Physico-Chemical Characteristics of Shungite Rock of Kazakhstan

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Abstract

Physico-chemical characteristics of shugite rocks of Kazakhstan (Bakyrchik deposit) were studied using the methods of elementary analysis, IR-spectroscopy, scanning electron microscopy, Raman spectroscopy and X-ray phase analysis. The content of carbon in shungite rock was determined to be from 3% to 19 %. The flotation technology for shungite rocks of Kazakhstan was developed, the content of carbon in the concentrate reaching 40.0%. When studying the elemental composition, the mineral part of shungite rocks was stated to be presented, mainly, by silicon, aluminium, calcium, magnesium, potassium, sodium, iron and titanium oxides. IR-spectroscopic investigations showed that in the concentrate, apart from polycyclic hydrocarbons containing methylene groups, there appeared carboxyl groups. The results of scanning electron microscopy (SEM) showed that flotation and thermal activation of shungite rocks on carbon allow obtaining a more developed surface structure and porosity. The structure of shungite carbon was shown by the method of Raman scattering to be close to that of glassy carbon. The results of X-ray diffraction analysis (XRD) of natural shungite rocks showed that the samples under study contained a carbonaceous substance and a number of mineral components: quartz, illite, bassanite, burgerite, muscovite. It is shown that shungite carbon of “Bakyrchik” deposit is identical to shungite of Zazhogino deposit in Russia. The stated physico-chemical characteristics allow to determine the directions of the use of carbon concentrate for solution of ecological and technological problems.

Introduction

Contamination of water and soil with oil and oil products, heavy metals, pesticides and other pollutants is a grave ecological problem. The common methods of water, air and soil purification are adsorption methods. However, most of the known sorbents have common disadvantages (high cost, poor sorption ability and others). Production of sorbents by conventional methods is characterized by multistageness, complexity of the equipment being used, limited availability of raw materials, etc. Search and creation of new effective sorption materials is an actual task.

One of the interesting materials for a multi-purpose use is a carbon-mineral natural raw material-shungite rocks which are natural composition materials. Their composition is quite different in both the content of carbon and mineral components and the structure. Shungite is a trivial name of amorphous carbon with its inherent structural characteristics unlike those of soot, graphite, diamond and carbine; its deposits differ in age and the regularities of structure formation.

Shungite carbon is fossilized oil or amorphous, noncrystallizable, fullerene-like (i.e. containing) certain regular structures) carbon, its content in rocks ranges from 1% to 30% also it contains aluminosilicates, alkaline metal oxides and trace amounts of noble and rare metals [1]. In rocks, shungite carbon forms a matrix in which disperse silicates with an average size of about 1 μm are uniformly distributed. The presence of these elements and the structure of shungite determine its unique technological and rheological properties. In chemical technology, shungite is of interest as a complex sorbent, natural catalyst or a catalyst carrier [2] possessing the properties of both carbon and silicate materials. In

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practice, being an excellent sorption material, shungite can be used for purification of sewage from oil products, phenols and heavy metal salts [3-6].

Many authors consider shungite rocks to be a standard representative of this class of hard bitumen [7]. At the atomic-molecular level, the structure of Karelian and Kazakhstan: shungites of "Bakyrchik" deposit proved to be similar. According to the opinion of S.G. Glebashev and his coworkers [8], Bakyrchik group of shungite platinoid-gold-sulphide deposits can be subdivided into three types of shungite-bearing rocks-highly carbonaceous shungite rock (more than 25% of C_{org}), mean carbonaceous shungitous rock (5-25% of C_{org}), low carbonaceous shungite-containing rock (1-5% of C_{org}), and a number of mineral varieties of shungite-bearing rocks.

In additions to carbon and the mineral phase, shungite rocks usually contain insignificant amounts of soluble organic substances represented by compounds of an aliphatic series, first of all, saturated ketones and esters with a branched structure, with trace amounts of aromatic compounds [9].

Detection of fullerenes in shungite rocks using the methods of high performance transmission electron microscopy and mass spectrometry has sparked the interest to shungite carbon [10]. The experiments on extraction using conventional organic solvents did not clarify the question on the occurrence and concentration of fullerenes in shungites [11]. All these works were based on the supposition that fullerene bonds in shungits were of a molecular charter. Covalent and donor – acceptor compounds of fullerenes resulting from interactions with nucleophilic molecules are being widely studied now. It should be noted that trace amounts of C_{60} are extracted from shungite carbon by the method of colloidal extraction using polar solvents [12]. In this regard, once again we faced the question on the conditions of formation and conservation of fullerenes and fullerene – like structures in nature [13]. So, the morphological similarity of the globule of shungite carbon and fullerenes was revealed: the presence of the internal space and two – dimensional hexagonal – like cell of carbon atoms with characteristic anisotropy of distortions decreasing its symmetry to a trigonal one [14]. Nanosize carbon particles (gigantic fullerenes, bulbous particles, nanotubes) which are layered structures with the distance between graphite – like planes of 0.35 nm were detected in the powder of shungite carbon [15]. Multilayered spheroidal particles of carbon with the diameter of 100 nm form carbon films on the surface of quartz grains of lidite (shungite rock with the content of carbon equal to 3%). Aggregated nanoparticles were isolated in the course of autoclave dissolution of quartz in lipid [16].

Due to the presence of specific difficulties, different methods, namely X–ray diffraction, electronographic and electron microscopic methods, were used in complex for accurate diagnosis of the structural forms of the proper carbonaceous substance. It should be noted that all these methods characterize, first of all, the atomic – molecular structure and a number of other properties as well as microtextural peculiarities of the object under study. A supramolecular structure is one of the characteristic features of shugite which is the reason of comparison of supramolecular structure of Karelian shungites and the shungite – like substance of "Bakyrchik" deposit [17, 18].

The aim of this work is to investigate the structure of shungite rocks of "Bakyrchik" deposit forming natural layers and dumps after mining polymetallic ores, to reveal the possibility of using the materials obtained on their basis for solution ecological and technological problems.

Experimental

Representative samples of shugites were taken in the course of field works at "Bakyrchik" and "Zazhogino" deposits.

Concentration of shungite rocks

The necessary requirements for the raw materials used in the technological process stage is constancy of chemical and granulometric compositions. That is why we have carried out works on stabilizations of the composition of shungite materials by flotation which was performed on a flotation machine FM-2M. Stabilization of the composition provides reduction of the initial shungite rock, the content carbon varies from 1.5% to 30%, to the constant chemical composition. It is stated that the use of kerosene as a collector and foamer Flotol allows increasing the content of carbon up to 40.0% in one stage without additional refining. The conditions and results of flotation are presented in Table 1.

Elemental analysis of shungite rocks was performed using Optical Emission Spectrometer (Optima 4300 PV). The content of C, H, N, S in shungite rocks and concentrates was determined by combustion method on TruSpec CHN Macro and TruSpec Add-On Module S. Sample preparation was performed in MarsXpress microwave oven using the acid attack. This method of decomposition of organic substances is based on the oxidative action of nitric acid under high pressure with microwave heating, which causes their destruction.

Table 1
Reagent conditions and results of flotation

Number of experiment	Consumption of flotation reagents, cm^3 (per 1 kg of rock)			The yield of concentrate, %	Carbon content, % wt.	Extraction of carbon, %
	Collector, kerosene	Foamer, Flotol B	Regulator, water glass			
1	2	1	-	40.2	44.1*	93.4
					1.1**	
2	2	1	5	40.6	40.9*	93.8
					1.1**	

* - The content of in the concentrate

** - The content of carbon content in the tailings

IR-spectroscopic analysis of shungite rocks was carried out on IR-spectrophotometer IR-ft. For the preparation of solid samples, the tablets of KBr containing finely dispersed sample of the test material were pressed.

Scanning Electron Microscopy

It is known that electron microscopy is one of the most effective methods for studying the structure of materials composed of small size particles. Electron microscopic images of the obtained materials on the basis of shungite rocks were taken on the scanning electron microscope JSM-6360LV (JEOL, Japan).

Raman Spectroscopy

Raman spectroscopy is known as an effective nondestructive approach, which gives detailed molecular level information. Raman spectroscopy is widely used for the study of carbon in its various crystalline and allotropic modifications. Registration of Raman scattering (RS) spectra was carried out on INTEGRA SPECTRA probe scanning microscope. A laser with the wavelength of 473 nm was used in this method. The spectra were recorded with a 20-second accumulation.

X-ray Diffraction Analysis

When studying multi–component carbon systems, a special role is played by the radiographic quantitative phase analysis. This methods allows, alongside with reliable diagnosis of any carbon component, determining the dynamics and mechanism of phase transformations of natural or synthetic carbon systems in the process of action of different physico chemical factors on them. The radiographic analysis of shungit rocks was performed on Ultima IV X-ray diffractometer.

Results and Discussion

The results of elemental analysis (Table 2) show that the content of carbon, nitrogen, hydrogen and sodium in the samples of shungite rocks of “Bakyrchik” deposit considerably increases and the content of silicon, aluminum, magnesium, potassium, calcium and iron decreases after flotation.

Table 2
Elemental composition of shungite rocks

Components	Schungite rock from "Bakyrchik" deposit	Carbon concentrates of schungites from "Bakyrchik" deposit	Schungite rock from "Zazhogino" deposit
C	17.7	45.2	31.3
S	0.2	0.8	0.9
N	0.3	0.5	0.4
H	0.02	0.7	0.1
SiO_2	52.0	37.3	42.7
Na_2O	1.4	0.2	2.0
MgO	2.2	1.3	0.2
K_2O	2.3	0.2	1.1
CaO	2.8	0.5	0.2
Fe_2O_3 + FeO	4.2	3.2	9.5
Al_2O_3	16.3	9.7	11.4
TiO_2	0.7	0.3	0.1
P	0.1	0.1	0.1

The data on the chemical compositions of shungite rocks of “Bakyrchik” deposit show the identity with stratified shingites of "Zazhogino" II deposit of the variety on carbon, and depending on the compositions of the silicate basis – with the average silicate variety.

IR spectroscopic study of schungites allowed to gain additional information on the structure of shungite carbon and qualitative composition of functional groups on their surface. The IR spectra of the samples are represented by the compounds with carbonyl groups (1600-1800 cm^{-1}), carboxylic (1000-1300 cm^{-1}), hydroxyl (362520 ± cm^{-1}), carbonic acids (353020 ± cm^{-1}) and amine (3500-3300 cm^{-1}) groups, that characterizes their similarity with industrial activated coals of vegetable origin.

Figure 1 shows that the IR spectra of schungite ore from "Bakyrchik" deposit have characteristic absorption band of OH hydroxyl groups (3627.43 cm^{-1}), NH_2 (3412.46, 3480.92 cm^{-1}) , the OH group of carbonic acids (3551.38), C-H (2860.74 cm^{-1}), C=C (1617.02 cm^{-1}), C=O (1637.63 cm^{-1}), CH_2 (2973.92, 1375.85 cm^{-1}), C-C stretching vibrations of the aromatic ring (1424.51 cm^{-1}), C-O (1270,83 cm^{-1}), C-OH (1028.71 cm^{-1}), disubstituted benzene (797.76, 700.57 cm^{-1}). In the IR spectra of carbon concentrates of schungites of this deposit (Fig. 2) there are characteristic absorption bands of OH group of carbonic acids (3551.66 cm^{-1}), NH_2 (3474.66, 3412.88 cm^{-1}), C-H (2879.45 cm^{-1}), C=O (1640.28, 1613.81 cm^{-1}), CH_2 (2917.55, 1380.12 cm^{-1}), C-C stretching vibrations of the aromatic ring (1413.81 cm^{-1}), C-O (1215.37 cm^{-1}), C-OH (1087.69 cm^{-1}), C=C aromatic ring (1024.28 cm^{-1}), disubstituted benzene (793.29, 710.07 cm^{-1}).

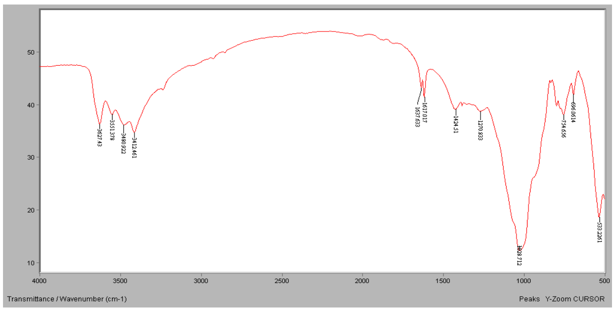


Fig. 1. The IR spectra of schungite rock from "Bakyrchik" deposit.

Figure 3 shows the IR spectra of schungite from " Zazhogino" deposit in which there are characteristic absorption bands of OH group of carbonic acids (3549,97 cm^{-1}), NH_2 (3473,68, 3411,58 cm^{-1}), C-H (2870,53 cm^{-1}), C=O (1638,93, 1619,86 cm^{-1}), CH_2 (2960,15, 1379,18 cm^{-1}), C-C stretching vibrations of the aromatic ring (1435,24 cm^{-1}), C-O (1207,15 cm^{-1}), C-OH (1085,96 cm^{-1}), C=C aromatic ring (1047.12 cm^{-1}), disubstituted benzene (754.65, 696.06 cm^{-1}).

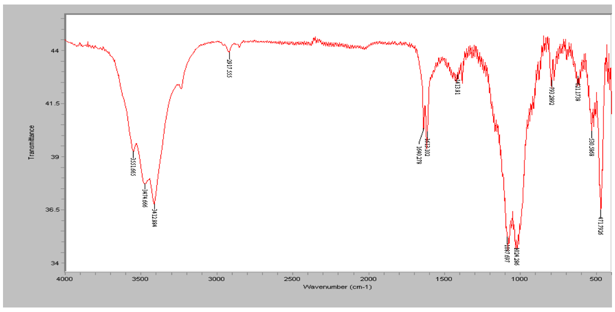


Fig. 2. The IR spectra of carbon concentrates of schungites from "Bakyrchik" deposit.

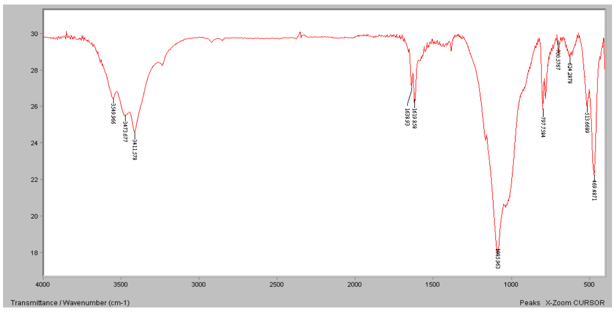


Fig. 3. The IR spectra of Karelian schungites from "Zazhogino" deposit.

The studies of elemental analysis of schungites of Kazakhstan have shown that even in the presence of high amount of mineral component in the carbon matrix, in contrast to the Karelian schungites, the surface of cleavage for the most part reveals the carbon matrix. Scanning electron microscopic pictures of such particle aggregations are presented in Figs. 4-6.

As it can be seen from Fig. 4 the samples are represented by dense formations with strong agglomerates. Physical and mechanical effects on schungite rock (crushing, grinding and froth flotation) a resulted in the change in the surface structure of the material (Fig. 5).

Scanning electron microscopic studies of Kazakhstan schungites and carbon concentrates showed the similarity of the morphological picture of the cleavage surface - plate-step, in contrast to the Karelian ores having generally rounded forms of submicroformation on the surface of cleavage (Fig. 6).The form and dimensions of the plates of Kazakhstan schungites were very diverse - from scaly to acute-angled. Although the faces of the plates are usually flat and straight, the jagged edges with triangular teeth were also observed. The layers are represented by both sub-parallel rows of plate-shape and fan-like divergent ones.

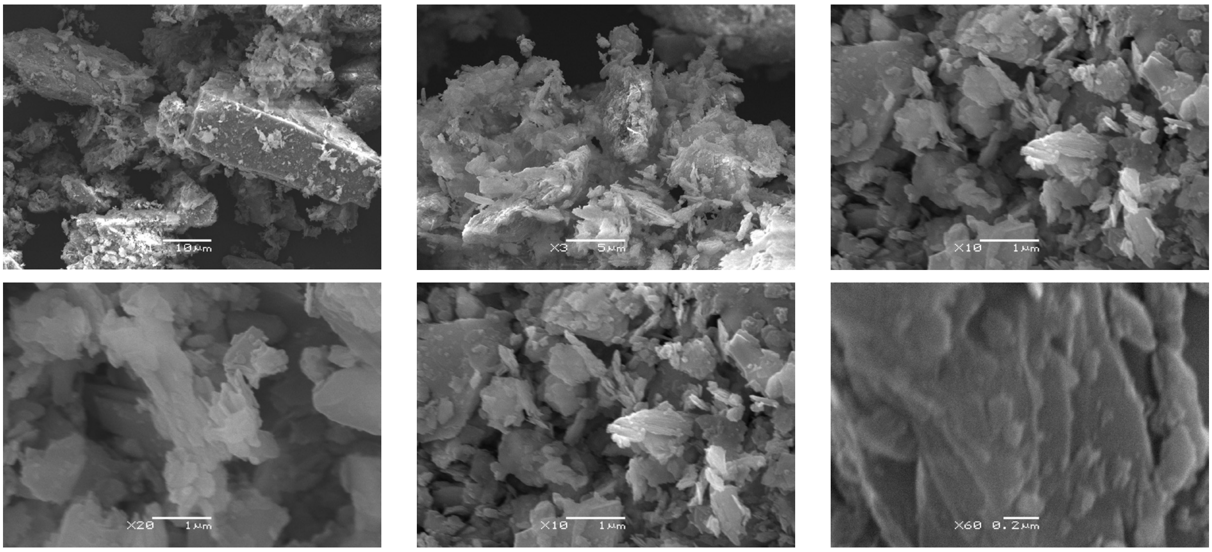


Fig. 4. Fragments of SEM images of schungite rock from "Bakyrchik" deposit at different magnification.

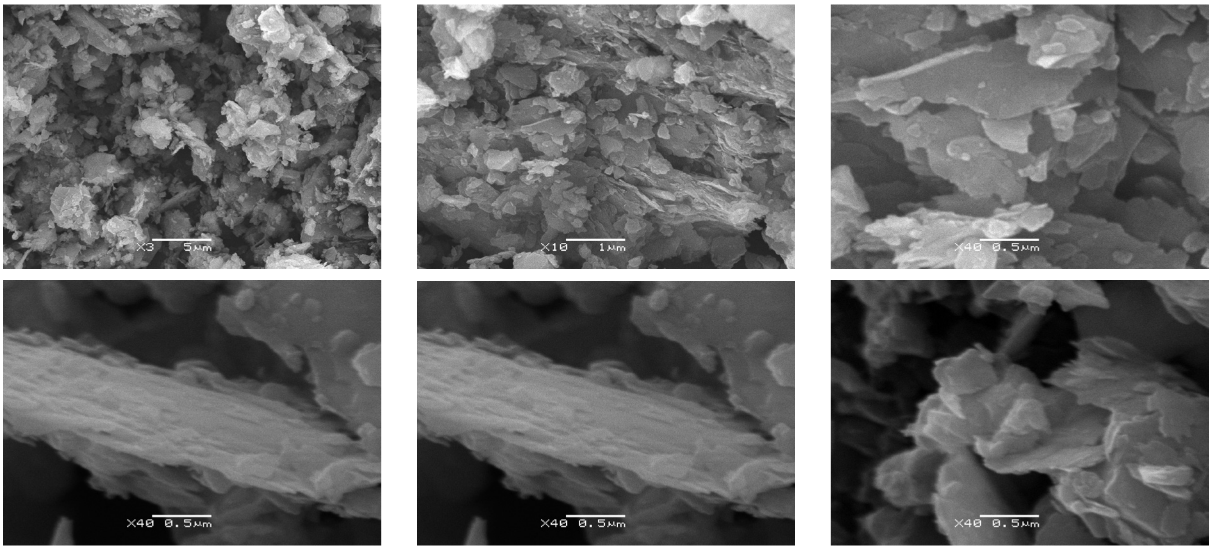


Fig. 5. Fragments of SEM images of carbon concentrate of schungite ore from "Bakyrchik" deposit at different magnification.

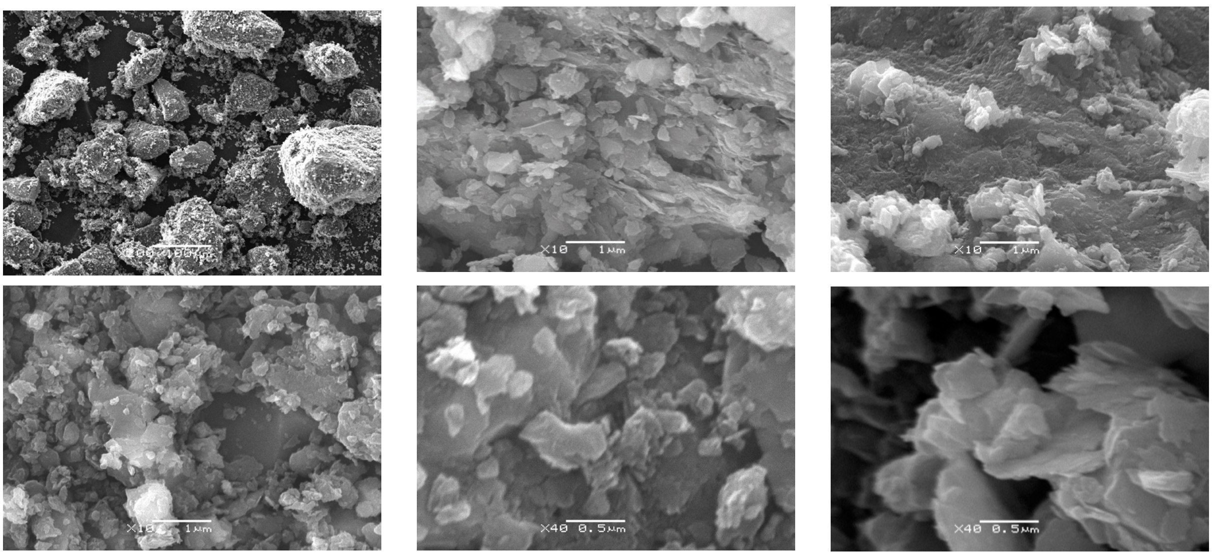


Fig. 6. Fragments of SEM images of Karelian schungites.

It was stated by scanning electron-microscopic studies of shungite rocks and concentrates that carbon materials with a more developed surface structure and increased porosity can be obtained as a result of physico-mechanical effects.

The structure of shungite rock was also studied using Raman spectroscopy. Figures 7-9 present Raman spectra of shungite carbon in range of waves of 200-3200 cm^{-1}. It is known that the Raman spectra of amorphous carbon usually have two bands - G (graphite) band with the wave frequency of about 1560 cm^{-1} and D (diamond) band with the frequency of about 1350 cm^{-1}, du to sp^2 bonds [19]. G band is conditioned by stretching pairs of sp^2 bonds in carbon rings and chains, and D band- by changes in crystallographic axes L_a, L_c in carbon chains. The intensity of D band is a measure of structural disarrangement [20]. For schungite rocks from “Bakyrchik” and “Zazhogino” deposits these bands are observed at 1353 cm^{-1} and 1589 cm^{-1}, 1356 cm^{-1} and 1576 cm^{-1}, respectively, i.e. "blue shift" for the G band and the "red" shift for D band take place (Figs. 7, 8).

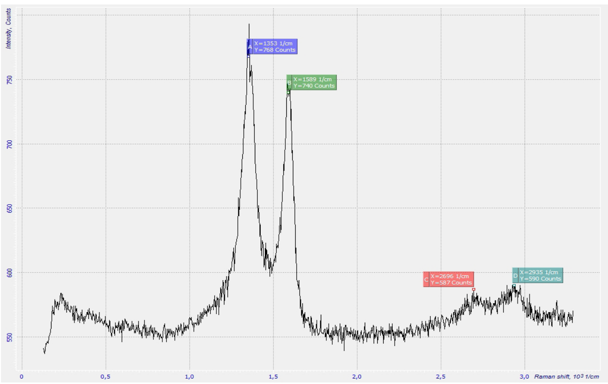


Fig. 7. Raman spectrum of schungite rock from “Bakyrchik” deposit.

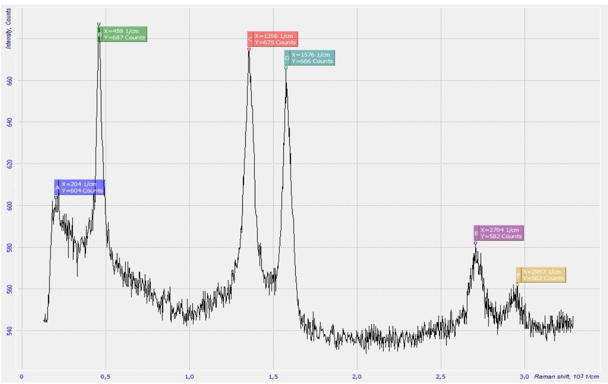


Fig. 8. Raman spectrum of schungite rock from “Zazhogino” deposit.

The oscillations in the region of 2696 cm^{-1}, 2935 cm^{-1} and 2704 cm^{-1}, 2957 cm^{-1} in the spectra of schungite rocks from “Bakyrchik” and “Zazhogino” deposits indicate the structural closeness of shungite carbon to vitreous carbon. In the spectra of schungite rocks from the deposit “Zazhogino” one can see absorption spectra at 204 cm^{-1} and 458 cm^{-1} which occur in the spectra of nanoparticles.

In the spectrum of carbon concentrates of schungites from “Bakyrchik” deposit (Fig. 9) the most intensive are also G and D bands characteristic of carbon structures. Comparison of Raman spectra of schungite rock and concentrates from “Bakyrchik” deposit (Figs. 7, 9) shows their similarity.

Raman spectra of samples of shungite carbon are typical spectra of carbon polycrystals of graphite structure with small grains, and consist of two broad bands with maximums at 1355-1360 cm^{-1} and 1586-1605 cm^{-1}, so-called D and G bands.

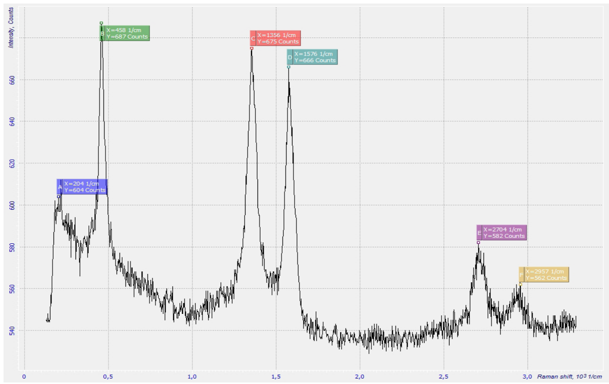
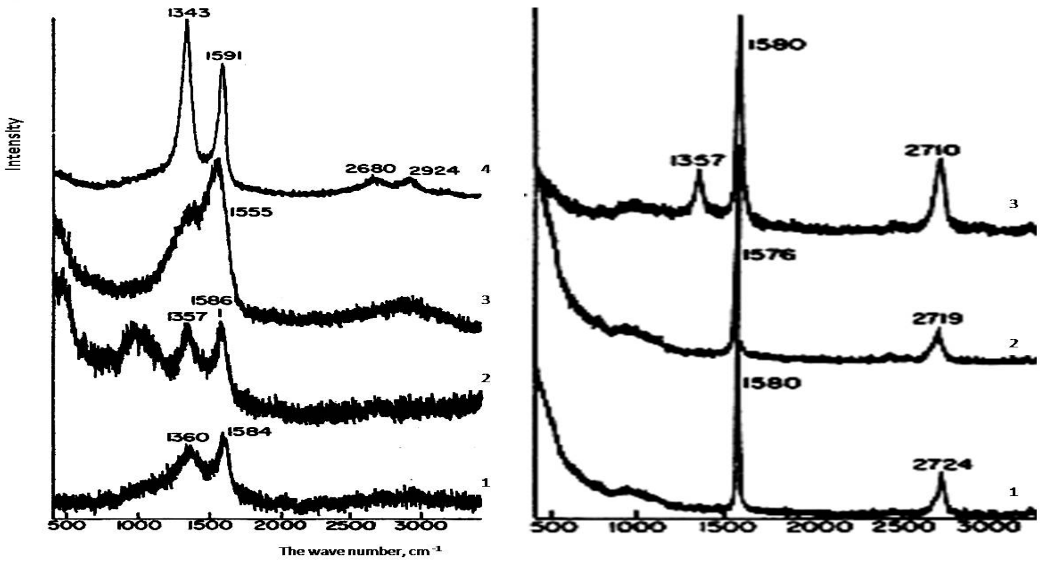


Fig. 9. Raman spectrum of schungite concentrates from “Bakyrchik” deposit.

Conclusions on the amorphous state of shungite carbon obtained by Raman spectroscopy verify the earlier results obtained by the radiographic analysis. This method confirms the conclusion that the material under the study is amorphous as crystallites are oriented randomly and have small sizes. Raman spectra in Fig. 10 are presented on the basis of [21, 22] for different forms of amorphous carbon. It is seen that depending on the structural state of carbon, in Raman spectra the width of lines and the ratio of D/G intensities change. For example, highly disordered carbon, such as charcoal or coke, has very wide peaks, while the peaks of glassy carbon and polycrystalline graphites are narrower. There is no D band in the spectrum of crystalline graphite. Comparison of Raman spectra in Fig. 10 shows the similarity of the spectra of shungite carbon with those of glassy carbon.



The wave number, cm^{-1}

Fig. 10. Raman spectra according to [21] of noncrystalline (a), mostly graphite (b). (a) 1 – charcoal, 2- coke, 3 – diamond – like carbon, 4 – glassy carbon; (b) 1 – natural graphite, 2 – highly oriented pyrolytic graphite, 3 – polycrystalline graphite.

Earlier, we carried XRD investigations of shungite rocks of Kazakhstan and compared them with literature data for shungites of Zazhogino [21]. Radiographic investigations of shungite rocks were aimed at the study of the structure and phase composition of shungite carbon. For shungite carbon of "Bakychik" deposit the following radiographic parameters were determined: interlayer distance d_{002}, graphitization degree Cg, the sizes of coherent scattering L_a and L_c along crystallographic axes *a* and *c*. Shungite carbon is diagnosed by the reflex with interlayer distance d_{002}~0.35 nm in the region $18^0 \div 32^0 \theta$.

The interlayer distance, the sizes of coherent region scattering along crystallographic axes *a* and *c* were calculated: L_a is an average diameter of packeted flat fragments of molecules, L_c is an average thickness of packs, the data are presented in the table. As is seen in Table 3, shungite carbon is characterized by insignificant sizes of coherent region scattering: within 8.2 nm – by the diameter of the network and 2.6 nm – by the thickness of the pack. The data of X–ray diffraction analysis allow to identify carbon of "Bakyrchik" deposit as shungite carbon similar in structure to shungite of "Zhazogino" deposit.

Table 3

The results of X–ray diffractions analysis and the mineralogical compositions of shungites

# of the sample	d_{002}, nm	L_c, nm	L_a, nm	$C_r = \frac{L_c \cdot 10^{-2}}{d_{002} - 3{,}35}$	C, %	Mineralogical compositions of shungite rocks
natural shungite	0.348	2.6	-	2.00	20.0	Hydromicas, quartz, pyrite, muscovite, bassanite and burgerite
concentrate	0.354	2.3	7.0	1.20	60.0	Quartz, hydromicas, bassanite and burgerite
Shungite of Zazhogino*	0.34	3.3	9.5	-	32.0	Quartz, muscovite, carbon

* – according to the data in [21].

The mineral part of shungite rock and carbon concentrate of "Bakyrchik" deposit contains hydromicas of hydromuscovite type (illite). Quartz, muscovite, bassanite and burgerite are detected in the rock, apart from silicom oxide bounds in hydromicas.

The data in Table 3 show that, when using the above mentioned methods of concentration, there are practically no significant changes in the structural parameters of the graphite – like component.

The revealed structural and physico–chemical peculiarities of shungite rocks undoubtedly indicate the fact that it is the summary effect of the presence of the carbon and mineral components that conditions the unique combinations of the properties of the rocks as a whole that makes them promising for practical use in effective solution of ecological and technological task [23, 24]. The obtained scientific result can be in many fields of chemical, food and petroleum chemistry industries. Realization of the proposed technology of shungite rock concentration considerably widens the raw material base of carbon materials.

Conclusions

Shungite rocks are stated to be a multiphase system containing a carbonaceous substance and mineral components. The mineral part of shungite rocks is represented, mainly, by silicon, aluminum, calcium, magnesium, potassium, iron, titanium oxides

The technological parameters of the concentration process were determined: the optimum fractional composition of the initial shungite rock for preparation of concentration pulp, the condition of the flotoreageants supply. The use of kerosene (250 g/t) as a collector and foamer – Flotol B (300 g/t) allows to increase the content of carbon up to 40.0% in one stage in the process of flotation without repurification, independent of the composition of initial shungite rock. The carbon component of shungite concentrates due to its higher adsorption activity can contact with sorbate by the hydrophobic part, and oxygen groups will be responsible for chemosorption processes.

The structure of shungite carbon, the diffraction pattern of which is characteristic for a turbostratic carbon structure consisting of polycondensed aromatical networks of a small size packeted in parallel way and azimutally not oriented in relation to each other, is determined. It is shown by the method of scanning election microscopy that shungite carbon is a spherical formation of an isometric and dendrite form. The value of interplane distance for the first ring varies depending on size and density of aggregation within 0.34-0.36 nm.

It was found that shungite has a turbostratic structure similar to crystallites of soot, i.e., composed of parallel graphite layers, randomly displaced relative to each other. It was shown that schungite carbon differs in the degree of ordering of the graphite-like layers, with the most disordered carbon observed in the rocks with its high concentration.

The possibility of using shungite rocks and products obtained on their basis for solution of ecological and technological tasks is shown.

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