene-like multilayer spherical globules with a diameter of 10–30 nm, comprizing inclusive packages of smoothly curved carbon layers covering the nanopores (Fig. 3). The globule structure is stable relative to shungite carbon phase transitions into other allotropic carbon forms. Fullerene-like globules may contain from a few dozen to a several hundred carbon atoms and may vary in shape and size [7]

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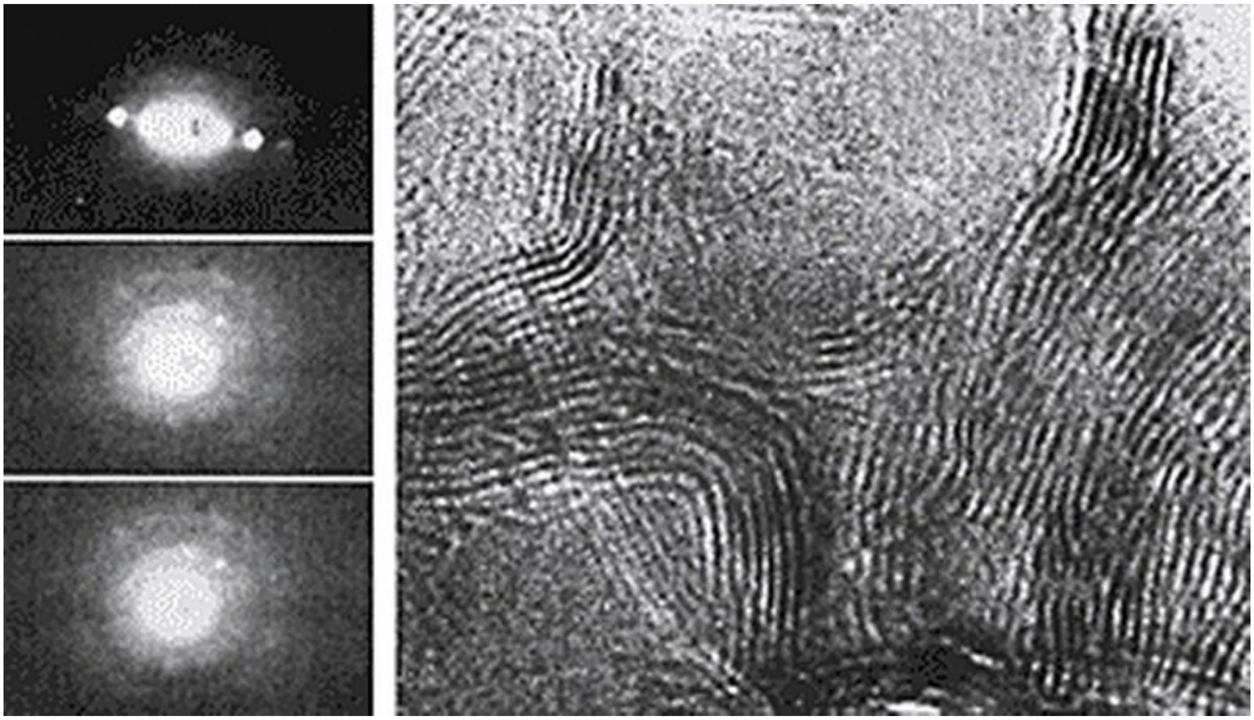

Figure 3: Electron diffraction of nanopattern of shungite carbon in the form of spherical multilayer fullerene globules with a diameter 10-30 nm, obtained by TEM (probe 0.5–0.7 nm, the energy of the electron beam 100–200 kV, the beam radius 10 nm, the range of the goniometer rotation -27 ... +27 ^{0}). On the left are shown fluoresent spherical fullerene-like globules, on the right – the multi-layered spherical fullerene-like globules with packets of carbon layers, recorded at a higher resolution

Fullerenes were discovered in 1985 by laser irradiation of solid graphite [8]. Later, fullerene-like structures were observed not only in the graphite, but also in carbon soot formed in an arc electrical discharge on graphite electrodes, as well in shungite (0.001–0.0001% (w/w)) [9]. Crystal formed from fullerene molecules (fullerite) is a molecular crystal, a transitional form between the organic and inorganic matter. Fullerite has a face-centered cubic cristal (FCC) lattice with the size of 1.42 nm, the distance between the nearest neighbors – 1 nm and the number of nearest neighbors in the FCC lattice – 12. At 249 K in fullerite crystall is observed a phase transition of the first kind, where the FCC lattice becomes simple cubic with an increase in fullerite volume on 1%. Density of fullerite crystall amounts 1.7 g/cm^3, that is somewhat lower than the density of shungite (2.1–2.4 g/cm^3), and graphite (2.3 g/cm^3).

The main characteristic feature of the fullerene structure is that carbon atoms are arranged at the vertices of regular hexagons and pentagons, covering the surface of a graphite formed sphere or ellipsoid making up the closed polyhedra consisting of three-coordinated even number of carbon atoms in sp^2-hybridization state. The carbon atoms constituting the sphere are linked together by covalent C–C-bonds, the length of which in the pentagon – 0.143 nm, and in the hexagon – 0.139 nm [10]. Fullerene molecules may comprise 24, 28, 32, 36, 50, 60, 70, etc. carbon atoms (Fig. 4). Fullerenes with the number of carbon atoms $n < 60$ are unstable. Higher fullerenes containing more carbon atoms ($n < 400$), are produced in small quantities and often have quite complex isomeric composition. In the carbonaceous material of shungite are presented identified fullerenes (C_{60}, C_{70}, C_{74}, C_{76}, C_{84}, etc.), as well as fullerene-like structures, as separated and related with other minerals as well. Additionally mixed varieties of carbon fullerene clusters having mixed composition have been described.

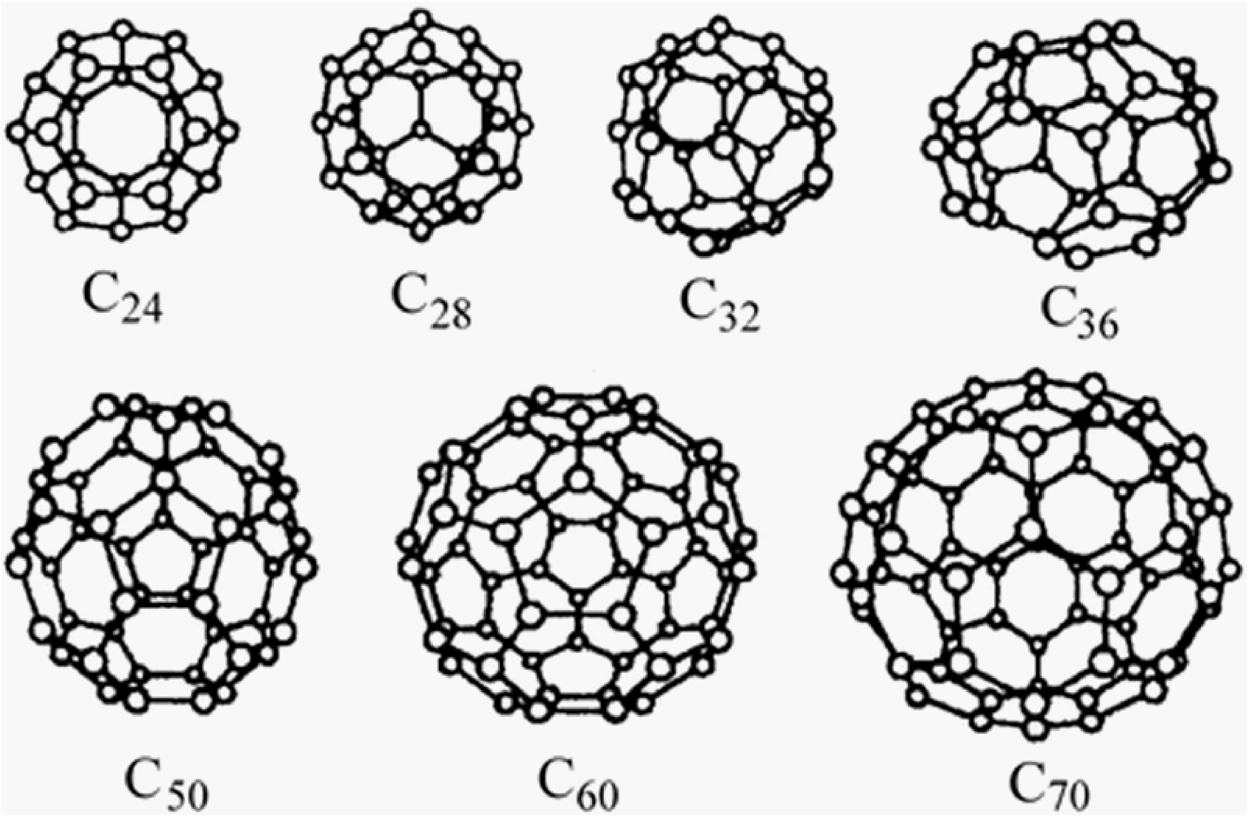

Figure 4: Varieties of natural and synthetic fullerenes with different numbers of carbon atoms: C_{24}, C_{28}, C_{32}, C_{36}, C_{50}, C_{60}, C_{70}.

Owing to the reticulated-spherical structure the natural fullerenes and their synthetic derivatives are ideal absorbents and fillers. The thickness of the spherical shell of the fullerene molecule C_{60} is ~ 0.1 nm with the molecular radius – 0.357 nm [11]. By placing within the carbon clusters various atoms and molecules, it can be possible to create a variety of materials and adsorbents with a wide range of physico-chemical properties. Currently, based on fullerenes are synthesized more than 3000 new compounds. Prospects of further development of the fullerene synthesis iare connected with the peculiarities of the chemical structure of the fullerene molecules, which are the three-dimensional analogues of carbon aromatic structures having a large number of conjugated double C=C bonds and reaction centers on a closed area of the carbon sphere. With their high electronegativity, fullerenes appear in chemical reactions as strong oxidizing agents. Allying to itself the radicals of different chemical nature, fullerenes are capable of forming a wide class of chemical compounds with different physico-chemical properties. The combination of fullerenes with a number of known classes of materials opens up the possibility towards chemical synthesis of numerous derivatives of these compounds. Fullerenes are used in bio-nanotechnology, electronics, medicine, aerospace and military technology, in the manufacture of new technical products, new steels and ferroalloys, construction and composition materials, refractory materials, paints, as well as they are used in water treatment. It is discussed the idea of using fullerens as a drug carriers on the basis of water-soluble endohedral fullerene compounds, within which are placed one or more atoms of an element with radioactive isotopes [12]. Also, it were found conditions for the synthesis of antiviral and anti-cancer drugs based on fullerenes, which introduction into the human body would act selectively on the affected cancer cells, preventing their further proliferation. The main obstacle to the use of artificially synthesized fullerenes is their high cost, which ranges 100–900 U.S. dollars per gram, depending on their quality and purity. That is why the discovery and development of new natural fullerene-containing minerals as domestic shungite and spheres of their practical using in industry has a great prospects for science and technology.

3.2. The use of shungite in water treatment technologies

Broad prospects are open for using shungit as a filter material in wastewater treatment and water purification. Natural shungite yealding activated carbon by a low porosity and inner surface, as a sorbent has a number of positive characteristics:

- High adsorption capacity, characterized by low resistance to water preasure;
- Mechanical strength and low abrasion resistance;
- Corrosion-resistance;
- Absorption capacity felative to many substances, both organic (oil, benzene, phenol, pesticides, etc.) and inorganic (chlorine, ammonia, heavy metals);
- Catalytic activity;
- Relatively low cost;
- Environmental friendliness and ecological safety.

The mechanism of interaction of shungite with water has not been completely understood. It is assumed that shungite can absorb oxygen actively interacting with them as a strong reducing agent in water and in air [13]. In this process is produced atomic oxygen, which is a strong oxidizing agent oxidizing adsorbed on shungit organic substanses to CO_2 and H_2O, thus freeing the surface of shungite for new acts of adsorption. Overexposure of shungite in respect to dissolved metal cations in water as Ca^{2+}, Mg^{2+}, Fe^{2+} and Fe^{3+} is explaned by the fact that the metals are transferred by the catalytically active shungite into the form of insoluble carbonates due to the oxidation of organic matter to CO_2 [14].

According to the data on absorption capacity shungite loses effectiveness before the activated carbon filter in the first stage of filtration, during the first 24 h, further shungite began purifiy water with a high and constant speed. This is explaned by high catalytic properties of shungite and its ability to catalytically oxidize organic substances absorbed on the surface.

The research of antioxidant properties of shungite in relation to organochlorine compounds, and free radicals have shown that shungite removes free radicals out of water in 30 times more effective than activated carbon [15]. This is a very important factor, because the free radicals formed during water treatment with chlorine and its derivatives, have a negative impact on the human health that is the cause of many diseases (cardiovascular diseases, cancer, etc.).

These positive qualities allow to use shungite as an effective filter material for wastewater treatment and purification from organic and chlorinated organic substances (oil, pesticides, phenols, surfactants, dioxins, etc.). Thus shungite is able to purify wastewater from oil up to threshold limit value (TLV) of water discharge into the water reservoir. Shungit adsorbs on its surface up to 95% of contaminants, including organochlorine compounds, phenols, dioxins, heavy metals, radionuclides, etc., removes turbidity and color, and gives the water a good organoleptic qualities, additionally saturating it with micro-and macro-elements (Table 3). Thus, adsorption activity of shungite relative to phenol makes up 14 mg/g , while for thermolysis resins – 20 mg/g, for oil products – more then 40 mg/g [16]. Model experiments showed that heavy metals (copper, cadmium, mercury, lead), boron, phenol and benzenecontained in water in concentrations being in 10–50 times higher than the TLVs, after the treatment by shungite in stationary or dynamic conditions on the shungite filter units, the content of these pollutants in water is reduced below the established levels of regulatory documents. In this case into the water does not enter any toxic elements from schungite adsorbents.

Table 3: Indicators of performance of filters based of mineral shungite

№	Common water pollutants	The removal degree, %
1	Fe^{2+}/Fe^{3+}	95
2	Zn^{2+}	80
3	Pb^{2+}	85
4	Cu^{2+}	85
5	Cs^{2+}	90
6	St^{2+}	97
7	Radionuclides	90
8	Fluorine	80
9	Ammonia	90
10	Chlorine and organochlorine compounds	85
11	Phenols	90
12	Dioxins	97
13	Helminth's eggs	90
14	Smell	85
15	Turbidity	95

In addition, owing to the shungite absorption activity against pathogenic microflora shungite has strong bactericidal properties, which allows to carry out the efficient disinfection of drinking water by this mineral in water treatment and water purification technologies. It is observed the bactericidal activity of shungite against pathogenic saprophytes and Protozoa. There is evidence that after the passage of water containing bacterium *E. coli*, through shungite filter there is an almost complete removal of this bacterium (the viral titer varries from 2300 cells/l in initial water up to 3 cells/l in treated water) [17]. Of 1785 cells/l of protozoa (ciliates, rotifers and crustaceans) contained in the initial water after the treatment by shungite were observed only a few exemplars (5 cells/l). In addition to these qualities, shungite has biological activity.

Owing to all these positive properties shungite may find its application in the preparation of drinking water in flow-through systems of any capacity for industrial and domestic purposes, as well as in the wells in order to improve the quality characteristics of water and give water its beneficial properties.

Especially effective and technologically justified is the use of complex filter systems based of the mixtures of shungite with activated carbon or zeolite, with possible subsequent regeneration of the absorbents [18]. When adding to the treatment scheme shungite and other natural absorbents (flint, dolomite, glauconite) purified water is enriched to a physiologically optimal levels by calcium, magnesium, silicon and sodium.

It is shown that the water passed through shungite or infused on shunfite has a general revitalizing effect on the body, reduces skin irritation, itching, rash, effective in vegetative-vascular dystonia, diseases of the gastrointestinal tract, kidney stones and other diseases [19].

The water filters based on shungite have been developed and applied in Russia since 1995. Now on the market of domestic producers of filters for water purification there is a certain number of large companies that produce household and industrial filters based on natural mineral shungite.

3.3. Other prospects for industrial using of shungite

The conducting properties of shungite minerals can create on their basis new conductive materials with radio shielding and radio absorbing properties to reduce the levels of electromagnetic radiation with a frequency 10–30 GHz and electric fields with a frequency of 50 Hz [20]. These properties of shungite also allow to create electrically conductive thermo-paints, concretes, asphalts, building and composite materials, plasters, etc. On the basis of shungite are designed electrical heaters, created the new environmentally friendly building and composite materials, etc.

The presence in shungite fullerene-like molecules opens wide prospects for their further use in various branches of industry – in the machinery for the production of various mineral additives and lubricants, in construction of bricks and plaster composite mixtures, to create screening compartments and facilities to protect against the impact of various types of radiation, in the power supply industry, as a substitute in the production of black soot. The limiting factor, however, remains extremely low percentage of fullerenes in shungite (up to 0.001% (w/w)).

Shungite, due to its structure and multi-component composition of its constituent elements has high activity in the oxidation-reduction processes, a wide range of absorption and catalytic properties. It makes good use of this mineral in various reduction-oxidation processes: including in the blast furnace casting high-silicon cast iron (1 ton of shungite replaces 1.3 tons of coke), in the production of ferro-alloys, in the production of phosphorus and carbide (SiC) and nitride (Si_3N_4) of silicon etc.

While dispersing shungite are formed tonkodisperstnye powders, mixing well with most organic and inorganic substances. This property of schungite powders allows their use as a black pigment paints on different basis (water and oil), fillers and rubber polymers (polyethylene, polypropylene, PTFE) substitutes of carbon in the rubber production, and as an adsorbent for various tipes or organic and inorganic compounds. Furthermore, shungite powders samples possess strong bioactivity. Their use in agriculture as mineral supplements to fertilizers may help to reduce the acidity of soil and increase the moisture conservation in 2–2.5 times longer than in the areas without shungite treatment that has a positive effect on the productivity of the total crop production.

Porous artificial material shungizit obtained after the thermal treatment of shungite at 1200–1400 ^{0}C is used as an insulation material and a filler for low-weight concrete (shungizitconcrete) production.

4. CONCLUSION

These data show that fullerene-containing natural mineral shungite can find wide practical applications in many branches of science and industry, and can be used as a substitute of carbon black soot in the production of various construction and composition materials, rubber, fillers and paints, as well as an alternative to activated carbon the natural mineral absorbent in water treatment. Efficiency of using shungite is stipulated by the high range of valuable properties (absorption, catalytic, regenerative, antibacterial, conductive), high environmental safety with relatively low cost of produced materials based on shungite as well as existence of the extensive domestic raw material base of shungite deposit. All these factors contribute to the further expansion of shungite and a big variety of materials based on it.

REFERENCES

[1]. Volkova, I.B. and Bogdanov, M.V. (1986) Petrology and genesis of the Karelian shungite-high rank coal. Int. J. Coal Geol. 6, 369–79.

[2]. Parfeneva, L.S, Volkonskaia, T.I. and Tikhonov, V.V. (1994) Thermal conductivity, heat capacity and thermal emf shungite carbon. Solid State Physics 36(4), 1150–1153.

[3]. Jushkin, N.P. (1994) Globular supramolecular structure shungita: data scanning tunneling microscopy. Reports. Acad. Science USSR 337(6), 800–803 [in Russian].

[4]. Kasatochkin, V.I., Elizen, V.M., Melnichenko, V.M., Yurkovsky, I.M. and Samoilov. V.S. (1978) Submikroporous structure of shungites. Solid Fuel Chemistry 3, 17–21.

[5]. Golubev, E.A. (2000) Local supramolecular structures shungite carbon / in: Proceedings of the Int. Symp. "Carbon-formation in geological history." Petrozavodsk: Publishing House of the Karelian Research Center, Russian Academy of Sciences, 106–110 [in Russian].

[6]. Kovalevsky, V.V., Buseckb, P.R. and Cowley J.M. (2001) Comparison of carbon in shungite rocks to other natural carbons: An X-ray and TEM study. Carbon 39, 243–256

[7]. Reznikov, V.A. and Polehovsky, Y.S. (2000) Schungite amorphous carbon – the natural environment of fullerene. Technical Physics Letters 26(15), 94–102.

[8]. Kroto, H.W., Heath, J.R. and O'Brien, S.C. (1985) C60: Buckminsterfullerene. Nature 318, 162–168.

[9]. Shpileuski, M.E., Shpileuski, E.M. and Stelmach, V.F. (2001) Fullerenes and fullerene-like structures. Journal of Engineering Physics 76(6), 25–28.

[10]. Stelmach, V.F., Strigutsky, L.V., Shpileuski, E.M. and Zhukovsky P.I. (2000) Fullerenes and fullerene-like structures. Minsk, 1–105 [in Russian].

[11]. Kovalevski, VV. (1994) Structure of shungite carbon. Natural graphitization Chem. 39, 28–32.

[12]. Andrievsky, G.V., Bruskov, V.I., Tykhomyrov, A.A. and Gudkov, S.V. (2009) Peculiarities of the antioxidant and radioprotective effects of hydrated C60 fullerene nanostuctures in vitro and in vivo. Free Radical Biology & Medicine 47, 786–793.

[13]. Cascarini de Torre, L.E., Fertitta, A.E., Flores, E.S., Llanos, J.L. and Bottani, E.J. (2004) Characterization of shungite by physical adsorbtion of gases. J. Argent. Chem. Soc. 92(4–6), 51–58.

[14]. Gorshteyn, A.E., Baron, N.Y. and Syrkina, M.L. (1979) Adsorption properties of shungites. Izv. Vysshykh Uchebn. Zaved. Khimia i Khim. Technol. 22(6), 711–715 [in Russian].

[15]. Mosin, O.V. and Ignatov, I. (2012) New natural mineral sorbent – shungite. Nanoingenerija 3, 34–36 [in Russian].

[16]. Mosin, O.V. and Ignatov, I. (2013) Structural properties and composition of fullerene containing mineral shungite. Nano- i microsystemnaja technika 1, 12–20 [in Russian].

[17]. Khadartsev A.A. and Tuktamyshev I.S. Shungites in medical technology. Vestnik novih medicinskih technologii 9(2) 2002, 83-86 [in Russian].

[18]. Podchaynov, S.F. Mineral zeolite – a multiplier of useful properties shungita / Shungites and human safety // in: Proceedings of the First All-Russian scientific-practical conference (3–5 October 2006) / ed. J.K Kalinin. Petrozavodsk: Karelian Research Centre of Russian Academy of Sciences (2007), 6–74 [in Russian].

[19]. Kibardin, G.M. Shungit and its healing properties. (2010) Moscow: Amrita-Rus, 48–50 [in Russian].

[20]. Parfen'eva, L.S. (1994) Electrical conductivity of shungite carbon. Solid State Physics 36(1), 234–236.