

Ключевые слова: дейтерий, тяжелая вода, протиевая вода, долгожитие, горная вода, ИК-спектроскопия, НЭС, ДНЭС.

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ГІРСЬКА ВОДА ЯК ГОЛОВНИЙ ФАКТОР ДОВГОЛІТТЯ В МУЛЬТИФАКТОРНОМУ ДОСЛІДЖЕННІ ФЕНОМЕНУ ДОВГОЛІТТЯ В ГІРСЬКИХ РАЙОНАХ БОЛГАРІЇ

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У роботі представлені дані про гірську воду як головний фактор довголіття в гірських районах Болгарії. Авторами була встановлена залежність між різними внутрішніми та зовнішніми чинниками на феномен довголіття болгарських довгожителів - місця проживання, стану здоров'я, статі та спадковості. Було показано, що вода є одним з найбільш важливих факторів для довголіття. Природні води з різних болгарських

джерел були досліджені методами нерівновісного енергетичного (НЕС) і диференціального нерівновісного енергетичного (ДНЕС) аналізу. Також вивчено біологічні ефекти води з різним вмістом дейтерію. Показано, що підвищений вміст дейтерію у воді призводить до фізіологічних, морфологічних і цитологічних змін клітини, а також чинить негативний вплив на клітинний метаболізм, а вода із зниженим вмістом дейтерію на 20-30% цілком впливає на здоров'я. За допомогою ІЧ-спектроскопії були досліджені зразки води з різним вмістом дейтерію, отримані з деяких болгарських водних джерел, а також сироватка крові хворих на рак. В якості основного оціночного фактора використовували значення середньої енергії водневих зв'язків ($\Delta E_{H...O}$) між молекулами H_2O , а також локальні максимуми в ІЧ-спектрах різних зразків води і сироватки крові людини при $-0,1387$ eV і довжині хвилі $8,95$ мкм. Показано, що для групи людей у критичному стані життя і хворих із злоякісними пухлинами найбільші значення локальних максимумів в ІЧ-спектрах зміщуються у бік менших енергій по відношенню до контрольної групи. Отримані результати свідчать про доцільність споживання чистої природної води, якості якої задовольняє гірська вода з болгарських джерел.

Ключові слова: дейтерій, важка вода, протієва вода, довголіття, гірська вода, ІЧ-спектроскопія, НЕС, ДНЕС.

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THE PECULIARITIES OF INTERACTION OF CARBONACEOUS MINERAL SHUNGITE AND MICROPOROUS CRYSTALLINE ALUMINOSILICATE MINERAL ZEOLITE WITH WATER

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Introduction

Shungite and zeolite – the minerals refer to new generation of natural mineral sorbents (NMS). Shungite is an intermediate form between the amorphous carbon and the graphite crystal, containing carbon (30 %), silica (45 %), and silicate mica (about 20 %) [1]. Shungite carbon is a fossilized organic material of sea bottom Precambrian sediments of high level of carbonization containing the fullerene-like regular structures. Shungite got its name 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 territory of the Russian

Federation. The total shungite reserves of Zazhoginsky deposit amount to approximately 35 million tons of shungite. The plant production capacity for the mining and processing of shungite makes up 200 thousand tons of shungite per year.

Zeolites are the aluminosilicate members of the family of microporous solids known as “molecular sieves”, named by their ability to selectively sort molecules based primarily on a size exclusion process. The natural zeolites form when volcanic rocks and ash layers react with alkaline groundwater. Zeolites also crystallize in post-depositional environments over periods ranging from thousands to millions of years in shallow marine basins. Naturally

occurring zeolites are rarely pure and are contaminated to varying degrees by other minerals, metals, quarts, or other zeolites. For this reason, naturally occurring zeolites are excluded from many important commercial applications where uniformity and purity are essential.

As natural minerals shungite and zeolite has unusually broad scope of application in industry. Shungite was used initially, 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 filler in rubber production. Subsequently there were discovered other new valuable properties of shungite – adsorptional, bactericidal, catalytic, reduction-oxidation properties, as well as the ability of shungite 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 shungite 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 shielding off the radio and electromagnetic radiation. Adsorptional, catalytic, and reduction-oxidation 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.

Zeolites as shungites are widely used in industry as a desiccant of gases and liquids, for treatment of drinking and sewage water from heavy metals, ammonia, phosphorus, as catalyst in petrochemical industry for benzene extraction, for production of detergents and for extracting of radionuclides in nuclear reprocessing. They are also used in medicine as nutritional supplements having antioxidant properties.

A wide range of properties of shungite and zeolite defines the search for new areas of industrial application of these minerals in science and technology that contributes to a deeper study of the structure with using the modern analytical methods. This paper deals with investigation of the structural properties of shungite and zeolite and evaluation of the mathematical model of interaction of these minerals with water.

Experimental Part

Material and methods

Material

The study was performed with samples of shungite obtained from Zazhoginsky deposit (Karelia, Russia) and zeolite (Most, Bulgaria). Samples were taken and analyzed in solid samples according to National standard of

the Russian Federal Agency of Technical Regulation and Metrology. Samples were put into 100 cm³ hermetically sealed glass tubes after being washed in dist. H₂O and dried in crucible furnace, and homogenized in homogenizer by mechanical grinding. For the decomposition of the shungite samples a system of microwave decomposition was used. Other methods of samples processing were watching with dist. H₂O, drying, and homogenization on cross beater mill Retsch SK100 (“Retsch Co.”, Germany) and Pulverisette 16 (“Fritsch GMBH”, Germany).

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, and SEM.

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.

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, equipped with plasma atomizer (under argon stream), Mega Pixel 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.

Gas-chromatography

The total amount of carbon (C_{total}) in shungite 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 °C.

Transmission electron microscopy

The structural studies were carried out with using transmission electron microscopy (TEM) on JSM 35 CF (JEOL Ltd., Korea) device, equipped with X-ray micro-analyzer “Tracor Northern TN”, SE detector, thermomolecular pump, and tungsten electron gun (Harpin type W filament, DC heating); working pressure: 10⁻⁴ Pa (10⁻⁶ Torr); magnification: 300000, resolution: 3,0 nm, accelerating voltage: 1–30 kV; sample size: 60–130 mm.

IR-spectroscopy

IR-spectra of water samples obtained after 3 day contacting with shungite and zeolite were registered on Fourier-IR spectrometer Brucker Vertex (“Brucker”, Germany) (a spectral range: average IR – 370–7800 cm⁻¹; visible – 2500–8000 cm⁻¹; the permission – 0,5 cm⁻¹; accuracy of wave number – 0,1 cm⁻¹ on 2000 cm⁻¹).

NES- and DNES-methods

NES- and DNES-methods were used for the estimation of energy of hydrogen bonds of shungite zeolite solutions in water in order to evaluate the mathematical model of interaction of these minerals with water. The device measured the angle of evaporation of water drops from 72 ° to 0 °. As the main estimation criterion was used the average energy ($\Delta E_{H...O}$) of hydrogen O...H-bonds between individual H₂O molecules in aqueous samples. NES-and DNES spectra of shungite and zeolite solutions in water were measured in the range of the energy of hydrogen bonds 0,08–0,387 eV or $\lambda = 8,9–13,8 \mu\text{m}$ with using a specially designed computer program.

Results and Discussion***The composition and the structure of shungite and zeolite***

According to the last structural studies shungite is a metastable allotropic form of carbon with high level of carbonization (carbon metamorphism), being on prior to graphite stage of coalification [2]. Along with carbon the shungite, obtained from Zazhoginsky deposit in Karelia (Russian Federation) contains SiO₂ (57,0 %), TiO₂ (0,2 %), Al₂O₃ (4,0 %), FeO (0,6 %), Fe₂O₃ (1,49 %), MgO (1,2 %), MnO (0,15 %), K₂O (1,5 %), S (1,2 %) (Table 1). The product obtained after the thermal firing of shungite (shungizit) at +1200...+1400 °C contains in small amounts V (0,015 %), B (0,004 %), Ni (0,0085 %), Mo (0,0031 %), Cu (0,0037 %), Zn (0,0067 %), Co (0,00014 %), As (0,00035 %), Cr (0,72 %), Zn (0,0076 %) 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 ₂ O ₃	4,0
5	FeO	0,6
6	Fe ₂ O ₃	1,49
7	MgO	1,2
8	MnO	0,15
9	CaO	0,3
10	Na ₂ O	0,2
11	K ₂ O	1,5
12	S	1,2
13	H ₂ O	1,7

Table 2

The chemical composition of shungit after heat treatment at +1400 °C

№	Chemical component	Content, % (w/w)
1	C	26,25
2	SiO ₂	3,45
3	TiO ₂	0,24
4	Al ₂ O ₃	3,05
5	FeO	0,32
6	Fe ₂ O ₃	1,01
7	MgO	0,56
8	MnO	0,12
9	CaO	0,12
10	Na ₂ O	0,36
11	K ₂ O	1,23
12	S	0,37
14	P ₂ O 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 ₂ O	0,78
28	Calcination (burning) losses	32,78

In comparison with shungite, zeolite comprises a microporous crystalline aluminosilicate mineral commonly used as a commercial adsorbent, three-dimensional framework of which is formed by linking via the vertices the tetrahedra [AlO₄]²⁻ and [SiO₄]²⁻ [3]. Each tetrahedron [AlO₄]²⁻ creates a negative charge of the carcasses compensated by cations (H⁺, Na⁺, K⁺, Ca²⁺, NH₄⁺, etc.), in most cases, capable of cation exchange in solutions. Tetrahedrons formed the secondary structural units, such as six-membered rings, five-membered rings, truncated octahedra, etc. As a result the zeolite framework comprises interacting channels and cavities forming a porous structure with a pore size of 0,3–1,0 nm. Average crystal size of the zeolite may range from 0,5 to 30 μm .

The empirical formula of zeolite can be represented as follows:



where n – the cationic charge ($n = 1–2$), γ – the molar ratio of oxides of silicon and aluminum in the zeolite framework, indicating the amount of cation exchange positions in the structure ($\gamma = 2–\infty$), w – the amount of water.

The composition of zeolite is analogous to that of shungite (Table 3), except for carbon which does not occur in zeolite. The amounts of core elements (SiO_2 , TiO_2 , Al_2O_3 , FeO , Fe_2O_3 , MgO , CaO , Na_2O , K_2O , S) constituting this mineral differ from that of shungite: their content is higher than that of shungite, except for TiO_2 and K_2O , the contents of which in zeolite were decreased (Table 3). The content of microelements as V (0,0272 %), Co (0,0045 %), Cu (0,0151 %), Mo (0,0012 %), As (0,0025 %), Ni (0,0079 %), Zn (0,1007 %), Zn (0,1007 %) was somewhat increased in zeolite, while the content of Ba (0,0066 %) and Cr (0,0048 %) was increased (Table 3).

Table 3

The chemical composition of zeolite (Bulgaria),
in % (w/w)

№	Chemical component	Content, % (w/w)
1	SiO_2	22,14
2	TiO_2	0,01
3	Al_2O_3	17,98
4	FeO	23,72
5	Fe_2O_3	1,49
6	MgO	14,38
7	MnO	0,61
8	CaO	0,36
9	Na_2O	0,5
10	K_2O	0,4
11	S	0,32
12	P_2O_5	0,06
13	Ba	0,0066
14	V	0,0272
15	Co	0,0045
17	Cu	0,0151
18	Mo	0,0012
19	As	0,0025
20	Ni	0,0079
21	Pb	0,0249
22	Sr	0,0021
23	Cr	0,0048
24	Zn	0,1007
25	H_2O	1,43

The physical and chemical properties of shungite have been sufficiently studied recently [4]. The density of shungite makes up 2,1–2,4 g/cm^3 ; the porosity – up to 5 %; the compressive strength – 1000–1200 kgf/cm^2 ; the conductivity coefficient – 1500 Sl/m ; the thermal conductivity coefficient – 3,8 $\text{W}/\text{m}\cdot\text{K}$, the adsorption capacity – up to 20 m^2/g .

Shungites differ in composition of their 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 % C), medium-carbon (5–25 % C), and high-carbon schungites (25–80 % C) [5]. The sum of (C + Si) in shungites of Zazhoginsky deposit (Karelia, Russian Federation) is varied within 83–88 % as shown in Fig. 1.

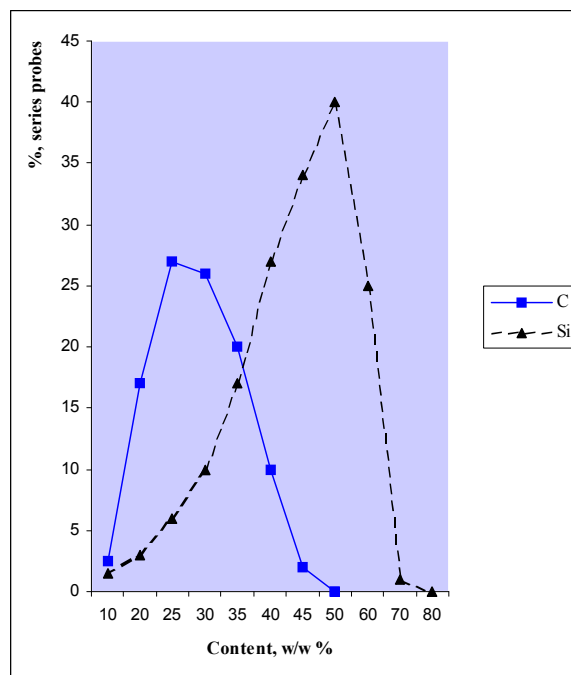


Fig. 1. The distribution (%) of carbon (C) (solid line) and silicon (Si) (dotted line) in shungite samples from Zazhoginsky deposit (Karelia, Russian Federation) according to atomic emission spectrometry (AES)

The crystals of crushed, fine ground shungite possess strong bipolar properties. This results in a high adhesion, and the ability of shungite to being mixed with almost all organic and inorganic substances. Besides, shungite has a broad spectrum of bactericidal properties; the mineral is the actively adsorptive against some bacterial cells, phages, and pathogenic saprophytes [6].

The unique properties of the mineral are defined by nanostructure and composition of its constituent elements. Shungite carbon is equally distributed in the silicate framework of fine dispersed quartz crystals having the size of 1–10 μm [7, 8], as confirmed by studying of ultra-thin sections of shungite by transmission electron microscopy (TEM) in absorbed and backscattered electrons (Figure 2).

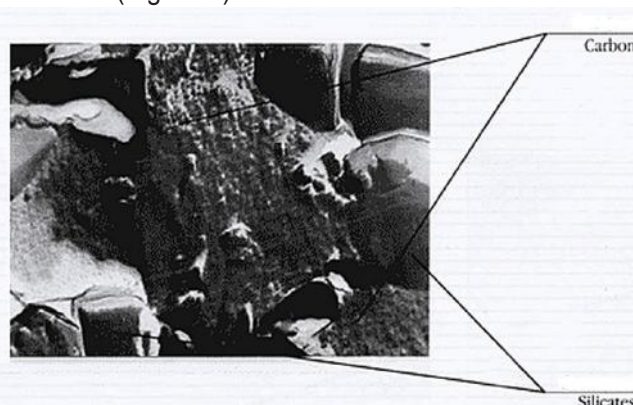


Fig. 2. Structure of shungite rock obtained by TEM method [7]. Scanning area 100×100 nm, resolution 0,5 nm, magnification 300000 times. The arrows show the silicate framework of fine dispersed quartz with the size 1–10 μm , and uniformly distributed carbon

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 [9]. With virtually constant elemental composition of shungite, the carbonaceous matter is demonstrated the variability in its structure – both molecular and supramolecular, as well as surface, and porous structure. X-ray studies showed that the molecular structure of shungite carbon is represented by a solid uncrystallized carbon, which components may have been in a state close as to the graphite and the carbon black and the glassy carbon as well, i.e. the maximally disordered [10]. Carbonaceous matter of shungite having a strongly marked structural anisotropy shows a significant increase in the diamagnetism at low temperatures that is a characteristic feature for fullerites [11].

The basis of the 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 (Figure 3). The globule structure is stable relative to the shungite carbon phase transitions into other allotropic carbon forms. Fullerene-like globules (the content of fullerenes makes up 0,001 %) may contain from a few dozen to a several hundred carbon atoms and may vary in shape and size [12].

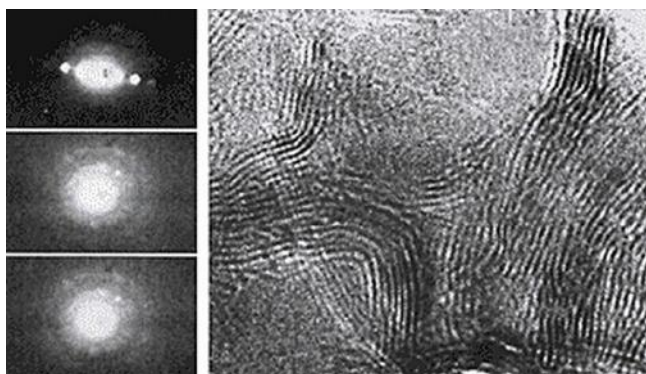


Fig. 3. Electron diffraction of nanopattern of shungite carbon in the form of spherical multilayer fullerene globules with a diameter 10–30 nm, obtained by TEM method [8] (the probe size 0,5–0,7 nm, the energy of the electron beam 100–200 kV, the beam radius 10 nm, the range of the goniometer rotation $-27^{\circ} \dots +27^{\circ}$). On the left are shown fluorescent spherical fullerene-like globules, on the right – the multi-layered spherical fullerene-like globules with packets of carbon layers, recorded at a higher resolution

Evaluation of the mathematical model of interaction of shungite and zeolite with water

By the measurement of IR spectra in the range of vibrations in the crystal mineral framework it is possible to obtain the information:

- a) on the structure of the framework, particularly type lattice ratio $\text{SiO}_2/\text{Al}_2\text{O}_3$;
- b) on the location of cations and structural changes in the structure during the process of the thermal treatment;

c) on the nature of the surface of the structural groups, which often serve as adsorption and catalytically active sites.

Other method for obtaining the information about the average energy of hydrogen bonds in an aqueous sample is measuring the spectrum of the water state. It was established experimentally that at evaporation of water droplet the contact angle θ decreases discretely to zero, whereas the diameter of the droplet changes insignificantly [13]. By measuring this angle within a regular time intervals a functional dependence $f(\theta)$ can be determined, which is designated by the spectrum of the water state (SWS) [14–16]. For practical purposes by registering the SWS it is possible to obtain information about the averaged energy of hydrogen bonds in an aqueous sample. For this purpose the model of W. Luck is used, which consider water as an associated liquid, consisted of O–H...O–H groups [17]. The major part of these groups is designated by the energy of hydrogen bonds ($-E$), while the others are free ($E = 0$). The energy distribution function $f(E)$ is measured in electron-volts (eV^{-1}) and may be varied under the influence of various external factors on water as temperature and pressure.

For calculation of the function $f(E)$ the experimental dependence between the water surface tension measured by the wetting angle (θ) and the energy of hydrogen bonds (E) in an aqueous sample is used:

$$f(E) = b f(\theta) / [1 - (1 + b E)^2]^{1/2},$$

$$\text{where } b = 14,33 \text{ eV}^{-1}; \theta = \arccos(-1 - b E)$$

The energy of hydrogen bonds (E) measured in electron-volts (eV) is designated by the spectrum of energy distribution. This spectrum is characterized by non-equilibrium process of water droplets evaporation, thus the term “non-equilibrium energy spectrum of water” (NES) is applied.

The difference $\Delta f(E) = f(\text{samples of water}) - f(\text{control sample of water})$

– is designated the “differential non-equilibrium energy spectrum of water” (DNES).

DNES is a measure of changes in the structure of water as a result of external factors. The cumulative effect of all other factors is the same for the control sample of water and the water sample, which is under the influence of this impact.

The research with the NES method of water drops, received after their being stayed for 3 days with shungite and zeolite in deionized water, may also give valuable information on the possible number of hydrogen H...O-bonds as a percent (%) of individual H_2O molecules with different values of distribution of energies (Table 4). These distributions are basically connected with the re-structuring of H_2O molecules with the same energies.

Table 4

Characteristics of spectra of water after 3 day infusion with shungite and zeolite, obtained by NES-method

-E(eV) x-axis	Shungite, % $(-E_{\text{value}})/$ $(-E_{\text{total value}})$	Zeolite, % $(-E_{\text{value}})/$ $(-E_{\text{total value}})$	-E(eV) x-axis	Shungite, % $(-E_{\text{value}})/$ $(-E_{\text{total value}})$	Zeolite, % $(-E_{\text{value}})/$ $(-E_{\text{total value}})$
0,0937	2,85	6,3	0,1187	0	12,4
0,0962	8,8	6,3	0,1212	5,9	6,3
0,0987	5,9	0	0,1237	0	0
0,1012	11,8	12,4	0,1262	0	0
0,1037	11,8	6,3	0,1287	0	18,7
0,1062	0	6,3	0,1312	8,8	6,3
0,1087	0	0	0,1337	2,85	0
0,1112	5,9	0	0,1362	0	0
0,1137	11,8	0	0,1387	11,8	2,4
0,1162	11,8	6,3	-	-	-

Another important parameter was measured by the NES method – the average energy ($\Delta E_{\text{H}\dots\text{O}}$) of hydrogen H...O-bonds among the individual molecules of H₂O after treatment of shungite and zeolite with water, to be compiled at -0,1137 eV for shungite and -0,1174 eV for zeolite. The result for the control sample (deionized water) was -0,1162 eV. The results with the NES method were recalculated in comparison with the DNES method. The result for shungite measured with DNES method was +0,0025±0,0011 eV and -1,2±0,0011 eV for zeolite. This difference may indicate on the different mechanisms of interaction of these minerals with water, but also may has been the result of the different composition and the structure of these two minerals, resulting in different behavior while the interaction with water.

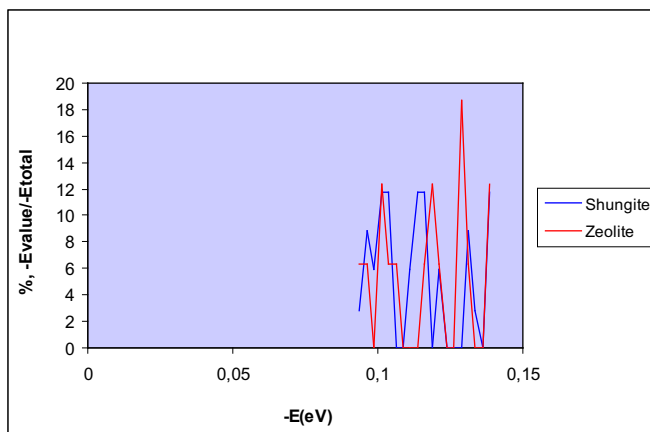


Fig. 4. The distribution ($\%, (-E_{\text{value}})/(-E_{\text{total value}})$) of water molecules in water solution of shungite/zeolite according to energies of hydrogen bonds ($-E_{\text{value}}$) to total result of hydrogen bonds energy

The results also suggest the restructuring of energy values among the individual H₂O molecules with a statistically reliable increase of local maximums in DNES-spectra. For the value -0,1387 eV there was a local

maximum with positive values for shungite and zeolite. In this regard it should be noted that A. Antonov early demonstrated that in the aqueous suspension of tumor cells there was detected a decrease of local maximums; DNES-spectra of aqueous solution containing Ca²⁺ cations have a local minimum of energy at -0,1 eV and a local maximum at -0,11 eV. The interesting fact is that due to the present of calcium in shungite, the aqueous solution of shungite has a local minimum of energy at -0,0987 eV and a local maximum at -0,1137 eV that closely corresponds with the DNES-spectrum of aqueous solution containing Ca²⁺ cations. Thus, by the analyzing the NES- and DNES-spectra of aqueous solutions of shungite and zeolite in water it is possible to evaluate the base of the mathematical model of interaction of these minerals with water, judging by the structural properties, the energies of of hydrogen H...O-bonds and the distribution the individual H₂O molecules in samples with different values of energies.

Practical applications of shungite and zeolite

Owing to the unique porous structure the natural minerals shungite and zeolite are ideal absorbents and fillers [18], and as adsorbents have a number of positive characteristics:

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

According to the data on adsorption capacity shungite loses its effectiveness in comparison with the activated carbon filter in the first stage of filtration, during the first 24 h; but further on shungite began purify water with a high and constant speed. This is explained by high catalytic properties of shungite and its ability to catalytically oxidize organic substances absorbed on its surface. The mechanism of interaction of shungite with water has not been completely understood. It is assumed that shungite can adsorb oxygen actively interacting with them as a strong reducing agent in water and in air [19]. In this process is produced atomic oxygen, which is a strong oxidizing agent oxidizing adsorbed on the shungite organic substances to CO₂ and H₂O, thus freeing the surface of shungite for new acts of adsorption. Overexposure of shungite in respect to the dissolved metal cations in water as Ca²⁺, Mg²⁺, Fe²⁺ and Fe³⁺ is explained 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 CO₂.

The research into antioxidant properties of shungite in relation to organochlorine compounds, and free

radicals have shown that shungite removes free radicals out of water in 20 times more effective than activated carbon [20]. 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 and cause many diseases (cardiovascular diseases, cancer, etc.).

These positive qualities allow use shungite as an effective filter material for wastewater treatment and the purification of water 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. Shungite 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 good organoleptic qualities, additionally saturating it with micro-and macro-elements (Table 5). The adsorption activity of shungite relative to phenol makes up 14 mg/g, while for thermolysis resins – 20 mg/g, for oil products – more than 40 mg/g. The model experiments showed that heavy metals (copper, cadmium, mercury, lead), boron, phenol and benzene contained 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 the regulatory documents. In this case into the water does not enter any toxic elements from the shungite adsorbents.

In addition, owing to the adsorption activity of shungite against pathogenic microflora, shungite has strong bactericidal properties that allow 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 the shungite filter there was the almost complete removal of this bacterium (the viral titer varies from 2300 cells /l in initial water up to 3 cells/l in treated water) [21]. 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 a strong biological activity.

Owing to all these positive properties shungite may find its application for 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 to return 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 subsequent regeneration of the adsorbents [22].

When adding to the treatment scheme to shungite other natural absorbents (zeolite, dolomite, glauconite) the purified water is enriched to a physiologically optimal levels by calcium, magnesium, silicon and sodium ions.

Table 5

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

Conclusions

The fullerene-containing natural mineral shungite and microporous crystalline aluminosilicate mineral zeolite due to its physical-chemical properties and the structure can find wide practical applications in many branches of science and industry, and can be used as an alternative to activated carbon the natural mineral absorbent in water treatment. Efficiency of using these two natural minerals is stipulated by the high range of valuable properties (absorption, catalytic, antioxidant, regenerative, antibacterial), high environmental safety and relatively low cost of filters based on shungite and zeolite as well as existence of the extensive domestic raw material base of shungite and zeolite deposits. All these factors contribute to the further expansion of these minerals and a big variety of materials based on it. As the result of our studies the base of the mathematical model describing the interaction of these two minerals with water was established. It allows better understand, how these minerals interact with H₂O molecules in water solutions in order to explain the adsorption properties of these minerals.

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THE PECULIARITIES OF INTERACTION OF CARBONACEOUS MINERAL SHUNGITE AND MICROPOROUS CRYSTALLINE ALUMINOSILICATE MINERAL ZEOLITE WITH WATER

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We studied the composition and structural properties of the amorphous, uncrystallized, fullerene analogous, carbon containing natural mineral shungite from Zazhoginskoe deposit in Karelia (Russian Federation) and the microporous crystalline aluminosilicate mineral zeolite (Most, Bulgaria) for evaluation of the mathematical model of interaction of these minerals with water. There are submitted data about the nanostructure, obtained with using of transmission electron microscopy (TEM-method), IR-spectroscopy (NES and DNES-method), as well as composition and physical chemical properties of these minerals. For evaluation of the mathematical model of interaction of these minerals with water, the methods of non-equilibrium spectrum (NES) and differential non-equilibrium spectrum (DNES) of water were applied. The average energy ($\Delta E_{H...O}$) of hydrogen H...O-bonds among individual molecules H₂O after treatment of shungite and zeolite with water was measured at -0,1137 eV for shungite and -0,1174 eV for zeolite. The calculation of $\Delta E_{H...O}$ for shungite with using DNES method compiles +0,0025±0,0011 eV and for zeolite -1,2±0,0011 eV. This result suggests the restructuring of $\Delta E_{H...O}$ values among the individual H₂O molecules in the samples, with a statistically reliable increase of local maximums in DNES-spectra.

Key words: shungite, zeolite, nanostructure, fullerenes, water, DNES

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ОСОБЕННОСТИ ВЗАИМОДЕЙСТВИЯ УГЛЕРОДСОДЕРЖАЩЕГО ФУЛЛЕРЕНОПОДОБНОГО МИНЕРАЛА ШУНГИТА И МИКРОПОРИСТОГО КРИСТАЛЛИЧЕСКОГО АЛЮМОСИЛИКАТНОГО МИНЕРАЛА ЦЕОЛИТА С ВОДОЙ

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Исследованы состав и структурные свойства аморфного, некристаллизирующегося, фуллереноподобного углеродсодержащего природного минерала шунгита из Зажогинского месторождения в Карелии (РФ) и микропористого кристаллического алюмосиликатного минерала цеолита (Болгария) для построения математической модели взаимодействия этих минералов с водой. Приведены данные о наноструктуре, полученные с помощью сканирующей электронной микроскопии (СЭМ), ИК-спектроскопии (НЭС и ДНЭС-метод), а также состав и химико-физические свойства этих минералов. Для построения математической модели взаимодействия этих минералов с водой использовали методы неравновесного энергетического спектра (НЭС) и дифференциально-неравновесного энергетического спектра (ДНЭС) воды. Измерена средняя энергия ($\Delta E_{H...O}$) водородных H...O-связей между индивидуальными молекулами H₂O после обработки шунгита и цеолита водой, составляющая -0,1137 эВ для шунгита и -0,1174 эВ для цеолита. Расчет $\Delta E_{H...O}$ для шунгита с использованием ДНЭС-метода составляет +0,0025±0,0011 эВ, а для цеолита -1,2±0,0011 эВ. Полученные результаты свидетельствуют о реструктурировании значений $\Delta E_{H...O}$ между отдельными молекулами H₂O в исследуемых образцах, со статистическим повышением локальных максимумов в ДНЭС-спектрах воды.

Ключевые слова: шунгит, цеолит, наноструктура, фуллерены, вода, НЭС, ДНЭС

ОСОБЛИВОСТІ ВЗАЄМОДІЇ ВУГЛЕЦЬВМІСНОГО ФУЛЕРЕНОПОДІБНОГО МИНЕРАЛУ ШУНГІТУ І МІКРОПОРИСТОГО КРИСТАЛІЧНОГО АЛЮМОСИЛІКАТНОГО МИНЕРАЛУ ЦЕОЛІТУ З ВОДОЮ

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Досліджено склад і структурні властивості аморфного, некристалізуємого, фуллереноподібного вуглецьвмісного природного мінералу шунгіту із Зажогінського родовища в Карелії (РФ) і мікропористого кристалічного алюмосилікатного мінералу цеоліту (Болгарія) для побудови математичної моделі взаємодії цих мінералів з водою. Наведено дані про наноструктуру, отримані за допомогою скануючої електронної мікроскопії (СЕМ), ІЧ-спектроскопії (НЕС і ДНЕС-метод), а також склад і хіміко-фізичні властивості цих мінералів. Для побудови математичної моделі взаємодії цих мінералів з водою використовували методи нерівновісного енергетичного спектру (НЕС) і диференційно-нерівновісного енергетичного спектру (ДНЕС) води. Обмірювана середня енергія ($\Delta E_{H...O}$) водневих H...O-зв'язків між індивідуальними молекулами H₂O після обробки шунгіту і цеоліту водою складала -0,1137 еВ для шунгіту і -0,1174 еВ для цеоліту. Розрахунок $\Delta E_{H...O}$ для шунгіту з використанням ДНЕС-методу складав +0,0025±0,0011 еВ, а для цеоліту -1,2±0,0011 еВ. Отримані результати свідчать про реструктурування значень $\Delta E_{H...O}$ між окремими молекулами H₂O в досліджуваних зразках зі статистичними підвищеннями локальних максимумів у ДНЕС-спектрах води.

Ключові слова: шунгіт, цеоліт, наноструктура, фуллерени, вода, НЕС, ДНЕС.

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