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CENTER OF PHYSICO-CHEMICAL METHODS OF RESEARCH AND ANALYSIS

SHUNGITE MINERALS OF KAZAKHSTAN: PROPERTIES AND APPLICATIONS

A collective monograph

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The monograph contains information on the fundamental research of shungite minerals of Russia and Eastern Kazakhstan. It was shown that the possibility of enrichment of shungite minerals to concentrations of 40, 60 and 90 mass.% on carbon, as well as the processes of modification of the resulting concentrates were studied. The physico-chemical properties of shungite minerals and concentrates of the Eastern Kazakhstan region of RK were studied as well as the areas of practical uses of the obtained shungite materials were discussed.

The monograph is intended for scientists, undergraduate and postgraduate students, PhD students and specialists in the field of chemical technology of non-organic substances, minerals, carbon sorbents.

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SYMBOLS AND ABBREVIATIONS

CLRF	Components of liquid rocket fuel
PC	Place of crash
SPLV	Separable parts of the launch vehicle
d ₀₀₂ -	Interlayer distance
L _a	Area of coherent scattering along the crystallographic axis a
L _c	Area of coherent scattering along the crystallographic axis c
E _{0 ef} -	Effective reduced activation energy
n _i -	Degree of order
M _p	Potassium module
HM	Hydrolysis module
IM	Iron module
BKc	Butyl xanthogenate
$\overline{\Delta G}_{a\phi c.}$	Free energy of adsorption
FM-2,5	Flotation machine
S : L	Weight ratio of solid and liquid phases in a substance
H _φ	Polynaphthenic phase
Γ _φ	Graphite-like component
C _z	Graphitization level
Γ _p	Degree of transformation of the X-ray amorphous component
DTA	Differential thermal curve
TC	Thermogravimetric curve
DTC	Differential-thermogravimetric curve
CTC	Symmetric singlet signal
CJY-3	Laboratory mixer
PMИ-60	Testing machine
f , kgs/cm ²	Tensile strength
θ, %	Relative residual elongation
RTP	Rubber-technical product
масс. ч.	Mass fraction
M ₂₅	Crushability
M ₁₀	Abrasion
Q _θ ^z , kJ/kg	Heat of combustion of the combustible mass in a bomb
CPhChMRA	Center of Physico-Chemical Methods of Research and Analysis
CMS	Carbon-mineral sorbent

Complex use of natural resources and the creation of waste-free technologies are the actual tasks of modern productions. In this regard, it has undergone a significant change in attitude towards waste in recent decades. In terms of environmental management, industrial wastes are secondary material resources. Waste produced and not demanded in certain industries could be used as valuable raw materials in other industrial sectors. Waste recovery and recycling with the production of secondary materials have been transformed into a multi-million profit business with high growth rates. Thus, it is widely known the great importance of carbon materials (ash, activated charcoal, etc.) for various industries. The volumes of world and Kazakhstan's consumption of these types of solid carbon have been raised significantly in recent years. However, the food and chemical industries of our country are experiencing deficient in carbon materials due to the lack of own production of many of these materials. Today, for this reason, it is necessary the production of carbon materials (composite materials, sorbents, rubber fillers, etc.) on the basis of advanced environmentally friendly and cost-effective technologies.

Due to continuously expanding needs for multi-functional adsorption systems, fillers of composite materials, it is of particular importance and relevance the development of the fundamental and technological bases for the creation of novel carbon-containing materials on the basis of coal and mineral raw materials of Kazakhstan. With a sufficient level of research of such systems, prerequisites arise for the creation of multi-purpose carbon-containing sorbents, polymeric composites, reducing agents for ore-thermal production, etc. Considering the complex mineral and chemical composition of carbon-containing raw materials, found in the ore body, and industrial mine dumps, the development of waste-free processing technology, the production of novel multi-functional materials, is an actual problem having both scientific and practical importance.

This book is devoted to the development of technologies for the production of composite materials from carbon-mineral raw materials of Eastern Kazakhstan – shungite minerals, for solving a number of technological and environmental tasks of the Republic of Kazakhstan. The authors have developed a technological scheme of enrichment of schungite rocks, which are contact ores in the mining and processing of polymetal ores. On the basis of carbon concentrates of shungite rocks, the technology of obtaining composite and nano-structured materials for various functional purposes is developed. The possibility of using carbon-containing materials in a number of technological processes is also shown. The production of nano-structured carbon-mineral powders and crushed stone on the basis of schungite minerals is created and put into operation.

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CHAPTER SHUNGITE-CONTAINING MINERALS

1

1.1. Types and properties of shungite-containing minerals

Shungite rocks are natural composite materials which are quite diverse in carbon content and mineral components, as well as their structure. Generally, each shungite rock contains a multi-component carbon (shungite) in its structure, which is associated with a combination of external (local geological) and internal (carbon-mineral crystallogeneses) factors. In spite of this diversity, carbon is characterized by the presence of globules – fullerene-like formations containing packages of smoothly curved carbon layers that enclose nanopores [1, 2].

In addition to carbon, shungite rocks contain a wide range of macro- and microelements. In previous studies, it was found that the macroelements (Si, Fe, Ti, Al, Ca, Mg, Mn, K, Na) are mainly included in such rock-forming minerals as quartz, mica, chlorite, albit, calcite and dolomite, while microelements (Cu, Zn, Co, Ni, Cr, V, Mo, Pb, S, As, Se, etc.) bound with accessory minerals, mainly sulphide minerals. Among them pyrite, violarite, chalcopyrite, sphalerite, millerite and others, and also layered silicates – roscoelite and paragonite [3].

Accessory microcrystals with a certain elemental composition have characteristic shapes and structures. Microcrystals with a predominant content of Fe, Ti, Ni and V are distributed quite evenly in a carbon matrix, often in association with complex aluminosilicates, and, as a rule, are monocrystalline, often rounded or with faint cuts. In contrast, As, Nb, Sb and Ba-containing inclusions are presented as polycrystalline aggregates of various forms. Between inclusions and the matrix of disordered carbon, the presence of two types of transitional areas was observed. The former consist of layers of more ordered carbon with an interplanar distance of 0.34 nm on the surface of microcrystals, and the latter consist of layers of a complex structure with interplanar distance varying from 0.2 to 0.5 nm. In some cases, a definite correlation has been observed in the mutual orientation of the layers in the crystals and transitional regions. At the same time, nanocrystals not only without transitional areas, but even without clear boundaries were found in shungite carbon, which indicates the possibility of their growth directly from the original shungite proto-substance. Non-carbon inclusions in the form of atomic monolayers intercalating carbon have a length of up to 100 nm and repeat the globular configuration of curved graphene layers. Whereas the interlayer distances (d_{002}) increase from 0.34 to 0.6 nm. Nano-sized clusters of non-carbon elements are detected by an increased contrast in the plane carbon layer and have dimensions of the order of a nanometer.

Thus, the following features of the natural crystallogeneses of shungite rocks can be highlighted:

- shungite carbon is a fullerene-like meta-stable carbon;
- mineral components are characterized by fine dispersed distribution in the form of crystals, layered inclusions and nanoclusters in shungite carbon;

- shungite rock is the result of a complex carbon-mineral structure formation which is directly reflected by the presence of transitional areas at the borders between carbon – minerals.

Currently, there is no doubt that it is the total effect of the presence of carbon and the mineral components that causes a unique combination of the physico-chemical properties of the rocks as a whole, which determines the prospects of their practical use as coke in metallurgy, as a catalyst in chemistry, in water treatment – effective sorbent, as well as an active filler for composite materials [4, 5]. In general, these directions are based mainly on the use of structural features and properties of rocks formed during natural processes. However, at the current stage of the development of shungites, the most relevant is the decision of the schemes of their rational use and the further development of science-intensive technologies that give the greatest economic effect.

It is therefore the most effective is the direction associated with the study and use of products of deep modification of shungite rocks, which lead to a fundamental change in their structure and properties.

Today, a number of stereotypes have arisen with regard to shungite rocks, which, on the one hand, due to the properties of rocks in certain physico-chemical and technological processes, and on the other hand, it does not take into account the subtle features of natural crystallogenes and can slow down the development of fundamentally new ways of using shungite rocks. Among them, in particular, as follows: the main active component of rocks is shungite carbon, and the more carbon in the rock, the better that assumes the enrichment of shungite rocks; the finer the crushing of the rocks, the more become active the carbon that determines the need for fine grinding.

Moreover, the mineral components of shungite rocks are divided into useful and ballast, for instance, carbon is useful in all processes, quartz is used in some processes, and layered aluminosilicates (ballast minerals) – in the majority of processes, whereas sulphides, including pyrite as sulfur compounds, are harmful components [6].

According to the content of shungite substance and mineral impurity, shungite rocks are divided into 5 types: shungite I (with a carbon content of more than 98% in the rock), shungite II (35-75%), shungite III (20-35%), shungite IV (10- 20%) and shungite V (less than 10%). This classification does not take into account the characteristics of the shungite itself and the composition of the mineral part. Given this, and also considering the geological location of the diverse shungite rocks, the latter, in term of their forms, were divided into two unmatched by volume combination [7, 8]:

- 1 – migratory shungites (non-stratified), *слагающие жилы, гнезда*;

- 2 – shungite rocks forming stratified layers in sedimentary and volcanogenic-sedimentary rocks

Non-stratified shungites, regardless the carbon content, belong to I species of shungites. In terms of composition, it is mainly the mostly high-carbon compounds. The carbon content in the rock exceeds more than 90%. Stratified shungites by the amount of carbon are divided into species of II, III, IV, V, and also into types, depending on the silicate base composition: high-silicon – A, medium-silicon – B, low-silicon – C. Later, concentrated carbon of stratified formations was also attributed to type I [6].

The data available in the literature regarding the elemental composition, although it does not cover the entire variety of shungite carbon, but characterize the shungite of many of the selected groups of rocks. An interesting fact is that the results of the analyses of shungite of the same types, and of the type, obtained by different researchers, are significantly different. For example, Table 1 provides the data on the elemental composition of migratory shungite from Shungi field.

The authors [9] explain the reason for the observed scatter of compositions by the features of the surface structure of shungite. In mass-spectroscopic studies, it was established that water constitutes the main part of the volatile moieties released during the drying of the shungite substance. Derivative-graphical studies in the helium atmosphere showed that in different samples the distribution of volatile components by the binding energies is different. Thus, in the migratory shungite, a significant part is constituted by hygroscopic water in the composition of volatile substances, while in the non-stratified shungite the fraction of hygroscopic water is much smaller. The different binding behavior of volatile substances with shungite substance was also observed in the stratified rocks. It follows that the quantitative distribution of volatile components by binding energies depends on neither the genetic type of rocks nor on its material composition. Comparison of the derivatograph results in helium atmosphere and the structural characteristics of shungite substance demonstrated that a large part of hygroscopic water is in shungite substance, which has a reduced degree of structure ordering, i.e. less metamorphosed [10, 11].

Table 1

The elemental composition of migratory shungite according to different researchers (mass %)

Elements	I*	II*	III*	IV*	V*	VI*	VII*	VIII**
C	93.45	94.20	99.12	95.13	96.80	97.30	93.00	98.11
H	0.99	0.83	0.44	0.73	0.55	0.80	0.80	0.43
N	0.70	4.97	0.44	2.72	1.20	2.20	5.50	0.43
O	4.86							1.03
S	-	-	-	0.43	0.44	-	-	-
Вода сверх 100 %	-	2.23	7.76	4.79	6.52	-	-	-
* I – VII – data from [10]								
** VIII – data from [9, 10]								

The difficulty of elimination of water and the tendency to thermal destruction, according to the authors, is a consequence of the fact that in shungite rocks there was a reduction of pore channels which acquired a “bottle-like” shape in the process of metamorphism. The stomata of such pores have low throughput and delay the release of vapors of strongly bound water. In the less metamorphosed rocks, the section of the pore channels varies slightly and does not create obstacles to the removal of the vapors of both hygroscopic and strongly bound water. This explains the fact that in the data on the elemental composition of shungite substance of heat-resistant rocks, which has an open character of porosity, there are no discrepancies even with different methodological approaches to the analysis [12].

Therefore, if the effect of the character of porous structure on the results of the analysis is excluded, then the elemental composition of shungite substance of all rocks, according to researchers, is within (mass.%) [9]: C – 98.6÷99.6; H – 0.15÷0.5; (N+O) – 0.15÷0.9; – 0.0015÷0.005. From H:C ratio value, it could be concluded that shungite substance has a high degree of carbonization similar to graphitic anthracites (H:C = 0.0052), cryptocrystalline graphites (H:C = 0.0045), etc. [13, 14].

Shungite of various types was studied by X-ray diffraction analysis by a number of scientists. The first X-ray diffraction studies of graphite, anthracite and migratory shungite from Shunga deposit was conducted by A. Boldyrev and T. Kovalev [15].

Noted by them, the general X-ray feature of these substances is the reflex (002), which, in their opinion, indicates the presence of a crystalline phase – graphite. Absence of weak reflexes of graphite is explained by the fact that the graphite phase is in a dispersed state in shungite. The authors [15] assume that the degree of graphitization of anthracite is fairly higher than shungite. Later, it was also noted by other researchers that on the basis of X-ray studies a highly dispersed graphite is present in the migratory shungite of Shunga deposit [12].

The authors [16] while studying the changes in the structure of a successive series of de-ashed fossil coal of Donetsk bassine: long-flame, gas, vapor-fat, coke, steam-fusible, lean and anthracite (at various stages of metamorphism) supplemented this series with brown coal (South Ural), shungite and, for comparison, with graphite. It was noted that interference fringes on X-ray diffraction patterns of anthracite and shungite matched with graphite lines of (002), (100), (004) and (110). However, reflections with indexes that characteristic for “oblique” atomic planes of graphite crystal grid, for example, (103) and (112) were not evident. This fact was considered as direct evidence that there were no three-dimensional order regions of carbon atoms in the form of the crystal grid of graphite in the examined materials.

The second and forth maxima in X-ray diffraction patterns of anthracite and shungite that are similar to reflections of graphite of (100) and (110) were considered as intramolecular interference on planar carbon atomic networks, similar to basic graphite atomic grids corresponding to periods of 0.260 and 0.142 nm. Hence, two-dimensional indexes of (10) and (11) were attributed to these maxima. The first and third maxima are the result of intermolecular interference, which are characterized by the formation of packages of parallel atomic grids located at a distance of 0.340 nm and differ by the angle of rotation around the direction that perpendicular to the planes of the grids [16].

The most detailed X-ray diffraction studies of Karelian schungite were performed by K. Usenbayev [9-12]. He chose shungite of I type of a deposit near the country of Shunga as the main object and studied also the solid products of its heat treatment in a wide range of temperatures (100-2800 °C).

It was found that the initial shungite is characterized by: broad blurred lines of (002), and very weak (004) and (11); no lines of (hkl) type; lines of (10) and (11) are asymmetric. Blurred lines of (002) and (004) refer to interlayer, whereas (10) and (11) are attributed to two-dimensional intralayer reflections. Such diffraction pattern is characteristic to a turbostratic carbon structure, i.e. structures that consist of polycondensation aromatic grids of small size arranged approximately parallel to the packages and azimuthally non-oriented relative to each other.

From the analysis of the line profile and its angular position the X-ray diffraction characteristics were calculated: d_{002} – interlayer distance, L_a and L_c – sizes of coherent scattering areas along the crystallographic of axes a and c . Natural shungite is characterized by an average interlayer distance of 0.3497 nm and a block of coherent scattering, the dimensions of which along a and c crystallographic axes are equal to $L_a = 6.7$ nm and $L_c = 1.8$ nm, respectively. Consequently, the area of coherent scattering consists of 5-6 layers, each of which contains 20-25 aromatic rings by diameter. Such structure is almost retained unchanged during heat treatment up to 1400 °C [12].

Starting from 1400 °C during heat treatment, d_{002} decreases sharply, and L_a and L_c begin to grow monotonously. Increasing the temperature up to 2800 °C does not lead to the formation of the crystal grids of graphite: the interlayer distance decreases up to

0.3436 nm, which indicates the formation of a structure that is characteristic to non-graphitizable carbon.

Coherent scattering areas during such heat treatment increase to $L_a = 16.4$ nm and $L_c = 5.8$ nm; when recalculated, gives 58 aromatic rings by the diameter of the layer and 25 layers in the package. However, it should be noted that the measurable coherent scattering region does not determine the true size of the packages. This is explained by the fact that the coherent scattering region decreases accordingly due to the presence of defects in the carbon layers and defects in their package.

The course of change in the interlayer distance d_{002} during heat treatment process of shungite is different to other non-graphitized carbonized organic substances. If in the case of latter, a monotonic decrease in d_{002} is observed with an increase in the temperature of the heat treatment, however there is no change found in d_{002} up to 1400 °C in shungite [11-12].

It is known that for coke that is thermally processed to a certain temperature, its repeated calcination to the temperature of the previous treatment also does not cause any change in d_{002} , however the reduction of d_{002} occurs only at a higher temperature. Similarly, it could be concluded that under natural conditions shungite was subjected to high-temperature heating at about 1400 °C. However, according to geological data, the natural process of shungite formation proceeded under conditions in which the temperature could not exceed 500 °C. The authors assume that the cause of such deep structural and chemical transformations of the initial parental substance of shungite at relatively low temperatures is due to the action of the time factor [11-12]. It is believed that the chemical structure features of the carbon substance of shungite is due to the result of the duration of slow carbonization reaction of parental substance. Moreover, the peculiarity of the entire set of chemical reactions of carbonization in the slow process is their selectivity. Therefore, the mechanism of carbonization of the original organic substances in the natural process, obviously, differs from the artificial thermal carbonization. The formation of particular form of carbon during the thermal carbonization of organic polymers depends on the nature and elemental composition of the original polymer. In particular, the presence of oxygen and other elements causes dehydrogenation in carbonization that directs the process towards the formation of the non-graphitized form of carbon [17]. Thermal transformations could be schematically presented as a set of chemical reactions of dehydrogenation and subsequent structural transformation of the products. The effect of dehydrating agents contained in the initial substance contributes to the acceleration of the chemical process of dehydrogenation and, therefore, to an increase in the heat resistance of transitional structures. As a result, the thermal process of structural transformation of carbon is inhibited, which leads to the formation of its non-graphitized form.

X-ray diffraction data confirm the presence of polycondensed aromatic layers in the original shungite and their packing in the turbostratic blocks. This does not contradict the proposed [17-20] general scheme of the polymeric structure of non-graphitized form of carbon as layers of atoms with sp^2 hybridization which are valently attached with each other by side chains of carbon atoms in other hybridization states (sp and sp^3). It is possible the inclusion of bridging oxygen bonds in atomic chains.

The observed thermal conversions of shungite at relatively low temperatures (up to 1400 °C) are explained by the thermal destruction of the weakest single carbon-carbon (C-C) and carbon-oxygen (C-O) bonds [11-12]. The formation of more thermally stable polyine ($-C\equiv C-C\equiv C-$) or cumulene ($=C=C=C=$) side bonds in shungite structure, which prevent the carbon layers from being packed into the crystal grid of

graphite during high-temperature processing [21-22], determines the inability of the shungite to proceed homogeneous graphitization [11-12]. The cause of generation of the polyine chains in the natural process of shungite formation should be attributed to the peculiarities of the parental substance and to the conditions of slowly proceeding selective dehydrogenation reaction [22]. The presence of carbon organized in cumulene chains along with aromatic carbon in the original shungite was also determined by K. Usenbayev as a result of the study the presence of coherent blocks anisotropy in natural deposits and near order of shungite-1 by plotting the curve of radial distribution function of the atomic density [22]. It turned out that the main structural unit of shungite substance is aromatic ring with interatomic distances of 0.139; 0.256 and 0.295 nm, while in crystalline graphite these distances are equal to 0.142; 0.246 and 0.284 nm [7].

Polycondensed aromatic mesh of shungite is defective and severely deformed. The distance between atoms present in adjacent non-oriented layers is determined to be equal to 0.38 nm. There is no absolute match between the radii of the coordination spheres as determined experimentally and obtained by calculation. This indicates the absence of a strictly regular structure in shungite [22].

Migratory shungites are thermally unstable substances in the temperature range of 170-370 °C, which is explained by the release of water [7]. The structural characteristics, calculated using the curves of radial distribution function of the density of heat-treated samples and initial shungite, remain unchanged. Therefore, this fact indicates the absence of a link between water and the main structural element of shungite, i.e. water, apparently, is attached only with the inner surface of shungite substance by chemisorption forces.

In shungite substance isolated from the rocks of II and III types, qualitative changes in the curves of the radial distribution function in comparison with the curve of migratory shungite is observed [23-24]. The diffraction spectra become narrower, false maxima appear at 0.075 and 0.175-0.186 nm, and the radius of the first coordination sphere becomes smaller (0.133-0.135 nm). The radii of the following coordination spheres are 0.251 and 0.300 nm. Consequently, the shungite substance of the studied stratified rocks also consists of polycondensed aromatic carbon atoms, which are approximately packed parallelly and azimuthally non-oriented relative to each other. But shungite substance of these stratified rocks is characterized by a greater structural orderliness compared to migratory shungite.

Using the method of derivatography, the values of the effective reduced activation energy of shungite combustion were determined [12]:

$$E_{0\phi} = 2.3RT \quad (1)$$

where T – end temperature of the combustion reaction of carbonaceous substance, K; R – universal gas constant, J/K×mol.

For migratory shungites, the values of this parameter vary within 3.93 – 5.39 kcal/mol. Between the effective reduced activation energy $E_{0\phi}$ and the interplanar distance of carbonaceous substances d_{002} , a clear relationship is established which is described by the expression [7]:

$$d_{002} = 3.70 - 0.143(E_{0\phi} - 3.30) \quad (2)$$

where d_{002} – expressed in Å, and $E_{0\phi}$ – in kcal/mol.

Interplanar distances linearly decrease with an increase in the effective reduced activation energy $E_{0\text{эф}}$ (Figure 1). Thus, the kinetic characteristics of the combustion process of carbon $E_{0\text{эф}}$ is in a direct functional dependence on the degree of its structural ordering, in particular, on the interplanar distances.

Equation (2) allows us to estimate the degree of structural ordering of any form of solid carbon. If the degree of orderliness of the most disordered carbon is considered as 0% ($E_{0\text{эф}} = 3.30$), and the most ordered graphite as 100% ($E_{0\text{эф}} = 5.75$), then the degree of orderliness n_i of the studied carbon substance can be expressed through the effective reduced activation energy by:

$$n_i = \frac{E_{0\text{эф}}^i - 3.30}{2.45} \times 100\% \quad (3)$$

The introduced degree of orderliness of carbon substance of the studied shungite rocks varies in wide range from 12 to 80%, and there is a continuous transition between them. Many other carbonaceous substances fall within these limits: soot, coke, thermoanthracite, glassy carbon, cryptocrystalline graphite, i.e. there are no particular differences between them according to the general molecular structure. The molecular-structure determined physical and chemical properties of carbon of this extensive association of substances can vary within wide range, which brings about the different practical and technological efficiency of the use of carbon with a disordered structure. In this regard, it is advisable to divide this carbon association into several groups.

It is known that on the basis of hardness all types of carbon were combined into two families by mineralogists [25]:

- 1) family of soft carbon species (graphite);
- 2) family of hard carbon species (diamond).

In turn, Vernadskiy divides the graphite family into two subfamilies [25]:

- 1) clear crystalline graphites – graphite itself and graphite;
- 2) dispersed systems (shungites) – natural coal, shungite, natural coke.

V. Veselovskiy divides graphite materials into groups based on two main features of a dispersed structure [13]: size and relative position of crystals. He allocates three groups: I – clear crystalline graphite with a crystal size of more than 1 μm ; II – cryptocrystalline graphites with a crystal size less than 0.2 μm ; III – graphytoids with a crystal size of about 0.01 μm . And V. Veselovskiy includes shungite into group III.

The authors [7] assume that the physico-chemical properties, as a matter of principle, do not depend on the dispersion, but on the molecular structure; present the classification carbon based on its molecular structure features. In this classification, five carbon groups are distinguished: I – clear crystalline graphite, of which the degree of structural order is $n > 94\%$; reduced activation energy $E_{0\text{эф}} > 5.60$ kcal/mol; interlayer distance $d_{002} < 0.336$ nm. II – неполнокристаллические graphites: $80\% < n\% < 94\%$; 5.30 kcal/mol $< E_{0\text{эф}} < 5.60$ kcal/mol; 0.336 nm $< d_{002} < 0.342$ nm. III – cryptocrystalline graphites: $70\% < n\% < 80\%$; 5.00 kcal/mol $< E_{0\text{эф}} < 5.30$ kcal/mol; 0.342 nm $< d_{002} < 0.345$ nm. IV – graphytoids : $57\% < n < 70\%$; 4.70 kcal/mol $< E_{0\text{эф}} < 5.00$ kcal/mol; 0.345 nm $< d_{002} < 0.350$ nm. V – shungites: $n\% < 57$; $E_{0\text{эф}} < 4.7$; $d_{002} > 0.350$ nm.

Using derivatograms the effect of temperature factor on the transformation of carbon structure of the samples from Shunga and Maksovo migratory deposits of shungite was also studied. These shugites have different degree of order in the natural state. Minor structural changes in shungite begin to occur at 700 °C, and the changes

appear more intense above 1000 °C. Primarily, drastic changes in the interlayer distances are recorded in the most ordered component, as a result, the structure of schungite becomes even more heterogeneous.

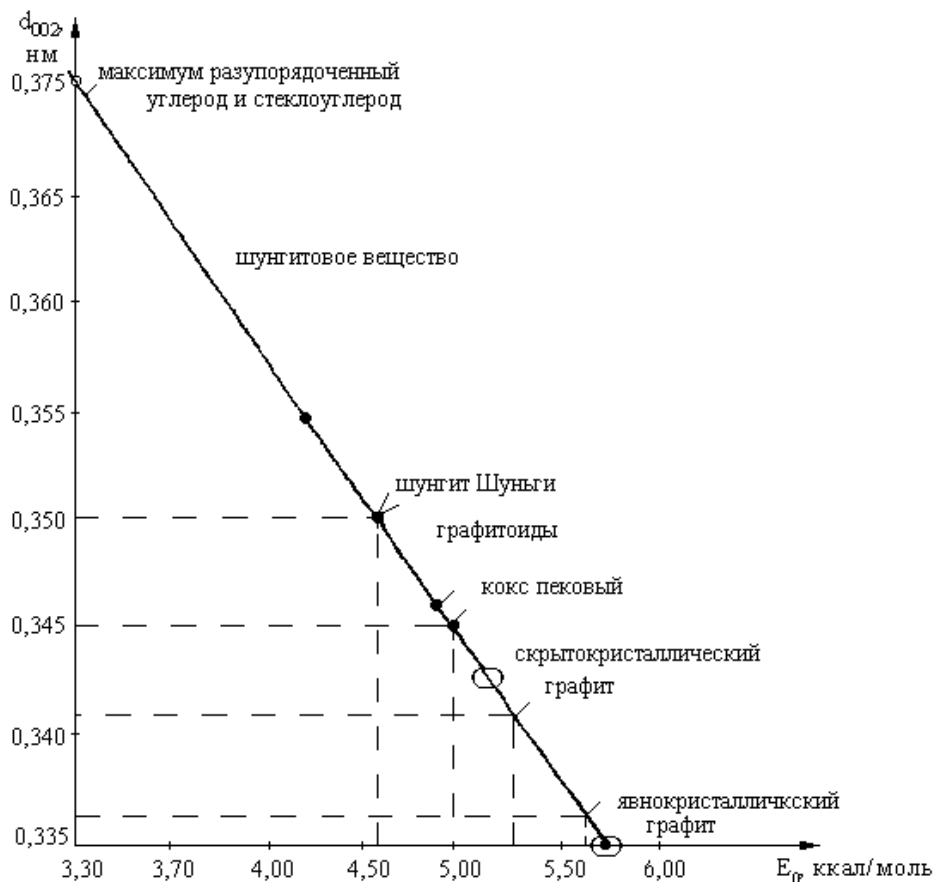


Figure 1 – Dependence of the interlayer distance d_{002} on the reduced activation energy E_0

Above 2000 °C intense crystallization of the least ordered structural component of shungite is occurred. After heat treatment at 2200 °C, Maksovo shungite exhibited one structural component with $d_{002} = 0.340$ nm. In Shungi shungite, the convergence of the interlayer distances of different structural components continues up to 2800 °C and reach 0.3425 - 0.3435 nm. Thus, the structural transformations in shungite during heat treatment are completed upon reaching the state of the cryptocrystalline graphite [26-27].

The study of the supramolecular structure of schungite was carried out using electron microscopy technique [7, 28, 29]. As a result of the study of fresh schungite cross sections, a variety of cleavage morphostructures was revealed, among which there are several types were identified: glassy, fiberglass, globular, scaly. The prevalence of two types of schungite cleavage morphostructures was recorded: globular and packed. Globular structure consists of particles (globules) with a size of 10-20 nm. Globules are concentrated in clusters, having a preferential orientation in the mutual arrangement. Packed morphostructure consists of individual areas (packs) in which the step-like fracture are clearly distinguished. All schungites had a layered structure. The layers of

shungites (depending on their type) have different length and thickness: in samples from the Nigozero deposit the layers have considerably extent length and thickness, 40 nm on average, Maksovo shungite layers have a greater thickness about 200 nm with a smaller length. In Chungaksha shungite the layered areas are large in size and go into one another. The structural diversity of shungite material predetermines large limits of fluctuations of their physical and chemical properties and therefore a wide range of practical applications.

When measuring the density of shungites, it was established that the density of shungite grows with a decrease in the degree of order of its structure. With minimal orderliness, the density of shungite approximates to the density of graphite (2260 kg/m³). The authors [8, 30-33] explain this fact that in the maximally disordered shungite all the pores are filled with water. In the process when shungite exposed to metamorphizing factors (including thermal), causing an increase in the degree of order of the substance, water was removed from the pores. This is an irreversible process as the pores are small and under normal conditions water is not able to penetrate into pores. The proportion of empty pores is 19% in Shunga shungite, in Maksovo – 12%, in Nigozero – from 0 to 5%. The decrease of density of shungite during heat treatment proceed only to a certain minimum, and then the value of density begins to ascend. At the same time, the degree of orderliness of shungite structure increases, i.e. crystallization is carried out, accompanied by a change in the porosity character, material compaction [34-37].

1.2. Carbonaceous porous materials, structure and methods of obtaining. Use of carbon-containing materials in adsorption

One of the important issues of the modern world is the aggravation of the ecological situation and, as a consequence, an increase in the toxic load on a living organism, primarily associated with the consumption of drinking water that does not meet the standards of SanPiN [38, 39]. High-quality water is a guarantee of the health of the nation, whereas poor-quality drinking water is the main reason causing to a decline in the population's health. The state legislates the rights of its citizens to clean and safe drinking water. It has been established that up to 80% of world's population get ill due to the low quality of water, as 20 – 40% of toxic substances enter the human body with water, including heavy metals and chlorinated polyaromatic compounds. It is known that toxic substances contained in water, even in subthreshold doses, are capable of causing teratogenic, embryotoxic, mutagenic and carcinogenic effects. Each water reservoir or water source is connected with its surrounding environment. It is influenced by the condition of formation of surface or groundwater flow, as well as man-made activities. The consequence of insufficient wastewater treatment of industrial and communal enterprises, large livestock farms, industrial waste in the development of ore minerals, etc. is the introduction into the aquatic environment of new, non-intrinsic substances – pollutants that worsen the natural balance of water [40-43].

Among the methods that has been successfully used to solve the problem of water treatment, and one of the most effective, is the sorption on activated coals and porous mineral materials that reduce the content of toxic substances to the maximum permissible concentration (MPC) standards. Activated coals are widely used to extract a variety of substances from the gas environment and solutions, various technical and food products, pharmaceuticals [44-46]. Activated coals are obtained from various types

of raw materials: wood and products of its processing, stone and brown coals, anthracite, peat, as well as from other materials [47-49].

The adsorption properties of carbon sorbents (graphites, soot, activated coals, carbon fibers and membranes) are due to the peculiarities of their structure: the dimensions of carbon crystals in the adsorbent skeleton, the structure of amorphous carbon, chemical compounds of carbon with other atoms, mainly with oxygen and hydrogen, as well as the degree of surface roughness, pore structure [50].

The most greatly developed porosity is in active coal obtained from natural materials; in the so-called molecular sieve coal, obtained by thermal decomposition of synthetic polymers [51,52].

In the recovery of organic compounds, almost frequently activated coals are used as adsorbents, which is associated with their high adsorption capacity, hydrophobicity, relatively low hydraulic resistance and sufficient mechanical strength.

The distribution of pores by radius in individual active coals could be quite different [50]. Extremely volatile solvents can be isolated from exhaust air with a sufficiently high degree of purity only on fine-porous activated coals. Substances with an average boiling point are also well adsorbed on coals of this type. For high boiling solvents, for example, xylene or high boiling gasoline, large porous activated coals are preferable.

If the exhaust air contains substances that reduce the pore volume due to "gumming", these harmful effects can be eliminated using coals with a sufficiently large capacity.

The work [50] considers the parameters of the porous structure of a series of coals, calculated from adsorption isotherms of benzene. The total pore volume ranges from 0.46 to 1.01 cm³/g, macropores – from 0.17 to 0.37 cm³/g, micropores – from 0.16 to 0.60 cm³/g. As the analysis of the obtained results showed, for the adsorption of aromatic hydrocarbons, the most reasonable activated coals are the ones with a total pore volume of more than 0.7 cm³/g.

The rate and heat of desorption are generally determined by the microporous structure of the activated coals. For instance, the degree of desorption of xylene from specified coals grows with increasing micropore volume.

The adsorption process depends not only on the nature of the adsorbent, but also on the adsorbate. Adsorption capacity is interrelated with the size of the molecules of organic substance. The results show that the dynamic activity of AP-3 coal is slightly lower for the solvent than for xylenes due to the faster breakthrough of low-boiling solvent components with small molecular sizes.

The presence of moisture in the gas stream and in the adsorbent significantly affects the dynamic parameters of adsorption. With the initial moisture content of 20% the value of dynamic activity of AP-3 coal falls up to 40%, while coal moisture content increases to 40% (i.e., when almost the entire volume of coal micropores is filled with water), the dynamic activity decreases to 90% [53].

The authors [54, 55] consider a possible mechanism of the adsorption of organic substances on activated coals. Breakthrough concentrations of organic substances coming out of the charge layer, at a time tending to zero, have very small values (10⁻¹⁶ – 10⁻¹⁰ g/cm³). With such small concentrations of adsorbate molecules in the gas phase, their concentration in micropores, i.e., in adsorbed state, also very small. In this case, it could be neglected the intermolecular interaction of adsorbed molecules with each other (adsorbate-adsorbent interaction). The adsorption process in this area will be determined by the intermolecular interaction of the adsorbent-adsorbate due to the dispersion forces caused by the fluctuation of the electron density in interacting systems.

When moistened, the sorbent is modified and adsorption layers of water molecules appear on the surface of micropore walls. The polarizability of water molecules is lower compared to the polarizability of organic substances and adsorbent. Therefore, a layer of water molecules should have minor effect on the force (adsorption) field, created by the walls of micropores, almost without changing the energy characteristics of micropores. Moreover, the surface of micropores is the most energetically active part of the volume of the adsorption space. Once in the adsorption volume, the molecules of organic substances diffuse through the water layer to the adsorption sites displacing part of water molecules.

The molecules of organic substances themselves are stable dynamic system of positively charged atomic nuclei and negatively charged electrons. The force field created by the “walls” of the pores deforms the molecule. Hence, easily deformable part of its electron cloud will shift towards opposite to the field direction, whereas atomic cores – to the direction of the field, i.e. towards the surface. Therefore, the kinetics of adsorption of organic substances should strongly depend on both the polarizability of the molecule and on the distance of its individual atoms to the surface.

The dynamics of the adsorption of aromatic hydrocarbons in the temperature range of 298 – 423 K on activated coals of CKT type of different granulation has been studied [56]; the adsorptive concentration in the gas stream was 0.5-2 vol.%. An increase in the adsorption temperature from 75 to 150 °C leads in all cases to an increase in the rate of motion of the front of the sorption wave and the length of the working layer by about three times.

Active coals poorly absorb polar compounds, for example, acetone compared to “pure hydrocarbons”. Authors studied [57] the adsorption capacity of samples of carbon and carbon-polymer sorbents obtained by pyrolysis of alfamethylstyrene, divinyl and diesel fuel on an aluminosilicate catalyst and aluminum oxide mark “A”. Benzene, toluene, ethylbenzene, styrene, acetone and ethyl acetate were used as adsorbates. It was found that after applying a large amount of coke (20 – 23% mae), the sorption properties of carbon-mineral sorbents, determined by the retention time of six model compounds, is fully consistent with the data obtained for activated coal; a small content of coke does not alter the properties of mineral sorbents of better retaining polar compounds; in spite of the large sorption capacity of carburized sorbents, their capacity is insufficient for practical use; treatment with steam at a temperature of 700 – 750 °C increases their activity by 70%.

The study [58] describes a method of purification of industrial gaseous emissions containing mixtures of toxic organic substances that can increase the sorption capacity and increase the time of protective action. The vapor-air mixture is passed through a layer of carbon sorption material made of activated carbon fibers and a layer of grains of activated coal. The mixture being purified is fed from the side of the layer of grains of activated coal. The technique provides an increase in the time of protective action by 1.5-2.0 times, and the adsorption capacity – by 1.5-2.5 times.

For removal of toxic gases, a non-woven filter with applied reagents is desirable. A mixture of potassium carbonate, calcium hydroxide, calcium sulfate and powdered activated coal or a mixture of potassium carbonate, alumina cement and powdered activated coal with addition of Pd and Pt catalysts are used as such reagents.

Low mechanical strength of activated coal results the formation of a large amount of coal dust, clogging the pores, ablation of the active component from the catalyst surface. By modifying the surface of inorganic sorbents with carbon using the method of cracking of carbon-containing substances on the catalytic centers of the surface of

sorbents, it is possible to obtain carbon-containing composites on a mineral basis, which combine the main advantages of mineral sorbents and active coals therefore superior mechanical strength and hydrophobicity [59, 60].

According to the adsorption characteristics carbon-containing composites and porous materials with a hydrophobic carbon surface are similar to activated coals, but surpass them in mechanical strength. Mechanical strength determines one of the most important characteristics of sorbents and catalysts – their lifetime. The mechanical strength of natural sorbents could be improved by the introduction of pyrolytic carbon. Therefore, carbon-containing composites on an inorganic matrix could replace activated coals in those processes that require strong carbon sorbents [61-63].

Wastewater containing hazardous substances can enter water bodies through various ways: directly from industrial premises or localities; through sewage systems with further entry to municipal wastewater treatment facilities; through local and off-site facilities with their own organized water outlets with or without cleaning. In addition, water bodies and watercourses may be contaminated with transport discharges, including accidentals.

Currently, over 5 thousand types of chemical substances enter the biosphere, i.e. products of technogenesis, most of which accumulate in the soil. Among contaminants, heavy metals take a significant place, the sources of which are wastes and emissions from industrial and fuel-energy plants, automobile and railway transport, mineral fertilizers, pesticides. Industrial and transport emissions to the atmosphere are the largest contributors of soil pollution with heavy metals [64].

The sources of heavy metals pollutants in the hydrosphere are very diverse [43]. The main part of the metals enters the hydrosphere with wastewater. The stream of large rivers on average consists of wastewater by 10–20%, whereas small rivers in industrial areas – by 30–40%, and sometimes by 90%.

According to the authors [65], every year more than 320 million tons of iron and 2.3 million tons of lead get into the seas with the waters of rivers. Sources of heavy metals into the world's ocean are different, but the major pollutant is wastewater. The discharged industrial wastewaters contribute to natural river stream pollution with 2-fold amount of mercury, 12-13-fold amount of lead, copper and zinc, 30-fold the amount of antimony. Furthermore, the total stream of heavy metals source into the northeastern part of the Atlantic Ocean with industrial and domestic wastewater is 9096 million m³ per year.

Mining industry and metallurgy have a significant impact on the occurrence of contracting and extensive anomalies in water systems. The appearance of the latter is due to the loss of substance in the technological chain and its involvement in the migration. All anomalies are polymetallic in nature, which is consistent with the composition of industrial effluents, the most abrupt and stable anomalies are expressed for suspended substances which move to bottom sediments. Even after the termination of exploitation of deposits, contaminated bottom sediments could be a secondary source of pollutants that get into the waters. The removal of chemical elements from the aqueous phase to the bottom sediments indicates only a temporary self-cleaning of the “water mass”, but not the water body [65]. As a result of migration, heavy metals that did not leave the stream into bottom sediments are carried by surface waters to the oceans.

Thus, it can be concluded that wastewater is the main source of pollution of the hydrosphere with heavy metals. Wherein, both industrial and domestic wastewater contain a significant amount of heavy metals. To reduce the amount of metals

discharged into natural watercourses with wastewater, it is necessary to carry out preliminary wastewater treatment. This requires inexpensive, easily recoverable sorbents.

There are a large number of patent literature on wastewater treatment from heavy metal ions and radioactive substances are available. Below some examples and comments are given.

There is a well-known method of obtaining granulated adsorbent for wastewater treatment [66-68]. It involves the mixing of activated carbon, oxides of iron, copper and aluminum.

An inorganic sorbent based on aluminum oxide with a carbon-containing material (10-70 wt.%) was prepared by the researchers from the Institute of General and Inorganic Chemistry [69].

A study report that the preparation of a sorbent, used in wastewater treatment, by mixing a carbon material containing activated coal and an organic auxiliary agent, which is sintered in contact with carbon dioxide [70].

Mansurova et al. reported a method of obtaining carbo-mineral sorbent [71]. This method involves the heat treatment of aluminum-containing compounds in an inert atmosphere or in a vacuum. Aluminum hydroxide and lithium salts or bivalent metals with anions of carbonic acids are combined and heat treated.

Abramov [72] described a method of obtaining a filtering-sorbing material for wastewater treatment, which includes the treatment of the carrier with an iron-containing reagent. The method involves the modification of natural zeolite with a copolymer based on the quaternary salts of diallylalkylammonium chloride or phosphate. This increases the mechanical strength of the sorbent and the degree of wastewater treatment. The modification is carried out at 343 – 353K, after which the product is mixed with peat preliminarily modified at the same temperature with the copolymer on the basis of quaternary dialkyl ammonium salts.

Authors [73] describe a method of treating a mineral base with an organic substance at an increased temperature initially in an inert atmosphere, then in an oxidizing atmosphere. The method characterized by increasing the heat resistance of sorbents; as a mineral base, ash from electrofilters of brown coal power plants or flocculants based on iron hydroxide or ammonium hydroxide in combination with silicates developed in wastewater treatment are used; and residues from chemical processing of brown coal are used as an organic substance – tar and bitumen.

Authors [63, 74] describe the methodology of the preparation of a carbon sorbent that includes the carbonization of carbon-containing wastes, coal and increase the filtering ability of materials by demineralization using 1-1.5% hydrochloric acid solution.

In recent years, inorganic sorbents have attracted increasing attention of researchers – oxides of titanium, tin, antimony; phosphates of zirconium, titanium, tin and a number of other compounds [50, 75]. Silica gel and other dispersed silica materials are the most widespread, which is associated with their high sorption characteristics.

From the review of the literature on sorption and wastewater treatment from ions of heavy and radioactive metals, it can be seen that the carbon-containing composites used (obtained from polyacrylamide, coal, metal oxides) do not have high specific surface area and strength. The use of these sorbents for complete and effective cleaning is impossible as further difficulties arise with their regeneration.

As the global population grows, the problem of providing drinking water is a major concern worldwide.

A third of all mankind do not have access to drinking water, and more than 3.0 billion people are not provided with sanitary conditions. Thereby, the UN General Assembly in resolution 55/196 proclaimed the year 2003 as the International Year of Freshwater and at 58th session in December 2003 agreed to proclaim the years 2005 to 2015 the International Decade for Action “Water for Life”, beginning with World Water Day, 22 March 2005.

The relevance and importance of providing clean water to the population is confirmed by the adoption of the sectoral program “Drinking Waters” in the Republic of Kazakhstan developed in accordance with the Order of the President of the Republic of Kazakhstan dated 16th November 1998, No.4153 “About the state program “People’s Health” and the resolution of the Government of the Republic of Kazakhstan dated 7th March 2000, No.367 “About the Action Plan on the Implementation of the Action Program of the Government of the Republic of Kazakhstan for 2000-2002 years”

1.3. Methods of enrichment of carbon-containing rocks

The necessary requirements for raw materials used in the technological scale is the constancy of the chemical and granulometric compositions. Considering that the chemical composition of shungite rocks is not constant, we have carried out studies on the stabilization of the composition of shungite rocks [78, 79].

With all the variety of industrial enrichment processes of minerals, including coal, all of them are based on the use of differences in various physical and physico-chemical properties of minerals [78, 79].

The following are the main methods of wet and dry coal preparation: gravity, flotation, magnetic, electric and special. Each of these methods includes a number of processes based on the general physical or physicochemical properties by which the material is separated, and differing from each other by the use of additional separating forces (flotation reagents) and corresponding designs of machines and equipment [80-83].

Gravitational method of enrichment is based on the use of differences in the densities of minerals. It includes the following processes: enrichment in heavy media (liquids and suspensions) of отсадка; enrichment in a stream of water flowing along an inclined plane (concentration tables, etc.); enrichment in a centrifugal field, in curvilinear flows, etc.

Flotation method of enrichment is based on the use of differences in natural or reagent-generated wettability of minerals. Flotation is divided into the following processes: foam flotation; foam separation; oil flotation; film flotation.

Magnetic method of enrichment is based on the use of differences in the magnetic susceptibility of minerals. It includes the processes of magnetic separation and magnetic flocculation.

Electrical method of enrichment based on the use of electrical properties of minerals. It involves the separation of components due to the electrical conductivity and the process of electrical separation on the basis of differences in the dielectric permittivity of the coal substance and mineral impurities.

Special methods of enrichment, rarely used for coal, include radiometric separation, enrichment according to form and friction, magneto-hydrodynamic enrichment, chemical enrichment, selective coagulation, bacterial enrichment, etc. [82, 84-86].

The use of certain processes is determined by the qualitative characteristics of the raw materials, the current trends in the development of equipment and technology for enrichment and technical and economic considerations.

The classification of methods and processes of enrichment is presented in Figure 2.

The set of processes used and coal processing are combined into a technological scheme of enrichment. There are qualitative (principal), qualitative and quantitative, water-slurry, air-dust schemes and schemes of chains of apparatuses.

The technological (principal) scheme of enrichment describes the sequence of technological processes and operations that coal undergoes during enrichment.

The qualitative-quantitative scheme of enrichment includes data on the quantity and quality of products of enrichment. The qualitative-quantitative scheme allows to determine the amount of products in all operations of separation or mixing, the yield of products, ash and moisture contents.

Water-slurry scheme shows the water consumption in individual operations and the content of solid phase (slurries) in it [88].

The completeness of the technological process of enrichment is usually characterized by a combined qualitative-quantitative and water-slurry schemes depicted in one diagram.

The chain diagram of the apparatuses characterizes the sequence of arrangement of the machines and apparatus used to carry out the technological processes of enrichment, starting with the arrival of coal at the factory and ending with the issue of commercial concentrates and wastes. On the chain diagrams of apparatuses the type and number of machines and apparatuses illustrated with conventional signs are usually indicated [89].

Deep enrichment of high-ash and high-sulfur coals is possible only by crushing them to the required dimensions in order to expose sulfur-containing splices and using a combination of enrichment in heavy-medium hydrocyclones, on concentration tables, with floatation and magnetic separation [90, 91].

The use of advanced technology of deep coal enrichment with heavy-medium hydrocyclones instead of deposition will lead to a significant reduction in the grain size of coal up to 0.3-0.15 mm during flotation. This will set a number of tasks in the development of flotation technology for thin coal slurries and the creation of special structures of high-performance flotation machines [92].

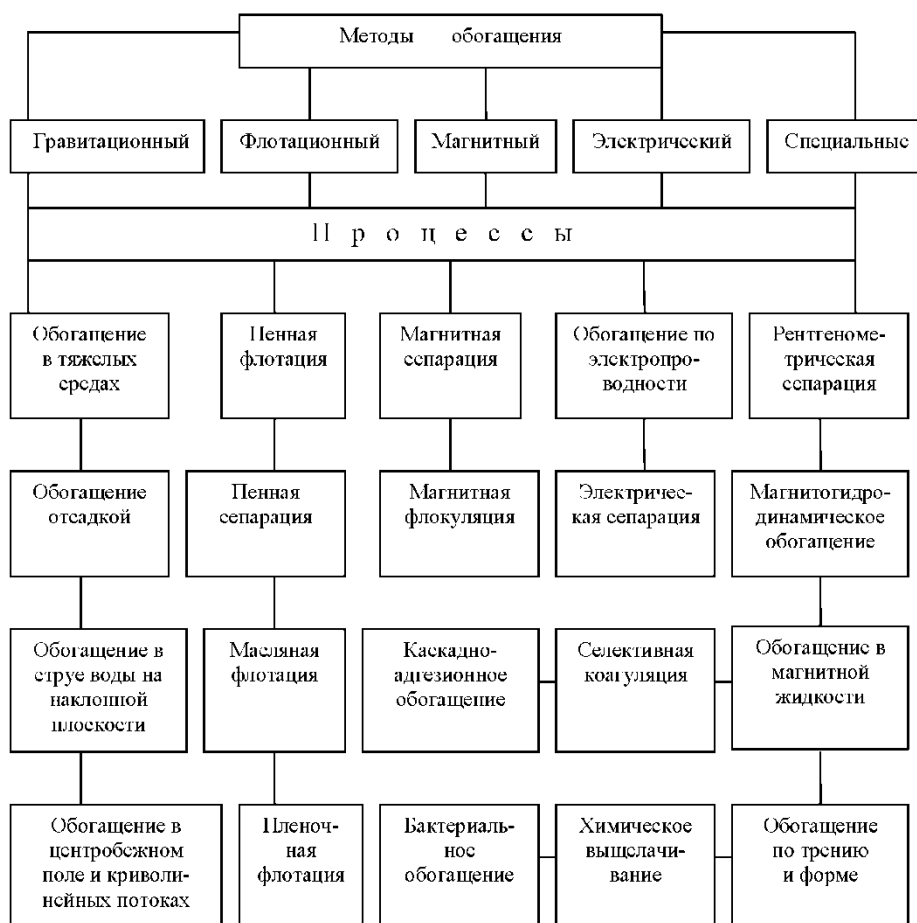


Figure 2 – Classification of methods and processes of coal enrichment [87].

Coal flotation as a process is carried out as a result of the so-called elementary flotation act (adhesion of particles to air bubbles), which is based on physico-chemical phenomena proceeded at the boundary of the three different phases: solid, liquid and gas. The most important of them are the wettability of the solid phase surface and the change of its properties during the sorption of flotation agents [93].

As it is known the flotation of coal is carried out using the flotation reagents that increase the floatability of coal slurries. In modern science the flotation of minerals is explained on the basis of the theory of hydrated layers. The hydrated layer consists of ordered dipoles of water located at the boundary of two phases. With a large thickness of the hydrated layer, the surface of the mineral will be hydrophilic (wetted with water), and with a small thickness of this layer – hydrophobic (not wetted with water).

Flotation reagents affect these layers as by reducing or increasing their thickness and stability. The preparation of mineral surfaces for flotation, therefore, is brought to a sharp increase in the differences in the wettability of the divided minerals. In this case, it is possible to selectively increase the hydrophobicity of the floatables and the hydrophilicity of the non-floatable minerals by supplying the reagents in certain combinations [94].

During coal flotation, in general, only the flotation component is affected, increasing its hydrophobicity by reagents-collectors.

Coal flotation takes place in an aqueous medium with minor changes in pH towards an increase in its acidity or alkalinity. Practically, this change does not affect the interaction of reagents-collectors with the surface of the coal particles. In this regard, the use of reagents-regulators of the medium is not necessary in coal flotation technology. However, they can be used, for example, in the case of selective isolation of pyrite.

The average consumption of collectors in the coal flotation is 1-1.5 kg/ton, foaming agents – from 50 to 300 g/ton [94].

Flotation machines [81] used in the coal enrichment are distinguished by a wide variety of types and technical parameters due to the need to create highly efficient and reliable designs in the absence of in-depth analysis of hydrodynamic and technological patterns of operation of machines and insufficient development of the theory of their action. The most common machines used in the coal flotation are ФМ-2.5, «Гипрококкс-52», ФМУ-50, ФМУ-50М, МФУ-6Я и МФУ-2-63 [95].

The technological factors of the coal flotation process include the qualitative, petrographic, granulometric, and fractional composition of the floatable material, preparation of the pulp for flotation, solid phase content in the pulp, method of dosing and consumption of reagents, duration of the coal flotation process.

The preparation of the pulp for flotation is usually considered as a process that includes the mixing of all streams of sludge feeded the flotation to obtain a homogeneous material (as for granulometric composition and the solids content in the pulp), material classification by size of 0.5 mm, carried out, for example, with the help of low-pressure hydrocyclones, and contacting (conditioning) of the pulp with reagents [95, 96].

The solids content in the pulp is an important technological parameter that determines the performance of flotation machines, the specific costs of reagents, electricity and water. The content of the solid phase in the pulp is expressed by the ratio of its mass to the mass of the liquid phase or the amount of the solid phase per unit volume (g/L or %).

The maximum solid phase content in the pulp during coal flotation should not exceed 300 g/L. In the conditions of each factory the optimal content of the solid phase depends on the ash content of the original sludge, their granulometric characteristics, the presence of clay-based rapid “slackening” impurities, etc.

1.4. Carbon black, a reinforcing rubber filler. The mechanism of reinforcement of polymers in the highly elastic state with carbon black

Carbon black is the most common and most active filler used to reinforce elastomers, in particular, rubber products [97-99]. It is one of the main materials that determine the technological and technical properties of rubbers, as well as the performance characteristics of tires [100, 101].

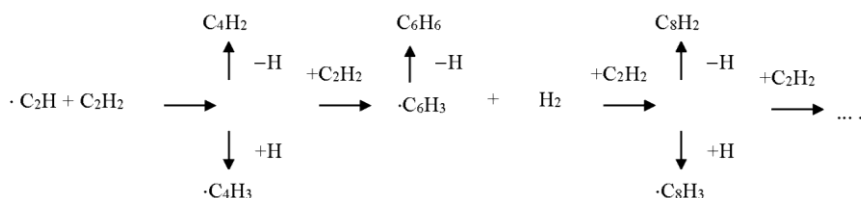
It is particularly important the role of soot in reinforcing synthetic rubbers, many of which, in the absence of carbon black, would have a very limited practical application [102, 103]. Currently, the rubber industry is the major consumer of soot produced (more than 94%) [104].

Carbon black is a finely dispersed powder-like material produced by the incomplete combustion of gas or liquid hydrocarbons [105, 106]. Depending on the method of

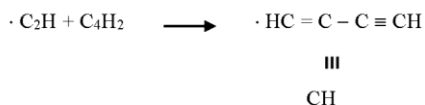
production and the raw materials used, carbon black is divided into five classes: diffusion (channel), furnace, thermal, acetylene and special [107, 108].

The formation of soot is quite complicated process. In the literature, several theoretical models of thermal processes of conversion of hydrocarbons into soot have been proposed. However, none of these methods can simultaneously explain the generation of soot over a period of 1÷10 ms and the implementation of the growth process through the cyclic compounds necessary for the formation of carbon black nuclei [109]. At the present time, it is believed that the formation of soot nuclei occurs by radical, ionic and carbene mechanisms [109-111].

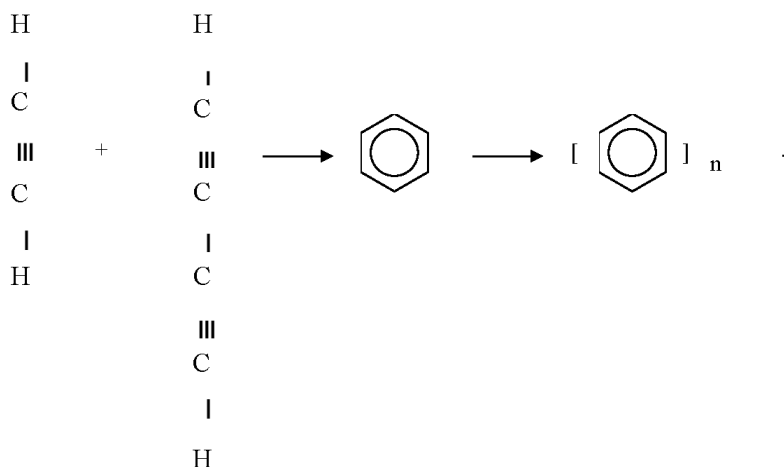
Polyacetylene mechanism has a great attention among the radical mechanisms. Polyacetylenes are formed through the radicals [112]:



Возможно протекание реакции:



Radicals, mainly $\cdot\text{C}_2\text{H}$ and $\cdot\text{CH}$, are preserved in the products of these and other reactions. These radicals contribute to the formation of acetylene and polyacetylene, between of which reactions can also take place the formation of benzene, as an intermediate product:

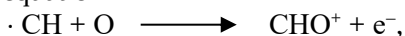


Active nuclei, which are the centers of formation of soot particles, are formed during successive polymerization and dehydrogenation of hydrocarbons. They have active centers capable of interacting with polyacetylene. With the growth of the chain and, accordingly, the amount of carbon in the particles, and also after their collisions, large particles are formed due to Brownian motion – primary aggregates that become inactive.

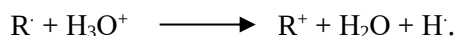
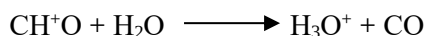
Based on many work done in various laboratories, it has now been confirmed that the resulting particles formed at intermediate stages of soot formation are liquid microdroplets that have the form of primary carbon black particles. The proof of their intermediate liquid state is given in [113,114].

The authors [115, 116] assume that the centers of the formation of carbon black particles are hydrocarbon ions present in the flame.

In this case, the condensation is considered as heterogeneous even in a narrow range of temperatures of the soot formation process. The basic mechanism of chemical ionization is described by equation



after which reactions proceed:



Ions found in flames C_nH_n^+ ($n = 3 \div 10$) Neutral molecules congregate around them, but the clusters retain a charge that interferes with their agglomeration, until a critical temperature-dependent size is reached which corresponds to the size of soot crystallites (2.0÷3.0 nm). Further, agglomeration of crystallites and surface growth due to a heterogeneous reaction take place, for instance,



since the carbon surface catalyzes the decomposition of hydrocarbon gases. Negative ions were also found in the flame [105]: CH_3^- , C_5H_2^- , C_5H_3^- and etc.

However, radical and ionic mechanisms have a common drawback [118]. The ratio of C/H in the precursor molecules of carbon black nuclei has been steadily increasing since the very beginning of the process, while it was experimentally found that up to a certain point this ratio is close to 1. Moreover, it is not very clear how the very fast transformation of the pyrolysis products into cyclic molecules is carried out.

In this regard, the third type of mechanism based on carbene reactions is of great interest [119, 120]. Carbenes are unsaturated uncharged particles, which contain a carbon atom with 6 electrons on the outer electron shell of R_2C : [121]. This atom has 2 non-binding p - and σ - orbitals. Carbenes are formed as a result of rearrangement of hydrogen atoms in a hydrocarbon molecule, in particular acetylene [122]. Acetylene is known to be one of the main products of the high-temperature pyrolysis of hydrocarbons [120]. Furthermore, it is believed that acetylene molecules precede the formation of nuclei of technical carbon black [123]. Carbenes are easily formed as a result of thermal pyrolysis of acetylene according to the following scheme:

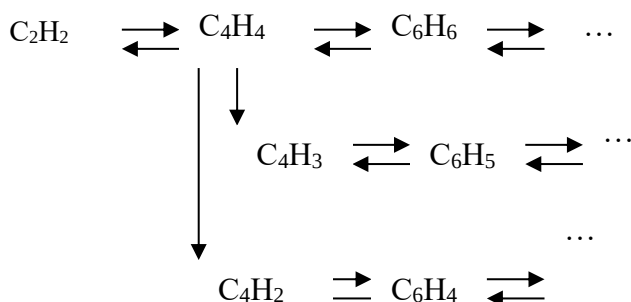


The presence of unpaired electrons determines the high reactivity of carbenes, this explains the rapid formation of cyclic molecules and the development of the process. Carbenes are capable of non-activationally introduce into π -bonds resulting in formation of unstable cyclic structures.

Based on the general scheme of the mechanism of pyrolysis of acetylene, the following main types of reactions could be highlighted [122]:

- 1) rearrangement reactions;
- 2) reactions of carbenes introduction into π - and δ -bonds;
- 3) cyclization reactions;
- 4) hydrogen elimination reactions.

Acetylene pyrolysis model can be expressed as [120]:



The time and temperature conversions of acetylene and yields of some cyclic products calculated for this mechanism are in good agreement with experimental data on acetylene pyrolysis. Thus, carbenes explain the multichannel process of the formation of soot nuclei and obtain a set of molecules-isomers with a C/H ratio close to 1 [122].

The main constituent of the soot is carbon. Most soot contains more than 90% of carbon, and it is believed that carbon in the soot is in a special form that is not found in natural materials [124].

Using X-Ray analysis technique [113, 125], it was found that the structural elements of carbon black particles are flat lattices consisting of six-membered rings (similar to benzene in the position of carbon atoms). The carbon atoms in these cycles are linked by the forces of the main valencies. Approximately 3-7 of such flat parallel lattices displaced relative to each other form elementary crystallite. The forces linking the carbon atoms of two parallel lattices are weaker than the forces between the atoms forming such lattices. The distance between the nearest carbon atoms in the lattice is equal to 0.142 nm, and between the carbon atoms in the nodes of two parallel lattices – 0.345-0.370 nm. Such structure of soot is not crystalline (there are no reflexes (hkl) on a typical soot X-ray diffractogram (Figure 1)) corresponding to three-dimensional ordering [126]. However, two-dimensional ordering and parallelism of layers in crystallites distinguish it from amorphous state. The structure of soot should be more accurately determined as disordered-layered or turbostratic [127].

Some carbon materials that are close in structure to carbon black (for example, petroleum coke), at the end of graphitization acquire many parameters of the graphite structure: two-dimensional ordering goes into three-dimensional, turbostratic modification into hexagonal. Such carbon materials are classified as graphitable substances. Soot, however, is limitedly graphitized, since the turbostratic form of carbon in most soot remains predominant even after high-temperature processing. In [114], it

was noted that in the case of homogeneous graphitization, an obstacle to the ordering of carbon layers of soot crystallites into the graphite structure is the presence of cross bonds linking the crystallites to each other.

The main physicochemical characteristics of carbon black, which determine its behavior in rubber compounds, are dispersity, structure, surface nature of the particles and their density [116].

In relation to soot, the concept of “density” needs to be clarified. One can talk about the density of crystallites, taking into account only their sizes and the number of carbon atoms located in crystallites. Such a density could easily be calculated from X-ray diffraction analysis data, and therefore the density of crystallites ρ_k is also called X-ray density. X-ray density is the true density of the material from which the soot is built up [124].

The density of soot particles ρ_u is a system of randomly packed crystallites. Basically ρ_u is determined by the pycnometric method and therefore it is called the pycnometric density.

Soot implies to dispersed materials, the small particle size of which is due to a natural result of their formation. Quantitatively, dispersion is characterized by three indicators [128]:

- particle size or particle diameter (for spherical particles);
- surface area;
- specific number of particles equal to the number of particles in 1 g of the material.

For soot, the geometric and adsorption specific surface areas of the particles are distinguished. The geometric specific surface area is determined in the case when the particle shape is taken as the spherical and is equal to the sum of the surfaces of the particles, which are 1 g. The adsorption specific surface area takes into account the roughness of the particles and is determined by the number of molecules adsorbed on the surface of the carbon soot in the form of a dense monomolecular layer. The dispersion indicators of the main types of soot are shown in Table 2 [129].

In the production of soot, it is usually determined by the level of its structure, regulating it by means of appropriate changes in the technological parameters of soot formation or the composition of the raw material. In the finished soot, the primary aggregates in contact with each other form secondary aggregates, which are weaker and could be destroyed during the manufacturing of rubber compounds [128].

Table 2

Soot dispersion parameters

Types of soot	Average diameter of the particles, nm	Surface area, m ² /g	
		Geometric	Adsorption
ДГ-100	30-033	93-103	130-160
ПМ-10В	29-032	95-105	<115
ПМ-90	29-032	85-92	95-105
ПМ-75	38-042	75-82	<85
ПМ-75Н	36-040	75-85	75- 85
ПМ-50	50-065	45-60	40- 55
ПМ-30В	88-100	20-26	18- 25
ПГМ-33	85-100	32-38	32- 38
ПМ-15	155-210	12-18	10- 20
ТГ-10	250-300	12-16	12- 15

High-structure carbon black brands contain a larger number of particles in the aggregates compared to normal and low-structure brands. The number of particles in the aggregates of high-structure and low-structure carbon black is 200-600 and from 2-3 to 15-20, respectively [129]. With an increase in the specific surface area of carbon black, its structure decreases.

Carbon black when introduced into the rubber mixture contributes to its strengthening, which, at first glance, seems unnatural. Indeed, the strength and stiffness of soot particles are much higher than of the rubber matrix. It follows that the latter should be the only deformable and destructible phase of the composite system [102]. Therefore, ultimately the strength of the rubber had to be determined by the strength of the rubber matrix and its bonding with soot particles. Hence, the primary microscopic damage to the rubber matrix during its deformation should occur much earlier than in an unfilled uniformly loaded rubber. Obviously, such damage could not directly contribute to the increase of stress rupture in the rubber matrix, though the matrix becomes stronger.

The phenomenon of reinforcing rubbers with dispersed carbon fillers is very complex and diverse [130, 131]. To date, there is no generally accepted theory of soot-reinforced rubber [109, 124, 130, 132-136]. A special role in enhancing the elastomeric compositions at the early stage of studying the above question was assigned to the structural formation of carbon-carbon network in rubber phase.

The author of [102] asked the question: “Why does soot make rubber stronger?” The answer is in the formation of chains of soot particles bonded with bound rubber. Such statement, at first glance, can be considered as something between the theory of “chain soot structures” of Dogadkin and the adhesion theory of Voyutsky’s reinforcement. However, the author’s approach to explaining the occurrence of this structure is peculiar.

As mentioned above, the introduction of a sufficient amount of very small filler particles, which have a huge surface area, turns a significant proportion of rubber into a bonded one, i.e. more tough state. Along with this, the use of very small particles simultaneously creates a large number of uniformly distributed microscopic discontinuities in the composite, which contribute to the transfer of the rubber phase from a complex (triaxial) stressed state into a system of numerous uniaxially loaded fibers oriented along the external load in the most effective way. As a result, according to the author of the theory [102], the formation of a fibrous structure occurs in rubber. Due to indicated structural rearrangement, fibers are the chains of soot particles sealed with bonded rubber. Therefore, the breaking forces of such fibers should be much higher than the corresponding values for the same rubber, but not in the “bound” state.

Indeed, it was established that the macroscopic strength of the structure, determined by the product of the number of fibers in a unit of cross section per average tensile strength of one fiber, is 5-10 times higher than the similar value in unfilled rubber. An additional factor of strengthening [102] is the fact that breaks of individual fine fibers could not substantially weaken the test specimen (as opposed to cracks in a continuous homogeneous medium, which after growth, usually distributed freely across all cross-sections of the sample).

Numerous studies of the mechanism of the action of fillers and their effect on the mechanical properties of vulcanizates show that the effect of reinforcing rubbers, to some extent, is due to the formation of links between carbon black particles and polymer chain molecules [137] and, primarily, links that reduce the mobility of polymer molecules [124].

In this general definition, reinforcement proceeds as vulcanization, which also aimed at the formation of cross-links that reduce the mobility of macromolecules. The difference is, firstly, in the quantity and nature of bonding. During vulcanization, a small number of strong valency links are formed, while the strengthening is likely to be associated with the formation of a larger number of less strong bonds. In each of the compared processes, bonds are formed in a wide range of energies. With amplified, this range is in the region of lower binding energies, but its upper limit may overlap with the lower limit of the range of energies of vulcanization bonds. Secondly, cross-linking during vulcanization only fixes the degree of order that the system has at the start of the process, while the interaction with the soot surface is immediately accompanied by an increase in orderliness. An increase in orderliness leads to an enhance in strength, i.e. reinforces the system.

The interaction of rubber with soot occurs not only when they are mixed, but also continues during the vulcanization stage, storage and operation of products. The mechanism of action of soot at each stage is different.

When mixing, the importance is the formation of the contact surface of soot with rubber and an increase in the degree of order or orientation of polymer molecules near this surface. The ordering of macromolecules near the contact surface of rubber-soot could occur, for example, via their orientation during physical adsorption on the soot surface, under the influence of asymmetric force fields around the soot particles that happen due to the non-equilibrium state and defectivity of crystallites of the surface layer.

The magnitude of the strengthening effect is greatly influenced by intermolecular interaction [132], therefore the smaller it is, the more noticeable is the effect of strengthening. In systems with a large initial intermolecular interaction, the effect of soot is much weaker. According to Aleksandrov and Lazurkin [138], in rubbers, containing active soot, local overstresses occur at higher loads than of in unfilled rubber. Moreover, if the molecules, that adsorbed on the soot surface, were in a critical position, then instead of break they can change their location to be more favorable one by desorption of one segment of a macromolecule and adsorption of another. For this, a complete separation of the molecule from the particle surface is not necessary, dissipation of overstress will occur if the molecule changes its position through "molecular slippage". In this case, the degree of orientation of the adsorbed molecules may still increase. A direct consequence of the equalization of stress is an increase in the tensile strength of the system when stretched. In a more complex way, the same effect enhances the wear resistance of vulcanizates.

The effect of strengthening is especially significant for rubbers that do not crystallize when stretched. In vulcanizates of crystallizable rubbers, the orderliness is also achieved by crystallization, however this does not revoke the need for soot. The crystallization of rubber on soot surface occurs only if there are mostly forces of physical nature act between them (non-localized physical adsorption).

The following experimental facts also indicate the action of physical forces between rubber and filler [124]:

- a decrease in the modulus and an increase in the equilibrium swelling of the filled vulcanizates upon heating indicate increased mobility of molecular chain segments that are relatively weakly linked on the soot surface;
- the introduction of soot practically does not change the glass transition temperature of the polymer due to the flexibility of the molecular chains; the formation

of strong bonds with soot would reduce the flexibility of the molecules and increase the glass transition temperature;

– NMR-spectroscopy, which is very sensitive to the mobility of molecules containing protons, reveals a sharp decrease in the mobility of polymer chains as a result of cross-linking during vulcanization; thus the introduction of soot, only a slight change in mobility is observed [139, 140]. However, according to [140], cross-linking formed during the vulcanization of natural rubber is closer to “physical” bonds in terms of strength, in synthetic rubber – chemical cross-linking. It is believed that only very weak links are formed in the case of filling the rubber with soot between the rubber molecules and the soot particles.

The predominance of physical interaction between rubber and soot is explained by the mechanism of stress balancing during stretching; interaction of a higher order would make desorption or molecular slip impossible. Apparently, adhesion forces play a major role in this mechanism, whose energy is less than the C–C bond energy in the polymer chain (otherwise, a rupture will occur before desorption) and more than the energy of intermolecular interaction of polymer macromolecules (otherwise the polymer molecules will not be adsorbed) [138].

It takes some time for the implementation of the mechanism of stress balancing upon stretching. At a high stretching rate, when the adsorption-desorption processes and molecular slippage do not have time to complete, the ultimate tensile strength of filled vulcanizates often differs slightly from the corresponding index for unfilled ones [141] (a similar relationship has also been established for tear resistance [135, 136]).

It is very likely, however, that the greatest increase in strength is achieved with a certain optimal ratio of strong (localized) and weaker bonds (non-localized). For instance, similar to how this happens during vulcanization, when weak bonds, easily regrouping, contribute to the dissipation of local overstresses, while stronger links – monosulfide bonds and C–C bonds ensure the integrity of the spatial network of the vulcanizate at high temperatures and large deformations [142].

Besides the above-mentioned aspects of strengthening the polymers with dispersed fillers, some factors should be noticed, whose role refers to the extent to which one or the other filler may affect the mechanical characteristics of the system. These factors primarily include the shape and size of the filler particles [133, 134]. The enhancing ability of the latter is directly related to their dispersion. The higher the dispersion, i.e. the smaller the particle size (consequently, larger specific surface of the filler and the surface of the interaction of the latter with rubber in the resin compound and in the vulcanizate), the greater the enhancing effect of the filler. By the nature of the action on rubber mixtures, carbon black is divided into highly active, active, medium-active, semi-active and low-active ones. Highly active carbon black has a specific surface area of 100 m²/g or more, active – 75-100 m²/g, medium-active – 40-75 m²/g, semi-active – 17-30 m²/g, low activity – 10-15 m²/g [128]. However, although carbon black with the highest dispersion ensures the production of vulcanizates with greater strength indices in the filling optimum, after reaching the optimum, the addition of more dispersed soot contributes to a decrease in the strength properties of rubbers.

The enhancing ability of finely dispersed fillers could not be fully implemented until their uniform distribution in a polymer medium is achieved. The better the filler is dispersed, the greater is its contact surface with rubber and the stronger is the interaction between them, leading to strengthening. Undispersed filler lumps weaken the rubber mixture forming structural defects and reducing the concentration of the filler in other

parts of the mixture. Therefore, another important factor in the enhancing effect of carbon black is its maximum dispersion for addition in rubber mixtures [128, 134].

Apparently, carbon black could be dispersed only up to a certain limit, namely, until complete destruction of the secondary structures while distributed in the mixture of primary aggregates of carbon black [128]. Therefore, more structural grades of soot are introduced and dispersed more easily than low-structural grades, but of the same dispersion.

The energy expended during dispersion of the carbon filler is consumed, primarily, in overcoming the interaction between the particles and the primary aggregates. The energy is consumed mainly upon dispersion of the carbon filler to overcome the interaction between the particles and the primary aggregates. This explains the significant difference in the dispersion speeds of various grades of soot. The greater the degree of dispersion of carbon black, the more difficult it is to disperse and, therefore, is more slowly introduced into the mixture.

Another important enhancement factor is wettability [143], i.e. the ability of a polymer to cover filler particles upon mixing, heat treatment or vulcanization of rubber compounds. Wettability is a measure of the compatibility of the filler and the polymer and it strongly affects the properties of the vulcanizates. Finely dispersed low-structure soot is more difficult to wet than high-structure soot. Particles of low-structure carbon black tend to form dense lumps into which rubber molecules can hardly penetrate. Poor rubber wettability of the agglomerate of particles leads to weakening the material due to the formation of structural defects and reduced filler content in neighboring areas.

A study of the experience of foreign countries [144] shows that recently in the rubber industry there has been a certain trend observed the changes in the range of raw materials used in the manufacture of rubber products. This tendency is explained mainly due to two reasons that are problematic for the countries of near and far abroad. Firstly, the economic inappropriateness of using carbon black as a filler for rubber mixtures caused by huge energy costs, depletion of hydrocarbon reserves (oil, gas, coal) and rising prices for them with a low yield of finished product (up to 2.5%). Secondly, environmental congestion, since large amount of carcinogenic substances are formed during the production of carbon black. Carbon black belongs to the third group of carcinogenicity [145, 146], which falling into the gas phase is then spread over hundreds of kilometres and at the same time poison the environment therefore leading to an increased risk of malignant neoplasms in humans and all living creatures as well as many other negative consequences.

1.5. Methods of soil detoxification contaminated with liquid rocket fuel components

Rocket and space activities have a specific impact on the natural environment. The specificity of the environmental impact of rocket and space technology (RST) due to the fact that it affects almost all geospheres of the Earth – from its surface to geostationary orbits. The main types of environmental exposure to RST include mechanical, chemical, acoustic and electromagnetic [147].

The start of a launch vehicle is always accompanied by the separation of stages, transition compartments, head fairings, which land in fields allocated to the falling grounds of separable sections of the launch vehicles (Figure 3) [148]. The result of the impact is the contamination of significant areas of the fall regions of the vehicle's separated parts. These lands are subjected to withdrawal from economic use. Industrial

areas, cities, power plants, railways, large rivers, canals and other infrastructure are located in zones adjacent to the falling grounds of flight paths [149].

The flight courses of carrier rockets launched from the “Baikonur” Cosmodrome stretch over thousands of kilometers over the territories of the Republic of Kazakhstan and the Russian Federation.

Initially, the flight paths were chosen over the semi-inhabited territories of semi-deserts, deserts, tundra, referred to as “low-value” lands, without understanding their real role in the landscape structure, their fragility and unique character. According to the data of the Agency for Land Resources Management of the Republic of Kazakhstan (2001), the total area of land allocated for fall of separable parts of carrier rockets in Kostanay, Northern Kazakhstan, Karaganda, Akmola, Pavlodar and Eastern Kazakhstan oblasts is more than 4.0 million hectares [148].

The prolonged impact of rocket and space technology on certain lands of the Russian Federation and the Republic of Kazakhstan led to the formation of zones of increased environmental risk as a result of soil contamination with residual amounts of toxic components of rocket fuel in the exhaust rocket units [150]. The results of experimental and theoretical studies to assess the impact of rocket and space technology on the environment show that the most vulnerable places, from an environmental point of view, are the falling grounds of the first stages of the separable sections of the launch vehicles, which account for the maximum load of pollution with toxic components of the rocket fuel [151].

The experience gained up to date showed that launches of carrier rocket have a negative effect on all components of the environment and biological species. It was planned that the products of fuel combustion and the separated parts of vehicles would settle within the limits of the allocated belts up to 100 km wide. However, as practice has shown, the spread of falling fragments of standard and emergency carrier rockets occurs with deviations (for example, 2 emergency starts of “Proton” launch vehicle from 05.07.1999 and 27.10.1999) up to 80-90 km from the flight path borders, whilst combustion products and unburned residues of fuel and oxidizing agents upon falling from a height of 20-100 km are disseminated hundreds of kilometers and settle on areas of thousands of square kilometres [149].

The falling areas of the first stages of “Proton” launch vehicle in terms of its environmental status correspond to the category of “ecological disaster zone”, and the impact areas correspond to the “zone of ecological crisis”. According to expert estimates, the total area of these zones is more than 7.0 million hectares. The evaluation was carried out using the method of analogy on the materials of five certified falling areas (1992) and environmental studies (1992-1994) in Karaganda oblast. The rest of the regions (there are about 70 of them) were not studied at all [149].

Upon discard of separable sections of the launch vehicle, primary contamination of the soil with rocket fuel residues takes place at the epicenter of the fall, in spillage areas and beyond as a result of spraying and dispersion of fuel during explosion and fire. Further, asymmetrical dimethylhydrazine (UDMH) evaporates and decomposes, absorbed in mineral and organomineral particles of soils, migrates with the surface and subsoil runoff deep into the soil section through cracks and root systems of the plants. Moreover, the initial level of soil contamination by UDMH could vary significantly for different places of incidence, although the amount of guaranteed residual rocket fuel during separation of the first stage of the launch vehicle has a relatively constant value. In this regard, the priority objective is to study the patterns of migration of asymmetric dimethylhydrazine in the soils of Central Kazakhstan, the results of which will make it

possible to carry out predictive assessments of the ecological state of the sites of incidence of the first stage of separable sections of “Proton” carrier rocket and will contribute to the development of novel optimal methods and technologies for treatment and detoxification of soils from UDMH.

In accordance with the stated objective, it was necessary to solve the following tasks:

1. Study the morphology of soil contamination with asymmetric dimethylhydrazine and the dynamics of its behavior on the falling sites of the first stage of separable sections of “Proton” launch vehicle located in the territory of Karaganda oblast of Central Kazakhstan.

2. Study the migration of asymmetric dimethylhydrazine along the profile of various types of soils at the places of incidence of the first stages of separable parts of “Proton” rocket carriers.

3. Study the patterns of diffusion mass transfer of UDMH and the kinetics of its destruction on model samples of dominant soil types of PII 15, 25 and 148 and the derivation of semi-empirical equations of diffusion migration of UDMH in different types of soils.

4. Perform mathematical modeling and numerical calculations of UDMH migration processes in various types of soil based on field data obtained in the territory of the falling grounds of the first stages of separable sections of “Proton” rocket carrier with a predictive environmental assessment of the distribution of UDMH concentration fields by soil profile.

The environmental load on the territory of the falling grounds is directly dependent on the number of space objects launched into orbit. According to telemetric measurements, the average value of the residual components of rocket fuel in the tanks at one launch was: fuel – 0.3–2.0 tons, oxidizer – 1.2–4.0 tons [152]. Thus, the fall of the first stages of launch vehicle from an altitude of 50–120 km is accompanied by a spillage into the atmosphere (into the soil and water bodies) up to 0.6–2.0 tons of UDMH and 1.4–6.0 tons of nitrogen tetroxide. The maximum permissible concentration of UDMH is $1 \mu\text{g}/\text{m}^3$ or $1 \text{ kg}/\text{km}^3$ of air, therefore, 2 tons of UDMH poison $200\,000 \text{ m}^3$ of air. This volume represents a pillar with a 2 km height and a cross-sectional area of $30 \times 30 \text{ km}$. An aerosol footprint from a height of 100 km is carried by the wind for 300–500 km. The evaporation of UDMH spot from the ground covers the area with a radius of 200–300 m [153].

Soil contamination with UDMH creates the risk of persistent changes in the functioning of ecosystems by disrupting biotic processes and changing the number of population and species composition of microbial and plant communities. High concentrations of asymmetric dimethylhydrazine may inhibit soil biological activity.

High degree of volatility and solubility in water, the ability to accumulate and stability in soils, plants, as well as the ability to migrate into the deep layers of the soil determine the high degree of danger of UDMH for environment.

In places of fuel spills, local, but more contrasting soil, biogeochemical and hydrochemical anomalies are formed. Also, the sources of secondary contamination of the area with UDMH and the products of its oxidation are rocket fragments on the surface of which rocket fuel residues are usually present [154].

Despite the possibility of the spread of pollutants over long distances, there is a localization of contaminants around the falling sites due to weak mobility of UDMH absorbed by the soil and rapid dilution of the component to safe concentrations (during rains and floods). One of the ways of UDMH removal far beyond the RP is ground or surface waters.

Once in the ecosystem, UDMH could be preserved unchanged or bind to natural substances mainly to organic compounds (fulvic acids, humic substances, etc.), and could also be partially transformed into N-nitrosoamines, including nitrosodimethylamine (NDMA), which has pronounced carcinogenic properties. In this case, tetramethyltetrazene (TMT), methyl methylenedihydrazine (MMH), dimethylamine (DMA) could be formed. The final products of the conversion of UDMH into OPS are nitrates, nitrites, formaldehyde, hydrazinecarboxylic acids and other substances [155-157].

Previously, the authors [156-157] concluded about the possible reactions of the transformation of UDMH in natural objects. The proposed scheme of UDMH transformations in soil and water is presented in Figure 4.

The mechanism of transformation of UDMH, as well as the formation of certain intermediate and final products may depend on a combination of the following factors: oxygen access; UV radiation; the presence of oxidizing agents; the presence of compounds capable of catalyzing the oxidation of UDMH; moisture in soil; soil microbiota; temperature.

As a result of field studies in falling areas of separable sections of "Proton" carrier rocket and studies of the dynamics of UDMH behavior, the main patterns of its migration were established and semi-empirical equations were derived which describe the processes of diffusion mass transfer and the kinetics of UDMH destruction in soils.

The analysis of the results of numerical calculations of the distribution of asymmetric dimethylhydrazine by the soil profile of the falling grounds for separable parts of launch vehicles, based on the calculations of diffusion mass transfer, showed a qualitative agreement of the results of numerical calculation with the data of field studies (Table 3)

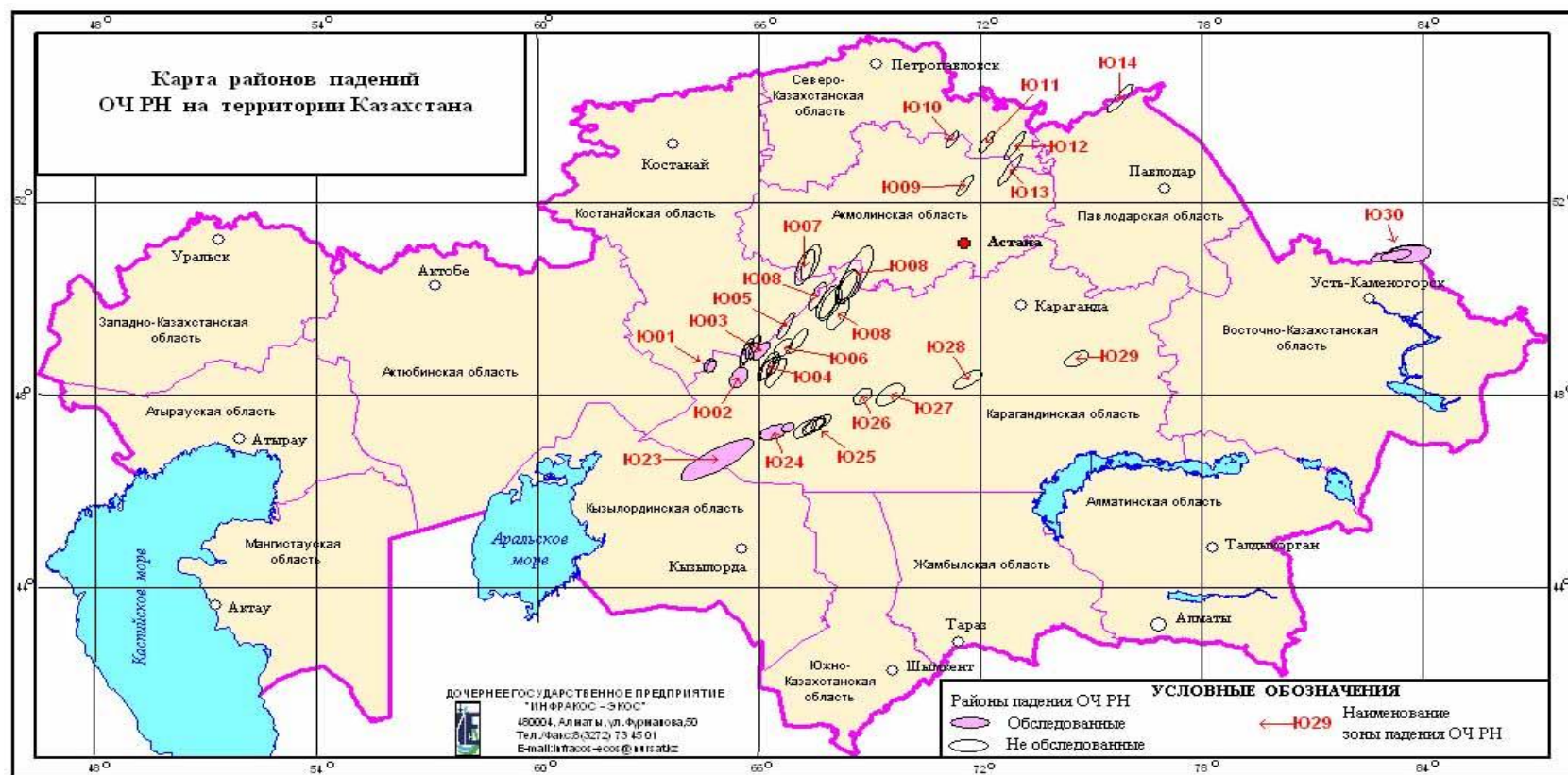


Figure 3 – Map of the areas of fall of separable parts of launch vehicles in the Republic of Kazakhstan

Table 3

The distribution of UDMH in the vertical direction at landing sites of separable parts of “Proton” carrier rocket on the territory of ПИ 148

Sampling depth, cm	CUDMH, mg/kg (field data from the expedition 09.06.2003)	Soil moisture, %	CUDMH, mg/kg (field data from the expedition 14.08.2005) in 2 years and 2 months	CUDMH, mg/kg (estimated data) in 2 years and 2 months
0	122	12	52.0	94.07
8	112	14	48.8	84.51
20	2.5	14	4.52	9.846
40	0.53	14	0.87	0.184
50	0.22	14	0.53	0.184
68	0.16	14	0.012	0.184

The estimated and experimental data from field studies showed that in the upper layers of the soil section adjustments to UDMH distribution pattern could be made through drying soil cracks by soil profile, sorption, desorption, filtration of aqueous solutions of UDMH, as well as work of soil microflora, plant root systems, contact with oxygen in the air and exposure to ultraviolet rays.

All these factors could take place since sites of falling of separable sections of carrier rockets are located in an arid climatic zone which is characterized by strong fluctuations in temperature and humidity. It is important to note that the soils of areas of fall of launch vehicles have different characteristics (chemical composition, type, dispersity, etc.) and are able to affect the processes of UDMH transformation [157].

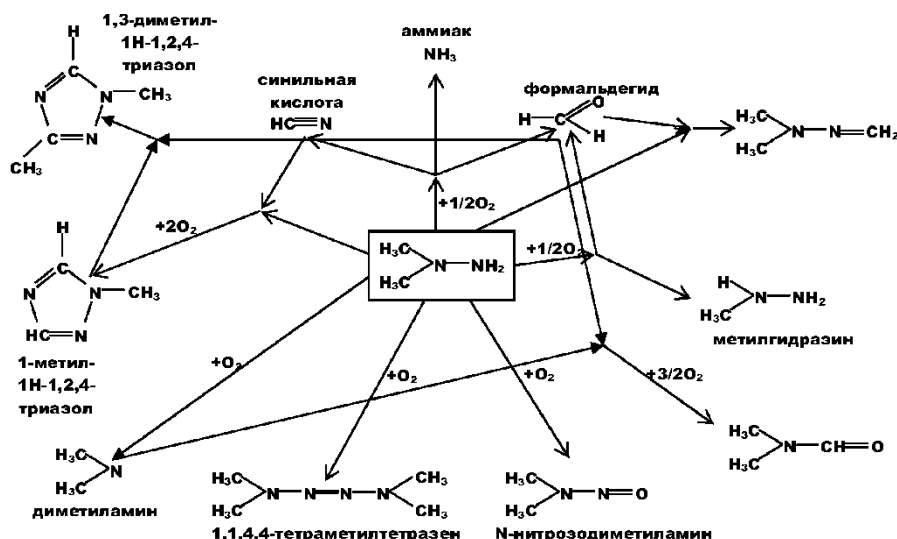


Figure 4 – The proposed scheme of UDMH transformations in soil and water

Operative work on localization has a significant effect on the size of damage caused by spillage of toxic substances, in particular CLRF. Significant lands of the impact area of SPLV are currently exposed to rocket fuel, therefore, the issue of effective localization of spill is particularly relevant.

When choosing one or another method of soil detoxification, the following requirements should be considered:

- express localization of places exposed to CRF and determination of concentration of the latter;
- development of the technological regulations of detoxification process, taking into account the material balance (soil-pollutant, the ratio of “cleaner-pollutant-soil”);
- minimal equipment design, which is especially important for hard-to-reach places;
- work in the shortest possible time;
- efficiency of neutralization (after laboratory studies, repeated field tests in a wide time interval, by season).

Currently, a number of methods have been proposed for decontamination of soil and water from CLRF.

Chemical methods are based on the expressed reducing properties of UDMH. Different types of oxidizing agents are used to reduce the level of contamination caused by UDMH. Among these oxidizing agents are hydrogen peroxide, atmospheric oxygen, ozone, chlorine oxidizing agents, sodium nitrite, etc. [158].

Chemical oxidative methods are very effective and can reduce UDMH concentration up to maximum permissible concentration (MPC). The efficiency of oxidation processes could be facilitated using catalysts. One of the promising methods is the oxidation of aqueous solution of UDMH in the presence of hydrogen peroxide with simultaneous initiation of its decomposition by adding a catalyst [159].

The use of chlorinated oxidants, among which the most effective reagent is liquid chlorine, allows to reduce the concentration of UDMH by 99% in a short period of time. Among chlorine oxidizing agents such as bleaching powder and ДТС-ГК are also used. However, choosing chlorine-containing substances to eliminate accidental spills of UDMH and neutralization of the sites of fall of SPLV, it is necessary to consider the amount of UDMH in the environment and products of its transformation. Consequently, extremely toxic substances could be formed when chlorinating one of UDMH products – triazole (an analogue of pesticides) [159].

Most of the oxidizing agents used cause secondary contamination in the soil and water or salinization. The formation of toxic UDMH derivatives is inevitable during oxidation. These toxic substances increase the overall toxicity.

Biotechnological techniques allow to avoid the disadvantages of chemical oxidative methods. Biological methods of soil treatment do not cause secondary pollution of the soil, but often improve soil fertility. The main advantage of biotechnological methods is the ability of biomass, as an autocatalytic system, to self-regulate the cleaning process in response to changes in the composition and concentration of the pollutant. Currently, a search for plants that are able to neutralize UDMH found in the soil is in progress. This method is very promising and should receive decent development [160]. The method of UDMH phytodetoxication in aqueous media with hyacinth aqueous solution has been developed. This method is highly effective and allows to dramatically reduce UDMH concentration within 20 days [161].

Sorption techniques are the most promising methods, the main development trends of which are in finding the cheapest and the most effective materials, improvement the technologies of regeneration and utilization of sorbents. The adsorption methods of UDMH detoxification have been considered as the most extensively used technique. These methods are used both for the localization of straits as well as for the treatment of natural waters and wastewater. Using the sorbents could substantially reduce the

amount of UDMH entering the biota. Various types of sorbents such as natural (peat, natural aluminosilicates) and synthetic (activated charcoal, ion-exchange resins, polymeric materials, etc.) substances are used in soil treatment. Nevertheless, these methods do not completely purify contaminated soil from UDMH. UDMH content in the soil is minimized by utilizing these methods. Sometimes, it is possible to collect up to 85% of spilled fuel. After treatment using sorbents, it is essential to carry out post-treatment in order to reduce UDMH concentration below MPC.

One of the proposed techniques to detoxify soils contaminated with UDMH is the use of a peat sorbent-catalyst. This method was developed in the Russian Scientific Center “Applied Chemistry” and is based on the use of top peat as a sorption material treated with orthophosphoric acid solution and additives that catalyze self-cleaning processes. Salts of transition metals such as Cu, Mo, Mn, etc. were chosen as catalysts [162].

Thus, to date, a number of techniques are known for detoxification of soil contaminated with CLRF. However, none of these techniques has been selected as a standard. In order to develop an advanced technology for soil treatment from CLRF, it is necessary to consider many factors, such as climate, geography, economy, etc. It is necessary to have a set of methods that would allow more effectively without causing additional damage to the environment and possibly with the least economic costs to perform neutralization of spilled rocket fuel.

1.6. The experience of using novel carbon reducing agents in electrothermal processes

Products of natural or artificial origin, in which carbon is the main component, are widely used in many electrothermal industries [163]. The most important of these are bituminous coal and anthracite.

Scarce and expensive blast furnace coke is mainly used in technological processes of electrothermal production. The need for coke, as a reducing material, has been significantly growing due to the rapid development of electrothermal industries (calcium carbide [164], phosphorus [165], ferroalloys [166]). Industrial inquiries are not fully provided by coke of small fractions [167]. Deficiency of small fractions of coke is acutely felt during the agglomeration of ores, too. Moreover, metallurgical coke by its physicochemical properties is not optimal for the operation of electrothermal furnaces. This is due to low specific resistance and low reactivity of metallurgical coke to metal oxides at the temperatures of the reduction processes [168].

In this regard, there was a demand for organizing the production of cheaper, special and optimal carbon reducers possessing higher electrical resistance and regeneration ability in comparison with metallurgical coke. A number of studies have been devoted to solve this issue [167, 169]. The study [167] reported the data on application of cokes from gas and poorly caking coals for electrical sublimation of phosphorus. Cokes were manufactured at Kemerovo Coke and Chemical Plant using already established technology. However, due to the high content of volatile substances, the coking period of these coals was increased to 10-20%. Furthermore, conventional equipment of coke industry turned out to be unsuitable for coking of poorly caking coal. Therefore, vertical and ring furnaces were required to coke these coals. The physicochemical characteristics of the obtained cokes are presented in Table 4 and compared with the properties of Donetsk coke used in phosphorus furnaces. The authors [167] note that utilizing coke, obtained from gas coals, in modern phosphorus furnaces showed the

suitability of these coke grades for the phosphorus industry. With the absence of deviations from the regulated technological standards all tested coke grades demonstrated a reduction in power consumption and an increase in productivity by 3-5% in practice. The economic efficiency of production has also significantly increased due to low cost of used coke from gas coals.

The advantage of шихты with coke from gas and low-caking coals is the possibility to prepare it on existing coke-chemical equipment. The cheapest coke is the coke made from low-caking coals of 2CC grade prepared in vertical furnaces. The study [170] report the use of inexpensive and special недоменные grades of coke in phosphorus furnaces, and technological parameters of furnaces were as good as above-mentioned ones.

The structure, chemical and granulometric composition of шихты are the most important parameters in the operation of the electrothermal furnace. It is known that the quality of the feedstock, to a large extent, determines the results of the operation of phosphorus furnaces [171]. Carbon materials are of particularly important for electrothermal production: firstly, carbon is the main component of шихты for the vast majority of electrothermal processes; secondly, carbon and graphite electrodes for electrothermics are made from carbon materials; thirdly, products from carbon materials (for example, coal blocks) are used for lining the electric furnaces themselves.

Rare and expensive blast furnace coke is mainly used in technological processes of electrothermal production. Currently, as already noted above [173, 174], the demand for coke, used as reducing material, is not fully provided by coke of small fractions [167]. The supplied large coke is then crushed into small pieces. Deficiency of small fractions of coke is acutely felt during the agglomeration of ores, too. Moreover, metallurgical coke by its physicochemical properties is not optimal for the operation of electrothermal furnaces. This is due to low specific resistance and low reactivity of metallurgical coke to metal oxides at the temperatures of the reduction processes.

In this regard, there is an urgent need to organize the production of inexpensive and special carbon reducing materials of proper dimensions, which have higher electrical resistance and regeneration capability compared to the metallurgical coke [175]. A number of studies have been devoted to solve this issue [167, 169].

The report demonstrated [176] the results of studying the possibility of application of phosphorus, used as a reducing agent for недоменных cokes, in the electrical sublimation process. These cokes were prepared using low-caking gas coals in a continuously operating ring pilot furnace of Nizhniy Tagil Iron and Steel Works. For laboratory studies, cokes were prepared at various coking temperatures (650, 700, 750, 800 °C). The results of studies showed that недоменные cokes were more active reducing agents than blast furnace coke with and without quartzite. With increasing temperature the difference in the degree of recovery of недоменным and blast furnace coke becomes less noticeable.

Experiments with недоменного coke showed that with an increase in the coking temperature the coke activity decreases. However, gas coke obtained even at 800 °C was more active than blast furnace coke. Table 3 shows that coke obtained in the ring furnace has a high reactivity by CO₂ (~ 4.5 times) and greater by УЭС (~ 9 times) than blast furnace coke.

Many authors [177-179] assume the partial briquetting of the feedstock as one of the possible ways of using low-grade coals for electrothermal sublimation processes. Coal briquetting is a mechanical processing of coal dust into lump fuel – briquettes having a certain geometric shape, size and weight. Coal briquettes must have the

sufficient strength, withstand mechanical stress, heat stability, i.e. keep the necessary strength and lump shape in the furnace during combustion.

Table 4

Physico-mechanical characteristics of недоменного and blast furnace coke

Sample	Moisture, mass. %	Ash, mass. %	Volatile, mass. %	Structural strength, %	Porosity, %	Reactivity, cm ³ /(g·s)	Electrical resistivity, Ω·cm
Недоменный coke	2.0	12.5	2.2	68	52.0	1.95	0.72
Blast furnace coke	-	-	-	82.9	40.0	0.45	0.08

Briquetting is based on the properties of friable and dust like materials being compacted and harden under the pressure. There are two methods of coal briquetting: compressed without binders at high values of pressure (above 78.4 MPa) and with the addition of a binder at low (14.7-24.5 MPa) pressures. Despite the fact that the technology of coal briquetting was developed at a sufficiently high engineering level, there is no single generally accepted theory of the mechanism of briquette formation, but only a number of hypotheses [180]:

- *the bitumen hypothesis* explains the formation of briquettes by gluing action of bitumen contained in coal;

- *the humim-acid hypothesis* describes the briquetting mechanism by the presence of free humic acids in the coal, which are substances extracted from coal using aqueous solutions of caustic alkalis and ammonia;

- *the capillary hypothesis* considers brown coal as a solidified colloidal substance (gel) having numerous capillaries filled with water: under the influence of pressure part of the primary capillaries of coal grains breaks up, and gaps between these channels (secondary capillaries) filled with water, causing the appearance of capillary adhesion forces, i.e. briquetted material must have a certain moisture content;

- *the colloidal hypothesis* explains the formation of a briquette by the action of molecular adhesion forces (Van der Waals forces);

- *V.M. Naumovich hypothesis of molecular adhesion* describes the reason for the particle bonding by the phenomenon of molecular sticking due to close contact under the pressure, while capillary-condensed moisture weakens the adhesion forces between the particles.

The last two briquetting hypotheses are more applicable to coals of a low degree of metamorphism, which have a developed capillary structure and are solid colloids – gels of humic substances.

In all phosphorus plants that have the most progressive performance indicators, great attention is paid to the quality of raw materials for powering electric furnaces and preparing them for production (for example, Pisteritsky plant, Germany) [181].

Karatau Basin is the largest phosphorite deposit and the main raw material base of the phosphorus industry. There are more than 30 different phosphorite deposits of which the biggest is Zhanatas deposit. Zhanatas deposit is characterized by the presence of several stratum of phosphate-containing rocks. In a typical cross-section of the deposit

there are 4 layers present: phosphate-siliceous, lower phospharite, phosphate-shale, upper phospharite.

Thanks to numerous studies, a rule for determining the suitability of ores by chemical composition for electrothermal processing was established:

$$[P_2O_5] ([CaO] + [MgO]) \geq \alpha \quad (4)$$

The value α is determined by the level of energy consumption and has 0.5–0.56 values at various plants.

In addition to the main components, phosphorites contain small amounts of alkaline oxides, sulfur compounds, organic substances, heavy and rare metals, which has a significant effect on the quality of phosphorus.

However, the data on the chemical composition of phosphorites is not sufficient enough. The same P_2O_5 content in the mixture could be achieved by different combinations of lithological components of ores (shale, sand gravelite, дайки диоритовой, etc.). During heating these rocks exhibit a different tendency to sintering, cracking and crushing. In this regard, due to the same P_2O_5 content in the feed, phosphorites behave differently in the furnace, therefore, the furnace performance and the yield of phosphorus are different.

Based on the analysis of the operation of powerful phosphorus furnaces, an equation was produced to calculate the productivity:

$$Q = S \cos \cdot K_M \cdot K_B T / w, \quad (5)$$

where S is the maximum power of furnace K_B -A; $\cos$ is the coefficient of furnace power; K_M – coefficient of maximum power consumed from the network; K_B – coefficient of the use of furnace working time; w – the specific power consumption; T – actual work hour.

From this formula it follows that the productivity of the furnace is determined by the ratio of K_M - K_B / w .

The dependence of w on the chemical composition of the feedstock was obtained theoretically and was repeatedly tested on industrial furnaces. The determining factor for the value of w is the ratio:

$$C = \frac{1,33[CaO] + 1,06([CaF_2] + [MgO]) + 5,59[CO_2] + 1,94[Fe_2O_3] + 6,8[H_2O]}{0,943[P_2O_5] - 0,556[Fe_2O_3] - 0,336} \quad (6)$$

The dependence of K_M and K_B on the composition of raw material could not be simply presented, because in this case, not the chemical, but the mineralogical composition of the raw material is important. For feedstock that prone to sintering, the gas-dynamic mode is disturbed, heat transfer processes is deteriorated, the temperature of the exhaust gases is increased. These factors lead to the need to reduce the power, i.e. decrease K_M . In that case, when the dust generation increases, between cleaning the electrostatic precipitators, the furnace run time decreases, i.e. K_B decreases. There are other possible reasons leading to a decrease in K_M , K_B and due to mineral composition of the feedstock. To assess the technological properties of the feedstock, it is recommended to determine the temperature T of liquid phase appearance and the temperature of complete melting T_2 . The minimum value of T_2 and the maximum value

$(T_2 - T_1) = DT$ correspond to the raw material of poor quality, for instance, shale's harmful effect on the furnace process has been practically proven.

The task of the feedstock preparation process is to meet the requirements on chemical, granulometric and phase composition of the raw material which applied by the electrothermal process. In the process of preparation carbonates and hydrates are decomposed and the organic part of шихты is removed.

There are two known methods of granulating small pieces – rounding and agglomeration. In the first case, the raw material is crushed and rolled on rotating plates by supplying water or a suspension of clay, boiler milk as binder.

During agglomeration, the starting material is phosphorite dusts with the size of less than 5-10 mm, which is mixed with coke powders and is fed onto a moving belt.

For normal furnace operation, it is necessary that the phosphate part of шихты should fulfill the following requirements: CO_2 content – less than 2%; H_2O – less than 1%; sizes of pieces, maximum – 50 mm; minimum – 5-10 mm. The temperature of the complete melting T_2 , K – more than 1620; the melting temperature range K – 150.

Quartzite must be dried and sieved before loading into the oven. The size of quartzite particles is 50-10 mm, however, large pieces should be eliminated, because quartzite is high-melting substance, its transition to a melt is associated with its dissolution, the speed of which depends on the size of the particles. Coke is also dried, crushed and sieved from small parts – 3 mm. Coke particles with less than 3 mm in size do not react with a phosphate-siliceous melt, but float on it, leaving the furnace with slag.

When preparing шихты, the dosage of coke and quartzite per unit mass of phosphorite is usually calculated [181].

The ratio of quartzite consumption K_{KB} to the consumption of phosphorite Φ in the шихте is equal to:

$$\frac{K_{KB}}{\Phi} = \frac{Mk([CaO] + [MgO]) \phi - ([SiO_2] + A_{12}O_3)}{([SiO_2] + [A_{12}O_3])_{KB} - Mk([CaO] + [MgO])_{KB}} \quad (7)$$

Coke consumption is calculated based on the carbon consumption required for the reduction of P_2O_5 , Fe_2O_3 , CO_2 , H_2O , S.

The total consumption of coke per unit mass of phosphorite:

$$\sum C / (\phi + K_{KB}) = 0,401 [P_2O_5]_{ш} + 0,18 [Fe_2O_3]_{ш} + 0,218 [CO_2]_{ш} + 0,6 [H_2O]_{ш} + 0,38 [S]_{ш} \quad (8)$$

Coke consumption:

$$K / (\phi + K_{KB}) = \sum C / Ca \cdot 103, \quad (9)$$

where C is the content of active carbon in coke.

Due to possible unaccounted loss coke, the calculated value increases by 3-5%.

To improve the technical and economic indicators of Karatau phosphate rock recovery in ore-heating furnaces, it is necessary to enhance ore preparation, introduce ore enrichment, sort by size and averaging of the composition. Deviations in the content of P_2O_5 between ore batches going into production should not exceed 0.5-3.0%.

The degree of extraction of phosphorus from ore is one of the main indicators of furnace performance. It depends on the content of phosphoric anhydride in the mineral part of шихты, on the rate of шихты loss, or in other words, on the residence time of

шихты components in the reaction zone, on the ratio of carbon and reduced oxides in шихте, on the granulometric composition of шихты, on the temperature in the reaction zone as well as on the electrochemical parameters of the reducing agent used.

In the production of silicon-containing ferroalloys (ferrosilicon, ferrosilicomanganese, ferrosilicochrome, ferrosilicocalcium, crystalline silicon, etc.), the source of silicon is quartzite, which is reduced by solid carbon of metallurgical coke to silicon in the presence of steel chips or various metal-containing ores [174]. The recovery proceeds through a complex scheme and a number of intermediate products are formed during the process. Under equilibrium conditions, the formation of SiO occurs in the temperature range of 1027-1689 °C mainly due to the interaction of condensed silica with carbon monoxide:



In the same temperature range at 1027-1483 °C the reactions proceed:



At 1483 °C, condensed carbon is disappeared and condensed silicon carbide is formed. While, at temperature range of 1483-1689 °C:



At 1689 °C, condensed silica is disappeared, and condensed silicon is formed (equation 14). At 1689-2027 °C, condensed silicon carbide and silicon remain in the equilibrium system.

When iron (manganese or chromium, or their mixtures) is present in the system, silicon intensively dissolves in them and quickly eliminated from reaction zone [174]. Silicon carbide is destroyed by liquid metals:



or with liquid silica by reaction:



The process of reduction of silica by carbon proceeds with the formation of intermediate products of SiO and SiC. Therefore, an important technological task is to provide favorable physicochemical conditions, in the ore reduction ferroalloy electric furnace, for the formation not only SiO and SiC, but also for easy implementation of the subsequent stages of their reduction to silicon with a minimum loss of silicon due to the escape from the furnace in the form of SiO and Si [164].

In real conditions of the production of high-percentage ferrosilicon in powerful open and closed electroferroalloy furnaces, these processes have direct link to such factors as the optimal size of шихтовых materials, gas permeability and electrical resistivity of

шихты. The physicochemical and electrical properties of carbon reducing agents are also of particular importance. Upon smelting ferroalloys in ore-reducing electrical furnaces mainly metallurgical coke of 10-25 mm grades, or after crushing, 25-40 mm grades is used as a carbon reducing material. In some cases, small amount of coal with different grades are added to coke.

This coke does not fully satisfy the requirements for carbon reducers used in electric furnaces, since it has low electrical resistivity and low reactivity to metal oxides at the temperatures of the reduction process. Nevertheless, the required deep electrode placing in шихте, maintenance of a high specific power in the reaction zones and rapid progress of the reducing reaction are not ensured. Due to the fact that blast furnace production, which is the main consumer of coke, imposes high demands on the mechanical properties and structure of coke, it becomes less reactive, more dense and electrically conductive, i.e. its properties are declined with respect to ferroalloy production [182].

The highest value of reactivity with respect to SiO_2 is charcoal – 97%, metallurgical coke – 62-68%. A special pilot coke, prepared to melt ferrosilicon, composed of a mixture of low-grade metamorphosed coals (gas and long-flame) has a reactivity of about 80%, which is a good value.

The second important requirement for the carbon reducing material, used in the production of ferroalloys in electric arc furnaces, is its high electrical resistivity at high temperatures up to 1500 °C. The higher the electrical resistivity of the carbon material, the greater secondary voltage (at a constant power strength in the electrodes) and it is possible to conduct electric melting. Providing the opportunities to conduct the process of smelting ferroalloys at high secondary voltages leads to prospect of creating three-phase furnaces of sufficiently high power – up to 50-100 thousand $\text{kV}\cdot\text{A}$.

The electrical resistance of ferroalloy шихт, to a great extent, is determined by the quality and quantity of the reducing agent (in particular, coke) than by other factors (the dimension of шихтовых materials, the amount of dust, properties and ratio of materials composing ore parts of шихт, etc.). In practice work of furnaces in the production of carbothermic ferroalloys shows that relatively small changes in the amount of coke in шихты composition lead to a significant change in its electrical resistance and, as a consequence, to a disruption of the electrical regime (change in secondary current and voltage). This, in turn, requires immediate adjustment of шихты or the choice of a new electric mode to prevent disruption of the smelting process [174]. In other words, a well-defined electric mode (secondary current and voltage) corresponds to a certain amount of coke of the same alloy in шихте, providing its most efficient melting. From this point of view, the quantity of the reducing material may serve as a distinctive to шихты and could be adjusted in its composition on existing furnaces with their optimal electric modes. A qualitative criterion of such peculiarity is the electrical resistance of шихт.

Experimental studies [183] of a number of physical characteristics of shungite rock and features of its recovery of silicon were conducted with the aim of a comparative assessment of the possibility and effectiveness of using such shungite rocks as a complex шихтового material in the production of simple and complex siliceous ferroalloys. Karelia's shungite rock (comprising of 50.5% silica and 33.5% carbon) was analysed in laboratory, semi-industrial, and pilot industrial scale for smelting ferrosilicon, silico-manganese, and ferrosilicoaluminum [170]. The experimental шихта for smelting ferrosilicon had the following composition: 45 kg shungite rock, 10 kg quartzite and 20 kg steel shavings. For comparison, a conventional шихта was prepared consisting of quartzite, coke and steel shavings of 50, 24 and 20 kg, respectively.

Smelting of ferrosilicon using both types of шихтовок was carried out in one electric mode at a current value of 1300–1400 A and voltage of 25–30 V. The obtained results of smelting of 45% ferrosilicon showed that the use of shungite rock facilitated daily productivity of the furnace and a decrease in the specific power consumption. The same result was observed in the case of smelting 75% ferrosilicon..

Similar tests [183] were also conducted in a semi-industrial furnace with a transformer capacity of 1200 кV·А. Шихтовые materials used in experiments (coke, quartzite, steel shavings) had standard chemical composition; shungite rock used in laboratory conditions had different chemical composition and contained 58.5% silica, 32.3% carbon and 3.63% alumina. The fractional composition (working fraction) of шихтовых materials was adopted as follows: quartzite 5-40 mm, coke 5-20 mm and shungite rock 5-40 mm.

Application of shungite rock, due to the increased silica content in the rock, made it possible to reduce quartzite content in the experimental шихте, the composition of which was as follows: shungite rock 100, quartzite 18, steel shavings 36 and 10 kg. Standard шихта was composed of quartzite 90, coke 15-46, steel shavings 40 and 9 kg. A smaller amount of steel shavings (10 and 9 kg) corresponds to шихте containing 75% ferrosilicon.

It was not possible to conduct smelting of ferrosilicon using shungite rock under conditions in which conventional шихта was melted, due to a sharp temperature increase in колошника, which led to sintering of шихты into a viscous aggregation. Comparison of smelting indicators of both grades of ferrosilicon according to two ways of шихтовок reveals that, when coke is completely replaced and 80% quartzite is substituted with shungite rocks, furnace productivity increased and specific energy consumption decreased [174].

The study [183] reported conducting a pilot industrial smelting of 45% ferrosilicon using shungite rocks of grade III with a gradual increase in the amount of shungite rock in шихты. Pilot batch of shungite rock had an average carbon content of 29.3%, silica 58.6%, alumina 3.9%, and the other – impurities. The technological fraction of shungite rock was accepted as 8-60 mm. However, upon preparing such technological fraction of shungite rock (from the initial 0-1000 mm feedstock), small fractions were formed on existing equipment: less than 6 mm (3.6%), 6-25 mm (48.7%), more than 25 mm (47.7%).

The smelting options for 45% ferrosilicon in шихтах of the following composition (kg) were compared:

	I	II	III	IV
Quartzite	300	300	300	200
Coke (20% humidity)	170	160	150	100
Shungite rock	-	51	102	342
Steel shavings	190	200-210	230	235-240

Pilot-industrial testing revealed that shungite rocks have good metallurgical properties. However, the process of ferrosilicon smelting is very sensitive to the growth of small fractions of шихты, which occurred when the content of shungite rock was increased in шихте. As a result, the process declined and there was a decrease in furnace performance [170, 183].

1.7. Prospects

Thus, an analysis of the scientific, technical and patent literature presented in this monograph shows that in recent years some progress has been achieved in the study of carbon-containing mineral raw materials, industrial wastes and the use of materials obtained on their basis in different fields, including for environmental purposes. Although, the issue of the mechanisms and technological principles of the use of natural and technogenic carbon-containing raw materials in the preparation of effective sorbent-catalysts for soil decontamination from components of rocket fuel, treatment of wastewater from ions of heavy metals and organic compounds, in the production of composite materials is still not well studied. By changing the technological parameters for the preparation of carbon-containing materials and considering the structural characteristics of shungite-containing materials, it is possible to construct the structure of carbon-containing composites of different purposes.

The topic about discovering novel materials – reducing agents for electrothermal production has remained very relevant for many years. Moreover these kind of studies are carried out both in CIS countries and in other foreign countries. There are essential results, for instance, on the use of special cokes from gas and low-caking coals for electric sublimation of phosphorus. Particular attention should be paid to the studies on the behavior of Karelian shungite rocks used as a complex шихтового material for electrothermal processes due to the fact that in 1970s, a mineral similar to shungite was discovered in the black shale stratum of the Eastern Kazakhstan [184]. However, until now, Kazakhstani shungite rocks have not found wide practical application.

The literature [36] reports a study of local shungite rocks of “Bolshevik” deposit conducted for the first time, in comparison with industrial carbon black in order to use them as a substitute to the latter upon filling composite materials. The authors [185] established that shungite rocks with a high carbon content (40÷50%) are more active fillers of elastomeric composite materials compared to low-carbon rocks and even industrial soot. It was shown the possibility of using Kazakhstani shungite rocks, as an alternative to carbon black, in the production of composite materials without modifying the technology and with the prospect of enhancing the physical and mechanical properties of finished products.

However, in the literature information about the industrial application of shungite rocks as a reducing raw material for electrothermics, as fillers for composite materials was not found, although there are prerequisites for studies in this direction [186]. In addition, scarce and high cost of blast furnace coke as well as a rapidly growing demand on carbon reducing agents both worldwide and nationwide, require the construction of installations to produce недоменных cokes from non-deficient and cheap raw materials. Considering that our country has reserves of unique and cheap shungite rocks that are sufficient for industrial use, it is therefore particularly interesting to study their behavior in technological processes when combined with carbon-containing raw materials.

In this regard, the team of authors chose the direction of study, the objective of which is to establish the physicochemical basis of formation of carbon-mineral systems based on wastes from the mining industry as well as carbon-containing raw materials found in the ore to identify patterns of morphology and microstructure of carbon-containing sorbents, reducing agents for ore-thermal production and fillers for composite materials.

CHAPTER 2 METHODS OF STUDY AND CHARACTERIZATION OF RAW MATERIALS

2.1. Characteristics of raw materials and reagents

The solution to the problem of finding rational ways to use any material starts with a detailed study of the material itself.

A team of authors studied black shale shungite rocks of “Bolshevik” polymetallic mine, Shar district, the Eastern Kazakhstan oblast. The study of the composition, structure of rocks and carbon content allows to determine the place of Kazakhstani shungite, “Bolshevik” deposit due to different forms of carbon, to establish its geochemical characteristics and to determine the ways of its use in technological processes.

Predicted amount of shungite resources at Bolshevik deposit, according to geological estimates of CJSC “Artel Trud”, is more than 30.0 million tons. To study the chemical and mineralogical compositions, 500 samples were taken in various directions of the southeastern horizon of the non-metallic side and averaged to 11 point, the opposite place of industrial production of polymetallic ores, at different heights of deposits. In addition, the following were used: metallurgical coke (GOST 18686-73); coal tar pitch (GOST 10200-73, Barnd A); resin (GOST 4492 69); liquid glass; kerosene; pine oil; 1,1-dimethylhydrazine, concentration of the main substance 1 mg/mL GOST (ЭАА «Экоаналитика», Russian Federation); HCl (GOST 3118-77); NaOH (GOST 4328-66); H₂SO₄ (GOST 4204-77); MnO₂; FeCl₃ 6H₂O (GOST 4147-74); phosphorite (GOST 6-19-25-744); quartzite (SiO₂ no less than 95%); NaOH (GOST 4328-66); HNO₃ (GOST 4461-77, ch.p.); HF (GOST 10484-77, ch.p.); HCl (GOST 3118-77, ch.p.); H₂SO₄ (GOST 4204-77, ch.p.); distilled water (GOST 6709-72)

2.2. Physico-chemical properties of shungite rocks and concentrates

2.2.1. Determination of the composition of shungite rocks

The chemical composition of shungite rocks was determined according to the general silicate analysis [187]. Samples were preliminarily abraded and dispersed through a 05 sieve. A fraction of 0.5 mm was used for analysis.

A sample of the test material with 0.5 g was melted by fusion in a platinum crucible with sodium carbonate at 850 °C for 30 min. In the resulting solution, silicon dioxide (SiO₂) was determined by a gravimetric method [188].

The precipitate on the filter was ashed, calcined to constant mass at 900 °C, weighed and analyzed for purity by distillation of silicic acid. Silicon dioxide content was calculated by the difference between the mass of the crucible with the precipitate and silicic acid and the mass of the crucible after distillation of silicic acid.

The determination of iron and aluminum content was carried out sequentially in a solution, obtained after dissolving the oxide precipitates, isolated from an aliquot (100 cm³) of the stock solution using complexometric technique at different pH values [188].

The determination of aluminum is based on the reverse titration of Trilon B solution that added to a solution in excess (in which iron (III) was titrated) with a solution of zinc salt with an xylene orange indicator at pH = 5.

In some samples, iron and aluminum were determined using complexometric titration technique [189].

Titanium was determined using colorimetric visual titration. The principle of this method is to compare the color of a solution formed by adding 3% hydrogen peroxide to a dilute sulfuric acid solution of the test substance with the color of titanium sulfate standard solution.

Calcium and magnesium were determined in the course of silicate analysis in the filtrate after elimination of silicic acid.

Potassium and sodium were determined from individual samples using flame photometry [190]. Organic carbon content was determined using previously reported protocol [190].

The total water content was determined using Brush-Penfield technique [188]; the errors in the determination of all quantitative characteristics by chemical analysis method did not exceed $\pm 2\%$.

The content of C, H, O in shungite was determined using elemental analysis [191].

The percentage content of carbon (X_C), hydrogen (X_H), sulfur (X_S) and mineral residue (X_{MO}) were calculated based on the weight gain of the absorbing devices and the mass of the undecomposed residue using the formulae:

$$X_C = \frac{0,2729 \times b \times 100}{a}, \quad (17)$$

$$X_H = \frac{0,1119 \times c \times 100}{a}, \quad (18)$$

$$X_S = \frac{0,3338 \times d \times 100}{a}, \quad (19)$$

$$X_{MO} = \frac{e \times 100}{a}, \quad (20)$$

where a – weight of sample, mg;

b – weight of CO_2 , mg;

c – weight of H_2O , mg;

d – weight of SO_4^{2-} , mg;

e – weight of ash, mg.

Errors determined by this method amounted to: for C – ($\pm 0.5\%$); for H – ($\pm 1.0\%$); for S – ($\pm 0.5\%$).

2.2.2. Determination of the heat of combustion

Combustion heat values were determined using a protocol described in [192]. The tests were conducted using a B-08MA calorimeter with a special mercury thermometer of constant filling.

The combustion heat value in the bomb of the test analytical sample (Q^a_{θ}) in J/kg was calculated using the formula:

$$Q^a_{\theta} = \frac{c \cdot K[(n_2 - \Delta n_2) - (n_1 + \Delta n_1) + \Delta n] - m_1 q}{m} \quad (21)$$

where c – heat capacity of the calorimetric system determined according to the instructions (GOST 8.219-76), J/°C;

K – thermometer scale interval, °C;

n_1 – thermometer reading corresponding to the initial temperature of the main period in the divisions of the thermometer scale;

Δn_1 – correction to a thermometer readings for gauge (when reading the thermometer n_2) in the scale divisions;

N_2 – thermometer reading corresponding to the final temperature of the main period in divisions of the thermometer scale

Δn_2 – correction to a thermometer readings for gauge (when reading the thermometer n_2) in the scale divisions

Δn – correction to a thermometer readings, considering the heat exchange of the calorimeter with the environment in divisions of the thermometer;

m_1 – weight of a wire taken for ignition, kg;

q – heat of combustion of a wire for ignition J/kg;

m – weight of a test fuel sample, kg.

Maximum heat of combustion of an analytical sample (Q_s^a), J/kg, was calculated using the equation:

$$Q_s^a = Q_o^a - (\beta S_o^a + \alpha Q_o^a) \quad (22)$$

where Q_o^a – heat of combustion in a bomb of the analytical fuel sample, J/kg;

β – a coefficient, considering the heat of formation of sulfuric acid from sulfur dioxide and the dissolution of this acid in water, that numerically equal to $94 \cdot 10^3$ J per 1.0% sulfur, converted to sulfuric acid during fuel combustion in a calorimetric bomb;

S_o^a – weight of sulfur converted to sulfuric acid during fuel combustion in a bomb, calculated for the analytical fuel sample test

α – a coefficient, considering the heat of formation and dissolution of nitric acid in water, equal to 0.0015 (for testing shale and peat)

Minimum heat of combustion of a working sample (Q_n^p) and a calorific value of a combustible mass (Q_n^c) in J/kg was calculated using:

$$Q_n^p = Q_o^p - \gamma(W_{\text{общ}} + 8,94 \cdot H_{\text{общ}}), \quad (23)$$

where Q_o^p – maximum calorific value of the working fuel, J/kg;

γ – 24.62, coefficient for expressing analysis results in kJ/kg;

$W_{\text{общ}}$ – total humidity, % mass.;

$H_{\text{общ}}$ – total hydrogen, % mass.

and

$$Q_n^c = Q_o^c - 8,94\gamma \cdot H^c, \quad (24)$$

where Q_o^c – maximum calorific value of the combustible mass, J/kg;

H^c – flammable hydrogen, % mass.

2.2.3. Determination of the reactivity

The determination of the reactivity was carried out according to a methodology described in the literature [193].

Реакционную способность исследуемых углеродных брикетов, вычисляли по формуле The reactivity of carbon briquettes (K), in $\text{cm}^3/(\text{g} \cdot \text{sec})$, was calculated using the formula:

$$K = \frac{V \cdot T}{m \cdot T_1} \cdot R, \quad (25)$$

where V – CO_2 feed rate, cm^3/sec ;

T – test temperature from test thermocouple readings, K;

T_1 – temperature of CO_2 supplied to the reaction tube, K;

m – mass of carbon in a sample of carbon briquette, is calculated using the equation:

$$m = m_1 \cdot \frac{(100 - A^d)}{100} \cdot \frac{C^{daf}}{1000}, \quad (26)$$

where m_1 – weight of carbon briquette sample, g;

A^d – ash content of the test sample, % mass.;

C^{daf} – dry ash-free carbon content, % mass. (when data is not available, C^{daf} is taken equal to 98%);

R – the degree of conversion of gas-reagent, calculated using the formula:

$$R = 2 \ln \frac{1}{1-r} - r, \quad (27)$$

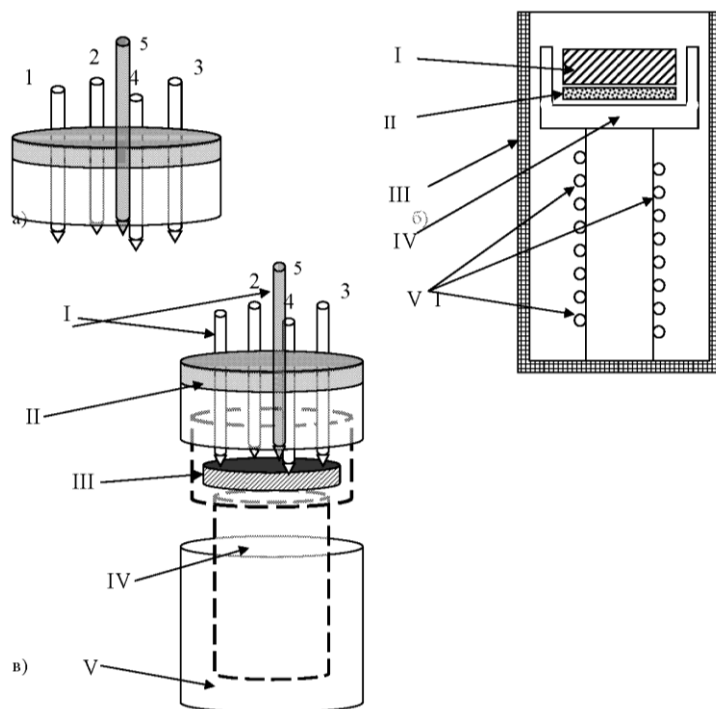
$$r = \frac{CO}{CO + 2CO_2}, \quad (28)$$

where CO and CO_2 – the content of carbon monoxide and carbon dioxide in the reaction products during the analysis, %.

The discrepancies between the results of three parallel determinations, for one sample, did not exceed $0.02 \cdot 10^{-3} \text{ m}^3/\text{kg} \cdot \text{sec}$.

2.2.4. Determination of electrical resistance

The resistance of the finished shungite briquettes was measured according to the report [194].



Измерительная головка (а): 1-4 измерительные зонды, 5 – термопреобразователь; печь с исследуемым образцом (б): I – исследуемый материал, II – изоляционный материал, III – алундовый стакан, IV – медная камера, V – электронагреватель; общий вид установки (в): I – измерительные зонды (1,2 – токовые; 3,4 – потенциальные, 5 – термопреобразователь), II – крышка зондовой головки с фиксаторами, III – исследуемый материал, IV – медный стержень с электронагревателями, V – алундовый стакан.

Figure 5 – Schematic illustration of an apparatus for measuring the electrical resistance

We have implemented a four-probe method for measuring the resistivity of shungite briquette samples pressed in the form of tablets. For this purpose, an installation for measuring the resistivity of materials was constructed, which consisted of a power source, measuring instruments, a switching device, a vacuum station, and a probe (Figure 5).

The probe head is made from a polytetrafluoroethylene plate with a fiberglass base reinforced on it. Metal needles (probes) were attached to the probe head, which by means of a clamping device pressed with 0.08-0.12 N force, were pressed to the test sample along the vertices of the square with 1 cm sides (Figure 5 a, в). A current was passed through a pair of contacts No.1 and No.4 and voltage was then measured between the other two contacts (No.2 and No.3).

The probe material is made from a copper capillary with a diameter of 1.53 mm and a length of 43-45 mm with pressed platinum needles of 0.5 mm diameter.

The current was set using B5-37 device, which had an output voltage adjustment from 0.1 to 29.9 V with an increment of 0.5 V.

The current value was monitored using a Ц4354 M-1 device. The voltage on the current contacts of the probe head was monitored using the B5-37 device. Both devices have an input resistance about 5-10 MΩ, which allows us to neglect the measurement error from the devices used.

Temperature dependent resistance of the samples was measured in the range of 20-900 °C. The samples were placed in an electric resistance furnace (Figure 5, 6), which was placed in the chamber of the vacuum station (the pressure applied was 10^{-2} Pa). Resistance measurements were performed with a rise in temperature.

It should be noted that in our installation the thermocouple was supplied through the upper hole of the probe holder directly to the tabulated sample, but not to the furnace, which allowed us to fix the temperature directly on the surface of the briquette in contact region with the probes (Figure 5, б).

Measurements for each sample were carried out at least three times, and in each experiment, the probe head was cross-connected to conduct measurements all combinations of connection.

The resistance was calculated using the formula:

$$\rho = \frac{U}{I} \cdot \frac{S}{L} \quad (29)$$

where ρ – resistivity, $\Omega \cdot \text{cm}$;

U – voltage, V;

I – current strength, A;

S – cross-sectional area, cm^2 ;

L – sample length, sm.

The error in measuring the electrical resistance of the samples was $\pm 4 \%$.

2.2.5. Determination of density and porosity

The effective (ρ_s) and apparent (ρ_k) density of shungites was determined according to the methodology described in [192] using the pycnometric technique in a 25 cm^3 glass pycnometer.

During the analysis, the following parameters are measured::

K – pycnometer constant, i.e. toluene mass in a pycnometer filled up to the mark, g;

M_n – weight of the sample, g;

M_1 – weight of the sample with toluene after filling the pycnometer with pycnometric fluid up to the mark, g;

M_2 – weight of the sample with toluene after complete impregnation with liquid and bringing the latter up to the pycnometer mark, g.

All measurements were carried out in a YT-15 thermostat at 20 °C. To remove air from the sample and the pycnometric fluid, the filled pycnometer was heated up to 100 °C (close to boiling point of toluene, $T_k = 110,6 \text{ °C}$), then it was thermostated at 20 °C.

The pycnometric (ρ_s) and apparent (ρ_k) densities were calculated using the following equations:

$$\rho_s = \frac{M_n}{K + M_n - M_2} \times \rho_m, \quad (30)$$

$$\rho_k = \frac{M_n}{K + M_n - M_1} \times \rho_m. \quad (31)$$

Using the obtained ρ_s and ρ_k values, the following structural characteristics were determined: effective porosity (Π_s), specific effective pore volume (V_s):

$$\Pi_{\vartheta} = \left(1 - \frac{\rho_{\kappa}}{\rho_{\vartheta}}\right) \times 100\%, \quad (32)$$

$$V_{\vartheta} = \frac{1}{\rho_{\kappa}} - \frac{1}{\rho_{\vartheta}} = \frac{\Pi_{\vartheta}}{100\rho_{\kappa}}. \quad (33)$$

Determination errors were: for ρ_{ϑ} and ρ_{κ} – ($\pm 0,5\%$); for Π_{ϑ} and V_{ϑ} – ($\pm 1\%$).

2.2.6. Determination of the material composition of shungite by thermal analysis

Thermal analysis was conducted on a derivatograph of system “Paulik F. - Paulik J. - Erdey L.” system (Hungary). Four curves were simultaneously recorded: temperature (T), thermogravimetric (TG), differential thermal (DTA) and differential-thermogravimetric (DTG) [195].

The determination of the qualitative composition of the rocks was carried out according to the temperature of thermal effects [196].

2.2.7. Analysis of shungite carbon using Raman scattering technique

The Raman spectra of the shungite carbon samples were recorded on a “Ramanor HG.2S” laser spectrometer (Jobin Yvon, France) in reflection from the surface of the pressed tablets during the sliding incidence of the laser beam (Figure 6).

Возбуждение комбинационного рассеяния света осуществлялось синей линией аргонового ионного лазера ИЛА-120 фирмы Karl Zeiss (Германия) с длиной волны $\lambda_{\text{возб}} = 488$ нм. Мощность излучения на линии составляла 200-300 мВт. Поляризация лазерного луча была линейной, а направление поляризации менялось при необходимости с помощью полуволновой пластинки.

Excitation of combination scattering carried out using a ИЛА-120 argon ion laser the blue line (Karl Zeiss, Germany) at a wavelength of $\lambda_{\text{excitation}} = 488$ nm.

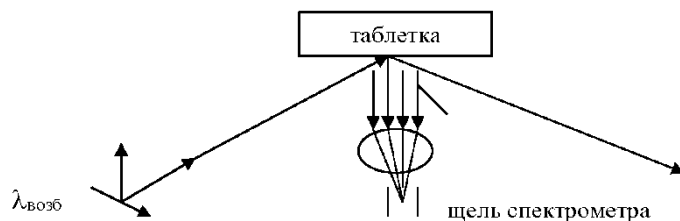


Figure 6 – Light path

2.2.8. X-ray analysis

X-ray diffraction analysis was performed on a ДРОН-1,5 X-ray diffractometer (CuK_{α} radiation, Ni – filter) using an ПП-14М electronic computing device and modernized collimation [197]. The use of these tools allowed to free the diffraction spectrum, especially in the small-angle region, from “parasitic” radiation while preserving the considerable light intensity of the device, which is very important when researching amorphous objects.

To reduce the effect of anisotropy and standardization of the testing conditions, the samples were exposed to reflection in a metal cuvette with a working volume of $17 \times 17 \times 1,5 \text{ mm}^3$. The registration of X-ray diffraction patterns in the range of θ angles from 4° до 30° was carried out in the continuous scanning mode with the scattering curve recorded on a diagram tape. The X-ray recording mode was selected depending on the mineralogical composition of the samples: voltage on the anode of the X-ray tube was varied from 28 kV to 36 kV, current strength was varied from 9 mA to 17 mA.

Processing the diffractogram that include the decomposition of a complex maximum, was carried out using iteration method according to [197]. X-ray quantitative phase analysis was used to determine the content of components by intensities values of the corresponding reflexes with an error of determination about 3-5% [198].

The interlayer distance d_{002} (nm) was determined using the Wulf-Bragg equation:

For shungite carbon, the following X-ray parameters were determined: interlayer distance d_{002} , degree of grafitization C_z , sizes of the areas of coherent scattering of L_a and L_c along the crystallographic axes a and c .

$$d_{002} = 0,0771 / \sin 2\theta_{002}, \quad (34)$$

where θ_{002} – reflex scattering angle (002).

The degree of grafitization C_z was calculated using the following formula:

$$C_z = \frac{L_c \times 10^{-2}}{d_{002} - 3,35}, \quad (35)$$

where L_c – average package thickness;

Вычисление размеров областей когерентного рассеяния L_{hkl} проводили по формуле [197]. Selyakov-Scherrer equation was employed to measure the apparent sizes of the coherent scattering regions. The sizes of the coherent scattering regions L_{hkl} was calculated using the formula:

$$L_{hkl} = \frac{K\lambda}{\cos\theta \sqrt{\Delta_{u3}^2 - \Delta_g^2}}, \quad (36)$$

where $K = 0,9$ – for basal reflections $00l$ and $K = 1,8$ – for hkl reflexes;

λ – X-ray wavelength;

θ – Bragg angle;

Δ_{u3} – value of the half-width of the reflex;

Δ_g – instrumental correction obtained during testing reference substances.

2.2.9. Study of the structure of shungite using electron microscopy

Electron microscopic images were taken on a Quanta-3D-200i scanning electron microscope in the National Nanotechnological Laboratory of the open type of Al-Farabi Kazakh National University. Shungite in the rock was studied using microdiffraction methods on single-stage carbon replicas with extraction. Fresh chips were prepared on the samples, on the surface of which a coal replica was sprayed. The replica was

removed mechanically with a heated solution of gelatin (gelatin concentration ~ 20,0%), followed by dissolution of gelatin in hot water. Microdiffraction pictures were then taken from the extracted particles.

2.3. Determination of fullerene clusters in shungites

The experiments to determine the presence of fullerenes in shungite rock were carried out according to a methodology described in [199]. The extraction of fullerenes was performed via solvent extraction in two ways:

a) Extraction with toluene using ultrasonic unit УД-1.

20 g of test sample was put into a 250 cm³ conical flask. Then, 5 mL toluene per 1 g of dry matter was poured into the flask and the solution was magnetically stirred. Then the flask was covered with a glass and placed in an ultrasonic bath and then sonicated for 1 h at 55±5 °C with ultrasonic vibration frequency of 2640 kHz.

Then the solution was allowed to settle. A large part of the sediment was separated via decantation. The solution was filtered through a “blue ribbon” ashless filter paper (tightly folded in 4 layers) on a Buchner funnel under the vacuum. The precipitate was washed several times with a small amount of toluene, filtered, and the filtrate was combined with the main part of the filtered solution. The extract was concentrated by evaporation of the extractant under the vacuum to a volume of ~ 8 cm³.

б) Extraction with xylene on a Soxhlet apparatus.

A Soxhlet apparatus was assembled and installed on a sand bath. 100 g of the extractable substance was wrapped in filter paper, tied with a thread, introduced into the extractor and then the solvent was pored. The extraction was carried out for 24 hours. Afterwards, the extractant was distilled off in the usual way, and the solution with the extract with a volume of ~ 20 cm³ was transferred into a specially prepared vessel.

The determination of fullerenes in prepared solutions by above-described methods was carried out using IR-spectroscopy in the wavelength range from 400 to 4000 cm⁻¹. Analysis was performed using KBr cuvettes. At the same time, IR absorption spectra of pure solvents were recorded. The presence of fullerenes was established by comparing the IR spectra of the studied solutions with the spectra of solvents.

2.4. Determination of physico-chemical characteristics of shungite concentrate used as a filler of composite materials

The pH values of the aqueous shungite suspension were determined according to the report in [188].

The absorption of dibutyl phthalate was determined according to the procedure described in [200]. The absorption of dibutyl phthalate (X) in cm³/100 g was calculated using the equation:

$$X = \frac{V}{m} \times 100, \quad (37)$$

where V – volume of adsorbed dibutyl phthalate, cm³;

m – carbon black sample weight, g.

The measurement error was ± (2.5 cm³/100 g). The mass loss during heating was determined using the methodology reported in [78], according to which, the test sample is heated in a pre-weighed glass bottle for 1 hour at 105 °C.

Loss of mass upon heating (X) was calculated using the formula:

$$X = \frac{m_1 - m_2}{m_1 - m_0} \times 100, \quad (38)$$

where m_0 – weight of weighing bottle with lid, g;

m_1 – weight of weighing bottle with lid and test sample prior to heating, g;

m_2 – weight of weighing bottle with lid and test sample after heating, g.

Error was $\pm 0,2 \%$.

The specific adsorption surface area was determined using previously reported protocol [95], according to which the inert gas was adsorbed by the test substance at the temperature of liquid nitrogen.

The desorption peak area (S) in mm^2 was calculated by the formula:

$$S = h \cdot a, \quad (39)$$

where h – peak height, mm;

a – peak width measured at half height, mm.

For each sample, two adsorption-desorption cycles were performed and the average value of the desorption peak area was calculated.

The specific adsorption surface (S_a) in m^2/g was calculated using the formula:

$$S_a = \frac{S_{cm} \times m_1 \times S_2}{S_1 \times m_2} \quad (40)$$

where S_{cm} – specific adsorption surface of a standard sample, m^2/g ;

S_2 – desorption peak area of a test sample, mm^2 ;

m_1 – standard sample weight, g;

m_2 – test sample weight, g;

S_1 – average desorption peak area of the standard sample, mm^2 .

Error was $\pm 10 \%$.

2.4.1. Preparation of rubbers

In the course of work, the rubber compounds were mixed on the basis of various rubbers: natural, butadiene-methylstyrene, butadiene-styrene, isoprene, or on the basis of their combinations. For the preparation of rubber compounds the following ingredients are used:

- vulcanization accelerators – captax, tiuram, altax, diphenylguanidine;
- vulcanization activators – zinc white, technical stearin;
- retardants of vulcanization – phthalic anhydride;
- vulcanizing agent – sulfur;
- softeners – petroleum jelly, KM-2 modifier, industrial oil, rubrax;
- plasticizers – coumaronic resin, oleic acid, dioctyl phthalate;
- fillers – soot II 803, soot 324, shungite, white soot BC 100, kaolin.

The compositions of the tested rubber mixtures are given in Tables 1 – 10 (Appendix A).

The preparation of rubber mixtures was performed in laboratory rollers in the course of one-stage and two-stage mixing processes. After cooling, the samples of the resulting

mixture were vulcanized in metal molds in the form of plates with a size of (150 × 150) mm, a thickness of (2 ± 0.3) mm in a vulcanizer at 120 °C under 150 atm pressure within 5 min, 7 min and 10 min for comparison.

2.4.2. Determination of mechanical properties of rubber compounds

Finished vulcanized plates with 2 ± 0.3 mm thickness were analysed to establish the mechanical properties. The determination of elastic and tensile strength properties of the obtained rubber samples was carried out according to the following procedure [201].

For the analysis, samples in the shape of a double-sided blade were cut out from rubber plates (Figure 7).

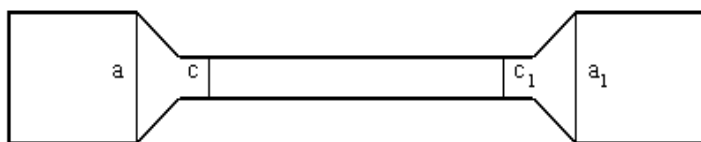


Figure 7 – Rubber test specimen for mechanical testing

Relative tensile strength upon stretching f (in kgs/cm²) was calculated using the formula:

$$f = \frac{P}{S_0}, \quad (41)$$

where P – stress load corresponding to elongation of the sample at the time of rupture, kgs;

S_0 – initial area of the test sample, cm².

The initial area of the sample section was calculated according to the equation:

$$S_0 = b_0 h_0, \quad (42)$$

where b_0 – initial sample width, cm;

h_0 – initial sample thickness, cm.

The elongation at break ε (in %) was calculated using the equation:

$$\varepsilon = \frac{l - l_0}{l_0} \times 100, \quad (43)$$

where l – the length of the working section of the sample at the time of rupture, mm;

l_0 – the initial length of the working section, mm.

The relative residual elongation θ (in %) was calculated using the formula:

$$\theta = \frac{l_1 - l_0}{l_0} \times 100, \quad (44)$$

where l_1 – the length of the working section of the test sample after “rest” within 1 min, mm;

l_0 – initial length of a working section, mm.

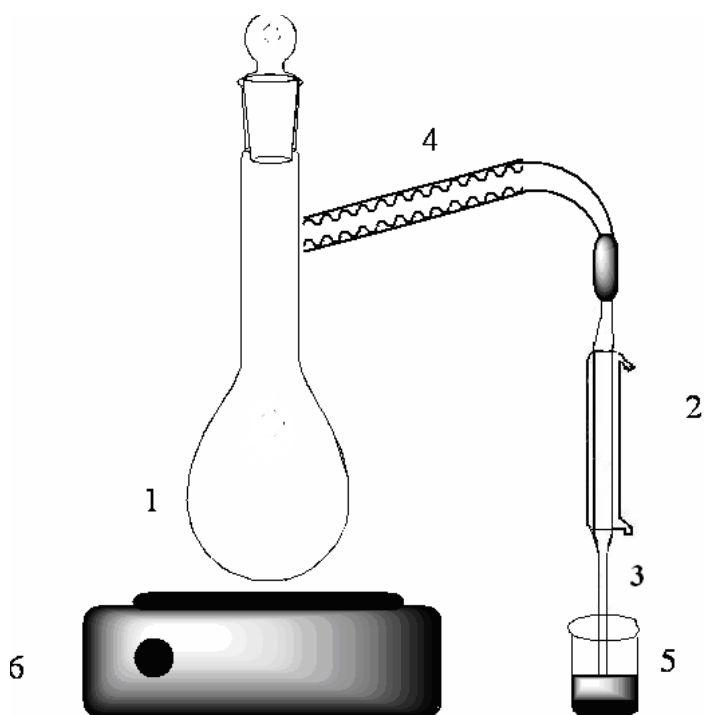
The errors of measurements and calculations of elastic and tensile strength properties were within tolerance, according to GOST 270 “Method of the determination elastic and tensile stress-strain properties”.

The rubber hardness was measured according to [201] using a TM-2 hardness tester. The error of hardness measurement was within the tolerance limits according to GOST 263 “Hardness of rubber”.

2.5. Methods of determination of the detoxification conditions of soils polluted with asymmetric 1,1-dimethylhydrazine

The identification and quantitative assessment of UDMH content and its transformation products were carried out using a chromato-mass spectrometric technique on a gas chromatography with mass-spectrometric detector an Agilent G890N5973N and a liquid chromatography with a diode-matrix detector, a four-channel gradient pump and a microdegasser of an Agilent +1100series. This equipment and the methodologies developed in CPhChMRA of Al-Farabi KazNU allow to determine the components of complex organic mixtures in soil, aqueous solutions, plants and living organisms with high reliability.

Identification was carried out using the library search program from the existing base of NIST mass spectral data and by comparison with the mass spectra of pure organic substances (H₂MA, TMT, ДМФА, МТА). Soil and sorbent in different ratios were placed in 500 mL plastic cups. The soil was thoroughly mixed with the sorbent and left in the open air at room temperature. After the set time elapsed, samples of soil and sorbent was taken and analysed to determine CLRT content and its transformation products. The soil was separated from the sorbent using a set of sieves of various diameters. After each sampling of the soil and the sorbent, this mixture was re-mixed. As a control experiment, in order to evaluate the effect of aeration in the given conditions, contaminated soil was placed in the plastic cups of the same volume and then was mechanically mixed as experimental samples. Analysis of the control soil samples for CLRT content and the products of its transformation was conducted after 1, 6, 16 and 24 hours, respectively.



1 – round-bottom flask; 2 – Liebig (straight type) condenser; 3 – pipe outlet; 4 – reflux condenser; 5 – receiving glass; 6 – electric hot-plate

Figure 8 – Installation for alkaline distillation of liquid samples, containing UDMH

2.6. The specific surface area of carbon-mineral sorbents based on shungite

It was determined using BET method. A mixture of gases with 95% helium and 5% argon was used as an adsorption gas. As a standard, γ - Al_2O_3 with a specific surface area of $S_{\text{yd}}=185 \text{ m}^2/\text{g}$ was used as a standard.

The calculation was carried out according to the areas of desorption peaks proportional to the total surface of the samples:

$$S/S_3 = sg/s_3g_3, \quad (45)$$

hence

$$s = Ss_3g_3/S_3g, \quad (46)$$

where S – desorption peak area (cm^2);

s – specific surface area of the sample (m^2/g or cm^2/g);

g – weight of the sample (g).

Values with index “3” refer to the reference sample.

2.6.1. Determination of the strength of shungite-based briquettes

The determination of strength was carried out according to the report [202]. Based on the obtained sieve analysis data, the class yield index of more than 25 mm (M_{25}),

which characterizes crushability, the class yield index of less than 10 mm (M_{10}), which characterizes abrasion, were calculated using the formulas:

$$M_{25} = (m_1 \times 100) / m, \quad (47)$$

$$M_{10} = (m_2 \times 100) / m, \quad (48)$$

where m_1 – weight of sample, remained in the sieve with holes of 25 mm diameter, kg;

m – weight of sample loaded into the drum, kg;

m_2 – weight of sample, passed through the sieve with holes of 10 mm diameter, kg.

The error in determination of M_{25} values was $\pm 2,0 \%$, and M_{10} – $\pm 1.0\%$ at confidence level of 95%.

2.6.2 Measurement errors of determination of sorption characteristics of carbon-mineral sorbents

Суммарная ошибка определения рассчитывалась по известному способу оценок ошибок [203], когда интересующая нас величина Z является суммой (или разностью) нескольких независимых измеряемых X и Y , для нахождения суммарной ошибки нужно складывать не сами ошибки, а их квадраты.

Measurement error values of a number of experimentally determined parameters, their size and measurement range are given in Table 5. The total error of the determination was calculated using the known method of error estimates [203], when Z value is a sum (or a difference) of of several independent measured X and Y ; in order to find the total error, it is necessary to add not the errors themselves, but their squares.

Table 5

Values of measurement errors, measurement units and their dimensions

Measured value	Measurement unit	Range	Error, %
Consumption of carbon-mineral raw materials	cm ³ /min	100 – 3000	2,0
Temperature of the reactor	K	373 – 1223	2,5
Degree of conversion	%	2-90	2,5
Process time	min	5-60	0,25

$$Z = (\Delta X)^2 + (\Delta Y)^2 \quad (49)$$

The reproducibility of adsorption values, upon determination of the specific surface area and porosity of carbon-mineral sorbents (height, weight and area of chromatographic peaks, $E_{дес.}$, etc.), was determined as the average quadratic deviation of individual absolute values of the measured units from the average values according to the formula:

$$\Delta = \frac{100}{\sum_1^n x_i} \cdot \sqrt{\frac{\sum_1^n (\Delta x_i)^2}{n - 1}} \quad (50)$$

$\sum_{i=1}^n x_i$ sum of measured values; n – number of experiments;

$$\sum_{i=1}^n (\Delta x_i)^2 \quad (51)$$

square deviations of individual absolute values from the average values.

All instruments used in the experiment had an accuracy class of 0.25-0.5. This means that the readings of the device are accurate with an accuracy up to 0.25-0.5% of the entire effective scale of the device. The amount of desorbed substance was estimated from the mass of the limited thermal desorption peak curve, the error in the determination of was $\pm 2\%$. The reproducibility of the results of chromatographic analysis of desorbed gases was also determined as the mean-root-square error of a series of measurements of the heights (or area) of the peaks and amounted to $\pm 1.1\%$.

CHAPTER SHUNGITE ROCKS OF KAZAKHSTAN

3

3.1. Characteristics of shungite rocks of Kazakhstan

The chemical analysis showed the heterogeneity of the composition of the studied rocks (Table 5). The results of the studies indicate that these rocks are a complex system, which consists of carbon, silicon dioxide, compounds of alkali and alkaline earth metals, as well as compounds of aluminum, iron, titanium. The majority of researchers consider the carbon substance of shungite rocks to as sorbent of metals [204].

The results of chemical analysis reveal a characteristic feature of shungite rocks of the East Kazakhstan oblast, particularly, inconsistency of the composition. Inconsistency of the composition manifested both in carbon and mineral parts. Thus, the amount of carbonaceous substance varies from a few percent to about 30%, the content of silicon dioxide reaches 60%, sometimes significant amounts of aluminum oxide (up to 23% Al_2O_3) are observed. To a lesser extent, the rocks are enriched with iron, titanium and other elements. However, carbon, silicon dioxide and aluminum oxide are extracted as the main structural components. This indicates the predominance of rocks with siliceous and aluminosilicate mineral parts.

All studied samples were divided into groups: according to the carbon content and the composition of the silicate base. Table 6 shows the two types of rocks marked among the selected samples: B and B.

Type B rocks, presented by samples № 3, 7 and 11, are characterized by an average silica content ~58% and constitute one type of V B with a low carbon content (from 1,5% to 3,6%), which allows these to be classified as low-carbon or shungite-containing rocks.

Shungite-bearing rocks of type B are low-siliceous rocks. They constitute a large part of the analyzed rocks. According to the content of carbonaceous substances, they are divided into three groups: II B, III B and IV B.

The studied rocks have rather high and practically equal values of the sum of alkalis Na_2O and K_2O , although, relative to each other, alkali metal oxides are present in sharply differing amounts.

For the chemical characterization of the rocks, K_2O/Na_2O ratio called the potassium module (M_k) was calculated (Table 6). However, this relation becomes most obvious when it is expressed through $lg M_k$ value. In terms of $lg M_k$ value, the stratum of shungite-containing rocks is subdivided into potassium (positive values of $lg M_k$) and sodium (negative values of $lg M_k$) stratum. According to the calculated $lg M_k$ values type B rocks can be divided into two subtypes: B (Na) is obtained when Na_2O prevails over K_2O , and B (K) when K_2O prevails over Na_2O .

The data in Table 6 indicate that potassium subtype species are predominate among the rocks: the vast majority of $lg M_k$ values are in the range of positive values. Groups II B and III B are represented by rocks of potassium and sodium subtypes. The rocks of the IV B and V B groups are purely potassium.

Group III B (Na) is formed by samples containing carbon from 24,0% to 66,74%. These rocks could be considered as high carbonaceous or actually shungite. These are called “Shungite rocks”. Actually shungite could also be attributed to rocks of group II B (K) with values of organic substances from 39,7% to 44,2%. The ranges of carbon content fluctuations in the groups are insignificant: III B (Na) (from 20,88% to 24,0%) and IV B (K) (from 10,05% to 14,30%). Group III B (K) is represented by one sample with an organic carbon content of 27,60%. The rocks that make up groups III B (Na), III B (K) and IV B (K) are medium-carbon type. They are called “Шунгитистые rocks”.

When comparing the value of carbonaceous substance content with the potassium module, the absence of any correlation between these indicators is revealed. Thus, in the framework of one species, the carbon content changes marginally upon transition from the potassium subtype to the sodium subtype, i.e. upon sharp changes in M_K .

The rocks of different groups, which are very different in average carbon content, have rather similar values of $\lg M_K$.

According to the analysis of the chemical composition, the dependence between shungite content and the composition of the silicate part could be easily determined. Upon transition from type B to type B, there is an increase in the content of carbonaceous substance in the rocks with a decrease in the amount of silica. Within the rocks of the same type (B) upon transition from II to IV species, there is a reverse process is observed: the carbon content decreases with increasing SiO_2 content.

In our opinion, Al_2O_3/R_2O ratio, where R_2O is the sum of alkaline oxides in the form of K_2O , is an interesting chemical attribute of the studied rocks:

$$R_2O = K_2O + 1,52 Na_2O, \quad (52)$$

where 1,52 – coefficient that expresses the ratio of K_2O/Na_2O molecular weight. Al_2O_3/R_2O ratio of Kazakhstani шунгитоносных rocks has mainly high values from 2,37 to 5,20 (the exception is the samples of group III B (Na), i.e. on average, it is equal to 2,37, which indicates the incorporation of Al_2O_3 mainly into alkali-free silicates composition, for example, chlorite [188].

According to the degree of oxidation-reduction, which could be characterized by the ratio FeO/Fe_2O_3 [39], the overwhelming majority of the samples belong to oxidized rocks, because value $(FeO/Fe_2O_3) < 2$ (Table 6). Normal rocks are also found in minor quantities, the oxidation-reduction degree of which lies in the range from 1 to 4. The data of chemical analysis indicate that the composition of the rocks, more precisely, mineral part of the composition contains substances that are capable to lose water at high temperatures (up to 1000 °C). This indicates a high content of total water (up to 4%) determined in the course of analysis according to the Brush-Penfield methodology, with a small content of adsorption water (about 1%) (Table 6).

Table 6

The chemical composition of shungite rocks and flotation concentrate

Content of components, % mass.														
	C	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	FeO	MgO	CaO	Na ₂ O	K ₂ O	п.п.п.	sum	H ₂ O _{ads.}	H ₂ O _{total.}
1	24,00	48,20	0,56	12,09	4,09	2,05	1,76	1,90	2,18	1,80	30,30	104,93	0,62	3,79
2	12,00	52,50	0,92	11,76	6,72	1,20	3,93	7,48	0,24	3,20	15,05	103,00	0,60	3,90
3	6,30	59,60	0,76	12,05	5,67	0,34	3,69	3,39	0,76	2,60	11,25	100,11	0,62	4,00
4	43,50	29,65	0,62	10,05	4,52	0,30	3,53	4,85	0,35	2,50	46,69	103,06	0,90	3,90
5	44,20	34,71	0,38	9,77	1,22	0,34	0,60	1,12	0,20	1,83	49,71	99,88	0,90	3,88
6	39,70	35,31	0,34	10,40	2,31	3,49	2,31	3,66	0,37	1,98	42,25	102,42	0,88	3,88
7	8,00	57,70	0,16	23,06	1,82	1,88	1,35	0,84	1,34	3,73	10,87	102,75	0,62	3,95
8	12,80	52,30	1,08	22,30	3,11	1,90	0,90	2,28	0,64	4,45	15,90	104,86	0,64	3,95
9	20,88	41,19	0,63	12,25	2,79	4,30	1,26	1,75	3,67	2,44	24,68	94,96	0,60	3,80
10	17,60	56,21	0,47	10,59	1,44	2,35	0,93	1,61	0,38	1,93	33,77	99,68	0,64	3,80
11	3,90	60,36	0,73	16,81	1,22	5,20	1,71	1,30	1,22	2,65	8,54	99,74	0,75	3,95
12-14 ФЛО	47,50	33,13	0,29	8,06	4,03	1,65	0,40	2,53	0,30	1,50	54,51	103,40	1,50	3,75

Table 7

Comprehensive data of the chemical composition of Kazakhstani shungite rocks

Group	№ sample	M _к	lg M _к	ГМ	ЖМ	$\frac{Al_2O_3}{R_2O}$	$\frac{FeO}{Fe_2O_3}$
II B (K)	6	5,35	0,73	0,47	0,54	4,09	1,51
II B (K)	4	7,14	0,85	0,52	0,45	3,86	0,07
II B (K)	5	9,15	0,96	0,34	0,15	4,59	0,28
III B (Na)	1	0,83	- 0,08	0,39	0,49	2,37	0,50
III B (K)	10	5,08	0,71	0,32	0,34	4,22	1,63
IV B (K)	9	2,95	0,47	0,48	0,30	5,29	0,91
IV B (K)	2	13,30	1,12	0,39	0,62	3,30	0,18
IV B (K)	8	6,95	0,84	0,54	0,21	4,11	0,61
V Б (K)	11	2,17	0,34	0,40	0,37	3,74	4,26
V Б(K)	3	3,42	0,53	0,32	0,47	3,20	0,06
V Б (K)	7	2,78	0,44	0,47	0,16	4,00	1,03

Table 8

The elemental composition of shungite rocks and concentrate

Group	№ sample	Content, % mass.			
		C	H	S	Ash
II B (K)	6	72,62	1,96	0,45	15,20
III B (Na)	1	24,13	2,15	0,36	67,05
II B (K)	4	50,05	2,08	0,43	41,06
III B (K)	10	32,96	2,17	0,33	60,20
IV B (K)	9	20,88	1,98	0,38	76,64
V Б (K)	3	9,04	2,03	0,40	86,86
V Б (K)	7	12,53	1,98	0,36	82,69
concentrate		54,61	4,03	0,61	38,75

Hydrolysis module (HM) was calculated in order to determine the type of Kazakhstani black shales in the system of chemical classification of sedimentary rocks:

$$\Gamma M = \frac{TiO_2 + Al_2O_3 + Fe_2O_3 + FeO + (MnO)}{SiO_2}. \quad (53)$$

This parameter is universal for the classification of most terrigenous and siliceous rocks. When calculating the HM, MnO value was neglected, because it was determined selectively for s samples and did not exceed 0,1%.

It is known that there are three types of rocks are distinguished according to HM parameter value: sillites (HM < 0,30), siallites and sypherlites (HM = 0,30 ÷ 0,55), hydrolysates (HM > 0,55). Therefore, these rocks should be classified as sialllites and sypherlites. These type of rocks include most clayey rocks, many clastic (greywacke) and volcanic sedimentary rocks [205].

Separation into subtypes was carried out by the dimension of the iron module (IM)

$$\mathcal{K}M = \frac{Fe_2O_3 + FeO + MnO}{TiO_2 + Al_2O_3}. \quad (54)$$

If IM < 0,75, then the rocks are referred to the sialllite subtype; if IM ≥ 0,75 – the subtype of sypherlites. The calculated values of the iron module (Table 7) of shungite rocks lie below 0,75 value, which determines their affiliation with the siallites, i.e. clay rocks.

Finally, rocks III B (Na), II B (K), III B (K) could be classified as high-carbon rocks by the content of carbonaceous substances (C_{opr.}>15 %). Such rocks include all high-carbon black shales.

Thus, according to chemical analysis data, the studied black shales of “Bolshevik” deposit are mainly clayey rocks of the potassium type with siliceous and aluminosilicate bases enriched to a great extent with the carbonaceous substance. This variety of shungite rocks, in our opinion, is due to the accumulation patterns of shungite substance in sediments and most likely of volcanogenic origin.

In parallel with a silicate method chemical analysis, the contents of C, H, and S in carbon-containing rocks were determined using quantitative elemental analysis technique. Some of the samples were selectively investigated that differ in type and variety and the results are presented in Table 8. A comparison the data presented in Tables 5 and 7 revealed that the carbon content, studied using elemental analysis, is higher. This is explained by the fact that in the case of using silicate chemical analysis methodology, the determination of only the carbon content was conducted, since the samples were preliminarily treated with hydrochloric acid to decompose thermoactive forms of carbonates. And, the total carbon content was determined using combustion elemental analysis technique, which explains the higher values of this indicator.

3.2. Floatation ability and adsorption properties of shungite rocks of “Bolshevik” deposit

In this section, we consider how flotation agents and electrolytes (activator or depressor) are adsorbed on the surface of shungites of various modifications depending on the pH of the medium. For instance, it was examined that how butyl xanthogenate (BX) is fixed on the surface of natural shungite (20,0% mass.) and flotation concentrate (40,0% mass.) and the results are depicted in Figures 9 and 10. It is seen that with an increase in the pH of the medium, the adsorption of BX decreases, which could be associated with hydrophilization of the surface of shungite by hydroxyl ions. This assumption could be explained by electrokinetic data presented in Figures 11-13. It was shown that with an increase in the pH of the medium, the negative charge of shungite increases due to the predominant adsorption of hydroxyl ions. Upon increasing BX concentration, the negative charge on the surface of shungites also increases due to hydrophobic interactions between hydrocarbon radicals of BX and aliphatic methylene groups of cyclic naphthenic phases of shungites. As a result, the polar groups of BX will be turned into the aqueous phase, which gives shungites an additional negative charge. It should be noted that BX molecules are absorbed due to the greater availability of hydrophobic sites on the surface of enriched shungite, which is a favorable condition for BX molecules. On the other hand, as was discussed in previous sections, the surface of shungite is heterogeneous due to the content of different phases. Therefore, it is impossible to exclude the electrostatical interactions between the polar groups of BX and hydrophilic polarized sites of shungite during the adsorption of ionic surfactants, which include BX.

It is well known that one of the main factors affecting the adsorption of surfactant ions at the interface between phases is the interaction in the double electric layer region. Therefore, in order to explain the adsorption process, it is necessary to know what causes the appearance of the surface charge, what is the structure of the double layer and electrokinetic potentials.

The formation of the surface charge upon contact of a solid phase with an aqueous solution is characteristic for almost all systems. Only under certain conditions existing in the solution, the total surface charge is equal to zero, which corresponds to the point of zero charge. In order for the system to remain electrically neutral, the solution must contain the same number of oppositely charged ions (excluding the excess charge in the solid phase); this set of electric charges of opposite signs forms a double electric layer due to the distribution of ions along the interface of two phases.

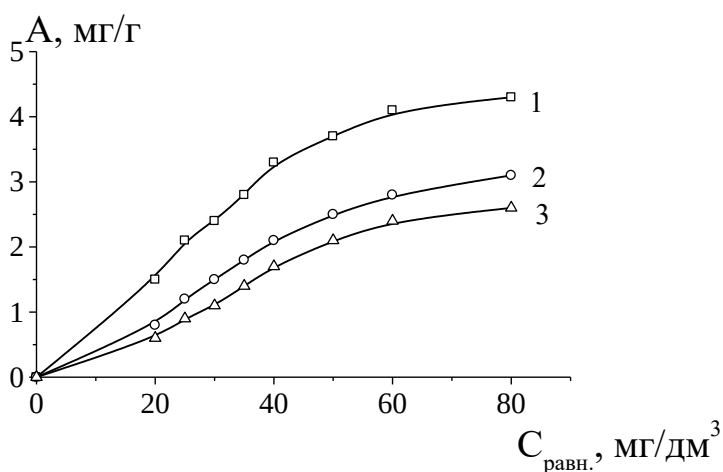


Figure 9 – The dependence of BX absorption on the surface of natural shungite at different pH of the medium (1–6; 2–8; 3–10)

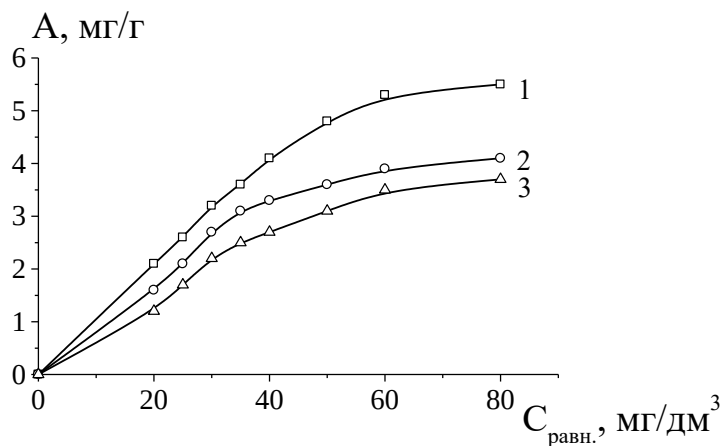


Figure 10 – The dependence of BX absorption on the surface of shungite concentrate (40,0% carbon) at different pH of the medium (1 – pH = 6; 2 – pH = 8; 3 – pH = 10)

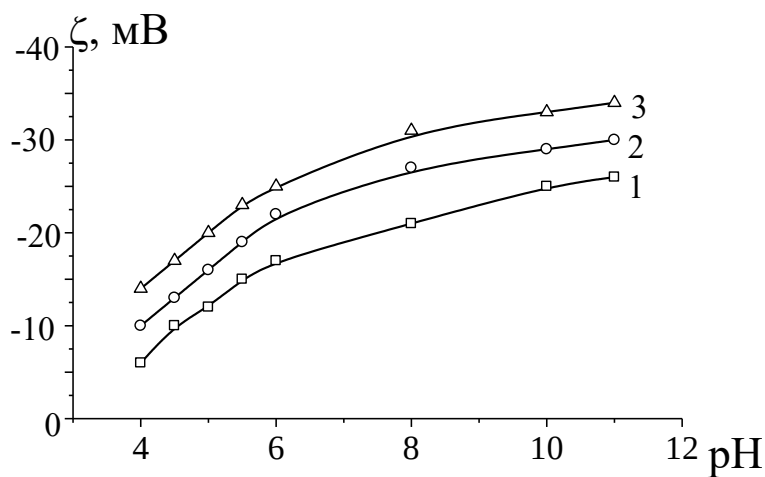


Figure 11 – The dependence of the electrokinetic potential of natural shungite particles (20,0% (1) carbon) and enriched shungites (40,0% (2) and 73,2% (3) carbon), respectively, on the pH of the medium

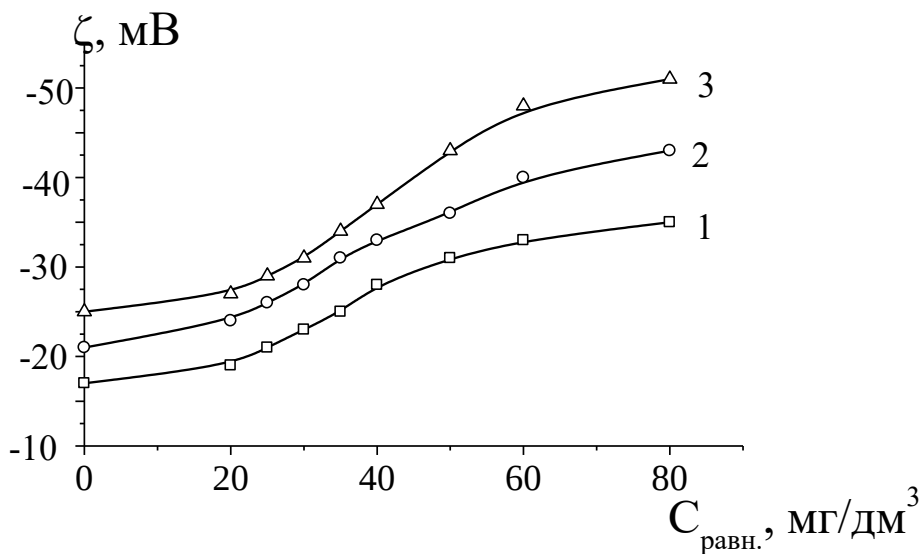


Figure 12 – The dependence of the electrokinetic potential of natural shungite particles at different pH of the medium (1 –6; 2 –8; 3 –10)

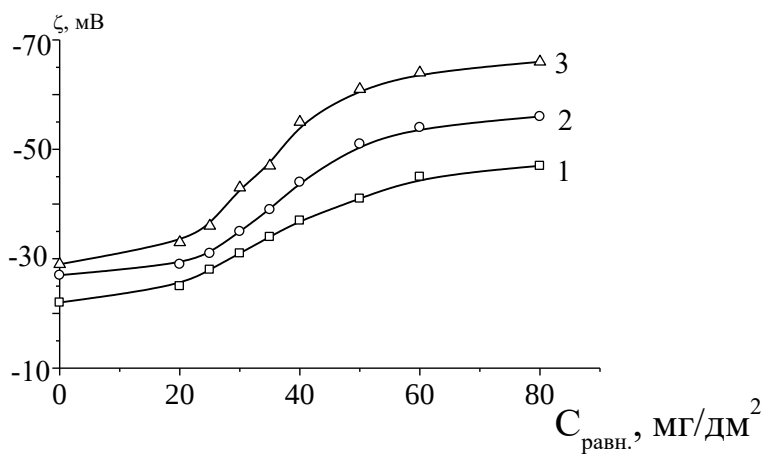


Figure 13 – The dependence of the electrokinetic potential of enriched shungite particles (40,0% carbon) at different pH of the medium (1 –6; 2 –8; 3 –10)

De Kaiser and Likhlema used the Frumkin – Fowler – Guggenheim (FFG) isotherm to study congruence type which best describes the adsorption of tetraalkylammonium ions on silver iodide

$$\theta / (1 - \theta) \exp(A \cdot \theta) = C_1 / 55,51 \exp(-\Delta G_{\text{ad.}}^0 / kT), \quad (55)$$

where the degree of surface filling θ is determined by the ratio Γ_1/N_u , N_u – the total number of adsorption centers (in moles) per unit surface for monolayer filling. It is believed that adsorption is reversible and localized, and the surface is energetically homogeneous. Lateral interactions are considered by coefficient A , the value of which, in accordance with equation (55), could be determined from the maximum slope of the isotherm ($d\theta/d \ln C_1$) under the condition of $\theta = 0.5$. In addition, substitution of A into equation (55) at $\theta = 0.5$ gives a ΔG_{adc}^0 value.

Although the above discussion points to a number of advantages that the use of the FFG isotherm compared to other types of isotherms, commonly used to describe the adsorption of surfactants, two significant limitations should be noted. Firstly, it is unconditionally accepted that coefficient A is constant at any degree of surface filling. In fact, however, this expression could change the sign, and also the absolute value with increasing θ . At low degrees of filling, A should reflect electrostatic repulsion between adsorbed ions. However, it is usually believed that for surfactant ions, the lateral “chain-to-chain” attraction begins to play a significant role at higher degrees of completion. It is often reported that the apparent adsorption energy becomes more preferable with increasing the degree of filling. Secondly, electrostatic interactions are strongly influenced by the charge that created due to the background electrolyte. Consequently, congruence of isotherms could only be expected if all measurements were carried out at the same ionic strength.

It is useful to compare equation (55) with the widely used Stern-Langmuir isotherm, which can be written as an expression

$$\theta/(1-\theta) = C_1 / 55,51 \exp\left(-\overline{\Delta G_{adc}} / kT\right) \quad (56)$$

In this case, free adsorption energy $\overline{\Delta G_{adc}}$ depends on the potential φ_β in the adsorption plane and on other factors. The possibility of separation of this energy into components is discussed below. At the same time, in equation (55), the term ΔG_{adc}^0 includes only electrostatic properties inherent to the interphase surface while there is no adsorption, and the change in the electrostatic member depending on filling is considered in the factor $\exp(A \cdot \theta)$.

When deriving the above equations, the following assumptions are made:

1. Ions of only one type – surfactant ions – are adsorbed specifically, therefore, $\sigma_\beta = z_1 e \Gamma_1$. This assumption is usually fulfilled upon low degree of surface filling in the presence of the electrolyte, which could probably be considered as “indifferent”.

2. One surfactant ion displaces one solvent molecule, i.e. the ion and solvent molecule are of the same size. Although in a wide range of filling, a better correlation could be achieved with a modified equation that considers the relative particle sizes, there is some uncertainty regarding the shape of the adsorption isotherm outside a region with a low degree of filling.

3. The surface is considered homogeneous, and upon deriving the Stern equation, an assumption is made about the possibility of consideration of electrical interactions through the average value of the potential.

4. Upon deriving the Stern equation, the dipole members and potentials of the intrinsic ionic atmosphere of the particles, as well as the lateral “chain-to-chain” interactions are not taken into account.

As a result, the Stern-Langmuir isotherm should be used at very low degrees of surface filling with surfactant ions or upon comparing adsorption of different surfactants with the same degree of filling (i.e. to obtain comparative information). Isotherms of the type described by equation (56) are often used to explain adsorption and electrokinetic data and the results of determinations obtained by “indirect” methods, for instance, by measuring the edge angle, and the limitations of the assumptions, used in their derivation, neglected. For example, authors studying the adsorption of surfactants at “mineral-water” interface deal with such conditions of surface filling in which lateral interactions between adsorbed surfactant ions are possible. Widely used isotherm

$$\Gamma_1 = 2rC_1 \exp\left(-\overline{\Delta G_{a\delta c.}} / kT\right), \quad (57)$$

where r – adsorbed ion radius.

This expression, proposed by Graham, is an analog of equation (56) with low filling ($\theta \rightarrow 0$). In interpreting the adsorption process using equation (57), the existence of lateral interactions between the hydrophobic parts of adsorbed ions is allowed, and this circumstance is very important. Thus, fundamental changes are made to the initial assumptions upon the general form of the Stern isotherm is preserved.

Let us consider the contributions of various energy parameters during the adsorption of ionogenic surfactants at the “solid-solution” interface.

It is generally accepted that $\Delta G_{a\delta c.}$ represents the sum of several contributions. Firstly, this could be written

$$\Delta G_{a\delta c.} = \Delta G_{\text{элек.}} + \Delta G_{\text{спец.}} \quad (58)$$

where $\Delta G_{\text{элек.}}$ – considers electrical interactions, while $\Delta G_{\text{спец.}}$ – specific adsorption and includes all other contributions to free energy that depends on the “specific” (non-electric) nature of the system. Although this recording is convenient, such separation $\Delta G_{a\delta c.}$ is conditional, since the electrical and chemical states of the molecule are not necessarily expressed by independent values.

Moreover, it should be noted that in the terminology of many authors $\Delta G_{\text{спец.}}$ refers to chemical free energy. It is generally believed that $\Delta G_{\text{спец.}}$ completely determined by Coulomb interactions. However, according to de Kaiser and Likhlema, it could be included in $\Delta G_{\text{элек.}}$ and the dipole member, therefore, it is:

$$\Delta G_{\text{элек.}} = \Delta G_{\text{кул.}} + \Delta G_{\text{дип.}} \quad (59)$$

$$\Delta G_{\text{кул.}} = z_1 e \varphi_\beta \quad (60)$$

$$\Delta G_{\text{дип.}} = \sum_j \Delta n_j \mu_j E_s \quad (61)$$

In equation (61):

Δn_j – change in the number of adsorbed dipoles j with a dipole moment μ_j ;

E_s – electric field strength in the plane of adsorbed particles.

It is believed that $\Delta G_{\text{дип.}}$ postulated due to the exchange processes between surfactant ions in the solution volume and in the adsorbed state, accompanied by the desorption of n water molecules. Surfactant dipoles, like water dipoles, are considered

in equation (61), and n must be associated with Δn_j in accordance with the type of adsorption of surfactant ions, considering the possibility of displacing oriented water dipoles with hydrocarbon chain segments. In the order of criticism of the equations (50-61), one could say that $\Delta G_{\text{кул.}}$ and $\Delta G_{\text{дун.}}$ are not mutually independent for the same reasons that have been advanced as arguments against the existence of a pure charge or congruence of adsorption isotherms with respect to potential. It is much simpler to explain what $\Delta G_{\text{элек.}}$ if neglect $\Delta G_{\text{дун.}}$. The following three cases could be considered.

1. If the charge of surfactant ions is opposite in sign to the total volume charge ($\sigma_\beta + \sigma_o$), then z_1 and φ_β have opposite signs, therefore $z_1 e \varphi_\beta < 0$ and the electrical interaction contributes to the adsorption process. In the absence of other specifically adsorbed ions (if σ_β is initially equal to zero), this case will occur at very low degrees of surface filling ($|\sigma_\beta| < |\sigma_o|$), where σ_o and σ_β have the opposite sign) for the combination “cationic surfactant – negatively charged surface” and “anionic surfactant – positively charged surface”.

2. If $(\sigma_o + \sigma_\beta)$ has the same sign as the charge of surfactant ions, then the signs z_1 и φ_β are the same and $z_1 e \varphi_\beta > 0$, i.e. electrical interactions interfere with adsorption. In the absence of specifically adsorbed ions, this case will occur for the combinations “anionic surfactant – negatively charged surface” and “cationic surfactant – positively charged surface”. The same will occur at higher surface fillings for the combinations listed in the first case, i.e. a sufficient amount of surfactant ions is initially adsorbed as counterions until $|\sigma_\beta| > |\sigma_o|$ (it is considered in the expression of the contribution $\Delta G_{\text{цней.}}$). In other words, at the isoelectric point σ_β changes the sign, therefore, $z_1 e \varphi_\beta$ becomes positive and opposite in the sign to the corresponding $\Delta G_{\text{цней.}}$ member.

3. In the considered conditions, IEP $\Delta G_{\text{цней.}}$ is equal to zero ($\Delta G_{\text{дун.}}$ neglected) and adsorption is determined by the expression $\Delta G_{\text{цней.}}$. The fact that the member $\Delta G_{\text{элек.}}$ may become predominant in $\Delta G_{\text{адс.}}$ at least at low degrees of surface filling, it follows from the examples available in the literature, in which it is shown that ionogenic surfactants are not adsorbed on certain similarly charged surfaces in an amount that sufficient to determine them.

Before proceeding to the consideration of $\Delta G_{\text{цней.}}$, it should be discussed about $\Delta G_{\text{элек.}}$. In the above explanation, the effects of the intrinsic ionic atmosphere or the effect of “charge discreteness” are not taken into account, and only the average potential φ_β in the adsorption plane is considered. In many cases, it is assumed that this quantity is known, and that the calculated values $\Delta G_{\text{цней.}}$ automatically include a correction for their own ionic atmosphere. This correction, which is an electrical quantity, depends on σ_β ; and indeed, this allows to explain the change in the calculated values of $\Delta G_{\text{цней.}}$ depending on σ_β . However, in conditions of very low surface filling, i.e. at low σ_β , the influence of the intrinsic atmosphere could be neglected.

Division of $\Delta G_{\text{цней.}}$ into individual interactions, which are considered to be independent, could be performed by several slightly different methods in accordance with the interactions of which type are combined into one group – either van-der-Waals interactions, or interactions between certain structural elements (for example, “hydrocarbon chain – surface” interaction). None of the methods of separation is perfect, and the choice of the type of interaction is determined primarily by the nature of the system under study and the experimental variables used. We use the following method of separation:

$$\Delta G_{\text{цней.}} = \Delta G_{\text{ц-ц}} + \Delta G_{\text{ц-а}} + \Delta G_{\text{нз-а}} \quad (62)$$

The first member in the right side of equation (59) ΔG_{u-u} characterizes the change in free energy during “chain-chain” attraction between the hydrophobic fragments of adsorbed ions; ΔG_{u-a} and ΔG_{n-a} relate to “chain-adsorbent” and “polar group-adsorbent” interactions, respectively. Some authors [206] describe ΔG_{u-a} referring to hydrophobic interaction, while other authors attribute ΔG_{u-a} to van-der-Waals dispersion interactions.

It is believed that in an aqueous environment hydrophobic interactions that associated with general tendency of non-polar groupings of molecules to aggregate, leading to partial or complete destruction of their interactions with water molecules. The free energy of this process is determined mainly by entropy factors that arise as a result of the destruction of short-lived molecular structures of water surrounding non-polar radicals. Perhaps, it makes sense to assume that both ΔG_{u-u} , ΔG_{u-a} include hydrophobic interactions, and ΔG_{n-a} strongly depends on the nature of the surface of a solid material, associated structured water and whether this structure is destroyed by hydrophobic chains or not. Dispersion interactions, which undoubtedly contribute to hydrophobic interactions, always exist, regardless of whether their existence is allowed or not.

Other physical components of ΔG_{u-a} could also be considered depending on the particular structure of the adsorbent and adsorbate. For instance, the adsorption of surfactant having an alkylaryl hydrophobic moiety could include “ion (or dipole) – induced dipole” interactions resulted due to polarization of π -electrons of aromatic rings at a close distance from the surface [206]. It is indicative that surfactants with fluorocarbon chains are adsorbed on fluorocarbon polymers efficiently than their hydrocarbon analogs, although the reverse process could be assumed considering van-der-Waals interactions. Such stronger adsorption may be due to the configuration compatibility of the fluorocarbon residue and polytetrafluoroethylene chain.

If adsorption is carried out on the surfaces of highly hydrated minerals, the main contribution to $\Delta G_{cneq.}$ introduces ΔG_{u-u} . This component, the meaning of which was explained above, evolves as a result of tendency of the hydrophobic groups of the adsorbed surfactant to be freed from the water environment by forming two-dimensional aggregates on the surface of the adsorbent. The hypothesized similarities between these structures and micelles in volume and free energy of their formation in each case are explained on the basis of the possibility of the formation of “half micelles”. A typical example of the experimental data on which this statement is based are the curves of the dependence of adsorption and ζ -potential on the concentration of surfactants obtained by Wakamatsu and Fürstenau for the SDS – aluminum oxide system. According to the data of these authors, the initial increase in adsorption, which is not accompanied by a change in the ζ -potential, indicates a simple exchange of surfactant ions with the indifferent counterions of the background electrolyte in the double layer. At a certain concentration, known as the critical concentration of the formation of half micelles, the adsorption sharply increases due to the formation of half micelles on the adsorbent and there is a concomitant change in the ζ -potential, as well as there are also sharp changes in other properties of the interface, for example the contact angle and sedimentation rate of aluminum oxide particles.

The above-mentioned authors put forward other arguments in favor of the concept of semi-micelle formation, which could be illustrated using electrokinetic data and flotation data obtained for systems of “acetylalkylammonium-quartz” with a negatively charged surface, as well as data on the adsorption of sodium alkyl sulfonates in aluminium oxide. Rapid changes in adsorption, ζ -potential and flotation degree to a

large extent depend on the length of alkyl chain, as expected by analogy with the process of micelle formation in volume.

3.3. Enrichment of shungite rocks of Kazakhstan

A necessary requirement for raw materials used in the technological process is the stability of the chemical and granulometric compositions. Considering the chemical composition of shungite rocks is inconsistent, authors conducted studies on the stabilization of the composition of shungite rocks [34].

Due to variety of processes of the industrial enrichment of minerals, including coal, all processes are based on the use of differences in certain physical and physico-chemical properties of minerals.

The technological factors of coal flotation process include the qualitative, petrographic, granulometric and fractional composition of the flotation material, preparation of the pulp for flotation, the solid phase content in the pulp, the dosage and consumption of reagents, and the duration of coal flotation.

The preparation of pulp for flotation is usually considered as an operation including mixing of all sludge streams entering the flotation to obtain a homogeneous material (both by granulometric composition and by the solid phase content in pulp), classification of the material by size (0.5 mm) carried out, for example, using low-pressure hydrocyclones, and contacting (conditioning) the pulp with reagents [77].

The content of solid phase in the pulp is an important technological parameter that determines the productivity of flotation machines, the specific costs of reagents, electricity and water. The content of the solid phase in the pulp is expressed by the ratio of its mass to the mass of the liquid phase (S:L) or the amount of solid phase in a unit volume (g/L or %).

The fractional analysis includes the method of separation of individual groups of mineral particles that differ in density. The fractional composition of the products of precipitation provides the most objective and complete information on the accuracy of the separation of the initial material by density. Fractional analysis of shungite ore was carried out in accordance with GOST 4790-93.

For separation shungite with a grain size of less than 0.63 mm, organic liquids with a density of 1300 to 2600 kg/m³ and a solution of zinc chloride with a density of 1100 to 2000 kg/m³, as well as organic liquids with a density of 2000 to 2600 kg/m³ were used. The composition of heavy liquids with a density of up to 2100 kg/m³ was determined by Table 9.

Table 9

Compositions of heavy fluids with a density of up to 2100 kg/m³

Density of the fluid, kg/m ³	Mass fraction of zinc chloride in the aqueous solution, %	Volume fraction of bromoform in the solution of "bromoform – white spirit", %	Volume fraction of bromoform in the solution of "bromoform – carbon tetrachloride", %
1200	22,0	19,0	-
1300	31,0	24,0	-
1400	39,0	29,0	-
1500	46,0	33,0	-
1600	52,0	38,0	-
1700	58,0	42,0	8,0
1800	62,0	47,0	22,0
1900	67,0	51,0	32,0
2000	72,0	56,0	42,0
2100	78,0	61,0	49,0
2200	-	66,0	55,0
2300	-	71,0	61,0
2400	-	76,0	67,0
2500	-	81,0	72,0
2600	-	86,0	77,0

The main properties of flotation pulp that affect the flotation process are its density, temperature and concentration of hydrogen ions.

Pulp density is measured by the ratio of the mass of the solid component to the mass of water $T:Ж$ or $p = Ж:T$; its content in 1 L of pulp (g/L) or in percentage. The ratio between these values is expressed:

$$p = \frac{1000\delta - T}{\delta T}; \quad (63)$$

$$T = \frac{1000\delta}{1 + p\delta}, \% / \text{ж}; \quad (64)$$

$$P = \frac{100}{p + 1}, \% \quad (65)$$

where δ – density of the solid component in the pulp, kg/m³; T – solid content, g/L; P – solid content, %.

With an increase in pulp density, flotation unit productivity increases, costs of reagent per unit volume of pulp, electricity and water decrease. However, with an excessive increase in pulp density, aeration decreases and the flotation of large particles deteriorates due to their separation from air bubbles while collision with neighboring particles. In this case, intense flotation of fine particles of the rock takes place, therefore contaminating the concentrate. Loss of carbon parts with waste increases.

Upon flotation of diluted pulps results in a better quality concentrate, but the productivity of the machines in terms of solid content decreases. Flotation of diluted pulps is recommended upon a significant content of fine sludge and complete regeneration of recycled water. However, it should be noted that the concentrate will

contain a large amount of water and is poorly filtered. In our case, upon flotation processing of shungite ore, the average pulp density was taken as $p = 2.8 \div 3.3$ or $T:\mathcal{K} = 300 \div 350$ g/L.

Considering the adsorption and electrokinetic characteristics of the shungite-containing minerals described in the previous section, synthetic 3-amyltetrahydropyran-4-ol acetate and 1-methyl-3-carbethoxy-1,2,5,6-tetrahydropyridin-4-ol xanthogenate were studied. These compounds were synthesized at the Center of Physico-Chemical Methods of Research and Analysis of Al-Farabi Kazakh National University , as well as industrial Flotol B [207].

Dosing flotation reagents was carried out from consumables with a capacity of 1 liter fractionally through dispensers. Consumables with dispensers installed in the immediate vicinity from contact tank. The operational parameters of the flotation process are presented in Tables 10-11 [92].

Table 10

Parameters of the technological process of flotation

Name of parameter	Unit of measurement	Value
Foaming agent consumption per 1 ton of ore	g	250
Collector consumption per 1 ton of ore	g	250
Class content (0,074 mm) in flotation feed	%	65
Main flotation feed density	% solid	25

Table 11

Weight of 1 liter of pulp depending on density and specific gravity

Solid content, %	S:F	Specific gravity of solid , g/cm ³						Solid content, %
		2,5	2,6	2,7	2,8	2,9	3,0	
5	19,000	1030	1031	1032	1033	1034	1035	5
6	15,667	1036	1038	1039	1040	1041	1042	6
7	13,281	1043	1045	1046	1047	1048	1049	7
8	11,500	1050	1052	1053	1054	1055	1056	8
9	10,111	1057	1059	1060	1061	1063	1064	9
10	9,000	1064	1066	1067	1068	1070	1071	10
11	8,091	1071	1073	1074	1075	1077	1078	11
12	7,330	1078	1080	1082	1083	1085	1087	12
13	6,692	1085	1087	1089	1091	1093	1095	13
14	6,144	1092	1092	1096	1098	1100	1102	14
15	5,667	1099	1101	1104	1107	1109	1111	15
16	5,250	1106	1109	1112	1115	1117	1119	16
17	4,882	1113	1117	1120	1123	1125	1128	17
18	4,556	1120	1125	1128	1131	1134	1137	18
19	4,263	1128	1133	1136	1139	1142	1145	19
20	4,000	1136	1141	1144	1147	1150	1153	20
21	3,762	1144	1149	1152	1156	1159	1163	21
22	3,545	1152	1157	1161	1165	1168	1172	22
23	3,348	1160	1165	1169	1174	1177	1181	23

Table 11, continued

24	3,167	1168	1173	1178	1183	1187	1191	24
25	3,000	1176	1181	1186	1191	1195	1200	25

26	2,846	1184	1190	1195	1200	1204	1209	26
27	2,704	1193	1199	1205	1210	1214	1220	27
28	2,571	1201	1208	1214	1220	1225	1231	28
29	2,448	1211	1217	1223		1234	1240	29
30	2,233	1220	1226	1233	1229	1244	1250	30
31	2,226	1229	1235	1242	1239	1254	1260	31
32	2,125	1238	1245	1252	1249	1265	1271	32
33	2,030	1247	1255	1262	1259	1276	1282	33

The flotation enrichment process was carried out on a column flotation machine and the basic technological scheme of the process is shown in Figure 14.

The principle of operation of the column type flotation unit is structurally and significantly different from the flotation machines of the chamber type. The contact tank designed for mixing pulp with reagents is a container of 1 cubic shape, in the center of which a shaft with two axial-type mixers 5 and 6 rotates with four-blade propeller. The drive of the mixers is carried out from the electric motor 4 through the pulleys. The mixers are located in the tank diagonally with a slight difference in height, which ensures uniform distribution of flotation agents in the pulp volume. The supply of flotation reagents to the contact tank is carried out using dosing devices 2 and 3.

Further, the pulp from the lower part of the contact tank using a slurry pump 7, proceeds to the middle part of the flotation columns 10 and 11, where the separation of valuable components and waste rock takes place. The pressure supplied to feed pulp is regulated by valves 8 and 9.

The pulp aeration unit 20 and 21 is located in the lower part of the columns, which contributes to a better distribution of bubbles in the pulp volume. The air supply is carried out using a compressor 17 and is regulated through manometers 18 and 19. The air pressure is set so that the foam is stable and does not undergo destruction from excessive air pressure.

Foam removals in the form of tubular drains 22 and 23 are located in the upper part of the columns, through which the ready-made flotation concentrate feeds the tank 12. The tank 12 is designed for dehydration of the concentrate using a vacuum pump 14. The waste rock (sludge) is discarded from the flotation column through the drain in the lower part to the slurry tanks 15 and 16.

3.4. Effect of physicochemical factors to the yield and quality of concentrates

The need to enrich shungite ore, as noted above, is due to the heterogeneity of the chemical and phase compositions.

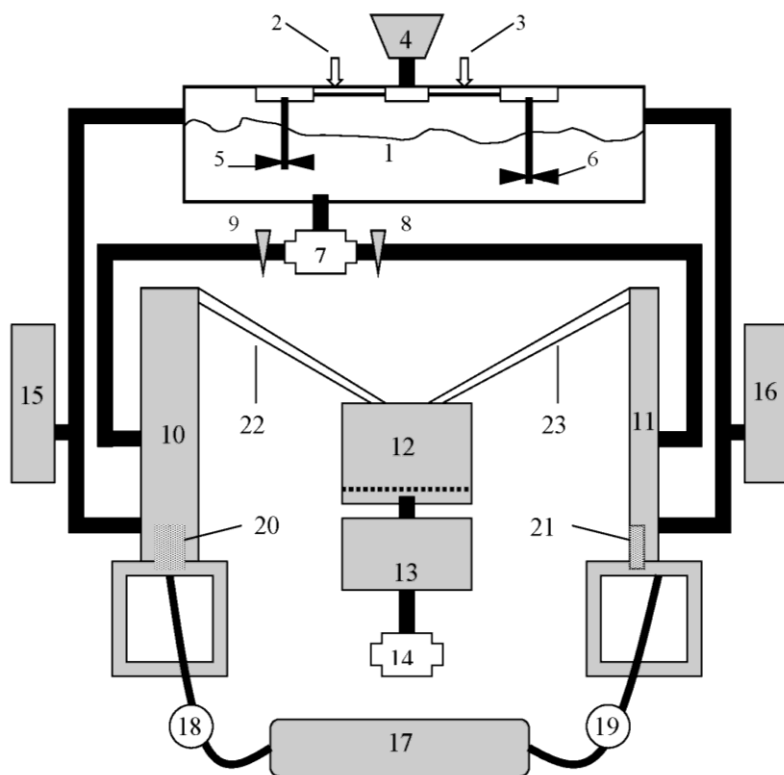


Figure 14 – Принципиальная схема флотационной установки колонного типа
 (1 – Контактный чан; 2–3 – дозировочные аппараты флотореагентов; 4 – электродвигатель;
 5–6 – мешалки осевого типа с четырехлопастными винтами; 7 – шламовый насос; 8–9 – краны регулировки подачи пульпы; 10–11 – колонны основной флотации и перечистой флотации соответственно; 12 – сборник флотоконцентрата; 13 – сборник избыточной воды; 14 – вакуумный насос;
 15 – 16 – шламовые емкости; 17 – компрессор; 18–19 – манометры; 20–21 – узел аэрирования пульпы; 22–23 – трубчатые пеноотводы)

In the process of enrichment of shungite rocks, it is necessary to know the main parameters of the enriched material, as well as the modes of the enrichment process.

Flotation of shungite is carried out as a result of so-called elementary act of flotation (particles sticking to air bubbles), which is based on physicochemical phenomena occurring at the interface between three phases – solid, liquid and gas. The most important of them is the wettability of the surface of the solid phase and the change in its properties during sorption of flotation agents. Although shungite material is a hydrophobic material, however, in practice, flotation of shungite could not be carried out without the use of flotation reagents that increase the floatability of shungite sludge. The floatability of minerals is explained by the theory of hydrated layers. The hydration layer consists of ordered water dipoles located at the boundary of two phases. With a large thickness of the hydrates layer the surface of the mineral will become hydrophilic.

Flotation reagents affect these layers by reducing or increasing their thickness and stability. The preparation of mineral surfaces for flotation, therefore, pointed towards to a sharp increase in the differences in wettability of separated minerals. At the same time, the hydrophobicity of floated and the hydrophilicity of non-floated minerals could be selectively increased by supplying reagents in certain combinations.

Traditionally, during flotation of coking coal, reagents affect only the floatable component, increasing its hydrophobicity by reagents-collector [83]. These reagents-collectors are organic compounds which being fixed on the mineral particles, hydrophobize them, i.e. give their surface the property not being get wetted with water. Thus, collectors contribute to the adhesion of particles to air bubbles. Collectors are divided into cationic, anionic and non-ionic ones. As collectors, reagent AΦ-2 and various kerosene (lighting, tractor, sulphurized) are used.

The flotation of shungite ore was carried out in an aqueous medium by adjusting the pH in a narrow region. Such change practically does not affect the interaction of the reagents-collectors with the surface of shungite particles. In this regard, reagents-regulators of the environment designed to regulate the flotation process in the direction of fostering the selective action of the collector to the flotability of minerals. In the technological scheme of flotation of shungite ore were not used.

Foaming agents are designed to create foam from mobile small mineralized air bubbles. Foaming agents (surfactants) reduce the surface tension at “air-water” interface. Various temperature fractions of higher alcohol were used as blowing agents for flotation of shungite ore; oil X; T-80; foaming agent; residual oil of butyl alcohol production; pine oil, etc. [83].

One of the important parameters of the enriched material is fractional composition. Fractional analysis of shungite with a grain size of less than 0.63 mm was performed using centrifugation. Zinc chloride solutions with a density of 1300 kg/m³ to 1800 kg/m³ were used in experiments. The results of the fractional analysis of shungite ore are presented in Table 12.

Table 12

Fraction analysis of shungite ore

Density of the fraction, kg/m ³	Yield of fraction, %	Sum, %	
		Floating fraction	Sunken fractions
< 1300	60,5	60,5	100,0
1300-1400	22,6	83,1	39,5
1400-1500	4,9	88,0	16,9
1500-1800	3,1	91,1	12,0
> 1800	8,9	100,0	8,9

In parallel with the fractional analysis, a sieve analysis of shungite ore used in the technological cycle was performed. The size class of the working rock was 0.63 mm (Table 13).

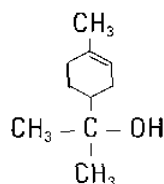
The effect of the temperature regime of the pulp on the flotation of shungite rocks is manifested in several directions. With an increase in pulp temperature, the stability of hydrated shells decreases, which is likely due to an increase in the thermal motion of molecules, which results in a decrease in the viscosity of apolar reagents and an increase of dispersion of their emulsions.

Table 13

The sieve composition of the initial of shungite rock sample

Fraction, mm	-0,63+0,20	-0,20+0,071	-0,071+0,044	-0,044+0,00
Content, % mass.	11,3	23,7	46,1	18,9

Upon initial increase in temperature the stability of the foam increases, the surface oxidation of the particles of the enriched material increases, therefore the stability of shungite concentrate foam increases. By increasing pulp stability, the initial dispersion of pulp air in the column type flotation machine also enhances, thereby the yield of concentrate by the content of the main component, in particular, shungite carbon, improves.



The studies showed that an increase in pulp temperature from 18 °C to 30 °C in all cases significantly enhances flotation, therefore increasing the technological indicators and the rate of the process, although this factor ultimately affects the increase in the cost of the final product.

Figure 15 shows the dependence of carbon yield in flotation concentrate on temperature.

As can be seen from Figure 15, increasing the temperature of the flotation pulp from 30 °C to 50 °C reduces the yield of concentrate. This fact is most likely associated with the pulp compaction in the flotation column, which prevents the free exit of the concentrate from the “leaks”.

The concentration of hydrogen ions (pH) in the pulp does not significantly affect the rate and quality of the flotation process of shungite rocks. According to the analysis of the chemical composition of shungite concentrate, the change in pulp acidity from pH 5.8 to 10.2 does not substantially affect the quality of enriched products. Thus, the index of the neutral medium pH = 6–7 should be considered as the optimum acidity of the pulp during enrichment of shungite rocks.

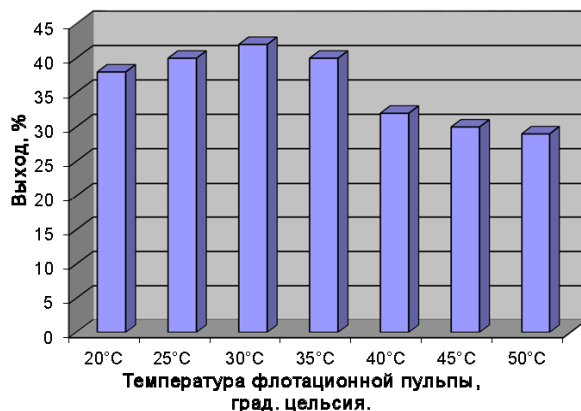
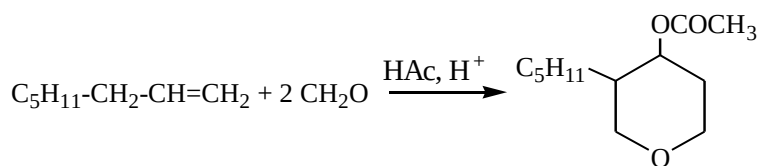


Figure 15 – Dependence of carbon yield in flotation concentrate (%) on temperature

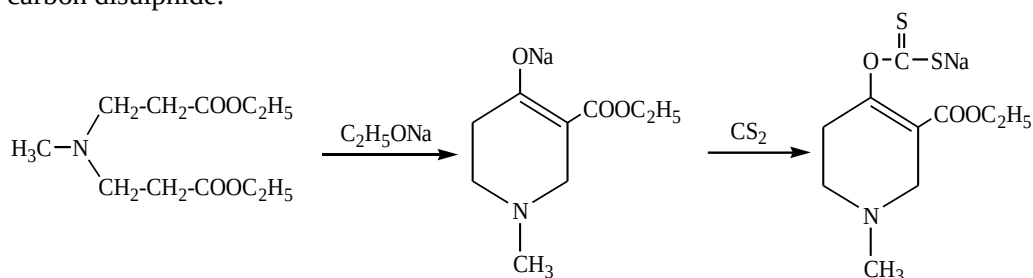
Flotol B, 3-amyltetrahydropyran-4-ol acetate and 1-methyl-3-carbethoxy-1,2,5,6-tetrahydropyridin-4-ol xanthogenate were used as flotation reagents in the process of enriching shungite rocks (oxal). It was shown that the first three flotation agents showed the great results in the processes of enrichment of polymetallic ores [207].

Flotol B is a high-quality natural pine oil, which is obtained by chemical treatment of oils obtained by distillation of pine wood. It consists mainly of terpene alcohols, in which terpeneol is the main component. Terpene hydrocarbons, esters and ketones are contained only in small quantities.

3-Amyltetrahydropyran-4-ol acetate was synthesized by reacting octene-1 with paraform in acetic acid in the presence of KY-2.



1-methyl-3-carbethoxy-1,2,5,6-tetrahydropyridin-4-ol xanthogenate was synthesized by reacting 1-methyl-3-carbethoxy-piperidin-4-one sodium enolate with carbon disulphide.



The main characteristic of the quality of flotation agents is the stability of the foam. The results of our studies of this indicator for the used flotation agents are presented in Table 14.

Table 14

Foam stability time for various flotation reagents

Type of flotation reagents	Stability time , min		
	Initial collection	Middle collection	Final collection
Flotol B	>60	10-15	<1
3-Amyltetrahydropyran-4-ol acetate	5-10	<1	<1
1-methyl-3-carbethoxy-1,2,5,6-tetrahydropyridin-4-ol xanthogenate	10-15	1-2	<1

The main characteristics of the flotation process of the studied flotation reagents are shown in Table 15.

Table 15

Shungite ore enrichment indicators, %

Indicator	Flotation reagent		
	Flotol B	Acetate...	Xanthogenate...
Carbon content in ore	19	19	19
Yeild of concentrate	40	22	31
Carbon content in concentrate	44	35	29
Carbon content in tailings	1,1	14,5	14,5
Removing carbon in the concentrate	93,4	40,5	47,5

Tables 14 and 15 show that the indices of the enrichment of shungite ore using 1-methyl-3-carbethoxy-1,2,5,6-tetrahydropyridin-4-ol xanthogenate and 3-amyltetrahydropyran-4-ol acetate [207]. inferior to enrichment when using Flotol B and clarified kerosene [207].

Thus, in further studies Flotol B (foaming agent) and kerosene (collector) were used as reagents for flotation of shungite. The optimal flotation reagents and their consumption for shungite ore enrichment in the column flotation machine are presented in Table 16.

The results of chemical analysis of flotation concentrate are presented in Table 5.

According to the results of an enlarged experiment on the enrichment of shungite rocks of “Bolshevik” deposit, a technological schedule and job descriptions for production personnel for the production of carbon-mineral concentrate with a capacity of up to 3 thousand tons were developed (Appendix B).

Table 16

Data on flotation enrichment of shungite rocks

№ sample	Flotation agent consumption , cm ³ (per 1 kg rock)						Products	Yield, %	Carbon content, % mass.	Carbon extraction, %
	collector		Foaming agent			regulator				
	kerosene	AAP-2	Flotol B	Xanthogenate *...	Acetate** ...	liquid glass				
1	2	-	1	-	-	-	concentrate	40,2	44,1	93,4
							tailings	59,8	1,1	-
2	2	-	1	-	-	5	concentrate	40,6	43,9	93,8
							tailings	59,4	1,1	-
3	2	-	-	-	5	-	concentrate	22,0	35,1	40,5
							tailings	78,0	14,5	-
4	-	8	1	-	-	5	concentrate	36,2	32,2	61,3
							tailings	63,8	9,6	-
5	2	-	-	5	-	-	concentrate	31,2	29,0	47,5
							tailings	68,8	14,5	-
Xanthogenate*... – 1-methyl-3-carbethoxy-1,2,5,6-tetrahydropyridin-4-ol xanthogenate Acetate** ... – 3-amyltetrahydropyran-4-ol acetate										

CHAPTER 4 PHYSICO-CHEMICAL PROPERTIES OF SHUNGITE ROCKS AND CONCENTRATES OF KAZAKHSTAN

At the end of the 70s, a mineral similar to shungite was discovered in the black shale stratum of East Kazakhstan [184]. The term “black slate” came from English-speaking, mainly American literatures, as a literal translation of the term “black shale” [198]. The interpretation of this concept has repeatedly become the subject of discussion. In domestic literature, “shales” are called metamorphic rocks. The term “black shales” does not seem to be applicable to sedimentary rocks. However, the author [100] defines the concept of “shale” as metamorphic rocks: combustible shales, siliceous shales, copper shale, etc., but all these are sedimentary rocks. Consequently, the term “black shale” is a term of widespread use. It covers a large group of sedimentary and sedimentary metamorphic rocks of different genesis, chemical and mineral composition, color and structure. But all these rocks have one common attribute – high content of organic matter of the non-angular series. Many researchers classify rocks with an organic carbon content of more than 1% as “black shales” [199].

Nowadays, the study of black shale formations, for a number of reasons, is interesting and relevant, too. Firstly, in the majority of black shale rocks are ore-bearing, i.e. represent containers of anomalies of a number of valuable chemical elements. Secondly, it is the accumulation of organic matter with a very versatile mineral composition of the components.

Visually, shungite rocks of “Bolshevik” deposit are a collection of accumulations, i.e. a compacted mixture of particles of a carbaceous substance with mineral components. Both are found in the form of local zones or runs of various thicknesses.

4.1. Characterization of shungite using Infra-red spectroscopy

Figures 16-18 show the IR spectra of shungite and concentrates of various degrees of enrichment by carbon (with carbon content of 20,0; 40,0 and 90,0%, respectively), for all samples the error in carbon content was $\pm 2\%$. According to the absorption spectra in the samples of natural shungite are present: quartz α -SiO₂ -1163, 1098, 800, 780, 695, 519, 477, 399, 374 cm⁻¹; muscovite KA₁₂[(OH, F)₂AlSi₃O₁₀] – 3620, 1033, 942, 532, 474, 428 cm⁻¹; calcite CaCO₃ – 1794, 1438, 877, 713 cm⁻¹; quartz – SiO₂ -1172, 798, 779, 695, 474 cm⁻¹; kaolinite A₁₄[(OH)₈Si₄O₁₀] – 1105, 942, 914, 474, 428 cm⁻¹; 5 HOH – 1610 cm⁻¹; H₂O molecules – 3448 cm⁻¹ molecules, but there are no absorption bands for aliphatic hydrocarbons. These data correlate well with the data of X-ray phase analysis, according to which, in natural shungite among its mineral components are identified: hydromica (1,01 nm), quartz (0,426; 0,334; 0,137 nm), dolomite (0,29; 0,22 nm), chlorite (0,353 nm), pyrite (0,271; 0,241; 0,220 nm), siderite (0,173; 0,1794; 0,1965; 0,234; 0,279; 0,357 nm) and feldspar (0,321 nm), the quantitative content of which varies from sample to sample due to the inconstancy of the composition of the studied rocks.

In the high-frequency region of the spectrum, absorption bands of stretching vibrations of methylene groups of aliphatic hydrocarbons $\nu \text{CH}_2 - 2926, 2855 \text{ cm}^{-1}$ are observed. In the long-wavelength region of the spectrum, the manifestation of valence vibrations of $\text{Ca-O } 342, 319 \text{ cm}^{-1}$, $\nu \text{OH} - 3424 \text{ cm}^{-1}$, $\text{HOH} - 1618 \text{ cm}^{-1}$ is observed.

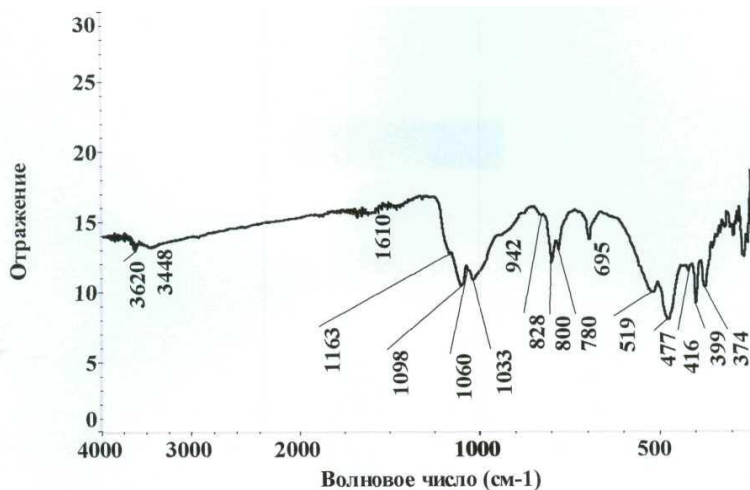


Figure 16 – Infrared spectrum of shungite, C - 20,5%

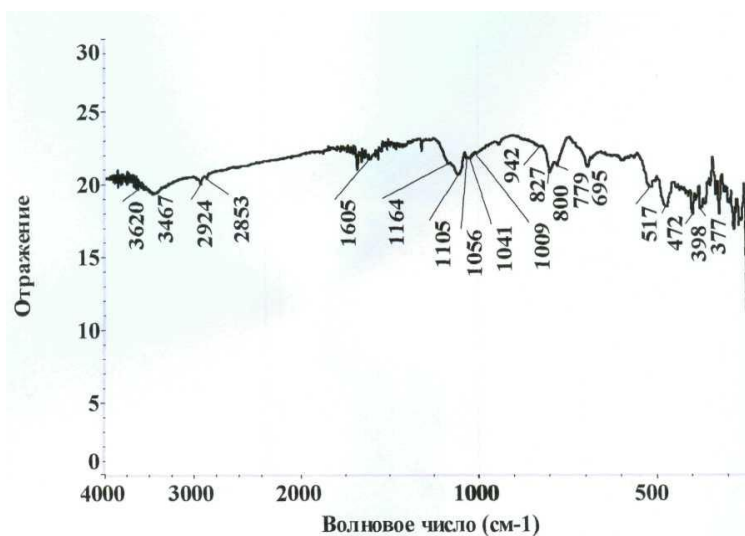


Figure 17 – Infrared spectrum of shungite concentrate containing 40,0% carbon

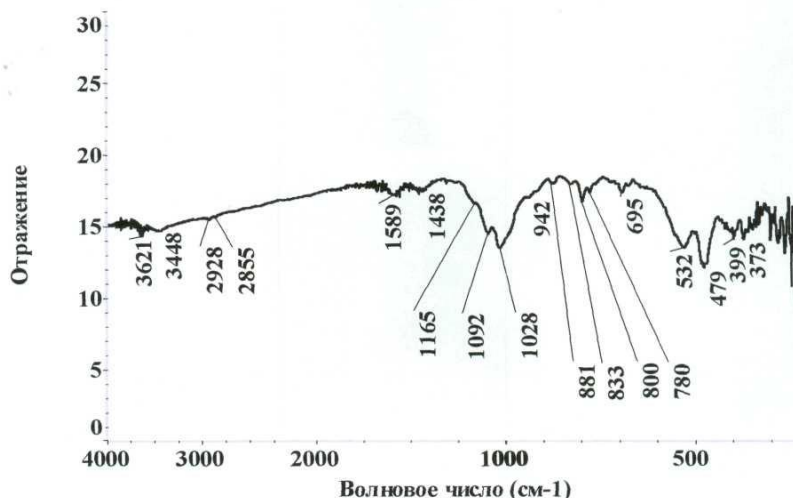


Figure 18 – Infrared spectrum of shungite concentrate containing 90,0% carbon

Upon enrichment of shungite with respect to carbon, absorption bands of methylene groups of aliphatic hydrocarbons νCH_2 – 2928, 2855 cm^{-1} appear. Most likely, because of the absence of aliphatic hydrocarbons, natural shungite has less pronounced adsorption properties compared to shungite concentrates, primarily due to the absence of chemical bonds. As a result of the increase in carbon component, the ratio of hydrocarbons, namely, C, O, H, N changes, which confirmed by the data of the microelement analysis. This could be explained by the fact that the layers of aliphatic groups of shungite concentrates are fixed with sorbate due to hydrophobic interactions.

Based on the data of X-ray diffraction analysis, the presence of one carbon or graphite-like phase (V) with $d = 0.357 \text{ nm}$ and three hydrocarbon (II, III, IV) phases with $d = 0.47; 0.8; 2.2 \text{ nm}$, respectively, are observed in the organic substance of shungites (in the sample with the maximum amount of carbon). The quantitative composition of the organic part is presented in Table 16, where, for comparison X-ray phase compositions of natural coals of various deposits are given.

From the data in Table 17, it could be concluded that shungites unlike coals of the low stages of metamorphism are characterized, like soots [125], by the absence of phase I so-called intermediate phase. By the quantitative content of graphite-like (V) and polynaphthenic (II) phases, as well as their ratio, shungites are close to coals of VI – VII stage of metamorphism. Shungites are able to graphitization with increasing the temperature. Therefore, after the heat treatment of the sample at 1500 °C, in the presence of argon the hydrocarbon phases disappeared due to their transformation into a graphite-like phase.

The polynaphthenic phase (H_ϕ) is a cluster structure (Figure 19) consisting of condensed (B) and naphthenic rings separated by methylene bridges (A) containing alkane chains.

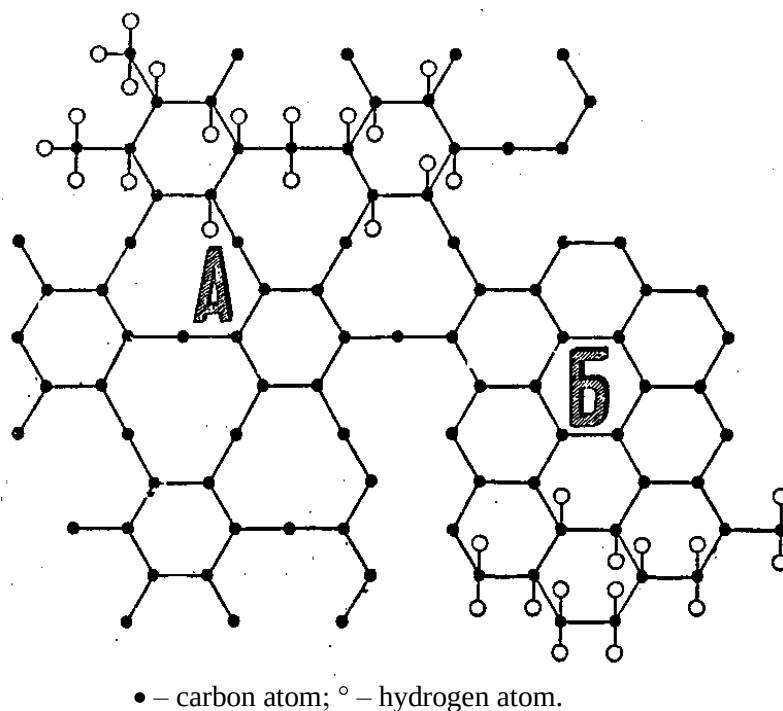


Figure 19 – The structure of the polynaphthenic phase

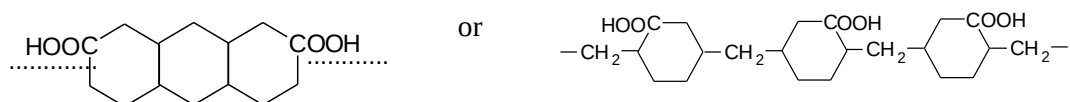
Table 17

X-ray phase composition of the organic part of carbon materials

Name of material	Phase content, %				
	I	II	III	IV	V
Shungite from East Kazakhstan	-	18,0	11,0	11,0	70,0
Coal from Aban deposit	41,0	28,0	7,0	-	24,0
Coal from Nazar deposit	43,5	28,8	4,5	-	24,0
Coal from Canada, mine Лайвейл	14,0	23,0	5,0	4,0	54,0

Помимо полициклических углеводородов, содержащих метиленовые группы, в результате окисления могут появляться кислородсодержащие группы, т.е. карбоксильные группы:

As mentioned above, indeed organic compounds are found on the surface of the enriched shungite. The content of polynaphthenic phase in shungites, depending on their types, reaches 18%. In addition to polycyclic hydrocarbons containing methylene groups, oxygen-containing groups may appear as a result of oxidation, i.e. carboxyl groups:



Consequently, the carbon particles of shungite concentrates could come into contact with sorbate hydrophobic part, while oxygen-containing groups will be responsible for chemisorption processes.

4.2. Determination of the material composition of shungite by thermal analysis

For many years, upon studying the kinetics of the decomposition of various solid substances the thermogravimetric method has been used under conditions of a uniformly increasing temperature [195].

Samples were preliminarily grinded and sieved through a 008 sieve. For analysis, powders with a particle size of less than 0.08 mm were taken. The weight of the sample was 600 mg. Calcined alumina (Al_2O_3) was used as an inert material.

Uniform heating of the samples was carried out in the air up to 1000 °C. The rate of temperature rise (20°/min) was selected on the basis of data from literature [195].

In the course of thermal analysis on one derivatogram, four curves were simultaneously recorded: temperature curve (T) – recording the temperature inside the sample; differential thermal curve (DTA) – the difference in temperature between the studied and inert samples; thermogravimetric curve (TG) – change in the mass of the sample; differential-thermogravimetric curve (DTG) – the rate of change in the mass of the sample.

Derivatives obtained during the experiment of thermal heating of shungite rocks were very similar to each other, which indicates the proximity of the material composition of the samples in a qualitative point of view. Derivatograms of natural shungite-bearing rocks are illustrated using sample No.9 (Figure 20) and a flotation concentrate sample (Figure 21). Figure 22 depicts a derivatogram of the concentrate after acid-base enrichment. These derivatograms indicate that the DTA curve is more informative, i.e. contains a greater number of thermal effects compared to mass loss curves. By the nature of DTA and DTG curves, a qualitative analysis of the phase composition of the rocks was carried out. On all derivatograms, the first peak on the DTG curve in the range of 20-200 °C indicates the process that occurs with a decrease in mass with a maximum rate around 110 °C. DTA curve also has a peak corresponding to the endothermic effect. Most probably, the removal of adsorbed water is recorded, which leads to a decrease in the mass of the samples. With an increase in temperature (500 ÷ 600) °C, another peak appears on DTG curve of samples No.9 and 6, indicating mass loss at a maximum rate at 567 °C (for sample No.9), 588 °C (for sample No.6) and 560 °C (for concentrate). In this temperature interval, a weak diffuse peak is recorded on DTA curve, indicating the endothermic nature of the chlorite decomposition process according to the X-ray diffraction analysis.

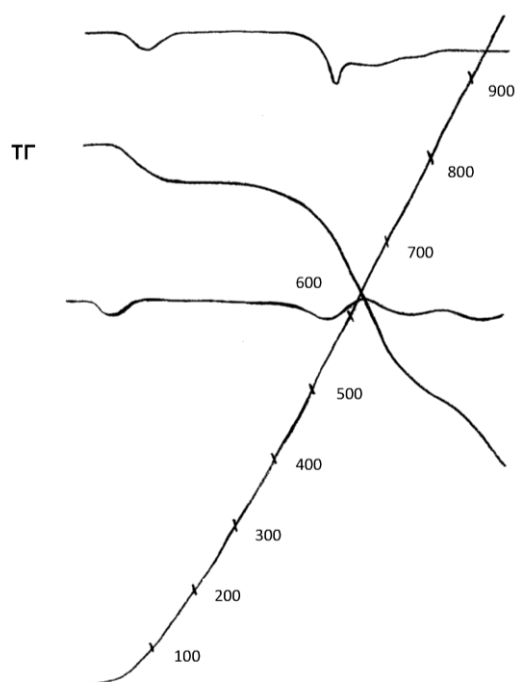


Figure 20 – Derivatogram of shungite sample №9

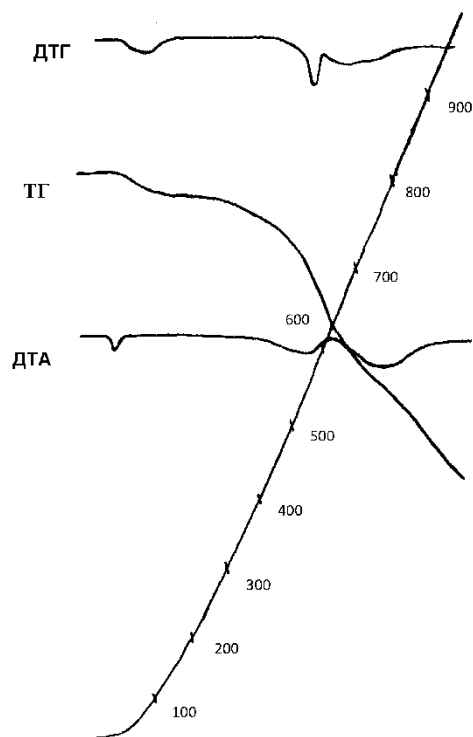


Figure 21 – Derivatogram of flotation concentrate sample

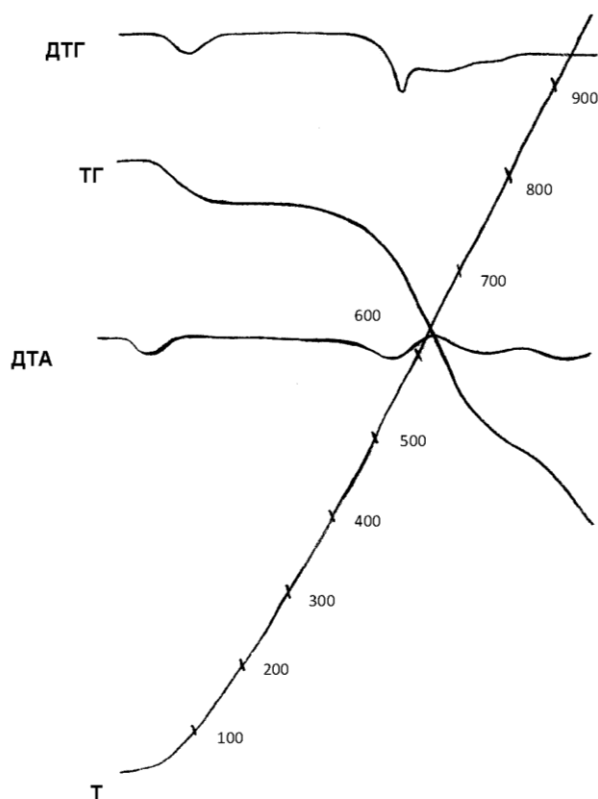


Figure 22 – Derivatogram of concentrate after acid-base enrichment

It should be noted that during the study of shungite rocks, it is difficult to accurately determine the initial and final temperatures of thermal effects due to overlay of sequential processes that occur upon heating of the samples. Thus, for example, it is impossible to accurately determine the boundaries of the temperature range of the decomposition of chlorite due to the overlay of an exothermic peak (540-750) °C in DTA curve, which is caused by the burning of shungite carbon. On the derivatogram (Figure 18) of sample with maximum carbon enrichment, the exoeffect of burning a carboneous substance in 540-680 °C interval with a maximum mass loss rate at 620 °C is clearly recorded. Upon moving up the temperature curve on DTA an endoeffect (790÷794 and ~ 830 °C) is observed, indicating the decomposition of carbonates [195]. An endothermic process with loss of mass at temperatures above 850 °C corresponds to dehydration of hydromica.

In the course of thermal analysis, a complex technique with the simultaneous study of curves of mass changes, differential mass changes and differential temperature changes with a uniformly increasing temperature was applied to determine the effective kinetic constants of the combustion reaction of shungite carbon. It was based on the method of data processing described in [208].

It was shown in the study [208] that the reaction corresponding to the combustion of carbon 1200 °C proceeds in the first order; when the carbon particles sizes are less

than 0.2 mm, the effect of diffusion is eliminated, and the oxidation reaction could be considered to proceed in the kinetic mode. The main characteristic of the quality of flotation agents is the stability of the foam. The results of our studies for the used flotation agents are presented in Table 14.

The overall rate of such reaction and the temperature dependence of the effective rate constant according to the Arrhenius equation:

$$\frac{dc}{dt} = -kc^n, \quad (66)$$

$$k = k_o \cdot e^{-E/RT}, \quad (67)$$

where κ – reaction rate constant;

κ_o – preexponential factor;

n – reaction order;

R – universal gas constant;

T – absolute temperature;

c – a portion of the substance determined by the expression:

$$c = (W - W_t) / (W_o - W_t), \quad (68)$$

where W – weight of sample at a given temperature;

W_t – final weight;

W_o – initial weight.

From equations (67) and (68):

$$\frac{dc}{c^n} = -k_o \cdot \exp(-E/RT) dt \quad (69)$$

If $q = dT/dt$ is the linear heating rate of the test substance, then for the case when $n=1$ equation (69):

$$\frac{dc}{c} = -\frac{k_o}{q} \cdot \exp(-E/RT) dT, \quad (70)$$

$$\text{or } \ln c = \int_o^T -\frac{k_o}{q} \cdot \exp(-E/RT) dT \quad (71)$$

Since the combustion reaction proceeds in a narrow temperature range, to integrate the right side of equation (71), it was proposed to choose the reference temperature T_s at which the reaction proceeds at the maximum rate and when

$$c = c_s = (W - W_t) / (W_o - W_t) = 1/e, \quad (72)$$

where e – base of the natural logarithm.

Instead of the variable T , another variable θ is introduced, which is defined as $T = T_s + \theta$. It could be shown that $1/T \sim (1 - \theta/T_s)/T_s$. Using this approximate expression, it is easy to integrate equation (71) and obtain:

$$\ln \frac{W - W_t}{W_o - W_t} = -\frac{k_o}{q} \cdot \frac{RT_s^2}{E} \cdot \exp \left[-\frac{E}{RT_s} \left(1 - \frac{\theta}{T_s} \right) \right] \quad (73)$$

Further simplification is achieved by using the fact that T_s is a function of another variable; when $T = T_s$, $\theta = 0$, and $c = c_s = (W - W_t)/(W_o - W_t) = 1/e$, then $\ln c = (W - W_t)/(W_o - W_t) = -1$. Therefore, when $\theta = 0$, equation (73) takes the form:

$$-1 = -(k_o/q)(RT_s^2/E) \exp(-E/RT_s). \quad (74)$$

By substituting this expression in the corresponding part of equation (73):

$$\ln \frac{W - W_t}{W_o - W_t} = -\exp(E\theta / RT_s^2), \quad (75)$$

$$\ln \ln \frac{W_o - W_t}{W - W_t} = E\theta / RT_s^2. \quad (76)$$

For different values of W and θ in the coordinates “ $\ln \ln \frac{W_o - W_t}{W - W_t}$ and θ ” straight lines are obtained whose slope is equal

$$\operatorname{tg} \alpha = \frac{E}{RT_s^2} \quad \text{or} \quad (77)$$

$$E = RT_s^2 \operatorname{tg} \alpha. \quad (78)$$

The use of a derivatograph makes it possible to significantly facilitate the processing of experimental data, since simultaneously with the integral mass change curve, the differential curve is also fixed. An extreme point is determined on the differential curve at which the rate of shungite decomposition is maximum. The projection of this point onto the temperature curve allows to determine the value of T_s , which is used in equation (77) to calculate the activation energy.

The data on the above derivatographs for determining the activation energy are summarized in Table 18. Figure 23 shows a linear dependence $\ln \ln \frac{W_o - W_t}{W - W_t}$ on θ for the combustion reaction of shungite carbon in various samples of shungite rocks. From the slope of the straight lines, the values of the effective activation energy were calculated, which amounted to (in kJ/mol):

№ sample	E , kJ/mol
----------	--------------

9	49,8
Float. conc	44,8
Acid-base enrichment	40,5

The data obtained during the studies indicate that the values of activation energy of the combustion of enriched samples are slightly lower compared to the activation energy of the combustion of natural highly mineralized rocks. Note that in [208] the values of the effective reduced activation energy ($E_{o\phi}$) of shungites calculated for:

$$E_{o\phi} = 2,3RT_{\kappa}, \quad (79)$$

where T_{κ} – temperature of the end of the shungite combustion process.

$E_{o\phi}$ should not be equated with the effective activation energy defined in this study. The fact is that the numerical values of the effective reduced activation energy ($E_{o\phi}$) are known to be less than the effective activation energy (E) due to the fact that there is a relationship between them, defined by the expression:

$$E_{o\phi} = \frac{E}{\lg k_o} \quad (80)$$

Knowing the value of the effective activation energy, one can also calculate the preexponential factor:

$$k_o = q \frac{E}{RT_s^2} \exp\left(-\frac{E}{RT_s}\right). \quad (81)$$

The calculated values of the preexponential factor and the values of the reduced effective activation energy calculated by formula (80) are given below:

№ sample	k_o , min ⁻¹	$E_{o\phi}$, kJ/mol
9		15,3
FR	$1,8 \cdot 10^3$	17,3
	$0,4 \cdot 10^3$	
Acid-base enrichment	$0,5 \cdot 10^3$	15,4

A comparison of $E_{o\phi}$ values with the literature [198] shows that the difference between them is not very large, and the dependence of the growth of $E_{o\phi}$ (or E) value upon transition from rocks with a high carbon content to highly mineralized rocks is preserved.

The author of [209] found that using the Arrhenius equation, it is possible with a sufficient degree of accuracy to describe only one derivatogram obtained at predetermined constant heating rate, since the heating rate of the test substance affects the parameters of the corresponding kinetic equation. Therefore, even the same samples at different heating rates have significantly different values of the parameters E and k_o . This means that when comparing the obtained kinetic parameters of various carbon-

containing substances, the conditions of the experiments should be taken into account, and, therefore, this comparison will have a very relative character.

Table 18

Derivatogram data for determining the activation energy

T, °C	θ , °C	W	$W - W_t$	$\frac{\ln \ln \frac{W_o - W_t}{W - W_t}}{T_s}$	$\frac{\theta}{T_s}$
Sample № 9: $T_s=620$; $W_o - W_t=0,6-0,234=0,366$					
588	-32	0,57000	0,33600	-2,459	-0,0516
600	-20	0,56750	0,33350	-2,375	-0,0323
620	0	0,56500	0,33100	-2,297	0,0000
640	20	0,55500	0,32100	-2,031	0,0323
660	40	0,54875	0,31475	-1,891	0,0645
680	60	0,54375	0,30975	-1,791	0,0968
690	70	0,54250	0,30850	-1,767	0,1129
Flotation concentrate: $T_s=710$; $W_o - W_t=0,6-0,42265=0,17735$					
607	-101	0,57250	0,14985	-1,781	-0,1423
620	-90	0,56875	0,14610	-1,641	-0,1268
640	-70	0,56625	0,14360	-1,555	-0,0986
660	-50	0,5650	0,14235	-1,515	-0,0704
680	-30	0,55625	0,13360	-1,261	-0,0423
700	-10	0,55375	0,13110	-1,197	-0,0141
710	0	0,55000	0,12735	-1,105	0,0000
720	10	0,548750	0,12610	-1,076	0,0141
740	30	0,54250	0,11985	-0,937	0,0423
753	43	0,54000	0,11735	-0,884	0,0606
Acid-base enrichment: $T_s=620$; $W_o - W_t=0,6-0,14315=0,45685$					
540	-80	0,572	0,42885	-2,761	-0,1290
560	-60	0,569	0,42585	-2,655	-0,0968
580	-40	0,567	0,42385	-2,591	-0,0645
600	-20	0,562	0,41885	-2,444	-0,0323
620	0	0,557	0,41385	-2,314	0,0000
640	20	0,550	0,40685	-2,155	0,0323
660	40	0,547	0,40385	-2,093	0,0645
680	60	0,540	0,39685	-1,960	0,0968

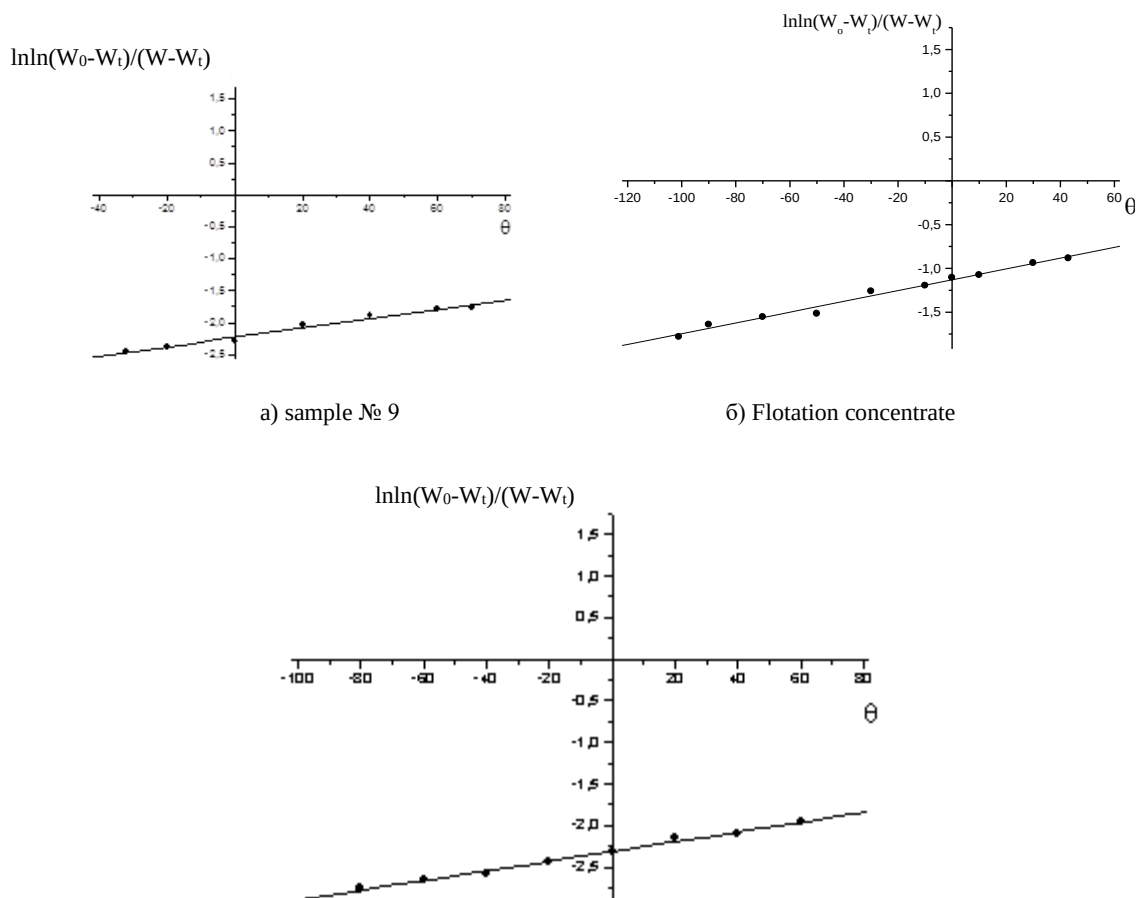


Figure 23 – Linear dependence of $\ln \ln \frac{W_0 - W_t}{W - W_t}$ on θ for the reaction of shungite carbon combustion

4.3. Characterization of shungite carbon using Raman spectroscopy

A study of the structure of shungite was also characterized using combinational light scattering. Raman-spectra of shungite carbon samples (Figure 24) is a typical spectrum of carbon polycrystals of a graphite structure with small grain sizes and consists of two wide bands with maximums at $1355 \div 1360 \text{ cm}^{-1}$ and $1586 \div 1605 \text{ cm}^{-1}$, so called bands. This method confirms the conclusion that the test material is amorphous, since crystallites are randomly oriented and are small in size.

Typical Raman-spectra of various representatives of amorphous carbon and, for comparison, crystalline graphites are shown in Figure 25. One can notice that depending on the structural state of carbon the line widths and the intensity ratio D/G change on Raman-spectra. For instance, highly disordered carbon, which includes charcoal or coke, has very wide peaks, whereas the peaks of glassy carbon and polycrystalline graphites are narrower. In the spectrum of crystalline graphite, the D band is completely absent.

By comparing the Raman-spectra in Figures 24 and 25 reveals their similarity, especially in the case of the spectra of shungite carbon, coke and charcoal. Natural shungite, like coke and charcoal, is characterized by a wider D band compared to the G band, upon a slight superiority in intensity of the latter. The data obtained indicate their structural identity.

The macro- and microstructure of cokes is evaluated using light microscopy, mainly in polarized light, as well as scanning and transmission electron microscopy. None of the coke used in industry has a uniform microstructure. It is always heterogeneous. A typical microstructure of ordinary coke of slow coking is shown in Figure 26, b.

With a relatively uniform distribution of one of the components the microstructure of cokes could be classified as pseudo-uniform. In this case, as a component of the microstructure, a morphological unit having statistically defined boundaries should be considered.

The microstructure of coke, characterized by a high ability to graphitization, is shown in Figure 26, b. In the absence of deformation a well-graphitized coke of a spheroidal structure (gilso-coke) is obtained. The main components of the microstructure include lamellar (plate-like), mosaic, and spherulitic. The morphology of the lamellar microstructure is clearly shown in Figure 26, c. Depending on the type of raw material used, the conditions of formation of the mesophase and its microstructure, technological factors and the design of devices of L_a , L_c values and the length of the lamellas may vary widely.

With an increase in the plate sizes, a scaly, not having a clear separation of lamellas (Figure 26, d), layered, consisting of lamellas entirely (Figure 26, c) and needle-shaped (Figure 26, e) microstructures, visible on a scanning electron microscope [210], are successively formed. An analysis of the microdiffractograms of the particles of the material torn by the replica showed that sections with a lamellar structure have basal reflexes in the form of arcs. Similar results are observed on X-ray diffraction patterns. This indicates different angles of inclination of crystallites, forming the examined fragments of the structure, to the plane of the section, which confirms its heterogeneity.

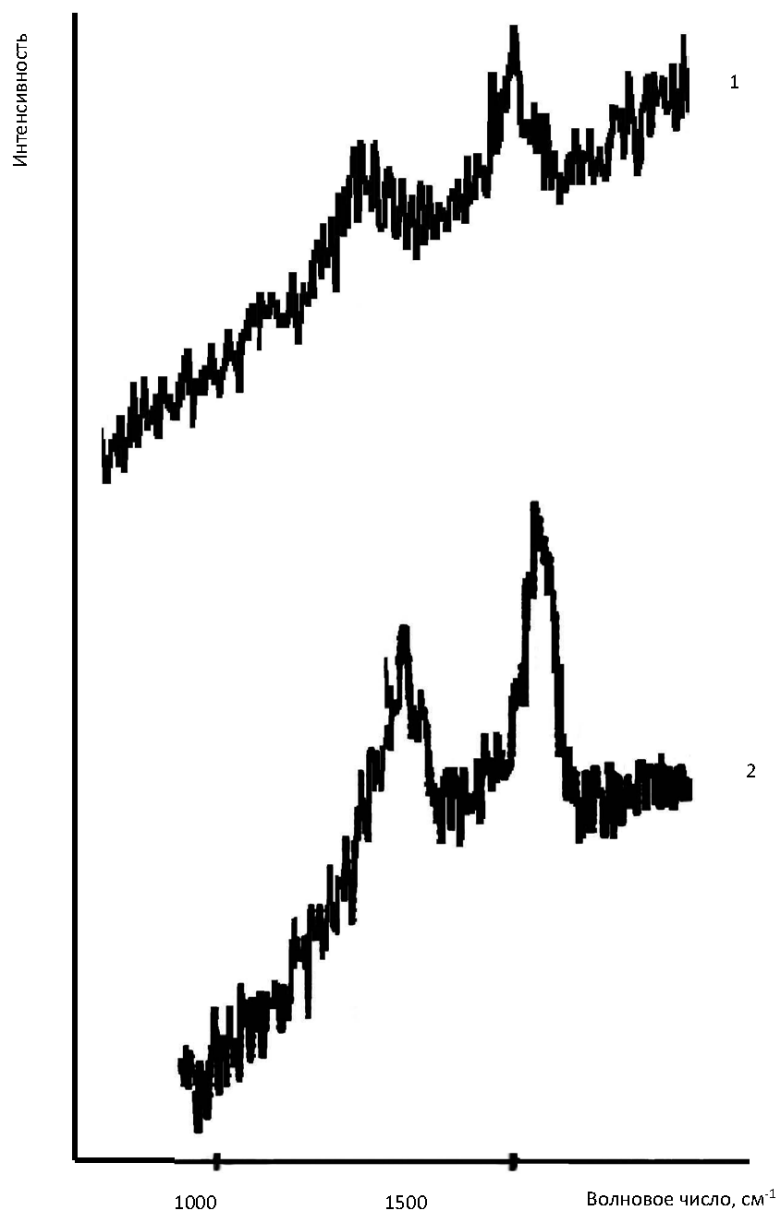


Figure 24 – 1 – shungite rock №9; 2 – shungite concentrate

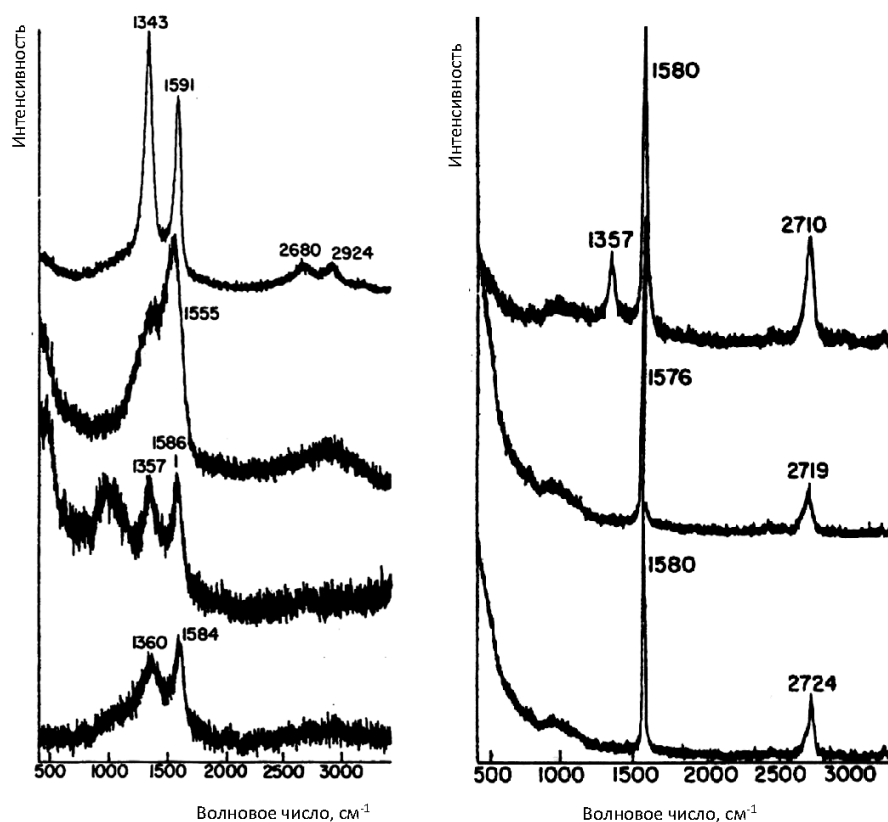
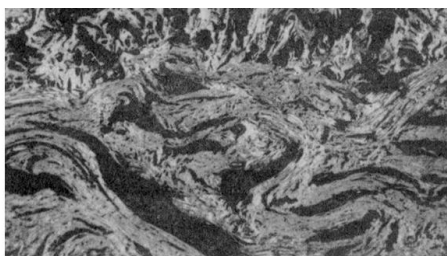
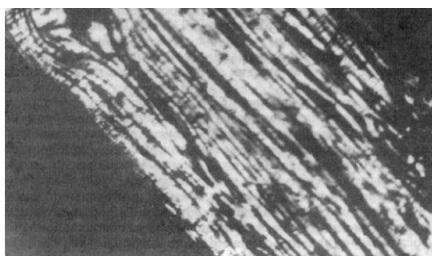


Figure 25 – Raman-spectra of different types of carbon
 а (1 – charcoal, 2 – coke, 3 – diamond-like carbon, 4 – glassy carbon); б (1 – natural graphite, 2 – highly oriented pyrolytic graphite, 3 – polycrystalline graphite)

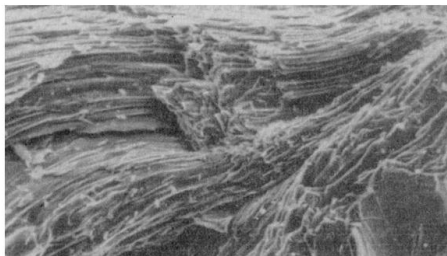
The spherulite structure (Figure 26, e) consists of aggregates of particles with spherical symmetry of spherulites 0,5–5 μm in size, morphologically very similar to spherulite polymers. They have characteristic disordered arrangement of the centers of formation of fragments with a well-defined molecular orientation. The central site of spherulites has a layered structure, however the radial character of the structure is typical for spherulites (Figure 26, e). Microdiffraction studies of spherulites show the presence of arcs corresponding to the basal planes, whose packs are located radially [210].



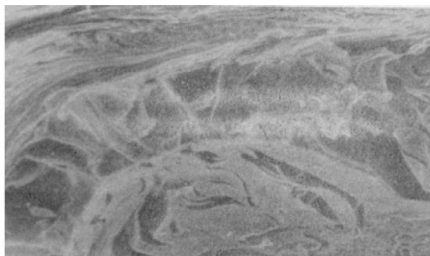
а) микроструктура рядового кокса, $\times 50$



б) микроструктура нефтяного замедленного коксования, $\times 50$



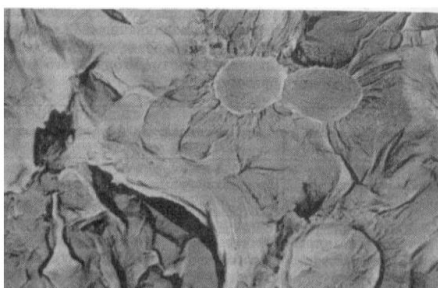
в) ламелярная микроструктура кокса (сканирующий электронный микроскоп), $\times 50$



г) микрофотография нефтяного кокса чешуйчатой структуры (сканирующий электронный микроскоп), $\times 50$



д) микрофотография нефтяного игольчатой структуры, $\times 50$



е) реплика сферолитовой микро-кокса структуры пиролизного кокса, $\times 200$

Figure 26 – Microstructure of coke

4.4. X-ray analysis of shungite rocks

Upon studying the multicomponent carbon systems, recently direct methods (that do not destroy the test sample) such as X-ray quantitative phase analysis, X-ray structural analysis have acquired a special role [197]. These methods, along with reliable diagnostics of any carbon component [198], allow to determine the dynamics and mechanism of phase transformations of natural or synthetic carbon systems in the process of exposure to various physical and chemical factors. The advantage of these techniques is the ability to gain information about the structure of not only crystalline, but also amorphous bodies, which could not be performed using other analytical instruments.

X-ray studies of shungite rocks were aimed at studying the structure and phase composition of shungite carbon. Interest in research in this direction was caused by the exclusion of one of the researchers of carbon materials, in particular, Karelian shungites, coal, etc., Kasatochkin V.I. By describing the origin of humus coals formed under aerobic conditions and sapropel coals accumulating under anaerobic conditions, he notes: “Shungite is special – the most ancient natural coal, dating back according to geologists’ estimates, at least two billion years. However, this is true only for Karelian shungite. As it is known, the formation of Kazakhstani shungites occurred in the Carboniferous period, therefore, their age is determined only 300-500 million years, in addition, the similarity of the Kazakhstani shungites and industrial carbon black was revealed [35].

X-ray analysis of shungite rocks was carried out on a DRON-1,5 X-ray diffractometer (CuK α radiation source and Ni as a filter) using an electronic computing device ПП-14М and modernized collimation. The application of the indicated means made it possible to free the diffraction spectrum, especially in the small-angle region, from “parasitic” radiation while preserving the significant aperture ratio of the device, which is very important when studying X-ray amorphous objects.

To reduce the effect of anisotropy and standardization of the shooting conditions, the samples were exposed to reflection in a metal cuvette with a working volume of 17×17×1,5 mm³. The registration of X-ray diffraction patterns in the range of angles θ from 4° to 30° was carried out in the continuous scanning mode with the recording of the scattering curve on a diagram tape. The X-ray recording mode was selected depending on the mineralogical composition of the samples: the voltage on the anode of the X-ray tube was from 28 to 36 kV, and the current was from 9 to 17 mA.

The processing of diffraction patterns, including the decomposition of a complex maximum, was carried out by the integration method according to the technique described in [197]. To determine the content of the constituent components an X-ray quantitative phase analysis was used according to the values of the intensities of the corresponding reflexes with an error of determination of $\pm 5\%$ [203].

For shungite carbon, the following X-ray parameters were determined: interlayer distance d_{002} , degree of graphitization C_z , sizes of the regions of coherent scattering of L_a and L_c along the crystallographic axes a and c .

The interlayer distance d_{002} (nm) was determined using the Wulf-Bragg equation:

$$d_{002} = 0,0771 / \sin 2\theta_{002}, \quad (82)$$

where θ_{002} - reflex angle (002).

The degree of graphitization of C_z was calculated using the formula:

$$C_z = \frac{L_c \times 10^{-2}}{d_{002} - 3,35}, \quad (83)$$

where L_c - average pack thickness;

To measure the apparent sizes of the coherent scattering regions, the Selyakov-Scherrer equation was employed. The calculation of the sizes the of coherent scattering regions L_{hkl} was calculated using the formula:

$$L_{hkl} = \frac{K\lambda}{\cos\theta\sqrt{\Delta_{u3}^2 - \Delta_9^2}}, \quad (84)$$

where $K = 0,9$ – for basal reflections $00l$ and $K = 1,8$ – for hkl reflexes; λ – X-ray radiation wavelength of; θ – Bragg angle; Δ_{u3} – the measured value of the half-width of the reflex; Δ_9 – instrumental correction obtained upon shooting reference substances.

An analysis of the X-ray spectra of carbon materials at different stages of lithogenesis allowed to conclude that the X-ray phase composition of these substances varies depending on the stage of formation. With an increase in the catagenesis stage, a gradual decrease in the content of I, II, III, and IV phases and a simultaneous increase in the concentration of graphite-like phase (V) are observed, which was shown in the consideration of the organic part in Section 2.1. It was established that the ratio of V and II phases changes regularly and grows with an increase in the stage of catagenesis, with each stage corresponds to a certain quantitative ratio of the indicated phases.

X-ray diffraction study of the natural shungite rocks of “Bolshevik” deposit showed that the test samples were represented by the sum of carbonaceous substances and a number of mineral components (Figure 27 a, 27 b, 27 c, sample numbers are indicated according to the numbering in Table 6). Moreover, X-ray diffraction patterns of samples of various degrees of carbon enrichment are similar, which indicates the proximity of their composition.

Knowledge of the structure of a substance allows predicting the ways of its application. A direct method for studying the structure, that does not destroy test sample, is the method of X-ray analysis.

The unique feature of this method is not only in the possibility of identifying the phase composition, but also in obtaining information about the structure of even amorphous bodies, which could not be done using other analytical instruments. X-ray diffraction analysis allows to study natural and synthetic substances, including amorphous carbonaceous substances in various aggregate (liquid, solid) states. X-ray phase analysis provides new perspectives in understanding the nature of the whole variety of sedimentary organic substances.

In this work, the main direction of X-ray studies is the investigation of X-ray phase composition of shungite rocks, the dynamics of its change depending on the used complex of technological operations of processing the initial samples which are carried out with the aim of increasing the content of the carbon structure itself, as well as to study the structure of the carbonaceous substance of local fossils.

The X-ray phase analysis showed that the test samples are a multiphase system characterized by the presence of a carbonaceous substance and a number of mineral components (Figure 27). Comparison of X-ray diffraction patterns of samples of various rocks indicates that the carbon-containing minerals of “Bolshevik” deposit have identical chemical and mineralogical composition, the difference is their quantitative content.

Shungite carbon is analysed by a reflex with an interlayer distance of $d_{002} \sim 0,35$ nm in the region $18^\circ \div 32^\circ \theta$ (in the figure, the reflex is indicated by a dashed line). The mineral part contains hydromica of hydromuscovite (illite) type, which is confirmed by the characteristic diffraction maximum at 1.01 nm.

In addition to silica bound in hydromica, quartz is detected in the rock, as evidenced by diffraction reflexes: 0,426 0,334; 0,137 nm. The diffractograms also show the

presence of dolomite (0,29; 0,22 nm), a few amount of chlorite (0,353 nm), pyrite (0,271; 0,241; 0,220 nm), siderite (0,173; 0,1794; 0,1965; 0,234; 0,279; 0,357 nm) and feldspar (0,321 nm).

Samples No.2 and 5, the carbon content was 20.4% and 44.7%, respectively. Sample No.4 was less mineralized: reflexes of chlorite, siderite and feldspar were absent on its X-ray diffraction pattern. As mineral impurities only quartz, dolomite, pyrite and hydromica were identified (Figure 27 c). This sample had a high carbon content of more than 70% as determined using X-ray quantitative phase analysis. It should be noted that the data of X-ray quantitative phase analysis to determine the content of organic carbon (Table 19) almost coincide with the results of chemical analysis (Table 5). The difference in the values of the discussed parameter is within the limits of the relative error of X-ray quantitative phase analysis, which is 5%.

The study of the structure of the carbonaceous substance is complicated by contamination with mineral impurities, which, however, is characteristic of all natural organic substances. Mineral components significantly reduce already weak diffraction spectrum of amorphous objects.

In order to free the organic phase from the influence of mineral impurities, samples of the initial rocks were subjected to flotation and chemical enrichment. Sample No.5 was prepared by flotation enrichment of the original sample No.9 (data are given in Tables 6). Sample No.4 is a product of sequential processing of the obtained flotation concentrate with concentrated hydrofluoric acid and a saturated solution of caustic soda at boiling points for 1 hour in each solution.

Based on the given diffraction patterns, it could be concluded that in test samples changes take place due to various processing methods and accompanied by an increase in carbon content.

Let us consider the behavior of shungite samples depending on the applied processing methods. The nature of the diffraction pattern of sample No.5 indicates that flotation enrichment of sample No.9 made it possible to increase the content of the shungite component from 20.0 to 40.0% while maintaining the qualitative composition of the mineral phase (Table 19). As a result of acid and alkaline treatment, the content of carbonaceous material increased to 90.0%. Whereas, carbonates, chlorite and siderite disappeared. Therefore, evaluation of X-ray diffractogram of enriched rocks showed that, although we could not completely get rid of all available mineral impurities, we were able to obtain a concentrate that was as close to saturation as possible. The line (002) in the region $18^\circ - 13^\circ \theta$ refers to interlayer reflection, while the line (100) ($21^\circ - 22^\circ \theta$) characterizes two-dimensional intralayer reflection.

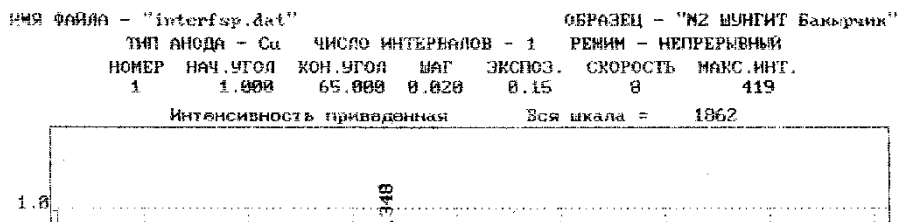


Рисунок 22 в

Figure 27 a – X-ray diffraction patterns of shungite rocks and concentrates (1)

SPECTRUM PEAKS						
№	2Θ	Площ	Іприв	Полушир	Межпл	%
1	8,72	217	367	0,57	10,117	26,3
2	11,48	65	67	0,94	7,708	4,8
3	12,44	74	113	0,63	7,126	8,1
4	17,66	115	147	0,75	5,028	10,6
5	19,90	155	200	0,77	4,466	14,4
6	20,79	167	320	0,52	4,274	23,0
7	23,96	194	180	0,82	3,717	12,9
8	25,10	321	220	1,34	3,551	15,8
9	26,60	648	1393	0,64	3,348	100,0
10	27,78	187	240	0,89	3,214	17,2
11	30,82	145	160	0,92	2,903	11,5
12	32,16	105	127	0,83	2,782	9,1
13	34,92	115	140	0,79	2,568	10,1
14	36,56	64	127	0,48	2,459	9,1
15	39,48	40	80	0,48	2,284	5,7
16	40,24	31	53	0,56	2,241	3,8
17	42,50	65	120	0,52	2,128	8,6
18	45,06	75	113	0,64	2,012	8,1
19	50,18	92	227	0,39	1,819	16,3
20	53,08	43	67	0,62	1,725	4,8
21	54,94	107	73	1,40	1,672	5,2
22	59,96	57	113	0,48	1,543	8,1
23	61,80	22	53	0,39	1,502	3,8

ИМЯ ФАЙЛА - "interfsp.dat"

ОБРАЗЕЦ - "N5 проба2 флотация"

ТИП АНОДА - Cu ЧИСЛО ИНТЕРВАЛОВ - 1 РЕЖИМ - НЕПРЕРЫВНЫЙ

НОМЕР НАЧ.УГОЛ КОН.УГОЛ ШАГ ЭКСПОЗ. СКОРОСТЬ МАКС.ИНТ.

1 1.000 65.000 0.020 0.15 0 500

Интенсивность приведенная Вся шкала = 2258

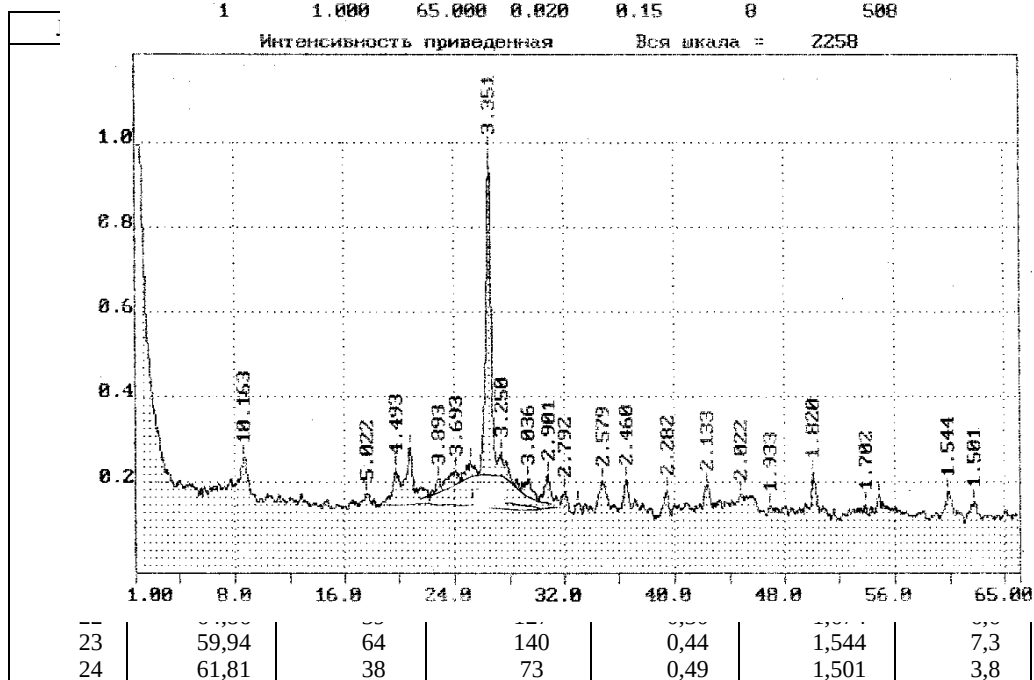


Figure 27 6 (2)

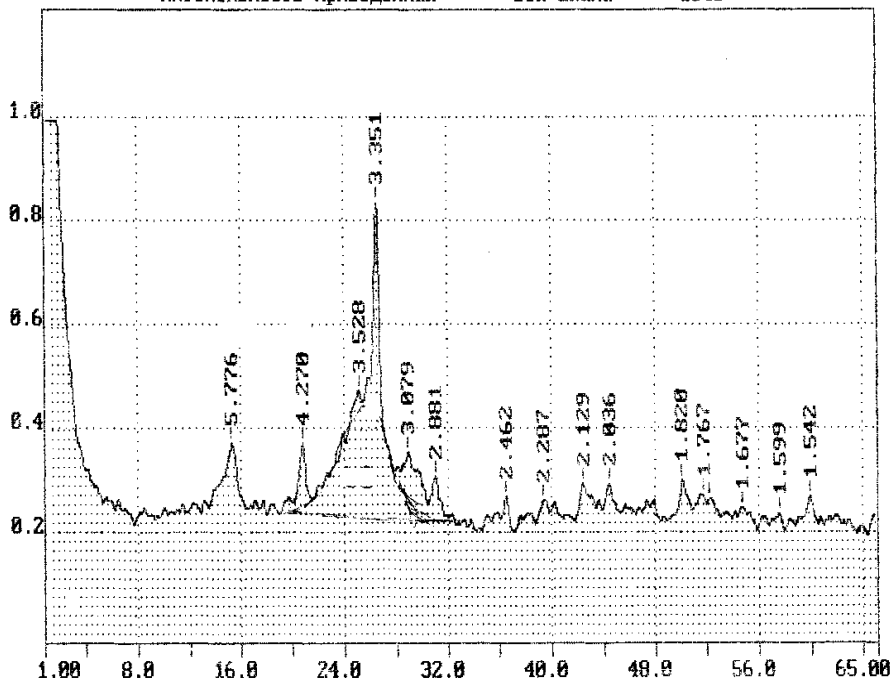
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ОБРАЗЕЦ - "Н4 проба1 HF"

ТИП АНОДА - Cu ЧИСЛО ИНТЕРВАЛОВ - 1 РЕЖИМ - НЕПРЕРЫВНЫЙ

НОМЕР НАЧ.УГОЛ КОН.УГОЛ ШАГ ЭКСПОЗ. СКОРОСТЬ МАКС.ИНТ.
 1 1.000 65.000 0.020 0.15 8 617

Интенсивность приведенная Вся шкала = 1645



SPECTRUM PEAKS

№	2θ	Площ	Иприв	Полушир	Межпл	%
1	15,32	309	253	1,17	5,766	24,8
2	20,80	162	253	0,61	4,270	24,8
3	25,24	509	420	1,16	3,528	41,2
4	26,58	646	1020	0,61	3,351	100,0
5	29,02	256	227	1,30	3,079	22,3
6	31,04	111	153	0,83	2,881	15,0
7	36,52	60	113	0,51	2,462	11,1
8	39,42	111	100	1,07	2,287	9,8
9	42,48	161	153	0,99	2,129	15,0
10	44,52	142	153	0,88	2,036	15,0
11	50,14	147	167	0,85	1,820	16,4
12	51,72	131	120	1,05	1,767	11,8
13	52,24	114	107	1,03	1,751	10,5
14	54,74	101	80	1,21	1,677	7,8
15	57,64	47	60	0,76	1,599	5,9
16	59,98	76	113	0,64	1,542	11,1

Figure 27 в (3)

The angular position of these maxima is quite close to the position of the main maxima of graphite. This indicates that the structure of shungite is very similar to

graphite, i.e. composed of similar graphite-like grids with a distance of C-C equal as in graphite, 0,142 nm.

Figure 28 shows the comparison of the diffraction curves of Karelian shungite I type, soot Π 803 and three-dimensionally ordered graphite. X-ray diffractogram of carbonaceous substances have generally have two, three or four diffraction maximum with different degrees of diffuseness. Here, the diffraction patterns of all the studied carbonaceous materials are represented with two bell-shaped reflexes. In general, the angular curve of the scattering intensity by carbon material of shungite rocks is very similar to that amorphous or low crystalline substances.

However, as can be seen from X-ray diffraction patterns (Figure 27 and 28), the maximum (002) of shungite carbon, however, like soot, is shifted towards small angles relative to the maximum (002) of graphite. This is explained by an increase in the average interlayer distance d_{002} for polycondensed shungite nets ($d_{002} \sim 0,35$ nm) and soot ($d_{002} \sim 0,36$ nm), laid approximately parallel to the packages, but having no azimuthal orientation relative to each other, in comparison with the interlayer distance of graphite ($d_{002} \sim 0,3354$ nm) [197]. In other words, the graphite-like networks in shungite are randomly displaced relative to each other in the plane ab , which indicates the amorphism of shungite carbon.

The imperfection of shungite structure, in comparison with the structure of three-dimensionally ordered graphite, is also indicated by the absence of diffraction lines with indices (002). However, despite the fact that, in comparison with the graphite monolayer, the polycondensed shungite net is defective, strongly deformed, the shungite itself could be considered to have a rather highly ordered structure. Such structure, by the nature of the diffraction pattern, could be attributed to a turbostratic carbon structure similar to carbon black crystals, which also have a two-dimensional order.

By analysing the profiles of (002) and (100) lines and their angular position, in addition to the interlayer distance, the sizes of the coherent scattering regions along the crystallographic axes a и c were calculated: L_a – the average diameter of the flat fragments of molecules placed in packages; L_c – average thickness of packages (Table 19). As can be seen from Table 18, shungite carbon of natural samples is characterized by small sizes of areas of coherent scattering: within 8,2 nm – according to the diameter of the grid and 2,6 nm – according to the thickness of the package. For graphite, the values of these indicators are 100 nm and 50 nm, respectively. It should be noted that the values of L_a and L_c parameters of test shungites are slightly less than those for Karelian shungite of I kind ($L_a = 9,5$ nm, $L_c = 3,3$ nm) and are close to the sizes of soot crystallites ($L_a = 6,5$ nm, $L_c = 2,9$ nm). In cases of a high content of mineral impurities in shungite-bearing rocks, L_a was not calculated.

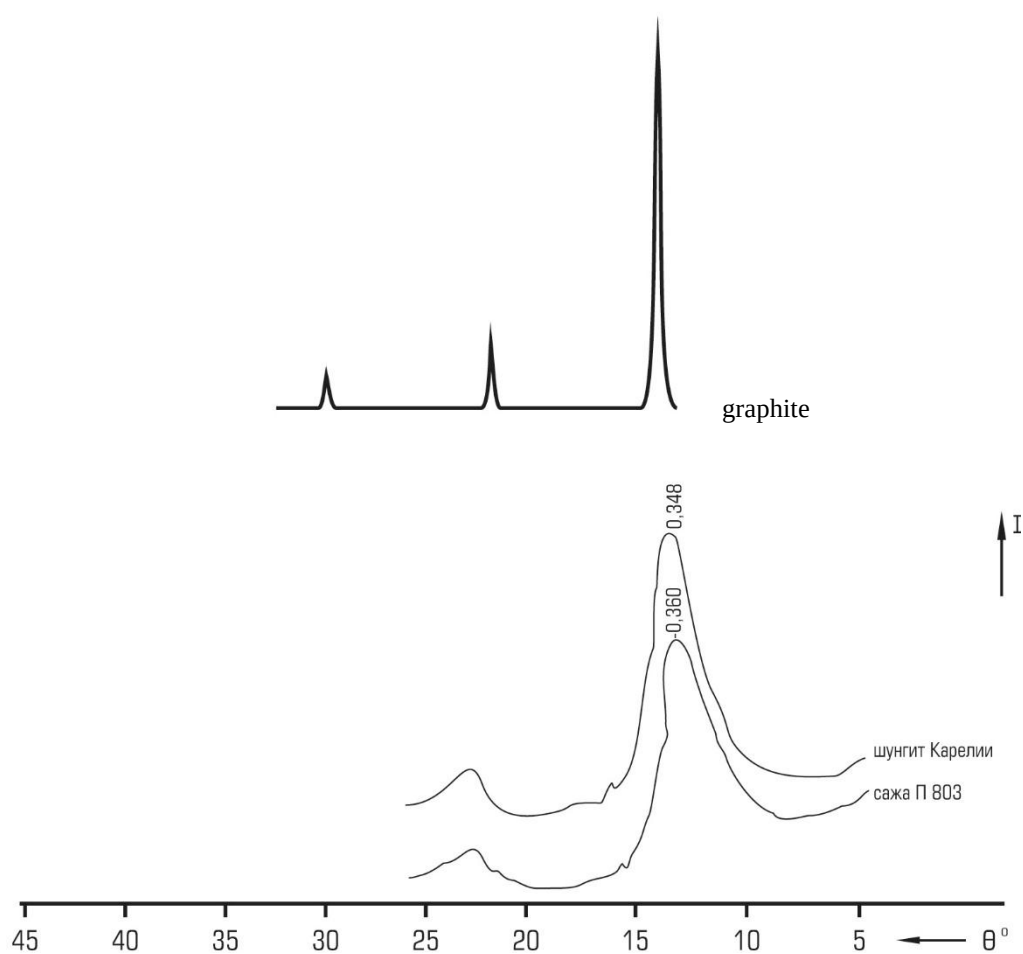


Figure 28 – X-ray diffraction patterns of carbonaceous substances

Figure 28 – Diffraction curves of Karelian shungite of I variety, soot П 803 and three-dimensionally ordered graphite

Based on the data presented in Table 19, it could also be concluded that there are practically no significant changes in the structural parameters of the graphite-like component when using the above enrichment techniques. For the graphite-like component (Γ_ϕ) of test samples, the level of graphitization (C_z) was determined, which indicates the degree of transformation of the X-ray amorphous component of Γ_ϕ into the crystalline state – graphite (Table 19). The higher the C_z parameter, the more perfect the structure of shungite. From an analysis of the data in Table 19, it follows that the most disordered carbon is observed in samples with a high content of carbon (sample No.4). With a decrease in the carbon fraction, its general ordering increases (sample No.2).

The presence of carbon with different structural ordering in an one microvolume of shungite rocks, perhaps, associated with the effect of crystals of the mineral base on the structure of the carbon in contact with it.

Table 19

X-ray diffraction analysis results

№ sample	d_{002} , nm	L_c , nm	L_a , nm	$C_z = \frac{L_c \cdot 10^{-2}}{d_{002} - 3,35}$	C, %	Mineral impurities
2, natural shungite	0,348	2,6	-	2,00	20,0	Hydromica, chlorite, quartz, pyrite, siderite, dolomite, feldspar
4, Acid-base enrichment	0,354	2,3	7,0	1,20	90,0	Quartz, hydromica, pyrite
5, floatation concentrate	0,355	2,3	7,0	1,15	40,0	То же
Явнок-ристаллический графит	0,335	50,0	100,0	-	-	Gneisses, mica shales, quartzites, shales, sedimentary rocks
Soot П 803	0,360	2,9	6,5	1,16	95,0	-

The dependence of the total order of shungite on its percentage content in the sample, i.e. from the area of contact with minerals, it is probably determined by the fact that the zone of catalytic effect has limited dimensions and is adjacent directly to the crystal. The catalytic effect of the mineral on the structural transformations of carbon of shungite rocks may be due to, at least, two main characteristics of the crystal – its elemental composition and structure [35]. For instance, the authors [186] established that quartz (a mineral with a tetrahedral structure) does not significantly affect the structural transformations of carbon, while layered silicates (muscovite, chlorite) contribute to the formation of carbon black. The study of carbon materials and their composites using X-ray diffractograms is associated with special difficulties, since almost all materials, except known crystalline modifications of carbon, are multiphase (multicomponent) mixtures. The main maxima of various phases of carbon systems merge into one broad (from 2° to 15°) reflection. Therefore, to characterize the structural state of a particular carbon substance, knowledge of “classical” parameters, such as the interlayer distance d_{002} and the sizes of the coherent regions of scattering L_a and L_c is insufficient. For qualitative and quantitative analysis, it is important to know the position and intensity of the main reflexes of each component. For qualitative and quantitative analysis, it is important to know the position and intensity of the main reflexes of each component. Therefore, upon conducting X-ray diffraction studies [197,198], it is necessary to decompose complex reflections of graphite-like phase into components by means of an iterative method using approximation based on experimental profiles of reflexes from a number of reference substances. As a result of such processing of X-ray diffraction patterns in sample No.4 (where the maximum carbon enrichment was achieved), it was found that the organic part of shungites is a complex mixture consisting of one carbon (Γ_ϕ) and three hydrocarbon (H_ϕ , O_1 , O_2) phases. The polynaphthenic phase (H_ϕ) is a clathrate structure (Figure 19) containing alkane chains, i.e. consisting of condensed (B) and naphthenic rings separated by methylene bridges (A). H_ϕ is analysed by a primary reflection of $d \sim 0.47$ nm (γ -band).

The structures of oxygen-containing phases with $d \sim 0.8$ nm (O_1) and with $d \sim 1.8 \div 2.0$ nm (O_2) have not been determined, as well as the amount of oxygen contained in them. The quantitative composition of the organic part is presented in Table 20. After heat treatment at 850 °C in the argon medium, the hydrocarbon phases disappeared.

It was established that most samples of industrial soot of different grades consist of two phases [113]: graphite-like and борхедоподобной-like (polynaphthenic), and the content of the latter could reach 30% depending on the degree of graphitization. The soot obtained at low-temperature combustion of rich methane-oxygen mixtures in stream conditions, according to the phase analysis, is a mixture of three phases: graphite-like, polynaphthenic and oxygen-containing. The presence of an oxygen-containing phase O_2 at an angle θ equal to $3,7^\circ$ is due to the formation of soot products in the presence of oxygen in the air. According to the quantitative analysis of low-temperature soot, the content of O_2 -phase varies from 12 to 14%, H_ϕ – from 27 to 31%, and Γ_ϕ -phase – from 57 to 60%. The dimensions of the coherent scattering regions of low-temperature soot are $L_a = 5,4$ nm, $L_c = 1,55$ nm (for soot obtained at 973 K) and $L_a = 5.1$ nm, $L_c = 2.2$ nm (for soot obtained at 1003 K), interplanar distances d_{002} are equal to 0,364 nm and 0,362 nm, respectively.

Comparison of these data with the results of X-ray analysis of test shungites reveals similarities and differences between the materials: the presence of oxygen-containing phases in shungites suggests that their formation occurred in the presence of oxygen similar to the formation of low-temperature soot.

Table 20

The composition of the organic part of shungite rocks

X-ray	Phase content, %	d , nm
Γ_ϕ	70	0,357
H_ϕ	18	0,470
O_1	11	0,800
O_2	11	2,200

The quantitative content of graphite-like and polynaphthenic phase, as well as the calculated values of the X-ray diffraction parameters characterize natural shungites, as a more ordered carbonaceous substance, because according to the literature [163], with an increase in the level of graphitization, the concentration of Γ_ϕ increases with a simultaneous decrease in d_{002} values. Consequently, according to the degree of graphitization, shungites are similar to industrial soot.

Thus, according to the results of X-ray studies, the structure of shungite rocks is characterized as multi-phase. X-ray phase analysis allows to establish both the mineral and organic parts of shungite rocks, as well as to trace the dynamics of changes in mineral and carbonaceous elements depending on the processing techniques used, record changes in the graphite-like component and determine its approximate content.

It was established that the mineral base is formed by hydromica, chlorite, carbonates, quartz and feldspar. The carbon of the organic part, defined as amorphous, is characterized by parameters similar to those of graphite. It was found that the structures of shungite and soot carbon are similar to each other. In addition to the graphite-like component, the X-ray diffraction technique reveals the presence of three hydrocarbon phases in the composition of the organic phase: polynaphthenic and two

oxygen-containing, which also indicates incomplete formation of graphite-like structures.

4.5. Characterization of the structure of shungite using electron microscopy

Electron microscopic images were taken on a Quanta-3D-200i scanning electron microscope in the National Nanotechnology Laboratory of the open type of Al-Farabi Kazakh National University. Different type of shungite powders were investigated by direct observation in the light transmittance using microdiffraction technique. Samples were prepared using dry preparation methods, i.e. dry application of the sample on a collodium film-substrate. Upon microdiffraction studies photographing of diffraction patterns were carried out.

Thus, the mineral composition of shungite rocks was studied using chemical, X-ray and thermal analyses techniques. The finely dispersed (X-ray amorphous) structure of the shungite phases was investigated using electron microscopy. The finely dispersed structure of the schungite phases was revealed using electron microscopy.

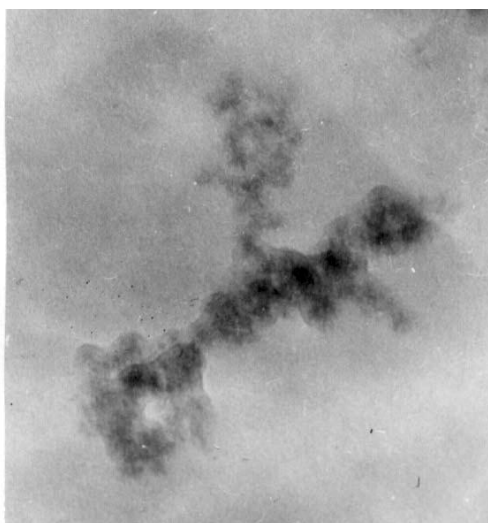
The samples of study were lump rocks with different contents of shungite carbon: ~ 20,0% (sample No.1), ~ 40,0% (sample No.2) and ~ 90,0% (sample No.3). Lump preparations were formulated for research using coal replicas methodology. Samples No.1 and No.2 are solid rocks, the major part of which was the mineral phase. Replicas of good quality were obtained from these samples. Upon mechanical separation of the coal replica, clusters of fine particles were extracted on its surface.

An electron microscope images of fine structure of shungite material sample No.1 is shown in Figure 29. As shown from the figure, the carbon structure of the sample is represented by accumulations of dendritic (Figure 29, a) and isometric (Figure 29, b) shapes. It was established that dendritic clusters are composed of small round shaped formations of 20–30 nm. The latter, in turn, are composed of fine particles of 1.5–2.5 nm in size. The same particles form clusters of isometric shape. Figure 29 shows the vicinity of clusters of fine particles of two types.

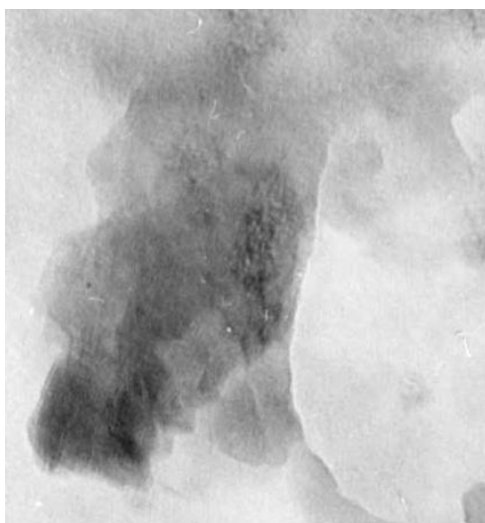
The microdiffraction pictures from such clusters are ring electron diffraction patterns shown in Figure 29, d. The value of the interplanar distance for first ring varies depending on the size and density of the accumulation in the range from 0,34 to 0,36 nm. This value of the interplanar distance is consistent with that determined during the X-ray analysis (Table 19).

In sample No.2 clusters of two types were also found which are similar to those considered for the first sample (Figure 29, a, b). Furthermore, in sample No.2, strictly oriented clusters of needle-like nature composed of translucent particles smaller than 0.5 nm were observed (Figure 29, c).

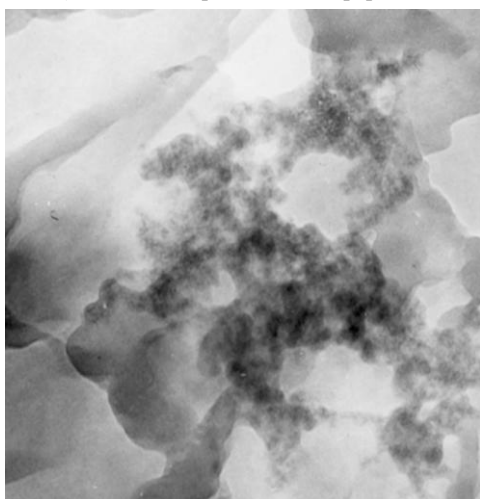
The microdiffraction pattern from needle clusters is a ring electronogram (Figure 29, d) with a set of interplanar distances of 4,47; 3,08; 2,6; 2,11; 1,95; 1,5; 1,24 nm, which could be attributed to SiO₂ or FeOH₃ except for the first reflex which corresponds to FeOH₂ [198].



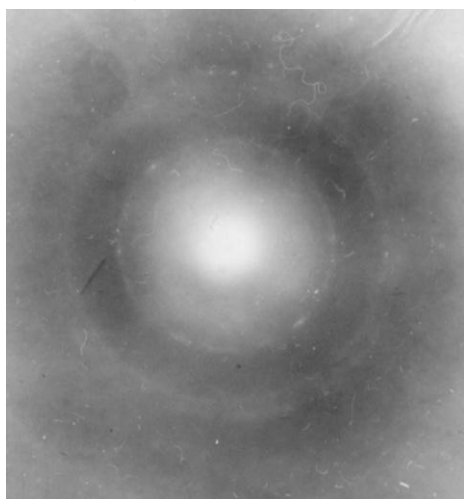
a) скопления гроздевидной формы



b) isometric clusters



c) replica of the fine structure of shungite



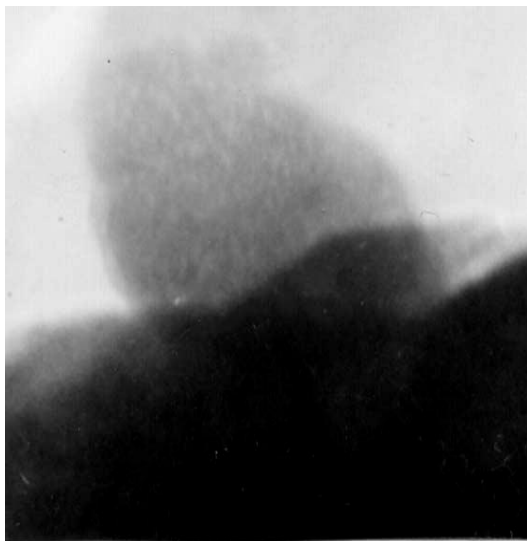
d) microdiffraction pattern

Figure 29 (1) – Electron microscopic images of shungites

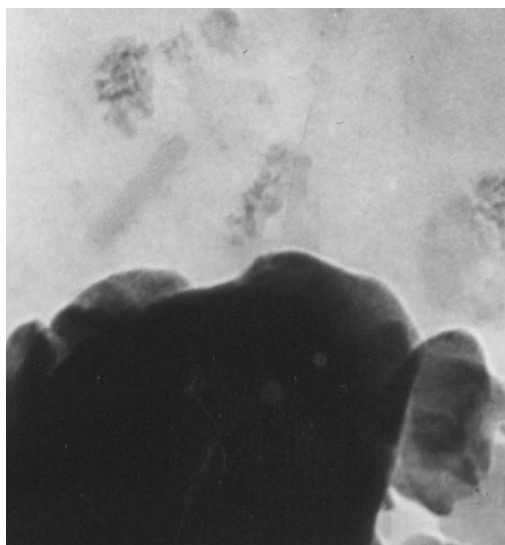
Figure 29a shows the vicinity of dendritic and needle clusters. The sample presented in Figure 29, f, unfortunately, is less informative. Due to the fact that it was sooty, brittle on the cleaved surface, it was not possible to separate the applied film well from the base. As it turned out, such method of preparation of replicas is not very suitable for the analysis of such samples. As a result, the replica was populated by large, dense formations (by particles of isometric shape identified as graphite), which overlap sections with finely dispersed particles.

Accumulations of finely dispersed particles could only be seen on the translucent edges of large, dense particles of graphite (Figure 29, b and 29, e). When considering the above photographs, it could be seen that these clusters are also isometric in shape.

The microdiffraction pattern from such sections, as shown in Figure 29, d, is diffuse rings due to overlapping of large particles of graphite.



e) porous shungite formation



f) shungite concentrate

Figure 29 (2)

Powder samples of shungite flotation concentrate were studied using “dry preparation” method. The analysis showed that the sample after flotation is characterized by the presence of several carbon phases. The major part is predominantly large, translucent, dense particles up to 1 μm (1000 nm) (Figure 29, e). Small accumulations composed of dense particles of up to 4 nm in size are less common (Figure 29, f). Such clusters could also be observed on the edges of large, dense particles (Figure 29, a, b, c).

Using the electron microscopy clusters of another type were discovered (Figure 29, a, c). These are less dense structures penetrated by voids. In other words, these are

porous formations. The pore size reaches 5 nm, the particle size is 4 nm. It should be noted that the structure of such formations coincides with the globular form of the Karelia shungite, for which the globule is a typical feature of the structure. However, the size of the globules of the studied shungites is much smaller than, for example, the migration shungite from Shunga. The size of the globules of the latter, on average, is determined to be equal to 30 nm (with a range of from 15 nm to 100 nm). Based on this, it could be assumed that the molecular chains of Kazakhstani shungite samples are more flexible compared to the Karelian shungite. This determines a larger bending angle during folding, which results in a smaller size of globules and pores of the test shungites.

The determined structural formations of different types give a microdiffraction picture corresponding to shungite (Figure 29, d). The interplanar distance for the first ring ranges from 0,345 nm to 0,351 nm. This is a typical silica particle: large, translucent, penetrated by dense formations, 5 nm in size.

4.6. EPR spectroscopic characterization of shungite rocks

The state of the theory of chemical reactions in a condensed phase is such that the theory and experiment are developed almost independently. The theory at present is only capable of giving general qualitative laws, but not quantitative forecasts. However, one of the main properties of chemical reactions in solids established – even in the kinetic regime, the reactions are controlled by the molecular dynamics of the solid, and the molecular organization of the transition state becomes the limiting stage, and not the actual chemical act. From this point of view, it is very important to understand how, for instance, macromolecules bind to solid surfaces.

The energy saturation of cluster-shaped materials means that the fundamentally incomplete crystal lattices in them correspond to a huge number of defects that cannot relieve excess energy.

A huge amount of this energy is concentrated on unpaired electrons localized on defects, which could be confirmed by EPR spectroscopy. Thus, it is known [27] that an intense G-signal is observed in the particles of carbon black, which corresponds to free radicals or conjugated carbon structures. In preliminary experiments our shungite samples also had an intense EPR signal.

EPR spectroscopy was used to study 3 samples of shungite sample. Sample No.1 is a flotation concentrate (carbon content ~ 40.0%), sample No.2 – natural shungite rock (carbon content ~ 20.0%); and sample No.3 is sample No.1 after acid-alkaline treatment (carbon content ~ 90.0%). EPR spectra were recorded using a Bruker ESP – 300 E spectrometer. Spectra were recorded in the X-band at frequencies of about 9,7 GHz with a change in induction from 0,05 to 0,6 T. The concentration of paramagnetic centers amounted to over 10^{19} спин/г, i.e. high enough, which, as usual, is characteristic for soot [26, 27].

The EPR spectra of all the studied samples markedly differ from each other. The simplest spectrum is observed in sample No.2. On a wide scan (Figure 30, a), the intense line of the ferromagnetic resonance is clearly visible due to paramagnetic impurities of iron oxide Fe^{3+} . Against its background in G-factor ~2.0 region, a line is visible that corresponds to a symmetric singlet signal that does not have traces of an ultra-thin structure (UTS). Probably, this signal corresponds to a system of conjugated carbon bonds (or cumulated), weakly developed because the exchange narrowing does not

occur. It is very interesting to compare the spectra of samples No.2 (Figure 30, a) and No.3 (Figure 30, b). On a wide scan in sample No.3, the signal of the ferromagnetic resonance is very small, which corresponds to the almost complete removal of Fe^{+3} oxide after acid treatment. Then the signal in $G \sim 2.0$ region (which is close to the value of G -factor for a free electron) has a somewhat unanticipated form. This is a very intense signal, symmetrical and without the signs of UTS, but its half-width (about 0,03 T) is very large. According to preliminary data, it corresponds to the presence of biradicals in the sample.

The most complex EPR spectrum is observed for sample No.3. A wide scan (Figure 30, c) clearly shows the ferromagnetic resonance of alkaline treatment of the flotation concentrate; in this sample the mineral ferromagnetic impurities apparently differ from Sample No.1. It should be noted that the amount of such impurities is also less than that of sample No.1. An intense peak with a G factor equal to approximately 2,0 is clearly evident in the spectrum. This signal is written in more detail on the average scan (Figure 30, d). Firstly, in G -factor ~ 3.0 region (and also at $G < 2,0$), the components apparently correspond to Fe^{3+} impurities in the paramagnetic state. Secondly, there is a narrow signal in $G \sim 2.001$ area, which is clearly visible on a narrow scan (Figure 30, e). Obviously, the last signal corresponds to the presence of a large number of unpaired electrons localized in free radicals or delocalized in a condensed system of conjugated bonds, with a strong exchange interaction narrowing the line.

Thus, the preliminary results of the study of paramagnetism of shungite samples are in good agreement with the results of studies carried out using other physicochemical methods, although the tasks of a more thorough clarification of the nature of the signal of ferromagnetic resonance remain unsolved. Nevertheless, it is clear that the number of unpaired electrons in shungite particles, in any case, is not less than their number in ordinary soot particles, which provides us grounds to propose a physical model for enhancing composite materials by shungite.

Segments in elastomers contain double bonds $>\text{C}=\text{C}<$, some of which, when in contact with the surface of shungite particles can diffuse into the composition of the macromolecule segments inside rather large pores, which, as revealed by electron microscopy, are observed in the structure of shungite carbon. Since $\text{H}_2\text{C}=\text{C}$: carbenes, as was noted in [105], could condense (connect) not only via a double bond, but could also be introduced via $\text{C}-\text{H}$ bonds, the carbon cluster formed by the multichannel scheme can contain a whole set of differently localized unpaired electrons in the defects.

A segment of a macromolecule that has entered into this environment inside the cavity could create chemical bonds with carbon atoms not only via opening a double bond, but it is also possible by introducing defects' biradicals in the $\text{C}-\text{H}$ bonds. The appearance of such strong bonds at interphase boundaries should significantly enhance the elastic-strength properties of composite materials due to a change in the supramolecular structure due to the interaction with the carbon-mineral component of shungite rocks.

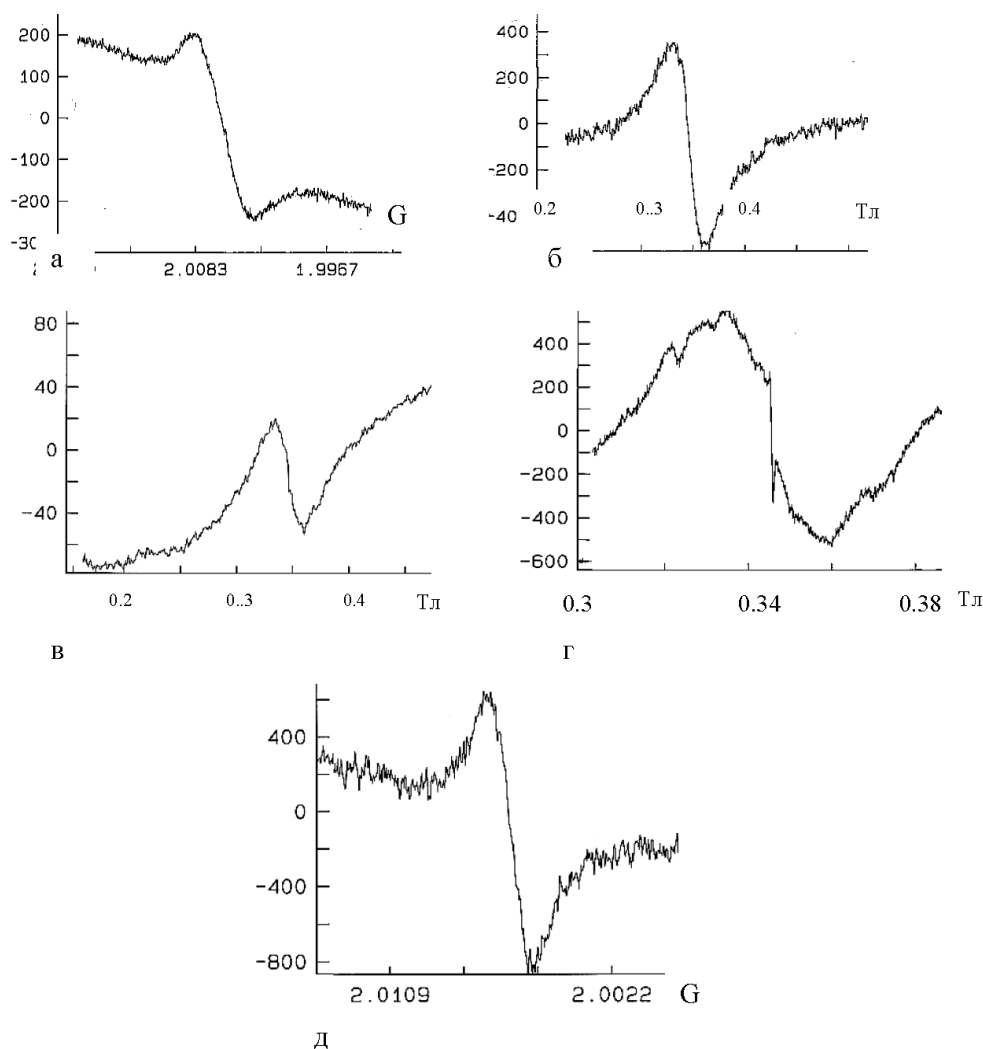


Figure 30 – EPR-spectra of shungite rocks of “Bolshevik” deposit (a-д)

4.7. Determination of fullerene clusters in shungites of Kazakhstan

For many years, it was believed that carbon could form only two crystalline structures – diamond and graphite. However, in 1985, Kroto and co-workers obtained carbon molecules of the new class now known as fullerenes [210].

Fullerenes are closed surface carbon structures that exhibit specific properties of a distinctive material as a physical object and chemical systems. Intensive efforts of specialists from various countries led to the discovery of many new interesting properties of fullerenes, which make it possible to relate to fullerenes not only as a new attractive object of fundamental science, but also as a basis for a wide range of applied developments.

Fullerenes, although they have structural elements that common with graphite, are a special form of carbon that is different from graphite, and also from diamond. The most popular one among fullerenes is C_{60} molecule, which is characterized by the highest stability. C_{60} molecule has the structure of a regular truncated icosahedron and resembles the surface of a soccer ball. C_{70} molecule, which has the shape of a closed spheroid, also has increased stability.

Fullerenes are a synthetic material. The most effective approach to obtain fullerenes is the thermal decomposition of graphite in an electric arc or by laser irradiation in helium atmosphere. However, it was reported [186] that after 7 years of discovery fullerenes were discovered under natural conditions in the North of Russia. The fullerene carriers were Karelian shungites, but scientists still could not explain the appearance of fullerenes in shungites.

Authors report [197] the structural similarity of shungite and fullerite (fullerites are fullerenes in a condensed state): firstly, the spherical hollow shungite globule is similar to fullerene molecules; secondly, the graphite-like layers of shungite are distorted in such a way that their hexagonal symmetry is reduced to trigonal, which is also characteristic of the carbon layers of fullerites. Therefore, globular shungite is considered as fullerene-like carbon expressed with intra- and interglobular porosity.

Study of fullerenes by researcher, scientists from different countries, as well as the discovery of fullerenes and fullerene-like structures in the globular shungite carbon of Karelia and, in addition, attempts to explain the high activity of shungites due to the presence of fullerenes in their structure [186] stimulated the group of authors to study shungite rocks of “Bolshevik” deposit in this direction. We have carried out a series of experiments to determin fullerenes in shungites. The experiments to determine the presence of fullerene clusters in the composition of shungites were carried out according to the technique described in [199].

Absorption bands that characteristic to C_{60} molecules, as shown in Figure 31, are absent in IR-spectrum of the test solution, which indicates the absence of fullerenes in shungite rocks of “Bolshevik” deposit.

It was reported [199] that the extraction of fullerenes from Karelian shungites was carried out by sequential treatment with ethanol and hexane, despite the fact that, as mentioned above, fullerenes are almost insoluble in these solvents. The analysis of extracts carried out using high-performance liquid chromatography revealed the presence of $C_{60} - C_{70}$ fullerenes in an amount of 0.0001%. In addition, the data of IR spectroscopy of Karelian shungite extracts are presented in [2]. In this work, the isolation of the organic phase was carried out using heptane and chloroform. It was found that the organic composition of Karelian shungite rocks from heptane extracts includes saturated hydrocarbons, the organic substance from chloroform extracts consists of aliphatic saturated compounds having carbonyl groups.

However, using the paramagnetic resonance technique, which is more sensitive compared to IR-spectroscopy, it has been established that the composition of organic shungite substance consists mainly of aliphatic hydrocarbons, primarily aliphatic saturated ketones and esters with a branched structure with a small presence of aromatic compounds.

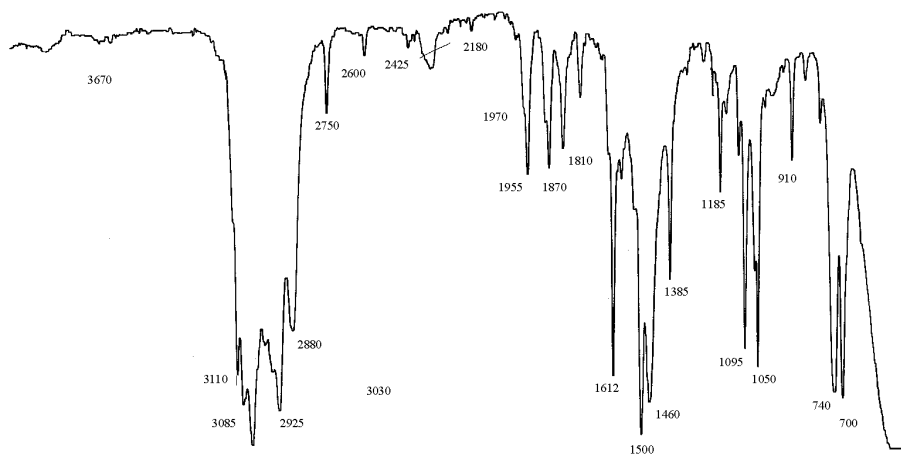


Figure 31 – IR-spectrum of shungite rocks extracts (1) (a - toluene extract from a high-carbon sample of shungite sample)

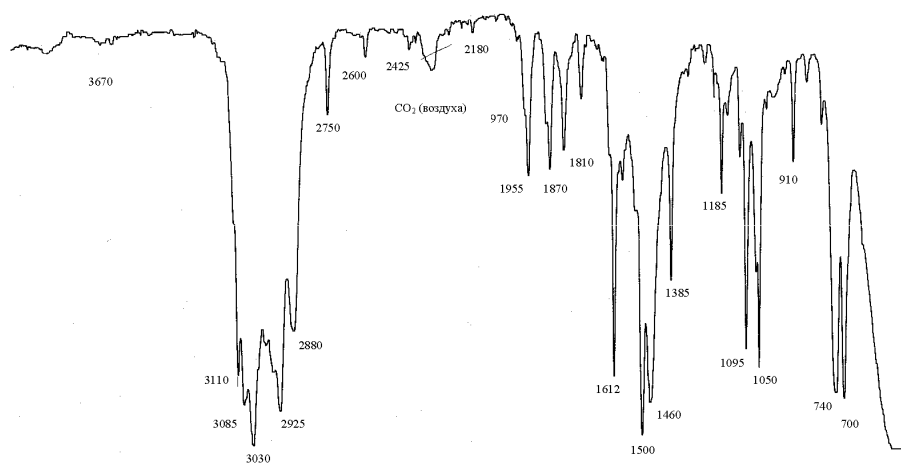


Figure 31(2) IR-spectrum of toluene (6)

CHAPTER 5 SHUNGITES AS FILLERS OF COMPOSITE MATERIALS

5.1. Study of shungite activity as a reinforcing filler of rubber compounds

The field of practical use of industrial carbon black (soot) is extremely diverse: from black pigment for coating, paint and printing industry to the production of carbon-graphite materials (electric brushes, carbon cathodes, etc.). Large quantities of soot are consumed in polymer manufacturing industries (the second largest in terms of material consumption). Carbon black is of particular important as a reinforcing filler for elastomers which enhances the strength properties and improves the specific properties of rubber and polymer vulcanizates. One of the actual tasks of the modern technology of composite materials is to find new types of raw materials for replacing scarce and expensive ingredients, which is also carbon black. The most significant consumers of carbon black in the Republic of Kazakhstan are companies manufacturing rubber products. Rubber enterprises in Kazakhstan at this stage are experiencing a soot deficiency, which is produced outside the country. The solution of the problem in place by traditional methods is inexpedient due to environmental and economic reasons [185]. In this regard, it remains an urgent task to find the possibility of obtaining highly dispersed fillers – partial or complete substitutes for expensive carcinogenic hazardous carbon black due to the expansion of local raw materials base (development of new deposits), or through the use of wastes from other industries.

The introduction of new types of fillers necessitates the development of specific requirements for these materials, considering the features based on the relationship “mineralogical composition, structure – technological and physico-mechanical properties of rubbers”. Based on this, it is very difficult to formulate specific requirements for all new fillers.

However, for a targeted choice of fillers, the following requirements must be considered [127]:

- the constancy of the chemical composition, “standard of raw materials”;
- the purity of the product (no impurities and contaminants);
- the moisture content is not more than 0,5%;
- dispersion, characterized by the absence of residue on sieve 014;
- non-toxicity of the product;
- availability of raw materials and its cost;
- the real prospect of new sources of raw materials.

A group of authors was guided by these general requirements in the study of the filler.

As follows from the foregoing, one of the main results of physicochemical studies of Kazakhstani shungite rocks and concentrates is the discovery of similarities in the structures of carbon shungite rocks and industrial carbon black. Such conclusion disturbs the well-established opinion that carbon in the soot is in a special form that not found in natural materials. Along with this, some differences between these carbon materials were also established. Firstly, shungite is characterized by the incompleteness of graphite-like layers (as evidenced by the presence of oxygen-containing phases in its

composition) and, accordingly, a lower degree of orderliness in their packing relative to soot. In addition, shungite carbon differs from industrial soot in the higher dispersion of primary particles. Therefore, we can conclude that the shungites of “Bolshevik” deposit, compared to other carbon materials, are closest to the maximally disordered soot. This suggests that shungite is highly active as the filler in composite materials. The results obtained served as the basis for experiments on the replacement of carbon black upon filling elastomers.

It is a promising of such a reinforcing filler of composite materials, a substitute for carbon black, can serve as a concentrate of shungite carbon with a carbon content of 40.5%.

Experiments on the replacement of carbon black with carbon concentrate based on ores in the manufacture of rubber products were conducted at the production base “Rezina” LLP (Esik, town). In this work, the standard rubber compounds used in the technological process of the company were adopted (Appendix A).

For the preparation of rubber compounds as fillers, samples of natural shungite rocks from “Bolshevik” deposit with a carbon content of 17.6% wt. (sample No.10) and a concentrate with a carbon content of 40.5% by wt. (sample No.14) were used. Shungite filler powders were prepared by crushing in a jaw crusher followed by additional grinding on a 75T – ДрМ vibratory grinder for 12 min. Fillers with a particle size of minus 30 μm were chosen for testing.

A number of physicochemical characteristics were revealed for the fillers obtained, and according to the literature report [201] special requirements for industrial carbon black were also established.

The pH of aqueous suspensions of shungite fillers were determined: 6,39 and 7,49 for samples No.10 and flotation concentrate No.14, respectively. The obtained values exceed the pH values corresponding to the soot oven grades (pH 6-11). According to the authors of the book, the high values of the hydrogen index of the test samples are due to the presence of mineral salts that dissociate in the aqueous medium.

Another regulated property of soot is its structurality. In practice, the structure of carbon black is determined by the absorption of dibutyl phthalate. Despite subjectivity and poor reproducibility, so far, this method is the most objective indicator of the structure of soot [200]. The structural nature of carbon black is determined by the presence of primary aggregates, their size and shape. In addition to carbon, shungite filler contains mineral compounds, as a result of which the original meaning of the discussion concept is lost. However, theoretically, the amount of absorbed dibutyl phthalate should correspond to the volume of the intermediates between the powder particles with their maximum packaging and the condition for maximum air removal. Therefore, the knowledge of this parameter is important, in our case, for the correct preparation of rubber compounds based on shungite filler and in the process of their preparation, similar to knowing the oil absorption of the dye, calculate the amount of oil needed to prepare a paint. Dibutyl phthalate absorption values found are shown in Table 21 (numbering of samples are according to Table 6).

Table 21

Absorption of dibutyl phthalate

No. sample	Absorption of dibutyl phthalate, cm ³ /100g
10	25
14 (floatation concentrate)	30
Π 803	35
T 900	29

From the data obtained it follows that the shungite filler corresponds to the low-structure grades of soot Π 803 and T 900.

One of the indicators, the value of which is strictly controlled in relation to carbon black, is the mass fraction of losses at 105 °C. In the course of chemical analysis of shungite rocks, mass losses during heating at 105 °C have already been determined. As seen from Table 20, the obtained values of the determined parameter were within normal limits established for industrial carbon black. So, for example, the indicator of the mass fraction of losses at 105 °C for soot Π 803 grade should not exceed 0.5%, and for T 900 – 1.5%.

However, with intended long-term storage of shungite rock under high humidity condition and also considering the fact that flotation enrichment is carried out in an aqueous medium, the test samples contained a significant amount of adsorbed water, and the indicator of the mass fraction losses at 105 °C considerably exceeded the established norm (3,6 and 4,1% for samples No.10 and 14, respectively). This could adversely affect the quality of the finished product (rubber), therefore, to avoid this issue the filler samples were pre-dried at 160 °C for 3 hours. As a result, the values of the mass fraction losses at 105 °C were obtained for shungite samples No.10 and 14 (only 0,5 and 0,2%, respectively), which corresponded to the regulated parameters. Nevertheless, upon storing the shungite raw materials under conditions that exclude the possibility of moisture, the above-mentioned heat treatment is not necessary when preparing the sample for use as fillers for rubber compounds. One of the main characteristics of carbon black is its specific surface area. With regard to shungite fillers, the values of the specific adsorption surface were determined, the results of these determinations are presented in Table 22 (numbering of samples are according to Table 6).

Table 22

Specific adsorption surface

No. sample	Specific adsorption surface, m ² /g
10	18
14 (floatation concentrate)	21
T 900 (carbon black)	15

From Table 22 it follows that shungite fillers in terms of specific adsorption surface correspond to soot grades with low indicators of adsorption surface: II 803 (18÷25 m²/g), II 705 (10÷20 m²/g), T 900 (15÷22 m²/g).

The mixture of rubber compounds, their vulcanization and subsequent study of the physicomechanical properties of the finished experimental rubbers were carried out according to the technological regulations and methodsologies applicable at an enterprise (Appendix A). In the course studies experiments were carried out on the possibility of implementing full and partial replacement of industrial carbon black with shungite fillers.

Experiments with the partial replacement of a standard filler were performed using a shungite filler with the carbon content of 17.6% and a floatation concentrate with the carbon content of 40.5%. At the same time, the deficiency of carbon was compensated by adding industrial soot. Thus, upon conducting pilot tests for the production of “Irrigation tubes” at a rubber plant (Test Report in Appendix 3), the optimal amount of carbon black and its substitute for given mixture was 30 and 70%, respectively, with the carbon content of 17.6% and floatation concentrate with the carbon content of 40.5 and 60%, respectively.

Determined mechanical properties during testing the experimental products are given in Table 23 and the results were compared with the physicomechanical properties of the products obtained based on those standard mixture. According to these data, the physicomechanical properties of experimental rubbers were higher than those for products obtained according to the standard formulation (i.e. filled only with technical carbon grade II 803) and comply with the requirements of TY 640 PK № 2977375-02-95 for rubber products.

Table 23

Physico-mechanical properties of rubber products “Irrigation tube”

Наименование показателей	Irrigation tube		
	experimental		standard
	Shungite rock (C-17,6 %)	Flotation concentrate (C-40,5 %)	
Tensile strength, MPa	7,84	9,33	7,35
Elongation at break, %	520	320	300
Residual elongation, %	19	21	40

Moreover, it established that upon using the substitute in the production of rubber goods, the consumption of the industrial oil of I-8-A brand was reduced by 10% while maintaining the standard amount of the remaining ingredients, which is explained by the low value of the absorption index of dibutyl phthalate by shungite filler compared to the soot of II 803 grade.

Thus, the results of pilot tests have demonstrated the possibility of using shungite filler as a partial substitute for carbon black.

As mentioned in the literature review, in addition to reinforcing fillers in the composition of various rubber compounds, inactive fillers, so-called diluents, are also introduced. The latter include kaolin, which consists mainly of the mineral kaolinite ($\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$) and various impurities (quartz, feldspar, etc.). Based on this and considering the data on X-ray and chemical analysis of the composition of shungite rocks, along with complete replacement of carbon black, the replacement of kaolin was also tested. The outcomes on how this affected the properties of the finished products will be discussed based on the comparison of the physical and mechanical properties of test and standard rubbers. Tables 24–25 show the results of testing the properties of rubbers produced according to the standard and experimental methodologies are presented. In the case of test samples the composition of mixture No.1 corresponds to the replacement of not only the standard carbon filler, but composition No.2 corresponds to the replacement of both fillers (i.e., soot and kaolin).

Table 24

The results of determination of mechanical properties of RTP “Irrigation tube” from standard mixture, experimental mixture of No.1 and No.2

№ composition of the mixture	№ shungite filler samples	Breaking load, N	Tensile strength, MPa	Elongation at break, %	Residual elongation, %	Hardness based on TM-2, cond. units
1	10	158,9	6,37	350	16	62
	14	175,5	5,97	300	15	68
2	10	167,4	6,57	360	16	62
	14	119,8	4,80	300	14	61
Standard mixture		104,9	4,13	210	9,3	60

Table 25

The results of determination of mechanical properties of RTP «Techplastina» from standard and experimental mixtures

№ composition of the mixture	№ shungite filler samples	Breaking load, N	Tensile strength, MPa	Elongation at break, %	Residual elongation, %	Hardness based on TM-2, cond. units
1	10	149,5	5,10	180	9	66
	14	139,5	4,70	130	7	63
2	10	189,9	6,37	210	12	67
	14	149,6	4,95	140	7	65
Standard mixture		158,4	5,39	180	8	66

The studies showed that the introduction of shungite as the filler allows to prepare rubbers mainly having higher physical and mechanical properties relative to standard vulcanizates containing carbon black grade II-803. The data presented in Table 26 indicate that if rubbers filled with sample No.14 of shungite-containing rock have a conventional tensile strength value of slightly lower compared to soot-filled rubber, then the tensile strength of rubbers filled with sample No.14 of shungite rock is much higher than the strength of standard rubber. The values of relative elongation at break of rubbers reinforced with high-carbon shungite filler are significantly higher than those

rubbers filled even with low-carbon samples of shungite-containing rocks and soot. Consequently, with an increase in the amount of carbon in the composition of shungite-containing rocks, an increase in the tensile strength properties of rubbers is observed. However, at the same time, an increase in the parameter of the relative residual elongation is observed in comparison with soot-filled vulcanizates. Upon filling rubber compounds with high-carbon shungite rocks, an increase in the numerical value of the hardness is also observed.

In addition, a comparison of the obtained test results indicates that the strength properties of rubbers filled only with shungite are higher than those for rubbers filled with both shungite and kaolin. Indeed, taking into account the phase composition of shungite rocks, the filler based on them could be considered as a complex mixture of active and inactive fillers. Therefore, upon introducing the proposed filler and kaolin together into the rubber mixture, it might be possible that the filling occurs higher than the permissible optimum limit, which leads to some deterioration in the properties of the end rubbers. Consequently, in the manufacture of rubber products it is advisable to replace both the active (carbon) filler and the inactive filler (in this case, kaolin) simultaneously.

According to the results of laboratory tests, the consent from “Резина” LLP was obtained to conduct industrial testings for the production of rubber products using shungite filler with subsequent introduction of the latter into production (see Appendix B).

In experiments with the complete replacement of soot, we attempted to evaluate the reinforcing effect of filling rubbers with shungites with different carbon contents. Despite the successes achieved in the field of reinforcing polymer materials with dispersed carbon black, theoretical concepts about the mechanism of enhancement using specified filler of elastomers (in particular, rubber compounds) remain the subject of discussion [102]. The reinforcing effect of filling is still estimated mainly empirically by the increase in the strength properties of rubbers or resistance to abrasion, a change in the temperature dependence of the mechanical parameters of rubbers, etc. Hence, when determining the reinforcing effect of filling elastomers with shungite fillers, we were based on measurements of the elastic-strength properties of shungite-filled products.

Table 26

Physico-mechanical properties of rubber irrigation tubes

Name of parameters	The composition of the rubber compounds				
	1	2			Standard
	vulcanization time, min	vulcanization time, min			vulcanization time, min
	5	5	7	10	7 ÷ 8
Conventional tensile strength, MPa	4,6	5,1	5,4	3,6	No less 3,9
Relative elongation at break, %	410	430	408	485	No less 250
Relative residual elongation, %	24	17	26	26	No less 30
Hardness, cond. units	50	53	50	52	50-65

Upon comparing the properties of rubbers filled with shungite with different carbon contents and standard soot of grade П 803, we determined that with the increase in the amount of carbon in the composition of shungite-containing filler, the strength properties of rubbers increase. Indeed, increasing the carbon content in the shungite filler and, thereby in the system as a whole, we increase the contact surface area of rubber – active filler, which is of great importance at the stage of mixing rubber with filler and contributes to an increase in the degree of orderliness of the system. Orderliness increases due to an increase in the number of points of application of binding forces (most researchers classify them as physical forces – adsorption and adhesion [132, 135]) evolving between the rubber and the filler, as well as the interaction forces between the filler particles, which lead to the formation of a chain-network structure of the filler permeating the rubber phase. To overcome all the available binding forces, it is necessary to carry out some work of rupture. Apparently, the stronger the system, therefore, the higher the reinforcing effect of the filler created in this system, the greater the amount of work necessary for its rupture. According to Виганду [103], the increase in the work of rupture is a quantitative measure of the activity and the effect of enhancement is expressed by the difference:

$$\Delta U = U - U_0,$$

where U – work of rupture of the filled mixture, U_0 – work of rupture of the unfilled mixture.

If we assume that the work of break is directly proportional to the breaking force, and the latter, as shown from the data presented in above tables, increases from samples of rubbers containing fillers with a low content of shungite to samples with a high content of shungite, then it might be concluded that the work of rupture increases during the transition from mixtures filled with low-carbon fillers to mixtures filled with high-carbon shungite rocks. The growth of the work of rupture shows that the reinforcing effect of filling elastomers with high-carbon content shungite fillers is greater than that of filling with low-carbon samples. Moreover, the breaking force corresponding to vulcanizates containing shungite fillers with the high carbon content exceeds that for rubbers containing soot. This, eventually, shows that the reinforcing effect of filling rubbers with high-carbon shungite rocks is greater than the reinforcing effect of filling with carbon black.

5.2. Mechanism for reinforcing elastomers with shungite filler

As mentioned above, one of the most important processes of rubber manufacturing technology is elastomer reinforcement with dispersed fillers, the main of which is carbon black. For a number of reasons, the economic and environmental nature of the current need to replace the standard carbon filler with new ones that able to meet all the growing requirements for the properties of technical rubbers of various purposes.

In search of a substitute to soot, we tested the shungite rocks of “Bolshevik” deposit as a reinforcing filler for dark rubber compounds, which led to positive results. An important factor is the fact that the use of shungite fillers does not require changes in the technological process of production of rubber goods. However, as it turned out, the replacement of standard carbon black in rubber compounds with equal amounts of

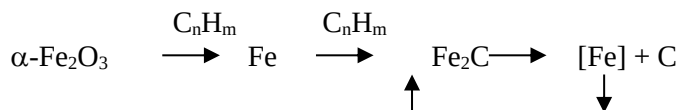
(mass.%) shungite filler leads to a significant decrease in the content of elemental carbon in rubber (in case of sample No.10, for example, 2.2 times) due to the dilution with a large amount of the mineral part. Nevertheless, as a result of this, the strength properties of the finished rubbers not only do not deteriorate, on the contrary, as the studies have shown, to some extent are improved.

We will consider this question in more detail. Why are shungite rocks a more effective filler for dark rubber compounds compared to industrial carbon black? The question posed is rather complicated, and one cannot answer it unambiguously.

According to the action applied to rubber compounds, according to the authors, the shungite filler should be considered as a natural binar composite, which includes shungite carbon with graphite impurities (as revealed by electron microscopy images), as well as mineral components. The main role in reinforcing elastomers upon filling with shungite fillers, of course, belongs to the carbon component. The mechanism of action of shungite on polymer, primarily due to its structural features. The versatility of shungite carbon is due to that this natural material, as studies have shown, has a structure close to that of industrial carbon black. The reason for this similarity probably lies in the conditions of abiogenic [6] shungite formation.

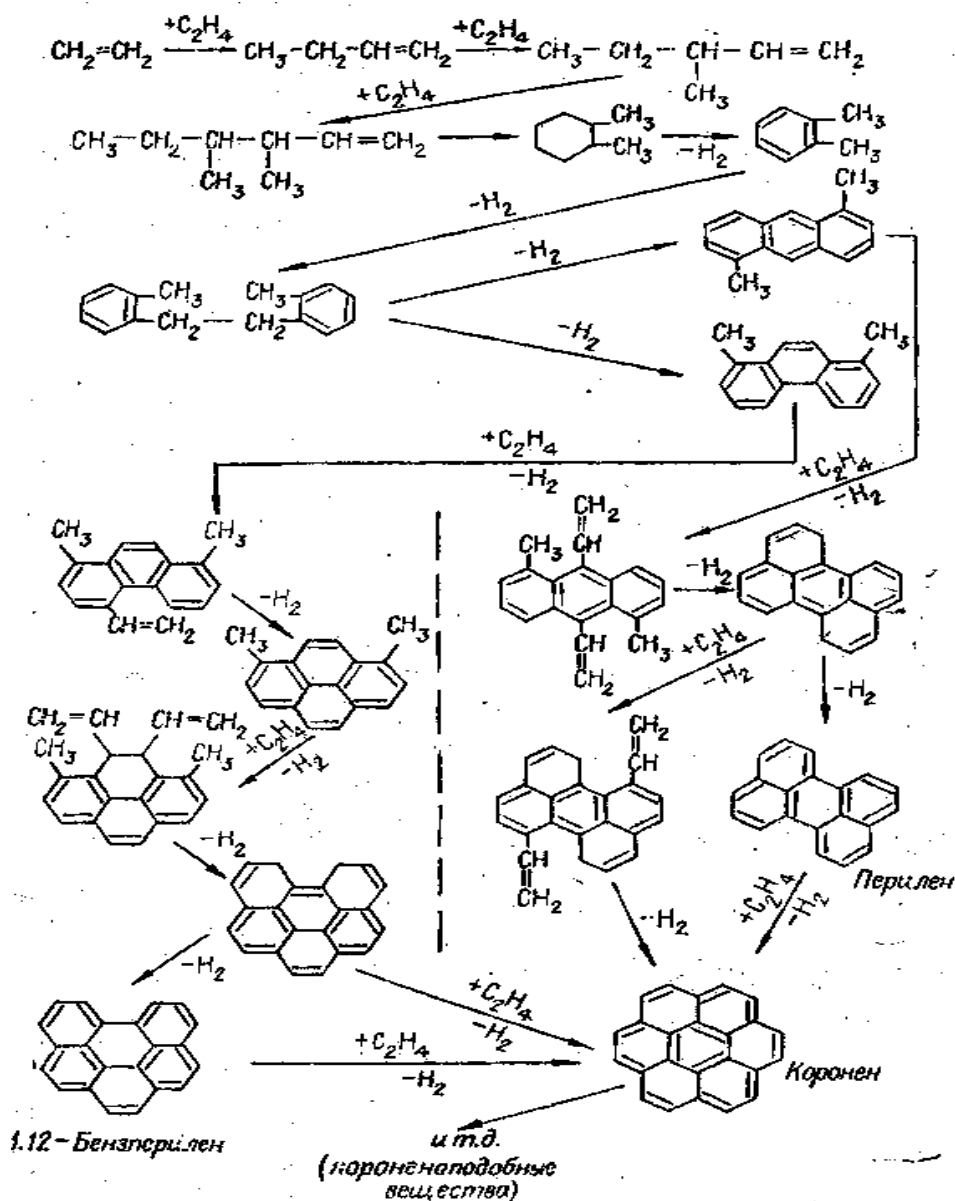
The genesis of the carbonaceous substance of the test rocks is very complicated. Apparently, shungites discovered in the territory of Kazakhstan in the volcanic sedimentary strata of Carboniferous age [184], formed as a result of thermal decomposition of hydrocarbons. In [6] it was shown that the reactions of these processes vary depending on the nature of the initial hydrocarbons, process conditions and the nature of the catalyst. Therefore, considering the issue of the formation of shungite carbon, it is impossible to disregard the effect of the mineral part, which in this natural process could act as the catalyst. Depending on the temperature of the formation processes of solid carbon, two polycondensation mechanisms were found: low-temperature (up to 700÷750 °C) and high-temperature (above 750 °C). In studies [57,71] on carbonization of the natural mineral raw materials surfaces (for example, Narynkol clay, Chilik clay), it was shown that ethylene is one of the products of the low-temperature conversion of hydrocarbons, the polycondensation of which on aluminum oxide is described by a consecutive (from latin “consecution” – result, consequence – next; a distinctive sign of the concept that derived from another) scheme.

Considering the role of the clay mineral component of shungite rocks in the formation process of shungite carbon, it could be assumed that this process took place according to the well-known carbene mechanism which is described by the general scheme [48]:



According to this mechanism, the formation of carbonaceous deposits happens during the interaction of hydrocarbons with metal oxides, as a result of which, at the first stage, the latter is reduced to metals. Metals, upon interacting with hydrocarbons form carbides, the decomposition of which again leads to the formation of metals and free carbon, on the basis of which carbonaceous deposits of various structures are formed.

Mansurov and co-workers in the studies [57,105,117] on preparation of carbonized materials based on local clays and mining industry wastes (chromite and bauxite sludge) investigated the patterns of formation of carbonaceous deposits on the surface of different solid sorbents depending on the time and temperature of carbonization (Scheme 1). The formation of carbonaceous deposits leads not only to chemical (the formation of metal carbide and the removal of carbide into a carbon fiber), but also to physical processes – the removal of particles into the carbon mass. At a constant carbonization time (30 min), the morphological features of carbon deposits are determined by the effect of the temperature factor. An amorphous phase of catalytic carbon is formed at 650 °C, which with the further increase in temperature becomes fibrous carbon. The growth of fibrous carbon particles and the removal of metal particles to the end of the thread occur at 750-800 °C. However, at these temperatures (800 °C), the formation of amorphous carbon could also occur, but with a significantly shorter contact time (5 min). With increasing carbonization time, a fibrous structure forms and the length of the carbon fiber increases.



Scheme 1

Some similarities are found when comparing the electron-microscopic images of shungite, soot П 803 and carbonized clay. The structure of carbonized clay is also represented by clusters of quite dense beads forming a chain structure, and the sizes of these beads (20-30 nm) correspond to the sizes of spherical shungite formations (20-30 nm).

However, the interplanar distances d_{002} of carbon obtained as a result of carbonization of the surface of Chilik clay and Turgay slime of bauxite production (0,336 nm) are much closer to the value of this parameter for graphite (0,3354 nm).

Indeed, for shungite $d_{002} = 0,355-0,356$ nm and even for the most ordered shungite carbon $d_{002} = 0,348$ nm. Consequently, the formation of shungite, apparently, took place for significantly short periods of time, and due to this carbon particles therefore unable to be ordered.

In addition, the initial clay mineral compositions, according to X-ray analysis, have the form “SiO-FeO-NiO-TiO₂” and after carbonization “SiO-FeC-NiC-TiC-SiC”. Thus, X-ray phase analysis of carbonized clay samples identifies carbides of metals, and also free metals as confirmed by X-ray fluorescence analysis. X-ray phase and electron-microscopic analyzes of local shungite rocks, however, do not reveal the presence of carbide-like materials and free metals. Perhaps this is due to the time factor. Moreover, in carbonized systems fibrous and filamentary carbon were observed, the latter being a hollow tube, at the end of which there was a metal particle. As a result of electron-microscopic studies carbon with a similar morphology in shungite was not found. Therefore, it is difficult to explain the high activity of shungites, as fillers for elastomers, based on the conclusion that amorphous carbon is formed only by carbide mechanism. The formation of shungite substance according to the scheme of the carbene mechanism of the thermal pyrolysis of acetylene seems to be more reliable, similar to the mechanism of formation of carbon black. As mentioned above, acetylene is one of the main products of high-temperature pyrolysis of hydrocarbons [105], and the generation of its molecules precedes the formation of soot nuclei. Thus, the formation of shungite and carbon black apparently proceeds according to the same scheme, as a result of which Kazakhstani shungite and carbon black have an almost identical structure.

It follows from the foregoing that the mechanisms of elastomer reinforcement with soot and shungite carbon, in general, should coincide. However, as we pφmy seer in the course of the research, shungite in rubbers demonstrates itself as a more active filler. The increased activity of shungite filler, in contrast to soot, is explained, firstly, by the smaller sizes of particles of shungite carbon, and secondly, by a lower degree of ordering. This fact is also described by the conditions of the formation of shungite carbon. According to geologists [184], the origin of the Kazakhstani shungite, as mentioned above, is of an abiogenic nature. Therefore, the authors of the book assume that the formation of shungite occurred as a result of rapid pyrolysis, possibly even not of gases, but of vapors of hydrocarbons that are present in earthen strata, in contact with magma layers. Considering by the relatively shallow bedding of shungite rocks of “Bolshevik” mine, it could be assumed that a rapid decrease in temperature occurred in the “reaction zone”. As a result of this, the formation of shungite carbon ended quite quickly, perhaps, in some cases, far from reaching completion with the corresponding structural reorganization. This explains the higher dispersity of shungite (sometimes even with respect to soot particles). The shallow bedding of shungite rocks could be considered as evidence of the absence of effect of high pressure on shungite rocks strata, which explains the low degree of ordering of the particles of Kazakhstani shungite in relation to graphite, and in some cases to carbon black.

A study [138] shows that a lower degree of ordering of the structure of graphite-like layers of carbon black increases its interaction with the polymer, while an increase in L_c parameter leads to a decrease in the strength characteristics. The obtained research results are in good agreement with this statement.

To summarize, the authors propose the following model of elastomer reinforcement with shungite carbon. As a result of the formation of shungite particles via carbene mechanism, the formation of graphite-like layers of shungite with the so-called “holes” (“voids” or “potholes”) should occur consistently (Figure 32). The free ends of rubber

macromolecules fall into these “potholes”, where they are attached not only mechanically, but also chemically due to the formation of links at the location of the most reactive carbon atoms of the amorphous disordered part of the carbon structure, peripheral carbon atoms in the base layers of crystallites, defects in the crystal lattice of carbon. Moreover, due to vibrations of elastomer macromolecules, their ends turn out to be firmly “stuck” inside “potholes” and are unable to “unhook” themselves. Of course, it is not only about the end groups of rubber macromolecules, but also about their segments.

The formation of “potholes” in the structure of graphite-like layers of shungite, firstly, causes an increase in interplanar distances d_{002} . The more such defects, the greater the distance d_{002} , and the less ordered the structure of graphite-like layers of shungite. This, firstly, as was shown above, should contribute to enhancing the interaction between the particles of shungite carbon and elastomer. Secondly, shungite, whose particles are composed of graphite-like grids with “holes”, is a “cluster-shaped” material, the surface of which is energetically heterogeneous. The places of the greatest accumulation of defects in the structure of graphite-like layers are the most energy-saturated. The “cluster-shaped” material with a more defective structure, which is more energy-saturated, is able to form links easier and, therefore, exhibits reinforcing properties more strongly.

The state of the theory of chemical reactions in a condensed phase is such that the theory and experiment are developed almost independently. The theory currently is only capable of giving general qualitative regularities, but not quantitative forecasts. But one can already consider one of the main properties of chemical reactions in solids to be established: even in the kinetic mode, the reactions are controlled by the molecular dynamics of the solid matter, and the molecular organization of the transition state becomes the limiting stage, not the actual chemical act. From this point of view, it is very important to understand how, for instance, macromolecules bind to solid surfaces. The energy saturation of the cluster-shaped materials means that the fundamental incompleteness of the crystal lattices in them corresponds to a huge number of defects that cannot relieve excess energy. A huge amount of this energy is concentrated on unpaired electrons localized on defects, which is confirmed by EPR- spectroscopy. Thus, it is known [131] that in soot particles an intense EPR signal is observed that corresponds to free radicals or conjugated carbon structures. In preliminary experiments, the samples of shungites also exhibited an intense EPR signal.

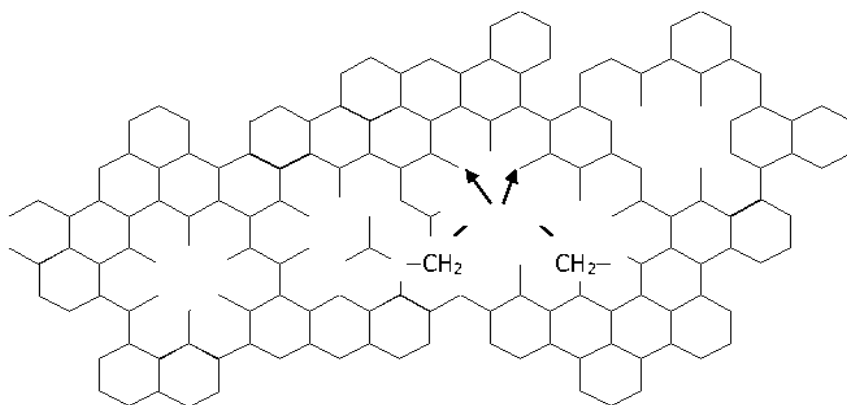


Figure 32 – Graphite-like layer of shungite with “potholes”

Therefore, the preliminary results of the study of the paramagnetism of shungite samples are in good agreement with the results of studies carried out using other physicochemical techniques, although the tasks of a more thorough clarification of the nature of the source of ferromagnetic resonance signal remain unresolved, as well as the nature of the source of paramagnetic resonance signal. Nevertheless, it is clear that the number of unpaired electrons in shungite particles, in any case, is not less than their number in ordinary soot particles, which gives us grounds to propose a physical model for reinforcing elastomers with shungites.

In elastomer macromolecules, the segments contain double bonds $>C=C<$, some of which, when in contact with the surface of shungite particles might diffuse into the composition of the macromolecule segments inside rather large pores, which, as shown by electron microscopy, are observed in the structure of shungite carbon. Since carbenes $H_2C=C:$, as was noted in [131], could condense (link) not only via a double bond, but could also be introduced through C–H bonds, the carbon cluster formed by the multichannel scheme could contain in the defects a whole set of variously localized unpaired electrons. A segment of the macromolecule that has fallen into their surroundings inside the cavity could create chemical links with carbon atoms not only via opening the double bond, as shown in Figure 25, but probably also through the introduction of biradicals of defects in the C–H bond. The appearance of such strong bonds at the interphase boundaries should significantly improve the elastic-strength properties of the composite material due to a change in the supramolecular structure.

It should be noted that the mineral components of shungite fillers also have an decent effect on the strength characteristics of rubbers. It is known [135] that the enhancement of strength properties depends on the total external surface of the filler in rubber, which is determined by the dispersity of particles and the degree of dispersion in the mass of rubber.

When shungite filler is introduced into rubber compounds, the effect of mineral components on the properties of the finished rubber is associated with an improvement in the distribution of finely dispersed shungite particles and the formation of the most favorable coagulation structures. On the one hand, larger and hard particles of the mineral part of the filler contribute to the destruction of shungite agglomerates upon milling, and on the other hand, the formation of a coagulation structure occurs due to the intermolecular interaction of colloidal particles and the stabilization of large particles by small particles of shungite.

However, an increase in the dispersity of shungite carbon aggregates in rubber due to their partial destruction at the mixing stage, on the one hand, causes an increase in the strength parameters of rubber due to an increase in the effective total surface of the filler. At the same time, with an increase in the number of dispersed shungite units in the vulcanizate, the friction between them during deformations also increases; as a result, heat formation and hysteresis losses rise in rubber. Indeed, in the case of filling rubber compounds with the sample of shungite rock No.10, the numerical value of the parameter of relative residual elongation is mainly higher in comparison with the rest of the samples.

Other reasons for increasing the strength characteristics of shungite-filled rubbers due to the action of mineral components, we believe that they contribute, firstly, to

loosening the structure of the rubber compound, and, secondly, to an increase in the number of weak “rubber-filler” links.

Previously, it was mentioned that an increase in the strength of the filled system is achieved by with a certain optimal ratio of strong and more weak bonds. Weak links, easily regrouping, contribute to the dissipation of local overstrain. A direct consequence of the equalization of stress is an increase in tensile strength. Consequently, the mineral components in shungite-filled rubber compounds contribute to the implementation of the mechanism of equalization of stresses upon the interaction of rubber with filler, which leads to an increase in the strength characteristics of filled rubber.

As studies have shown, the most favourable option is to use shungite filler with a carbon content of 30–50% while replacing standard carbon and mineral fillers. The introduction of too many mineral fillers, apparently, causes the formation of a large number of weaker links with the elastomer that cannot withstand large loads and leads to a decrease in the strength of the vulcanizate. So, for instance, the results of measuring the elastic-strength properties indicate that, in the case of using sample No.14 (flotation concentrate) as a filler, the prepared vulcanizates could not withstand the comparison of strength with standard rubbers. When kaolin is removed from the mixture, but the same amount of shungite filler is retained, an increase in the strength parameter of test rubbers is observed, which nevertheless remains less than the value of standard vulcanizate.

CHAPTER 6 MODIFIED CARBON-MINERAL SORBENTS FOR SOIL DETOXIFICATION FROM COMPONENTS OF LIQUID ROCKET FUELS

6.1. The technology for preparation of modified carbon-mineral sorbents

In order to develop a sorption technology for the detoxification of CLRF from soils, we have prepared carbon-mineral sorbents (CMS) based on shungite rock concentrate and sorbents modified with transition metal ions (MCMS).

Modification of the sorbent was carried out by mechanically interacting the flotation concentrate with modifying additives until a homogeneous distribution over the entire volume of the шихты was formed. Iron (III) chloride and manganese (IV) oxide in the amount of 5% of the total mass of the sorbent were used as modifying agents. Such ratio of the modifying additive and the sorbent was experimentally determined as optimal, since the result of the preliminary laboratory studies showed the possibility to efficiently neutralize CLRF in soils precisely by this ratio of components. The results of the detoxification activity of the studied materials are presented in Table 27. The developed process flow diagram for the preparation of modified shungite sorbents for these purposes is presented in Figure 33.

Table 27

The effect of the concentration of transition metals on the decontamination of soils polluted with UDMH

The content of iron and manganese ions, %	Sorption time, h	C ₀ , mg/kg	C _p , mg/kg	ε, %
5 (Fe ³⁺)	24	23,6	not available	100%
3 (Fe ³⁺)	24	23,6	1,4	%
2 (Fe ³⁺)	24	23,6	0,6	98%
5 (Mn ⁴⁺)	24	23,6	not available	100%
3 (Mn ⁴⁺)	24	23,6	1,2	98%
2 (Mn ⁴⁺)	24	23,6	0,5	94%

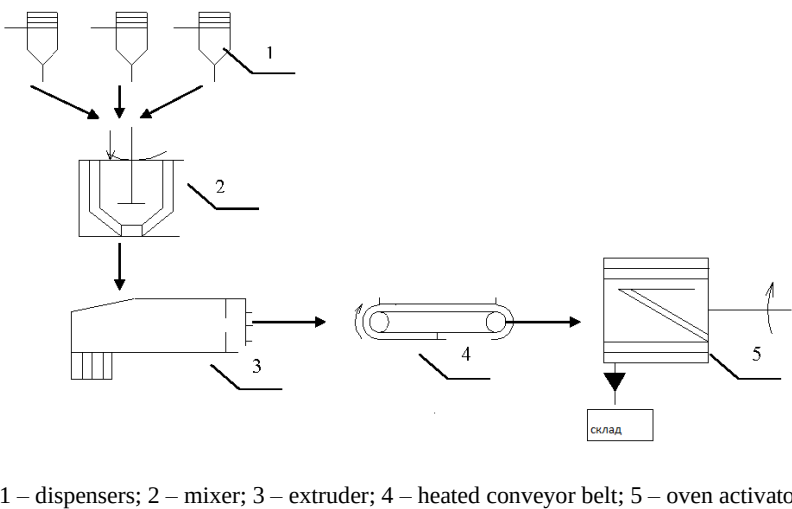


Figure 33 – Technological scheme for the preparation of modified shungite sorbents

6.2 Investigation of the physicochemical basis of the detoxification processes of soils contaminated with unsymmetric dimethylhydrazine and the products of its transformation using carbon-mineral sorbents modified with Mn⁴⁺ and Fe³⁺ ions.

In order to determine the optimal conditions for detoxification of artificially contaminated air-dry and moist soils with UDMH at room temperature, carbon-mineral

sorbents modified with MnO₂ and FeCl₃ (MCMS) and with such characteristics presented in Tables 28-30 were used.

Table 28

Physicochemical properties of MCMS and carbon sorbents

Name of parameter	MCMS- Mn ⁴⁺	MCMS - Fe ³⁺	ДАК*	БАУМФ**
Bulk density, g/cm ³	1,2	1,2	not normalized	
Humidity, %	1,5	1,5	no more 10	
Ash content, %			no more 6	no more 10
Specific surface area, m ² /g	24,0	24,0	not normalized	
Total pore volume by water, cm ³ /g	1,4	1,3	no less 1,4	not normalized
Adsorption activity by iodine, mg/g	44,6	43,5	no less 30	no less 70
Sorption capacity by methylene blue, mg/g	18,2	18,0	not normalized	
Sorption capacity by UDMH, mg/g	33,2	31,7		
Sorption capacity by kerosene, mg/g	35,5	31,9		
*- Crushed active charcoal for purification of steam condensate from oil and other impurities.				
**- Crushed active charcoal for adsorption from aqueous media in filter set [154].				

Table 29

The strength of CMS modified with manganese and iron ions

Type of sorbent	a, g	b, g	Π, %
CMS	27,63	10,56	38,21
MCMS (Mn ⁴⁺)	27,63	11,55	41,80
MCMS (Fe ³⁺)	27,63	11,50	41,60

Table 30

ε_{3a} Porosity of CMS and CMS modified with manganese and iron ions

Type of sorbent	G _{и.с.} , g	G _{и.с. , Γ} "	ρ, g/cm ³	V, cm ³	X, %
CMS	133.50	143.30	0.79	40.00	30.86
MCMS (Mn ⁴⁺)	133.50	144.80	0.79	40.00	35.58
MCMS (Fe ³⁺)	133.50	144.70	0.79	40.00	35.50

The study was conducted over time at a ratio of soil:MCMS equal to 9:1, 5:1 and 3:1, as well as at initial UDMH concentrations in soils of 13.6; 58.9 and 115 mg/kg. Control over the detoxification process was carried out using HPLC. The degree of detoxification of UDMH was calculated using the formula:

Table 31

The degree of soil detoxification using MCMS-MnO₂

№ experiment	Content soil:MCMS	Sorption time, h	C ₀ , mg/kg	C, mg/kg	ε, %
1	9:1	3	13,6	6,5	52,4

2	9:1	6	13,6	5,2	61,8
3	9:1	12	13,6	3,2	76,8
4	9:1	24	13,6	1,9	86,1
5	9:1	48	13,6	1,74	87,2
6	5:1	3	13,6	6,1	55,0
7	5:1	6	13,6	2,6	80,9
8	5:1	12	13,6	1,8	87,2
9	5:1	24	13,6	1,6	88,2
10	5:1	48	13,6	1,5	89,3
11	3:1	3	13,6	4,8	64,6
12	3:1	6	13,6	2,3	83,3
13	3:1	12	13,6	1,6	88,6
14	3:1	24	13,6	1,4	89,4
15	3:1	48	13,6	1,3	90,5
16	9:1	3	58,9	29,0	49,2
17	9:1	6	58,9	24,8	57,9
18	9:1	12	58,9	13,4	77,3
19	9:1	24	58,9	9,4	84,1
20	9:1	48	58,9	8,7	85,2

Table 31, continued

21	5:1	3	58,9	3,2	94,6
22	5:1	6	58,9	3,1	94,8
23	5:1	12	58,9	1,0	98,3
24	5:1	24	58,9	0,7	98,8
25	5:1	48	58,9	0,6	98,9
26	3:1	3	58,9	1,8	96,9
27	3:1	6	58,9	1,7	97,0
28	3:1	12	58,9	0,5	99,1
29	3:1	24	58,9	0,4	99,4
30	3:1	48	58,9	0,3	99,5
31	9:1	3	115	51,8	55,0
32	9:1	6	115	38,9	66,2
33	9:1	12	115	17,3	85,0
34	9:1	24	115	12,7	89,0
35	9:1	48	115	10,7	90,7
36	5:1	3	115	7,6	93,4
37	5:1	6	115	5,2	95,5
38	5:1	12	115	2,5	97,8
39	5:1	24	115	1,0	99,1
40	5:1	48	115	0,7	99,4

Table 32

The degree of soil detoxification using MCMS-FeCl₃

№ experiment	Content soil:MCMS	Sorption time, h	C ₀ , mg/kg	C, mg/kg	ε, %
1	9:1	3	13,6	7,1	47,8
2	9:1	6	13,6	6,3	53,7
3	9:1	12	13,6	3,8	72,0
4	9:1	24	13,6	2,7	80,1
1	2	3	4	5	6
5	9:1	48	13,6	2,0	85,3
6	5:1	3	13,6	6,4	52,9
7	5:1	6	13,6	3,6	73,5
8	5:1	12	13,6	2,3	83,1
9	5:1	24	13,6	1,9	86,0
10	5:1	48	13,6	1,6	88,2
11	3:1	3	13,6	5,0	63,2
12	3:1	6	13,6	2,5	81,6
13	3:1	12	13,6	1,7	87,5
14	3:1	24	13,6	1,5	89,0
15	3:1	48	13,6	1,4	89,7
16	9:1	3	58,9	29,2	50,4

Table 32, continued

18	9:1	12	58,9	13,9	76,4
19	9:1	24	58,9	9,8	83,4
20	9:1	48	58,9	8,9	84,9
21	5:1	3	58,9	3,4	94,2
22	5:1	6	58,9	3,2	94,6
23	5:1	12	58,9	1,8	97,0
24	5:1	24	58,9	1,0	98,3
25	5:1	48	58,9	0,9	98,5
26	3:1	3	58,9	1,9	96,8
27	3:1	6	58,9	1,8	97,0
28	3:1	12	58,9	1,2	98,0
29	3:1	24	58,9	0,7	98,8
30	3:1	48	58,9	0,5	99,2
31	9:1	3	115	52,9	54,0
32	9:1	6	115	39,5	65,7
33	9:1	12	115	20	82,6
34	9:1	24	115	15	87,0
35	9:1	48	115	11	90,4
36	5:1	3	115	8,5	92,6
37	5:1	6	115	6	94,8
38	5:1	12	115	3,5	96,7
39	5:1	24	115	2	98,3
40	5:1	48	115	1,2	99,0

$$\varepsilon = 100(C_0 - C) / C_0$$

where C_0 – initial concentration of UDMH in soil; C – the current concentration of UDMH in soil. The results of studies obtained for CMS modified with MnO_2 and $FeCl_3$ are presented in Tables 30 and 31.

As shown from Tables 31 and 32, the duration and degree of detoxification of soils are affected by the ratio of soil:MCMS and the initial concentration of UDMH in the soil. With an increase in the fraction of MCMS in the soil, the degree of detoxification increases, while the duration of detoxification decreases. The highest degree of detoxification is observed for the ratio of soil:sorbent – 3:1 and the smallest – for the ratio of 9:1. However, an increase in the degree of detoxification for the ratio of 3:1 is minor compared to an increase in the degree of detoxification for the ratio of 5:1. The highest rate of detoxification of soils is observed in the first 6 hours. The degree of detoxification in 24 hours is 90-95%, and in 48 hours – 98-99%, i.e., detoxification happens in the first 24 hours.

Thus, it was established that the optimal conditions for detoxification of soils contaminated with UDMH at concentrations of 10 – 115 mg/kg using a sorbent modified with MnO_2 or $FeCl_3$ is the ratio of 5:1 and the detoxification time is 24 hours.

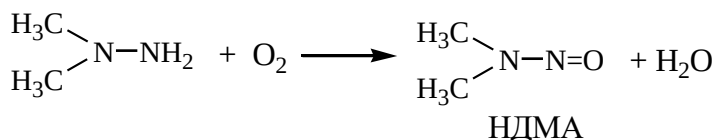
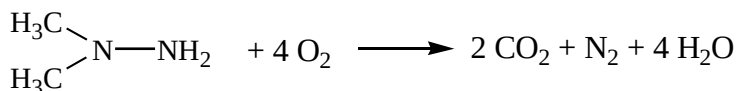
In order to study the detoxification process using MCMS – MnO_2 , MCMS – $FeCl_3$ and CMS, soil samples from the sites of crush of SPLV contaminated with UDMH and its decomposition products were used. Qualitative and quantitative compositions of the contaminated soil samples are given in Table 33. As shown in Table 33, the main decomposition products of UDMH are H_2DMA , $DM\Phi A$, MT, and TMT. Schematically the formation of these products could be explained by the incomplete oxidation of UDMH.

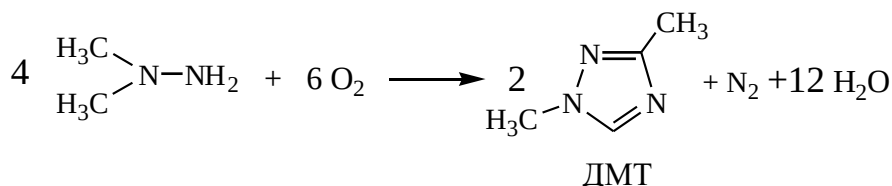
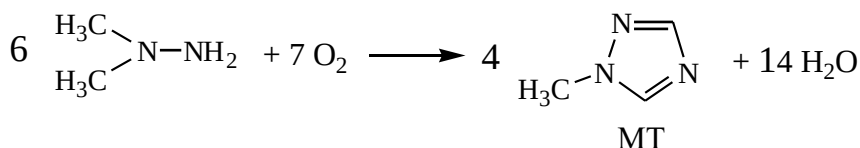
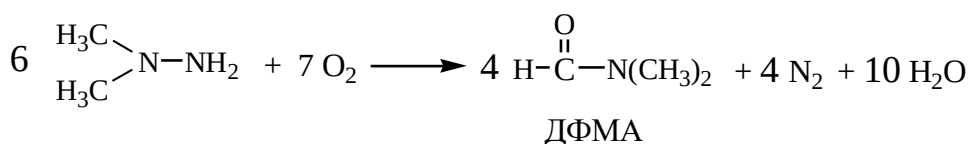
Table 33

Qualitative and quantitative compositions of the transformation of rocket fuel products in soils from the places of crush of SPLV

Content, mg/kg				
UDMH	H_2DMA	$DM\Phi A$	MTA	DMT
8,0	0,430	0,166	0,620	0,480
12,0	0,330	0,612	0,421	0,302
32,0	0,484	0,131	0,256	0,377

The oxidation of UDMH and its decomposition products





A study on the detoxification of soils from UDMH and its decomposition products was performed in time intervals at a ratio of soil:MCMS; soil:CMS equal to 5:1 in comparison with a control the data are presented in Table 34.

Table 34

The degree of detoxification CLRF in soils

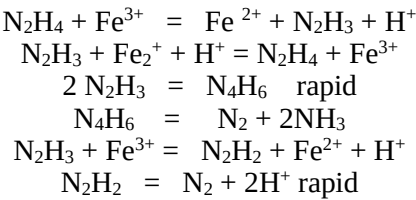
C ₀ , mg/kg	Sorbent	C, mg/kg				ε, %
		Time, h				
		1	6	16	24	
0,8	MCMS – MnO ₂	0,23	0,16	0,04	0,00	100,0
	MCMS – FeCl ₃	0,56	0,32	0,16	0,13	83,8
	CMS	0,75	0,18	0,08	0,00	100,0
	control	0,79	0,69	0,63	0,55	30,4
1,2	MCMS – MnO ₂	0,26	0,23	0,11	0,01	99,17
	MCMS – FeCl ₃	0,47	0,45	0,16	0,00	100,0
	CMS	0,62	0,53	0,27	0,00	100,0
	control	0,95	0,84	0,76	0,66	30,5
3,2	MCMS – MnO ₂	0,89	0,67	0,04	0,00	100,0
	MCMS – FeCl ₃	1,02	0,60	0,29	0,00	100,0
	CMS	1,79	1,56	0,84	0,00	100,0
	control	3,10	2,65	2,31	2,18	29,68

As shown in Table 34, the detoxification of UDMH and its decomposition products in the presence of natural and modified shungite sorbents occurs more rapidly than in the control. Modified shungite sorbents absorb and catalyze the oxidation of UDMH decomposition products better than natural shungite sorbent.

Figures 1-5 (Appendix B) demonstrate the dynamics of the accumulation of UDMH and its decomposition products in natural and modified carbon-mineral shungite sorbents. The figures display that the degree of accumulation of UDMH decomposition products in the natural shungite sorbent is greater than in modified sorbents. These results also confirmed the data in Figures 6-12 (Appendix B), which show that the degree of extraction (detoxification) of UDMH and its decomposition products from the soil is higher in the presence of modified shungite sorbents.

This is explained by the fact that not only UDMH and its decomposition products are absorbed in modified sorbents due to physical adsorption, but also their complete oxidation as a result of the catalytic action of Fe and Mn.

Complete oxidation of CRF and its components takes place mainly under the influence of oxygen in the air and in the presence of manganese (IV) oxide and iron (III) chloride, too. The mechanism of the catalytic oxidation of UDMH adsorbed on the shungite sorbent could be demonstrated by the interaction of hydrazine with Fe³⁺.



Thus, the results of the studies show that upon using shungite sorbents modified with manganese (IV) oxide and iron (III) chloride, in detoxification of soils contaminated with the components of liquid rocket fuels, almost complete neutralization of soils exposed to space-rocket activity takes place.

6.3. Study of the features of sorption of T-1 rocket fuel from the soil using natural and modified carbon-mineral sorbents

Table 35 shows the dependence of the extraction of T-1 kerosene from loamy soils contaminated with the different concentrations of the latter (using simple and modified shungite sorbents). It is seen that all three types of sorbents extract kerosene at the same rate from the soil within 24 hours. Table 36 shows the dependence of the accumulation of T-1 rocket fuel from the soil in natural and modified shungite sorbents, from which it is seen that a proportional dependence of the removal of rocket fuel by sorbents is observed.

As shown earlier, the optimal soil:MCMS ratio for the detoxification of UDMH and its decomposition products is 5:1. The same conditions were used to study the sorption of T-1 rocket fuel from the soil and tae data are presented in Tables 35 and 36.

Table 35

Degree of extraction of T-1 kerosene from the soil using natural and modified shungite sorbents

Kerosene T-1,	Sorbent	Content, mg/kg	ε, degree of recovery,
		Time, h	

mg/kg		1	6	12	24	%
8582,0	CMS	7940,0	3157,0	452,0	43,6	99,5
	MCMS – MnO ₂	6740,0	2685,0	347,0	53,6	99,4
	MCMS – FeCl ₃	6810,0	2548,5	347,0	26,8	99,7
	control	8503,0	8324	8241	8107,0	4,7
12434,0	CMS	11027,1	6423,0	943,0	51,2	99,6
	MCMS – MnO ₂	9689,0	5489,0	821,0	72,2	99,4
	MCMS – FeCl ₃	9673,0	5489,0	1242,0	92,4	99,3
	control	12154,0	11934	11657	11561,0	4,9
21571,0	CMS	18763,0	7641,0	1145,0	64,0	99,7
	MCMS – MnO ₂	17097,0	7497,6	1004,0	100,3	99,5
	MCMS – FeCl ₃	16971,0	8434,8	1345,6	124,0	99,4
	control	20310,0	20249	20108	20021	1,4

Thus, a comparison of the data on the extraction of UDMH and its decomposition products with the results of the extraction of T-1 rocket fuel using simple and modified shungite sorbents shows that hydrocarbons are not capable of oxidation under these conditions.

Table 36

The degree of accumulation of T-1 rocket fuel in natural and modified shungite sorbents

Kerosene T-1, mg/kg	The proportion S:S	Content, mg/0,5 kg				ε, degree of absorption, %
		Time, h				
		1	6	12	24	
8582,0	CMS	563,0	3425,0	5130,0	7034,7	82,0
	MCMS – MnO ₂	1657,0	3507,3	5611,5	8100,7	94,4
	MCMS – FeCl ₃	1311,3	2984,7	4613,9	7705,0	89,8
12434,0	CMS	883,0	1154,0	6011,4	10491,0	84,4
	MCMS – MnO ₂	1144,5	2470,5	6250,7	12070,0	97,0
	MCMS – FeCl ₃	2043,1	5139,3	9147,7	11042,7	88,8
21571,0	CMS	1547,0	1807,0	13929,0	18425,0	85,4
	MCMS – MnO ₂	1935,4	4025,7	9665,1	20509,4	95,0
	MCMS – FeCl ₃	1587,5	3403,3	9720,1	20966,7	97,2

6.4. Investigation of the places of fall where the separable parts of a launch vehicle

The fall area of the first stage of LV “Proton” PC 15,25 is located in the south-west of Ulytau region of Karaganda oblast.

The coordinates of the centers and the area of the site of falling are given in Table 37.

The results of field studies to analyse the soil cover showed that the territory of PC 15,25 is represented mainly by medium and heavy loamy, as well as clayey types of soils. Therefore, sections of the places of crush of SPLV were chosen for studies, and this is a characteristic type of soil for these soil cover. Information on the places of crush (PC) is given in Table 38.

Table 37

The coordinates of the areas of fall of the first stages of “Proton” launch vehicle

Zone number	Plot shape	Coordinates of center	Axle size, km	Azimuth of the major axis, град.	Area of land, thousand ha
Ю-24 (PC 15,25)	Ellipse	47°20'30" 66°46'30" 47°14'00" 66°23'00"	27x18 60x30	65 65	160

Table 38

General information on the key areas

№ PC of SPLV	№ zone	№ Area of fall of SPLV	Type of carrier rocket	Coordinates of the fall epicentre of SPLV		Launch date LV
				Northern latitude	Eastern longitude	
1	IO-24	25, 15	«Proton»	47°18'37,6''	66°28'05,1''	22.08.2002
7		71,30	«Soyuz»	48.50.00,0	65.58.11,4	~11.2001 г.

The first key section of PC No.1 is located in the southeastern sector of the area of fall 25, in the interfluvium of river Zhide and river Karasirek at coordinates 47°18'37,6'' northern latitude and 66°28'05,1'' eastern longitude. The date of the landing of SPLV – 22nd August, 2002. The landing point of the first stage of “Proton” SPLV is flat surface of the excavated foam. The soil cover of PC No.1 is characterized by zonal brown solonchak desert-steppe soils in a complex with meadow brown soil. The soil was identified as a brown desert-steppe solonchak-solonchak soil. The vegetative cover of PC is poor by species composition. It is represented mainly by the wormwood-дерновинно-злаковым species and is characterized by pronounced complexity and mosaicity and is highly sparse (projective cover 20-40%), but the root systems form a continuous network. Cereals are represented by steppe дерновидными species: festuca and agropyron. White-earth wormwood, биюргун, кокпек and прутняк are common among the shrubs (Figure 34).

Two anomalies were formed as a result of the fall of SPLV. One is about to the place of impact of the propulsion system on the ground, and the second is related to the place of fall of the fuel tank.

Immediately after the landing of the stage, the area of the epicenter of the fall of SPLV was plowed up by tractor and treated with a peat composition by the Russian services in order to test a new method of soil detoxification in the places of crush of SPLV. The use of such detoxification technique has produced great interest. In 2004, at this site of crush of the first stage of “Proton” LV, a шурфовый разрез at the epicenter of the landing of SPLV was made, and over the next two years, soil samples were analyzed for the presence of UDMH in order to monitor its distribution and evaluate the efficiency of the decontamination technique.

As the three-year observations showed, the proposed technology and the material itself – peat composition, turned out to be ineffective for this natural and climatic zone. Used peat wetted by 15-20%, was disseminated on the ground surface. At the time of conducting these studies, the temperature was over 53 °C, as a result of which the peat was almost instantly dried and most of its parts were taken out by wind erosion (Figure 35).



Figure 34 – Soil cover PC No.1 area of fall 25.15



Figure 35 – General view of the surface treated with peat on the territory of PC No.1 area of fall 25.15

In order to study the morphology of soil contamination with UDMH a section of 1,3 m deep soil was excavated. The soil characteristics of the laid *шурфового* section along genetic horizons are shown in Figure 36.

Testing the soil in 42 days after spillage showed that UDMH spread to migrate up to 1,3 m of the soil horizon depth with differentiation of the distribution of fields of toxic CRF concentration in the range of 0,13-18,0 mg/kg of soil. Such intense UDMH permeation deep into the soil section is apparently due to the flow of filtration of aqueous solutions of UDMH formed due to the accumulation of meltwater and precipitations inside the funnel, as well as the effect of gravity, which contribute to the acceleration the penetration of UDMH. This process is accompanied by the saturation of the volumes of the main canals with the active absorption of the CRF into the *межпладные* planes and the diffusion mass transfer of UDMH. The impact of such processes could be greatly reflected in the secondary distribution of UDMH over the soil horizon near the central points of the formed funnels by maintaining the maximum pressure of the aqueous solution of UDMH for a long period of time.

Results of physicochemical analysis of samples taken at the PC No.1 in 2003-2005 showed the presence of UDMH in the soil cover after treatment with the peat composition. UDMH content in the surface soil horizons ranged from 0,55-40 mg/kg, and in 2,5 months it amounted to 0,18–34,0 mg/kg (Figure 36).

Upon analysis of the soil in 2 years, UDMH content in them was 0-12,31 mg/kg. Therefore, the results of experimental studies at PC No.1 displayed that used methodology of soil detoxification with the peat composition is not effective enough.

The second key section of PC No.7 (71,30) the region of fall No.71,30 is located in the northeastern part of Ulytau region on the border of Karaganda and Kostanay oblasts. The region of fall No.71 is an ellipse and the region of fall No.30 is a circle overlapping each other.

	Area of fall 71	Area of fall 30
Coordinates of center	48°55'00" northern latitude 66°03'00" eastern longitude	48°56'00" northern latitude 65°48'00" eastern longitude
Tilt azimuth	38°	28°
The radius of the major axis	50 km	22 km
The radius of the minor axis	20 km	22 km

In these areas there are many water sources represented by rivers, reservoirs and springs. Such rivers flowing in the district as Ulken Zhylanshyk, Shagyrly Zhylanshyk, Kulenbai Baksy-zhylanshyk, Kanshabulgan, Aksay could be mentioned. The rivers Ulken Zhylanshyk, Shagyrly Zhylanshyk, Kulenbai Baksy-zhylyanshyk dry up in the summer in some areas. The banks of these rivers are mostly steep and precipitous. Other rivers dry up at the beginning of June. The water level in all rivers depends on the time of the year and the temperature. In winter all rivers freeze. They open at the beginning of April, upon this period a spring flood happens and water level rises 3-4 meters and sometimes overflows the coasts.

The areas are dominated by flat terrain, however, there are many small elevations. The altitude of ground surface above sea level ranges from 200 meters in river channels to 350 meters in elevations (Figure 36).

The vegetation cover of the regions is represented by steppe and semi-desert vegetation. The prevailing edificators are wormwood: white wormwood, small-

flowered wormwood, солянка деревцовидная, ежовник солончаковый, лебеда седая.

The analysis of the study of soil contamination of CLRF and their location at the key site are presented in Figure 36. Tracking the dynamics of CLRF behavior at the key site allows to conclude the following.

Firstly, the source of rocket fuel components in landscapes are spills of residual amounts of CRF and their secondary dissemination. Soil pollution is mainly of a local nature. The maximum degree of contamination of the soil with CRF is observed in the upper layers of the soil (up to 1,4 m depth), the greatest load is carried by the soil of the landing points of the fuel tanks and propulsion systems.



Figure 36 – General view of the landscape of PC 71.30

Secondly, funnels with a depth of 0,3-1,5 meters and a diameter of up to 10-14 meters are formed at the places of the fall of SPLV, which lead to the destruction of the surface of soil cover, the changes in the structure of packaging of genetic soil horizons along the profile, and the appearance of cracks in different directions and other defects.

Thirdly, modern methodologies for soil detoxification from CLRF on PC SPLV could not ensure full localization and disposal of the pollutant. Therefore, despite the application of various methods and technologies for the treatment of contaminated soils, CRF are able to migrate to the deep horizons of the soil profile.

Fourthly, the picture of the distribution of CLRF in the soil profile is controlled by gravity soaking of the profile. For the upper horizons mainly frontal percolation is characteristic, which completely saturates the mass of these horizons.

Residual CLRF permeate through drying cracks, molehills, along root systems of plants, worm passages and is sorbed in separate horizons depending on the type and properties of soils. This process is accompanied by the saturation of the volumes of the main canals, the active absorption into the межпачные planes, and the diffusion into the intercrack mass. As a result of such processes, “CRF containing zones” with high contents are created in the soil profile. Then, in the lower horizons of soils, as the influence of structural features of the soils (the minimum number of drying cracks, molehills) and root systems of plant decreases, due to the difference in concentrations in “accumulation zone of the CLRF – uncontaminated soil” system, diffusion mass transfer of CLRF inevitably occurs [61].

Thus, field experiments conducted on the sites of crush of SPLV shows that the sooner the detoxification of soils contaminated with CLRF is carried out, the more effective they will be.

6.5. Field detoxification experiments

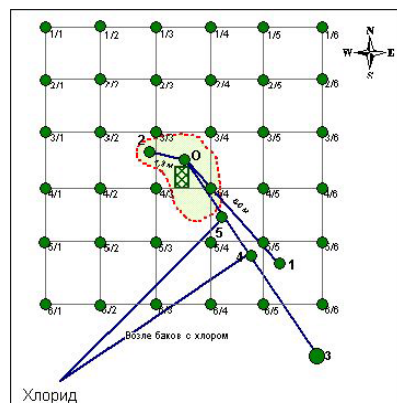
The main task upon performing the experiments on the elimination of spills of rocket fuel components remains the complete and rapid destruction (neutralization) of spilled components. The proposed adsorption method of soil detoxification from CLRF is primarily intended for conducting surface experiments to a depth of 15 – 25 cm, which are primarily associated with “fresh” falls.

The procedure for carrying out the tests on neutralization of contaminated soil using the modified CMS includes the following steps.

1. Prior to detoxification, the territory is cleaned from the mechanical parts of the launch vehicle (metal fragments, LV composite materials, etc.).
2. The amount (volume) of contaminated soil and the concentration of CLRF in soil are determined.
3. The ratio of soil:sorbent is determined considering the degree of contamination and the capacity of the modified carbon-mineral sorbent with respect to CLRF.
4. The sorbent is distributed in the contaminated soil, mixing throughout the area to the depth of permeation of CLRF. For these purposes, one can use agricultural equipment (tractors, seeders, plows, cultivators, shovels).
5. If necessary, the prepared soil is moistened. The relative humidity of the neutralized soil should be at least 5%. Water can be used from any source (water reservoir).
6. The exposure of the sorbent to the soil is calculated with periodic monitoring of the degree of neutralization. The time of neutralization of CLRF depends on specific conditions (concentration of CLRF, soil temperature and moisture, the amount of sorbent). When detecting CLRF in 24 hours with a concentration of more than TLV, the neutralization of the soil should be repeated with the addition of sorbent. Schematically the reclamation work is shown in Figure 37.

ХАРАКТЕРИСТИКА КЛЮЧЕВОГО УЧАСТКА № МП 7 (РП 71,30)

а) Схема ключевого участка с расположением точек отбора проб



УСЛОВНЫЕ ОБОЗНАЧЕНИЯ



10 см

20 см

30 см

60 см

95 см

120 см

в) Схема разреза почв

Суглинок средний, светло-каштановый, сухой, слабоуплотненный, корешковатый, непрочно-комковато-корковатый

Суглинок средний, светло-каштановый, сухой, слабоуплотненный, корешковатый, непрочно-комковато-пороховатый

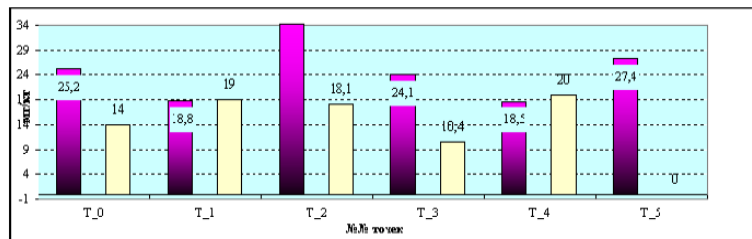
Суглинок средний, буроватый, слабоуплотненный, комковато-пороховатый, слабокорешковатый

Суглинок тяжелый, светлее предыдущего, уплотненный, комковатый с порошком и пылью, с единичными корешками

Суглинок тяжеловатый, средний, буровато-палевый, уплотненный, комковато-пороховатый, почти без корешков

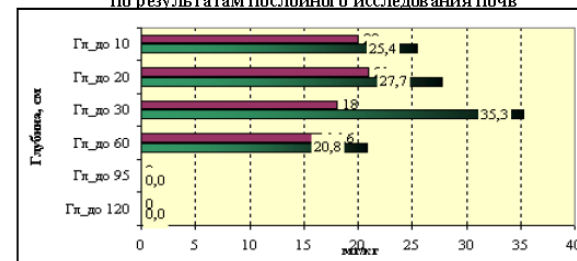
Суглинок средний, палевый, уплотненный комковато-творожистый

б) Гистограмма концентраций керосина Т-1 по результатам поверхностного исследования почв по точкам



Даты анализа 2006 г. , ИК-спектроскопия

г) Гистограмма концентраций керосина Т-1 по результатам послойного исследования почв



Даты анализа 2006 г. , ИК-спектроскопия

Тип РН	Союз	Координаты	48.50.00,0 с.ш.	Объект ОС	почва	Количество	поверх-
Вид ОЧ РН	1-я ступень	центральной точки	65.58.11,4 в.д.	Даты отбора проб		2006	ность
Дата падения	~11.2001 г.	Высота центральной точки	250 м			2007	шурф

The prospects of the presented method are as follows:

- the possibility of performing the experiments in hard-to-reach places in the shortest time after the spillage (pollution), without additional localization measures;
- no excavation works;
- prevention of the spread of toxic substances with air masses, surface and ground waters;
- the absence of environmental damage during soil detoxification (sorbent-catalyst is essentially a coal-mineral fertilizer, the content of trace elements does not exceed the phytotoxic level);

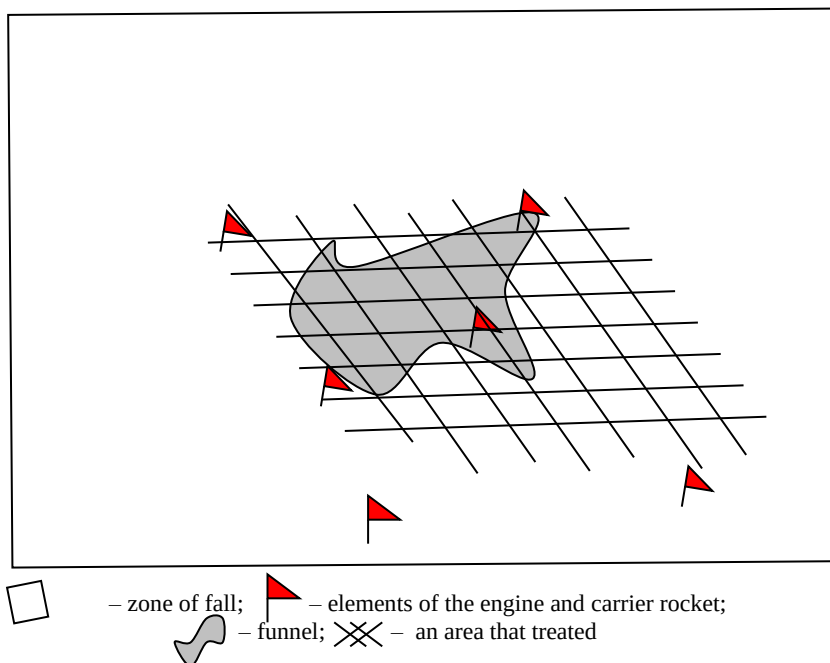


Figure 37 – Schematic illustration of reclamation works

- the possibility to carry out all operations either manually or using the existing means of agricultural, construction or transportation equipment, i.e. the development of special equipment is not required to perform the work;
- availability of raw materials, low cost, simplicity of preparation technology of sorbents-catalysts.

6.6. Material balance of the processes of preparation of a modified carbon-mineral sorbent and evaluation of their economic activity

Based on the results of research, a technology for the production of sorbent modified with manganese (IV) ions and iron (III) was developed, the modified carbon-mineral sorbent was obtained for the soil detoxification contaminated with CLRF, the mechanism of catalytic oxidation of products of CLRF with the modified carbon-mineral sorbent is shown.

A method has been developed for preparation of the modified carbon-mineral sorbent from shungite rocks. It was established that UDMH adsorbed from the soil in

the sorbent undergoes decomposition into products: ДМТ, МТА, НДМА, etc. Sorbent modified with manganese (IV) ions showed a high sorption capacity with respect to CLRF. The use of modified carbon-mineral sorbents fosters the decomposition of CLRF to non-toxic components and subsequently allows not to remove the sorbent from the soil, because it does not disrupt the general background and chemical balances of soils. The introduction of shungite sorbent will solve a number of issues of economic and environmental nature, which were discussed at the beginning of this work.

Conducted studies on the detoxification of soils contaminated with UDMH and its decomposition products suggest carrying out the work to deliver it to the place of CLRF spillage. Further operation involves dissemination it in a certain ratio and mixing it with the surface soil layer 25 cm in depth. The proposed scheme for the use of carbon-containing mineral sorbent is the most economical and technologically beneficial in the climate of Central Kazakhstan, since it does not depend on the climatic period (moisture content in the soil, wind erosion, etc.). The method of detoxification of soils contaminated with CLRF is protected by the innovative patent of the Republic of Kazakhstan "Method of detoxification of soils with modified carbon-mineral sorbents" (Appendix B).

It is known that the cost of production is expressed in monetary terms of a combination of all the material, labor and monetary costs incurred by the enterprise in the course of its business activities. Cost is characterized by the composition and the ratio of the individual elements of costs and cost lines to total costs of production. Typically, the structure of production costs is considered in two aspects: by cost elements, reflecting the expenses of the enterprise to main and auxiliary materials, fuel, depreciation, wages and salaries, etc., and according to the articles of calculation, which characterize the direction of cost-expenditures directly related to the production of this type of product, equipment maintenance, workshop management, etc.

The cost of production is a synthetic indicator that characterizes the success of the entire production work of the enterprise. The cost of production is affected by the expenditure of materials, fuel and energy, the use of advanced, efficient processing techniques, the labor, prevention of unproductive losses and expenses, i.e. essentially all the moments that characterize the organization of this production. Therefore, prevention to increase the cost of production with all sorts of unproductive losses and expenses is one of the most important tasks of economic policy.

The calculation of the annual economic effect is carried out by comparing the above costs before and after the start of the use of the invention or rationalization proposal. The above costs are the sum of cost and normal profit, i.e. in general:

$$З = C + E_n K, \quad (85)$$

where $З$ – reduced costs of a unit of production (work), tenge; C – unit cost of production (work), tenge; K – specific capital investments in production assets, tenge; E_n – normative coefficient of capital investments.

Savings are calculated by the equation:

$$\mathcal{O} = (З_1 - З_2) \cdot A_2, \quad (86)$$

where $\mathfrak{D}$ – annual economic effect, tenge; $\mathfrak{Z}_1$ and $\mathfrak{Z}_2$ – reduced unit costs before and after the start of use of the invention; A_2 – annual volume of production after the start of the use of the invention.

By substituting the formula (85) into formula (86):

$$\mathfrak{D} = [(C_1 + E_n K_1) - (C_2 + E_n K_2)] \cdot A_2 \quad (87)$$

$$\text{or} \quad \mathfrak{D} = [(C_1 - C_2) - E_n (K_2 - K_1)] \cdot A_2, \quad (88)$$

where C_1 and C_2 – the cost of a unit of production (work) before and after the start of the use of the invention, tenge; K_1 and K_2 – specific capital investments in production assets before and after the start of the invention.

The unit cost of production (work) in the specified equation is the sum of the changing cost of items, and not a workshop, factory or full cost, and the wholesale price of the enterprise.

Consequently, if as a result of use of the invention, material costs (C_M) (which relates to our case), salary (C_3), electricity ($C_{\mathfrak{D}}$), etc. are changed, C_{Π} – other costs, then the cost will be the sum of the changing cost item

$$C = C_M + C_3 + C_{\mathfrak{D}} + \dots + C_{\Pi} \quad (89)$$

$$\text{or } C = \sum_M^{\Pi} C. \quad (90)$$

By substituting this value in the formula (90):

$$\mathfrak{D} = \left[\sum_M^{\Pi} (C_1 - C_2) - E_n (K_2 - K_1) \right] \cdot A_2. \quad (91)$$

Since, in our case, new capital investments are not required, then in the formula (91) one can neglect the indicator $- E_n (K_2 - K_1)$. In addition, since using the invention in the equation (89), only the C_M index will change, then when calculating the cost of finished products and, further, the economic effect, we will consider only this indicator.

The material balance of the preparation of modified carbon-mineral sorbent is presented in Table 39.

Table 39

The material balance of the preparation of modified carbon-mineral sorbent

Income	kg	Expenditure	kg
Shungite rock	3000	Sorbent	1000
Water	9000	Wastes	2000,100
Kerosene	0,375	Water	8640,725
Fotol B	0,450	Losses	360,300
Catalyzing additives	0,300		
Total	12001,125	Total	12001,125

The costs of materials prior to the implementation of the invention are on average:

- cost for sorbents (peat type) – from 110000 tenge/ton;

Costs on materials after the implementation of the invention:

- the estimated cost of 1 ton of modified carbon-mineral sorbents is 87000 tenge/ton.

Consequently, the annual economic effect at $A_2 = 110000$ tenge, for the modified carbon-mineral sorbent 1 t is:

$$\Xi \text{ (for MCMS)} = (110000 - 87000) \cdot 1 = 23000 \text{ tenge}$$

Annual environmental contributions are currently in the millions of US dollars.

Consequently, the annual economic effect, even with the consumption of 100 kg modified carbon-mineral sorbent per drop allows to reduce costs by several times, while not taking into account moral and social factors.

CHAPTER 7 CARBON-MINERAL SORBENTS FOR THE DECONTAMINATION OF NATURAL OBJECTS FROM VARIOUS POLLUTANTS

7.1. The technological basis of the processes of production of carbon-mineral sorbents based on the concentrate of shungite rocks

Recently, during extraction and enrichment of non-ferrous metal ores, the growth of the gross product has been priority, rather than environmental protection measures, therefore, the level of environmental pollution by heavy metals has significantly increased in the zones affected by mining-and-processing and mining-and-metallurgical enterprises.

More than 35 elements are extracted in the composition of ores and chemical fuel from the bowels of the Earth to its surface. Huge amount of waste enter the atmosphere and water bodies due to ore processing, energy combustion, consumption of heavy metals. And the anthropogenic accumulation of mercury in the biosphere (mainly in the hydrosphere) is currently estimated at 1 million tons. Loss of cadmium in the biosphere is 5 thousand tons/year.

Annually, over 0,46 thousand tons of copper, 3,3 thousand tons of zinc, tens of thousands of tons of acids and alkalis are lost in the wastewater of electroplating plants. In addition to the indicated losses, copper and zinc compounds carried out by wastewater from treatment plants of galvanic production have a very harmful effect on the ecosystem [41, 64].

Among the methods that have been successfully used to solve the issues of water purification and being one of the most effective, one can name sorption on activated charcoal and porous mineral materials, which make it possible to reduce the content of toxic substances to TLV. The use of carbon materials and, in particular, activated charcoals in engineering and chemical technology is quite diverse. Activated charcoals are widely used to extract a wide variety of substances from gas medium and solutions, various technical and food products, and pharmaceutical substances. Activated charcoals are obtained from various types of raw materials: wood and its processed products, stone and brown coals, arthracite, peat, and also from other materials.

In recent years, the domestic industry has faced a shortage of activated charcoals, since there is no own production in Kazakhstan, primarily due to the lack of a traditional raw material base.

Activated charcoals, the need of which is very high, were fully imported until recently into our country. Considering the chemical composition of shungite rocks and their enriched products, as well as the high adsorption activity of shungite carbon, all the prerequisites for using it as a raw material for the production of a complex carbon-mineral sorbent are created.

We have carried out work on the development of a technological scheme for preparation of carbon-mineral sorbent based on the concentrate of shungite rock,

investigation of its physicochemical characteristics and use in the processes of domestic and industrial wastewater treatment.

In most cases, the concentration of metal ions from the aqueous phase is carried out in a dynamic mode. In this regard, the gas permeability factor becomes quite relevant, since the volumes of processing of industrial enterprises are significant.

As mentioned above, the concentrate of shungite rocks obtained as a result of flotation enrichment is a finely dispersed material, whose fractional composition is minus 73 μm , therefore, the first stage of work was the issue of preparing a granulated material with the predetermined fractional composition. The chemical composition of the concentrate of shungite rocks used as feedstock for the preparation of carbon-mineral sorbent was samples No.12-14 (Table 5).

Schematic technological diagram of the preparation of carbon-mineral sorbent is presented in Figure 38.

The production line consists of three main components: 1) a mixer, 2) an extruder, and 3) a conveyor belt dryer.

1) The mixer is a container for loading components with a screw mixing device. It is intended for mixing a flotation concentrate with a binder; an aqueous solution of saccharose was used as the binder. The optimal ratio S:L was determined as 1:10, which provides optimal physical and mechanical indicators of the quality of the resulting briquette and the minimum consumption of binder. The blend is mixed until the binder is evenly distributed over the volume of the concentrate. The prepared mixture is then fed into the extruder.

2) The extruder is designed in the form of a vertical press, which consists of a working cylinder 2, a cone nozzle 3 and a piston mechanism 4. A loading window 5 is placed on the working cylinder, into which the mixture is fed. The piston mechanism is driven by an electric motor 5 through a worm-type reducer 6. The motor is driven by a belt drive with pulleys 7. The briquettes are molded in the lower part of the nozzle, which has row openings with a diameter of 1.3 mm, and formed briquettes are further removed to the conveyor belt dryer.

3) The purpose of the conveyor belt dryer is that as the briquettes move on the belt, residual moisture is removed before the thermal activation process. The conveyor belt itself consists of a станины 8, along the edges of which two belt shafts 9 and 10 are mounted, through the shaft 9 the belt is driven by an electric motor 11. The temperature required for drying the sorbent is created using six air тены 12. The voltage on the тены is set using a voltage relay 13, in which the voltmeter 14 is built-in. The temperature of the drying process is monitored using an electric millivoltmeter 15, to which a platinum-rhodium-platinum thermocouple 16 is connected and that located directly in the heating zone. Briquetted carbon-mineral sorbent from conveyor belt dryer enters the collector 17.

The final stage in the preparation of the carbon adsorbent is thermal burning and activation with hot steam. The schematic diagram of this unit is shown in Figure 39. The reaction chamber 2 is built into the reactor in the form of a beaker in such a way that between the heat-insulating jacket and the chamber walls there is air space, in which five evenly distributed U-shaped air тена are built-in, which provide heating from the outside of the reaction chamber. Central heating is provided by a spiral built into cylinder 4, current supplied to it through the voltage relay. Four tubes 5 are uniformly located inside the reaction chamber, in which there are openings along the entire length with an interval of two centimeters for uniform distribution of the inert gas and vapor throughout the entire volume of the reaction chamber. These tubes emerge from the

bottom part 6 of the deployed system. Gas is supplied from the cylinder 7. The pressure is recorded by a pressure gauge 8 on the gear 9. After the carbonization process, a sharp steam is supplied to the reaction chamber from the steam generator 10 to generate steam activation. The steam is accumulated from the heating of the water by three water тенами 11 built into the steam generator. Switching the supply of gas-vapor to the deployed reactor system is carried out by crane 12. Figures 40-44 show photographs of a technological line for the production of granulated carbon-mineral sorbent with a capacity of 50 kg/day. Modes of the briquetting process of the concentrate of shungite rocks and carbonization of the carbon-mineral sorbent are presented inT 40 and 41.

Table 40

Modes of operation of the concentrate briquetting unit.

Speed of conveyor belt mechanism, mm/min	Temperature of conveyor belt mechanism, °C	Extruder piston pressure, MPa	The mixing time of the components in the mixer, min
250	170	50	90

Table 41

Modes of operation of the concentrate briquetting unit.

Temperature of carbonization, °C	Time of carbonization, min	Duration of activation, min	Steam consumption, Gcal / hour
750	45	30	2500

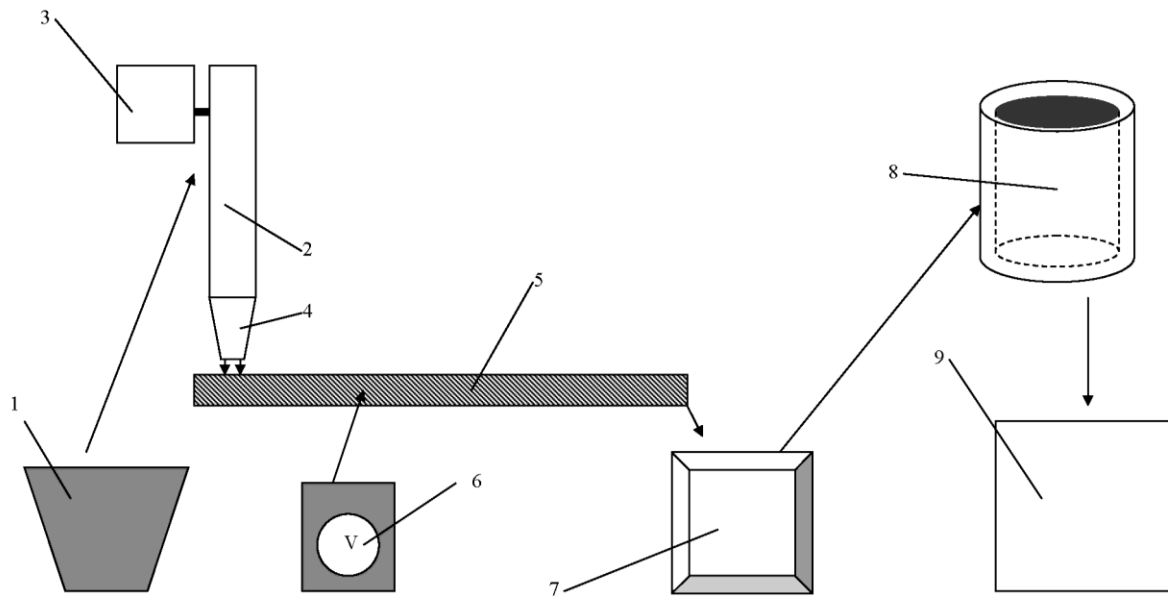


Figure 38 – The technological scheme for the production of carbon-mineral sorbent

(1 – a concentrate mixer with a binder; 2 – an extruder; 3 – an electric drive of the extruder; 4 – a replaceable nozzle of the extruder with a different diameter of dies; 5 – drying belt conveyor with a built-in temperature control; 6 – a conveyor heating regulator; 7 – a drying cabinet; 8 – a thermal activation reactor; 9 – a warehouse container).

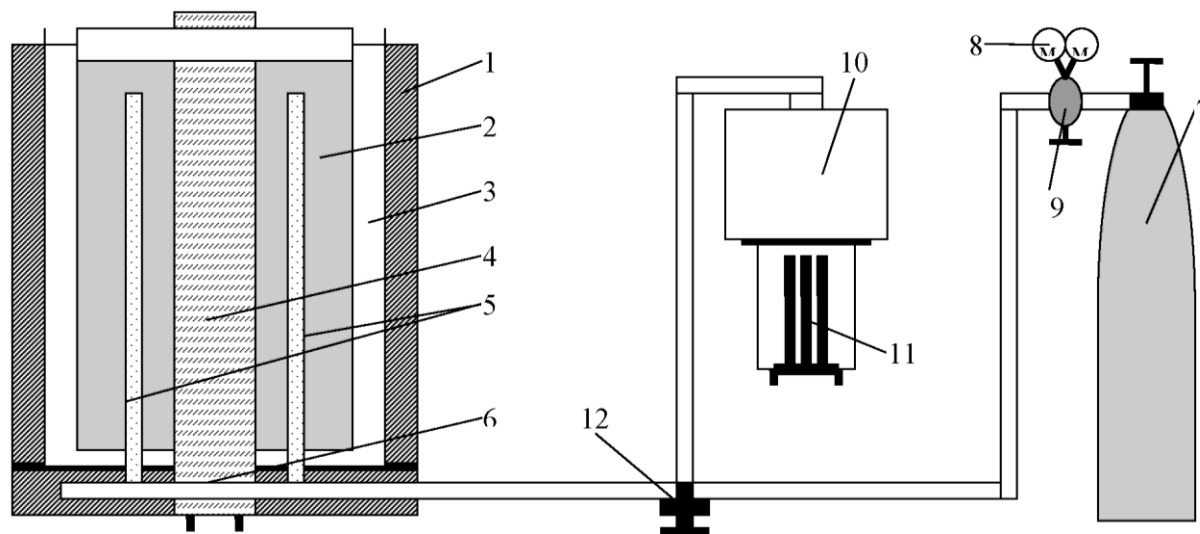


Figure 39 – Schematic diagram of the thermal burning and activation unit with hot steam

(1 – a thermal insulation; 2 – a reaction chamber; 3 – an external heating element; 4 – an internal heating element; 5 – elements of the uniform distribution of gas-steam; 6 – gas-steam delivery pattern in the bottom of the reactor; 7 – a gas cylinder (argon); 8 – manometers; 9 – a gear; 10 – a steam generator; 11 – water electric heaters; 12 – a gas-steam switching valve).



Figure 40 – A photography of the columns of the main and cleaner flotation



Figure 41 – Photography of the extruder briquette assembly



Figure 42 – A photograph of the conveyor belt dryer unit for briquetting



Figure 43 – A photograph of the briquette assembly mixer



Figure 44 – A photography of the thermal burning and hot steam activation unit

7.2. Study of physicochemical patterns and features of the sorption processes of metal ions by carbon-mineral sorbents based on shungite

Upon determining the physicochemical characteristics in these studies, two types of sorbent were used for comparison: 1) a sorbent prepared from shungite rock (“Bolshevik” deposit), crushed to the fraction – 71 μm , which has passed the stage of the steam-gas activation (sorbent No.1 – SGA) and a sorbent that not subjected to SG-activation (sorbent No.1 – without SGA); 2) a sorbent prepared from a flotation concentrate, also having passed the stage of steam activation (sorbent No.2 – SGA) and a sorbent that not subjected to SG-activation (sorbent No.2 – without SGA). In both cases, briquettes of fractional composition 2–5 mm were prepared [49].

One of the important characteristics of sorbents is their mechanical strength. Figure 45 shows the dependence of the compressive strength ($\sigma_{\text{сж}}$) on the size of particles and the temperature of activation of sorbents based on shungite concentrate.

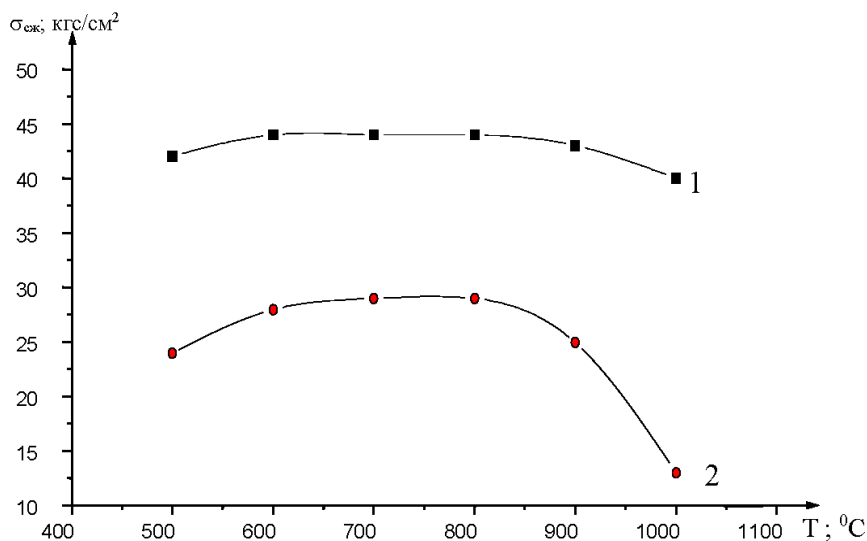


Figure 45 – The dependence of the mechanical strength on the activation temperature (1 – samples with a particle size of <100 μm; 2 – samples with a particle size from 100 to 315 μm)

As shown in Figure 45, for both types of samples of shungite sorbents, their mechanical strength decreases with an increase in the temperature of activation, since thermal decomposition of the obtained briquettes occurs upon raising the temperature. Figure 45 also shows that the mechanical strength of the samples with a smaller particle size (<50 μm) is almost 1,5 times higher and changes slightly with increasing temperature compared to sorbents with a large particle size (more than 95 μm). This is due to the denser packing of briquettes of shungite sorbents of the first series. As studies show, a longer mechanical treatment of the initial rock also strongly affects the size and constancy of the specific surface of the tested sorbents (Figure 46).

The specific surface area of shungite sorbents was determined using thermal desorption method. The measurement results are presented in Table 42. The specific surface area ($S_{уд}$) was calculated using the equation $s = S_{с3г3}/S_{с3г}$. Al_2O_3 with the specific surface area of $S_{уд}=243 \text{ m}^2/\text{g}$ and an area of desorption peak $S_3=15,3 \text{ cm}^2$ was used as a standard.

Figure 46 shows that for samples of the first series, an increase in the temperature of activation leads to a gradual decrease in the specific surface area of shungite sorbent. Most likely, this is due to the contamination of the inner surface by decomposition products of salts and oxides of various metals contained in shungite sorbents. Большое влияние

The temperature affects to the second series of samples. Here, a sharp increase in the specific surface area from 75 to $198 \text{ m}^2/\text{g}$ is observed with an increase in the temperature of activation from 500 to 700 °C. The maximum specific surface area is observed at an activation temperature of 700 °C.

With a subsequent increase in temperature, the specific surface area of shungite sorbents decreases. An interesting jump in the specific surface area for the sorbents of the second series at a temperature of 1000 °C was observed. According to the authors, this is due to thermal decomposition of the sorbent granules, the formation of cracks and chips which leads to a sharp increase in the specific surface area. Such an increase in the specific surface area practically does not affect the sorption characteristics of this

sample, since new adsorption centers are not formed, and, consequently, the effective (useful) specific surface area does not practically change.

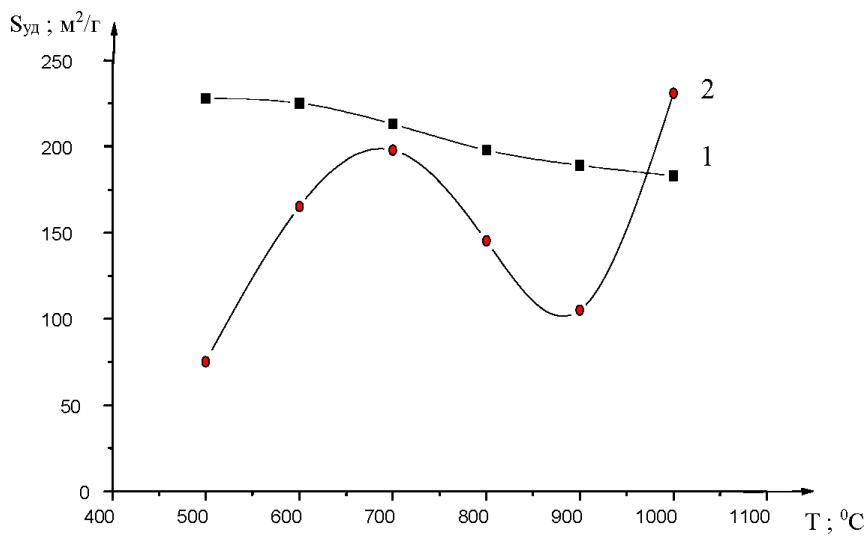


Figure 46 – The dependence of the specific surface area on the activation temperature (1 – samples with a particle size of <100 μm; 2 – samples with a particle size from 100 to 315 μm)

Table 42

The results of measurements of the specific surface area of shungite sorbents using thermal desorption method.

№ п/п	Size of particles, d, μm	Temperature of activation, T, °C	Desorption peak area, S, cm²	Specific surface area, Sуд, m²/g
1	< 50	500	14,4	228
2		600	14,2	225
3		700	13,4	213
4		800	12,5	198
5		900	11,9	189
6		1000	11,5	183
7	95 – 315	500	4,7	75
8		600	10,4	165
9		700	12,5	198
10		800	9,1	145
11		900	6,6	105
12		1000	14,5	231

The suggested assumption proves the promising sorption properties of shungite sorbents. Figure 47 shows the dependence of the methylene number M (mg/g) of shungite sorbents of series 1 and 2 on the activation temperature. The figure

demonstrates that for samples of the 2nd series, an increase in temperature from 900 to 1000 °C does not significantly affect the sorption capacity of the sorbent (it increases by only 1,2 mg/g), despite a substantial increase in the specific surface area.

Shungite sorbents were used to sorb 0,15% aqueous solution of methylene blue. Comparing the curves of the dependence of the specific surface area (Figure 46) and the sorption capacity (Figure 47) on the temperature of activation, it could be noted that the dependence of the sorption capacity on the temperature for both series of samples is proportional to the dependence of the specific surface area on the temperature (excluding the last part for the second series), which, in fact, was supposed to be expected.

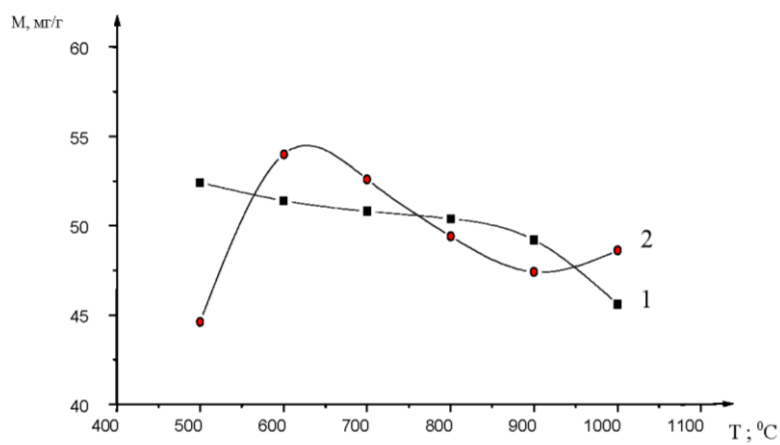


Figure 47 – The dependence of the sorption capacity on the activation temperature (1 – samples with a particle size of <100 μm; 2 – samples with a particle size from 100 to 315 μm)

It should also be noted that samples of sorbents of the series 2 are characterized by higher values of the sorption capacity (Figure 47) relative to the values of the specific surface area (Figure 46) compared to sorbents of the series 1. This is due to the different porosity of the sorbent samples. The results of determining the sorption capacity of shungite sorbents are presented in Table 43.

Table 43

The results of the determination of sorption capacity by methylene blue

Size of particles, d, μm	Temperature of activation, T, °C	Optical density of the solution, A	Concentration of the solution, C, g/L	Methylene number, M, mg/g
< 50	500	0,057	0,190	52,4
	600	0,065	0,215	51,4
	700	0,069	0,230	50,8
	800	0,072	0,240	50,4
	900	0,081	0,270	49,2
	1000	0,108	0,360	45,6

Table 43, continued

95 – 315	500	0,116	0,385	44,6
	600	0,045	0,150	54,0
	700	0,056	0,185	52,6
	800	0,080	0,265	49,4
	900	0,095	0,315	47,4
	1000	0,086	0,285	48,6

A longer crushing of the initial rock for the preparation of sorbents of the first series led to the formation of a larger number of small particles, which, in turn, caused the formation of additional micro- and meso- pores in the structure of these sorbents during further processing. For sorption of molecules of large sizes, which, in fact, are methylene blue molecules, the macro- and meso- porous structure of the sorbent is preferable. Hence, changing the conditions of processing the initial rock, one can obtain sorbents with various pore sizes, and, therefore, characterized by selective sorption.

Based on the physicochemical properties of the prepared shungite sorbents (mechanical strength, specific surface area and sorption capacity), it could be concluded that the optimum temperature of sorbent activation is the interval (600-700) °C, which shown in Table 44.

Table 44

The results of studies of the physicomechanical characteristics of shungite sorbents

Size of particles, μm	Temperature of activation, $^{\circ}\text{C}$	Mechanical strength, kgs/cm^2	Specific surface area, m^2/g	Sorption capacity, mg/g
< 50	500	42	228	52,4
	600	44	225	51,4
	700	44	213	50,8
	800	44	198	50,4
	900	43	189	49,2
	1000	40	183	45,6
95 – 315	500	24	75	44,6
	600	28	165	54,0
	700	29	198	52,6
	800	29	145	49,4
	900	25	105	47,4
	1000	13	231	48,6

7.3. The study of the formation of the porous structure of carbon-mineral sorbents upon steam activation process

In the first decades of our century, activated charcoals was usually considered as an amorphous type of carbon, although electron microphotographs make it possible to distinguish between a loose structure consisting of finest carbon particles about 3 nm in size. Hoffmann [198] for the first time proved using only X-ray diffraction analysis that these particles are crystallites with sizes of 1-3 nm. Therefore, nowadays, activated charcoal is referred to the group of microcrystalline carbon species. Although graphite crystallites consist of planes with a length of 2-3 nm, formed by six-membered rings, typical for graphite orientation of individual planes of the lattice relative to each other

is broken. This means that in activated charcoal the layers are randomly shifted relative to each other and do not coincide in the direction perpendicular to the plane of the layers. The distance between the layers of shungite carbon is greater than that of graphite (0,3354 nm) and ranges from 0,344 to 0,365 nm. The diameter of a building element connected in the same plane is 2,0-2,5 nm, and sometimes even more. The height of the pack of layers is equal to 1,0-1,3 nm. Thus, graphite crystallites in activated charcoal contain 3-4 parallel carbon layers.

Due to the presence of an ordered graphite structure, activated carbons are usually characterized by substantial electrical conductivity. Particularly, it depends on the activation temperature and increases at high temperatures, since the surface oxygen compounds acting as insulators are removed and larger elemental crystallites are formed.

At high temperatures corresponding to the preparation temperatures of activated carbon, the specific resistance is much lower than at 400-500 °C. The calcined samples were ground into powder and tested under pressure of 18 MPa in the form of pressed products.

In addition to graphite crystallites, the concentrate of shungite carbon contains, according to X-ray analysis, from one to two thirds of amorphous carbon; along with this, there are heteroatoms, in particular, oxygen, which is confirmed by microelement analysis.

The inhomogeneous mass consisting of graphite crystallites and amorphous carbon determines the unusual structure of shungite carbon. Between individual particles, cracks and cracks (pores) appear with width of the order of $10^{-7} \div 10^{-8}$ m, as was revealed earlier. These intermediate pores were formerly called “micropores” [53], and large cavities with a diameter of up to 1 μ m were called “macropores”. Through this system of pores, mass transfer is carried out in all processes occurring in the inner surface of the carbon-containing material. Cavities that do not interact with the external surface are generally called “cryptopores”. From the point of view of adsorption practice, they have no meaning.

Initially, the division into micro- and macropores turned out to be too crude for the description of adsorption processes. Therefore, Dubinin [53] proposed the following classification of pores: micro-, transitional and macropores. In accordance with this division, micropores are the thinnest pores that are filled with an adsorbate at low partial pressures, even before capillary condensation. The transition pores are pores in which capillary condensation takes place, and macropores have a large radii that the phenomenon of capillary condensation is no longer possible.

Currently, such classification, mainly its analytical and technical aspects, has been brought into line with the norms of the International Union of Pure and Applied Chemistry [65]. Pores with diameters up to 0,4 nm are called submicropores, pores with diameters in the range 0,4-2,0 nm are called micropores. For pores with diameters from 2 to 50 nm the name of the mesopore is proposed, larger pores with diameters above 50 nm are called macropores. idea

Using the notion about pore diameters or radii, which should be considered as effective parameters, one can assume that the pores have only a cylindrical I shape. However, V-shaped and slit-like pores predominate in activated charcoals along with pores of a J irregular shape. In most industrial active carbons, pores of various shapes are simultaneously present. Moreover, many studies prove the existence of so-called bottle-shaped pores with narrow entrances which are formed, in particular, in the classical chlorzinc activation process.

The distribution of pores by radii in individual activated charcoal could be quite different. In accordance with this, large-pore activated charcoals are distinguished, which, however, always contain thin pores, and fine-porous activated charcoals, which, in addition to micropores, might also include large pores.

Currently, it is still not possible to obtain an optical image of micropore systems of activated charcoals. Even with an unusually strong magnification, electron microscopic images allow to distinguish only pores with the diameter of about 10 nm. Significantly lower magnification is provided by images using a scanning electron microscope, which sufficiently clearly reproduces the structure of the particle surface.

Figures 48-51 show the kinetics of changes in porosity and pore distribution in a carbon-mineral sorbent depending on the preparation conditions and conditions of temperature activation.

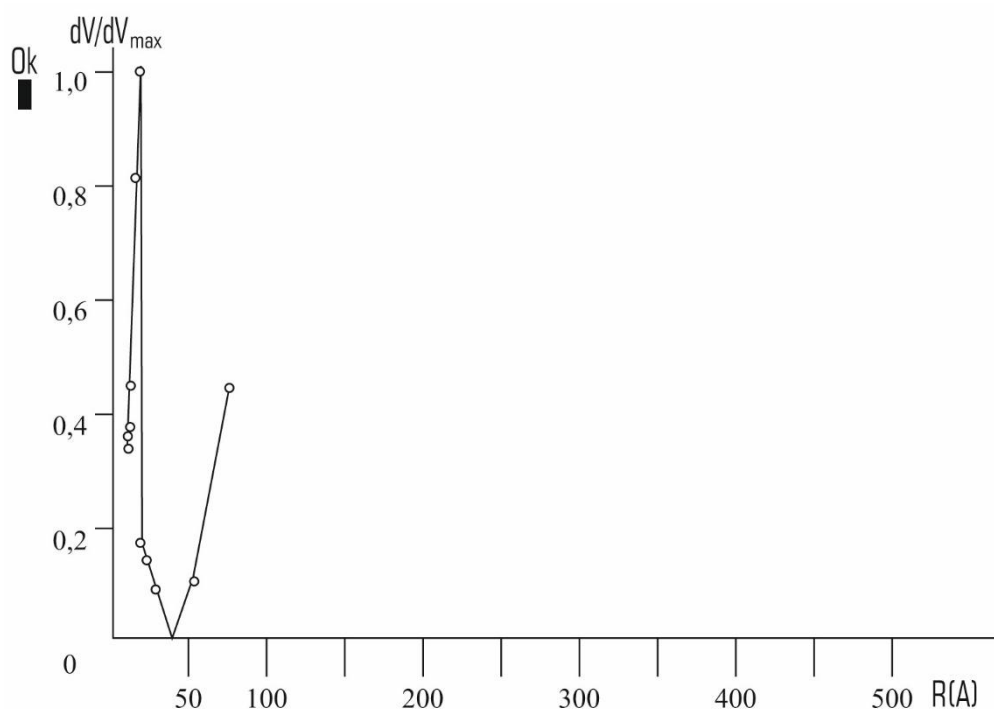


Figure 48 – Carbon-mineral sorbent (C – 40,0 %), temperature of activation 500 °C

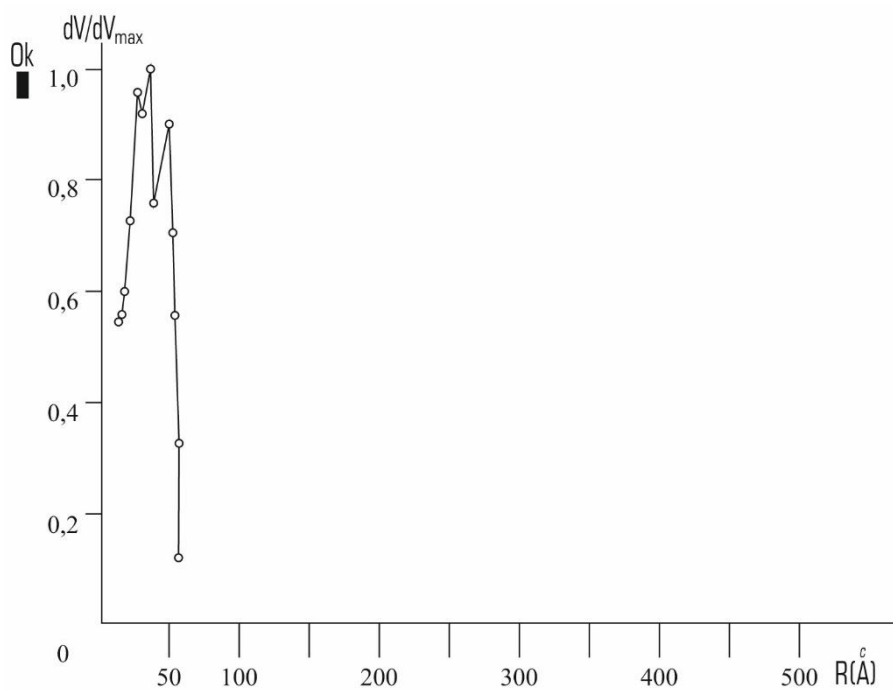


Figure 49 – Carbon-mineral sorbent (C – 40,0 %), temperature of activation 750 °C

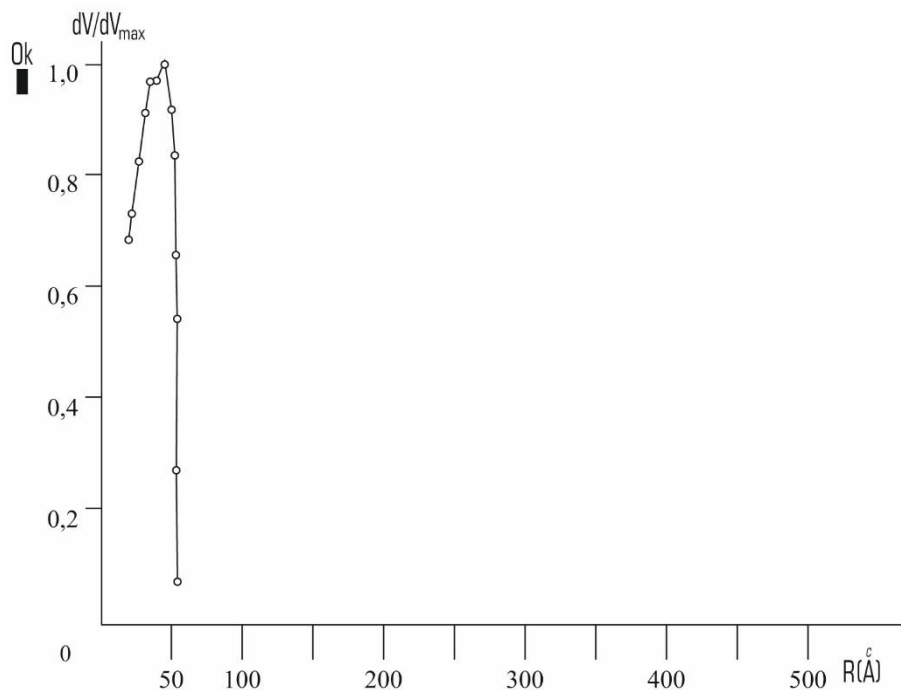


Figure 50 – Carbon-mineral sorbent (C – 20,0 %), temperature of activation 500 °C

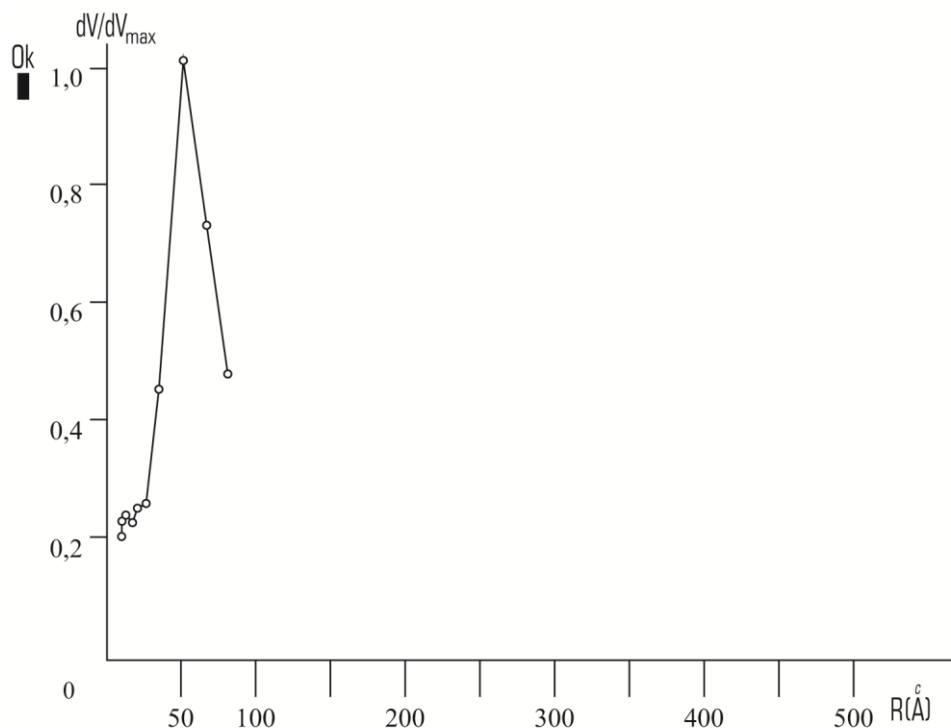


Figure 51 – Carbon-mineral sorbent (C – 20,0 %), temperature of activation 750 °C

7.4 The application of sorbents in water treatment processes

Adsorption of water by activated charcoals is of great interest from a practical point of view. Water fills up to 30-50% of the pores of coal, the diameter of which is less than 12-24Å. Meanwhile the “normal” carbon surface is hydrophobic, it repels water, the carbon body, the surface of which is covered with a large amount of oxygen, acquires a hydrophilic character. Coal sorption occurs due to the large specific surface area and porosity [71].

To determine the sorption ability, model solutions with a known content of the studied metals were used. Upon preparation of model solutions, chemically pure reagents ($\text{Pb}(\text{NO}_3)_2$, $\text{K}_2\text{Cr}_2\text{O}_7$, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, NH_4VO_3) were used. The sorption in the dynamic mode was carried out on the setup shown in Figure 52. The installation is based on the use of reverse pressure during the passage of solution from vessel 1 through a column with sorbent 3. The feed rate of the model solution was regulated by valve 2 and set during the experiment 10 mL/min. Samples were taken every 5 minutes into the collector 4. Determination of the content of metal ions in the samples was carried out using a “Shimadzu AA-6200” atomic absorption spectrometer.

In the static mode, the dependence of sorption ability on the time of contact of the sorbent with the solution was studied. The ratio of solid and liquid phases was 1:100, which corresponds to the optimal conditions for the use of the sorbent.

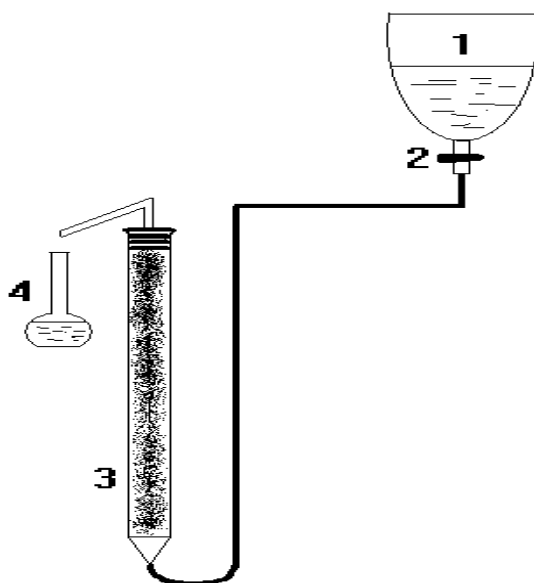


Figure 52 – Installation for carrying out the adsorption in a dynamic mode
(1-vessel with a model solution, 2-valve for regulating the supply of the solution, 3-column with a sorbent, 4-sampler)

Sorption of lead (II) in the dynamic mode

Figure 53 shows the data on the sorption of lead from a solution containing 10,45 mg/L of Pb^{2+} ions at pH = 6 and pH = 2,5. Samples were taken as the solution passed through the column at intervals of 5 min.

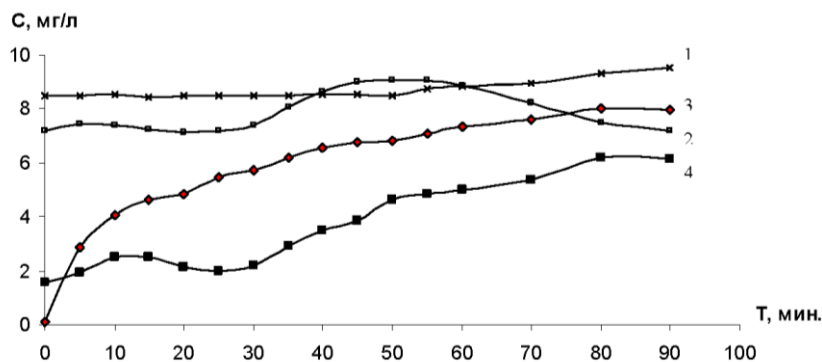


Figure 53 – Sorption of lead in the dynamic mode (1 – on sorbent №1 at pH=2,5; 2 – on sorbent №2 at pH=2,5; 3 – on sorbent №1 at pH=6; 4 – on sorbent №2 at pH=6)

Figure 53 shows that sorbent No.2 in a medium close to neutral (pH = 6) absorbs lead (II) ions better than sorbent No.1. Moreover, sorption takes place during the entire time of the experiments. In an acidic environment, sorbent No.2 also does not lose sorption activity during a long time period. A slightly different dependence is observed

for sorbent No.1. Here, after 60-80 min, a decrease in sorption activity is observed, which may be associated with the saturation of the sorbent with lead ions.

Sorption of lead (II) in the static mode

The dependence of the contact time of the sorbent with the solution was studied. Figure 54 shows the dependence of sorption on the contact time of the sorbent with the solution at pH values of 6 and 2.5 (the initial concentration of the solution was 10,45 mg/L).

At pH = 6 within 40 minutes of contact, the best sorption is observed in sorbent No.2, with prolonged interaction from the solution with a neutral medium, better absorption is observed in sorbent No.1.

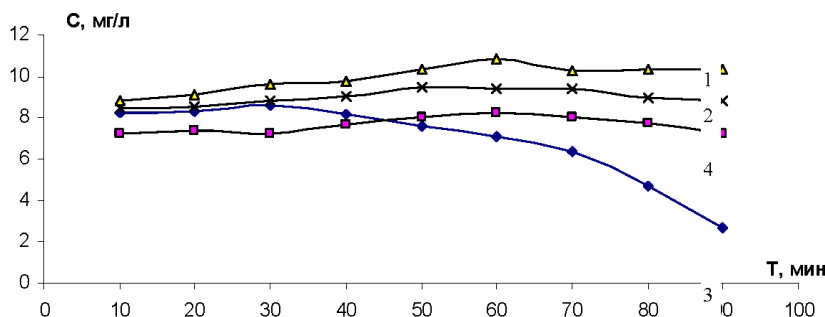


Figure 54 – Sorption of lead in the static mode (1 – on sorbent №1 at pH=2,5; 2 – on sorbent №2 at pH=2,5; 3 – on sorbent №1 at pH=6; 4 – on sorbent №2 at pH=6)

Sorption of chromium (VI) in the dynamic mode

Figure 55 shows the data on the sorption of chromium from a solution containing 12,67 mg/L of Cr^{6+} ions at pH = 6 and pH = 2,5. Samples were taken as the solution passed through the column at intervals of 5 minutes.

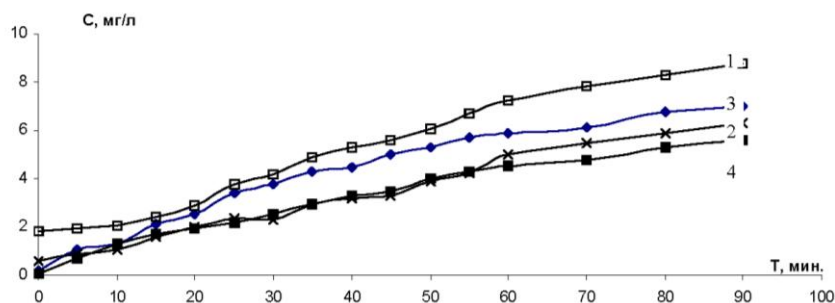


Figure 55 – Sorption of chromium in the dynamic mode (1 – on sorbent №1 at pH=2,5; 2 – on sorbent №2 at pH=2,5; 3 – on sorbent №1 at pH=6; 4 – on sorbent №2 at pH=6)

Figure 55 shows that sorbent No.2 in an aqueous medium with a hydrogen index equal to 6 absorbs chromium (VI) ions better than sorbent No.1. Moreover, sorption

takes place during the entire time of the experiments. At pH = 2,5, as seen from the figure, sorbent No.2 during the entire duration of the experiment extracts Cr^{6+} ions more actively than sorbent No.1.

Sorption of chromium (VI) in the static mode

The dependence of the contact time of the sorbent with the solution was studied. Figure 56 shows the dependence of sorption on the contact time of the sorbent with the solution at pH = 6 and pH = 2,5 (the initial concentration of the solution was 12,67 mg/L).

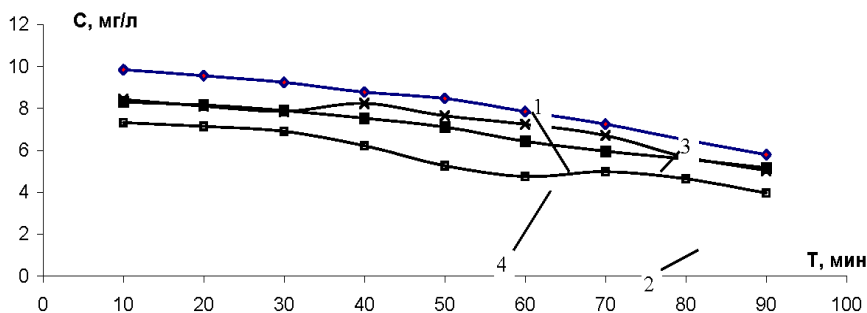


Figure 56 – Sorption of chromium in the static mode (1 – on sorbent №1 at pH=2,5; 2 – on sorbent №2 at pH=2,5; 3 – on sorbent №1 at pH=6; 4 – on sorbent №2 at pH=6)

In this case, both types of sorbents sorb metal ions better from solutions with pH = 2,5. Figure 56 clearly shows when sorbents No.2 and No.1 are compared with each other, sorbent No.2 has large sorption characteristics with respect to Cr^{6+} ions.

Sorption of nickel (II) in the dynamic mode

Figure 57 shows the data on the sorption of nickel from a solution containing 18,36 mg/L of Ni^{2+} ions at pH = 6 and 2,5. Samples were taken as the solution passed through the column at intervals of 5 minutes.

Figure 57 shows that sorbent No.2 in an aqueous medium at pH=6 and 2,5, absorbs nickel (II) ions better than sorbent No.1.

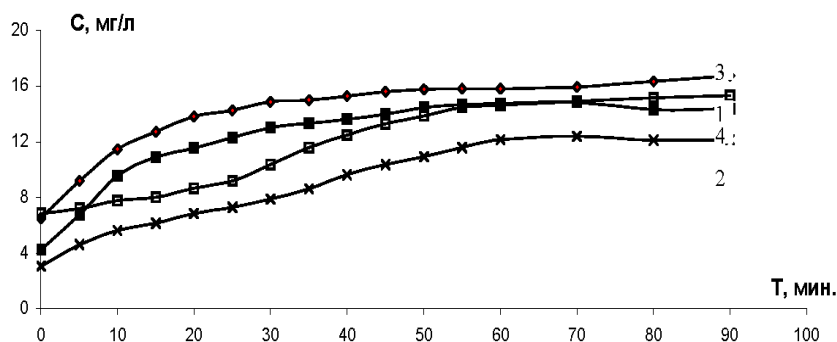


Figure 57 – Sorption of chromium in the dynamic mode (1 – on sorbent №1 at pH=2,5; 2 – on sorbent №2 at pH=2,5; 3 – on sorbent №1 at pH=6; 4 – on sorbent №2 at pH=6)

Sorption of nickel (II) in the static mode

Figure 58 shows the dependence of sorption on the contact time of the sorbent with the solution at pH = 6 and 2,5 (the initial concentration of the solution was 18.36 mg/L).

Throughout the experiments, effective sorption was observed in sorbent No.2 to a greater extent than in sorbent No.1.

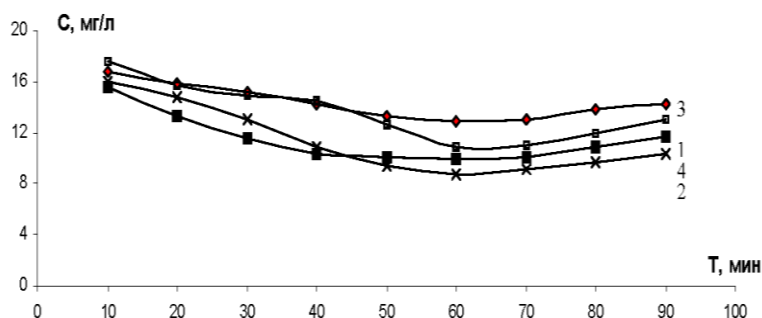


Figure 58 – Sorption of nickel in the static mode (1 – on sorbent №1 at pH=2,5; 2 – on sorbent №2 at pH=2,5; 3 – on sorbent №1 at pH=6; 4 – on sorbent №2 at pH=6)

Sorption of vanadium (V) in the dynamic mode

Figure 59 shows the sorption data of vanadium from a solution containing 14,75 mg/L of V^{5+} ions at pH = 6 and 2,5. Samples were taken as the solution passed through the column at intervals of 5 minutes.

1 – on sorbent №1 at pH=2,5; 2 – on sorbent №2 at pH=2,5;
3 – on sorbent №1 at pH=6; 4 – on sorbent №2 at pH=6.

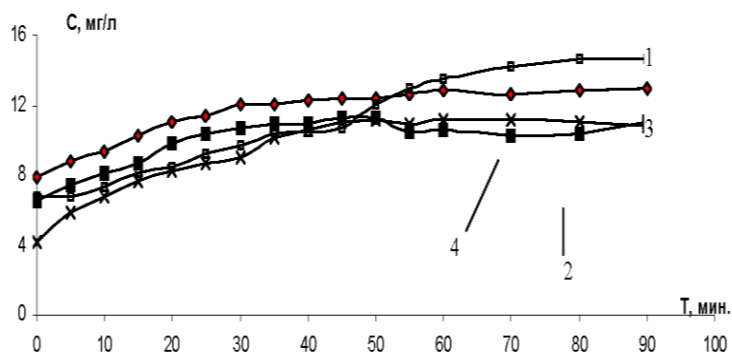


Figure 59 – Sorption of vanadium in the dynamic mode

Figure 59 shows that sorbent No.2 in a medium close to neutral sorb vanadium ions on average better than sorbent No.1. In this case, the sorption activity of the sorbents is gradually lost during the experiments. In an acidic environment, sorbent No.2 at the initial stage (45 minutes) is slightly inferior to sorbent No.1 in sorption activity. Sorbent No.2 became more active during the longer contact time.

Sorption of vanadium (V) in the static mode

The dependence of the contact time of the sorbent with the solution was studied. Figure 60 shows the dependence of sorption on the contact time of the sorbent with the solution at pH = 6 and 2,5 (the initial concentration of the solution was 14,75 mg/L).

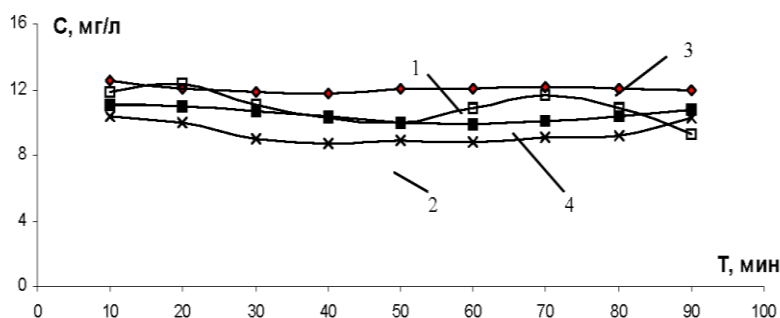


Figure 60 – Сорбция ванадия в статике (1 – на сорбенте № 1 при pH=2,5; 2 – на сорбенте № 2 при pH=2,5; 3 – на сорбенте № 1 при pH=6; 4 – на сорбенте № 2 при pH=6)

Figure 60 shows that the sorption activity of sorbent No.2 in solutions at pH = 6 and 2,5 is higher than that of sorbent No.1, which is explained by the chemical composition of the sorbents, in particular, the content of the carbon part.

Thus, the sorption of ions of lead (II), chromium (VI), nickel (II) and vanadium (V) has a significant effect on the pH of the medium, the contact time of the solution with the sorbent, and the ratio S:L. The sorbent used in the studies could be regenerated without a significant deterioration in its technical characteristics and sorption properties. The studies showed the promise of using carbon-mineral sorbents based on shungite in the sorption of heavy metal ions from aqueous systems. According to the studies, sanitary and hygienic conclusions were obtained, Technical conditions were developed and a certificate of product quality was received for the use of sorbents for drinking water purification (Appendix B).

7.5. Material balance of the preparation process of carbon-mineral sorbent and evaluation of its economic efficiency

The calculation of the material balance for preparation of the carbon-mineral sorbent allow to determine the consumption of components. According to the technological scheme presented in Figure 38, the calculations for the preparation of carbon-mineral sorbent were made, the results of the calculations are presented in Table 45.

Table 45

Consolidated material balance of the preparation process of carbon-mineral sorbent

Income			Consumption		
Name of the article	kg	Mass fraction, %	Name of the article	kg	Mass fraction, %
Circulating water	3000,0	54,0	Carbon-quartz briquettes	1000,0	18,1
saccharose	120,0	2,1	tailings	1640,0	29,5
Shungite rock	2429,5	43,8	Circulating water	2881,7	51,9
flotation reagents	0,5	0,1	Steam	28,3	0,5
Total	5550,0	100,0	Total	5550,0	100,0

The cost price of the carbon-mineral sorbent presented in Table 46 was calculated according to the requirements of technical and economic calculations of chemical production.

Table 46

Cost of shungite concentrate

Name	Costs per 1 ton of products, tenge							Cost of 1 ton of product
	raw materials	materials and reagents	salary	operation of the installation	electricity, water	depreciation and fuel	other utilities	
Carbon-mineral sorbent (with a volume of 100 t/year)	10952,0	7400,0	25160,0	6770,0	28120,0	4144,0	8140,0	90686,0

Technical and economic efficiency are calculated according to the rules of chemical production using the following equation:

$$\varnothing = [\Pi_{\text{опт}} - (C + E_{\text{н}} \times K_{\text{доп.}})] \times A$$

where $\Pi_{\text{опт}}$ – wholesale price of products, tenge; C – the cost of production of new products; $E_{\text{н}}$ – standard coefficient of economic efficiency, which is equal to 0,15 tenge; $K_{\text{доп.}}$ – additional specific capital costs for the development of this product; A – annual output in the estimated year, equal to 100 tons.

Based on this: $\varnothing = [180\,000 - (90686 + 0,15 \times 1)] \times 100 = 8\,931\,385$ tenge.

CHAPTER 8 THE USE OF CARBON-QUARTZITE BRIQUETTES BASED ON SHUNGITE CONCENTRATE IN ORE THERMAL PROCESSES

8.1. The technology for preparation of carbon reducing agents for ore-thermal production

The results obtained in the study of shungite rocks confirmed the feasibility of conducting tests to assess the properties and behavior of shungites as reducing agents for electrothermal processes. The presence of active amorphous carbon in shungite rocks in close contact with developed silica surfaces suggests that shungite rocks will exhibit high chemical activity and increased electrical resistivity in ore recovery processes [168].

Considering the fact that the concentrates of shungite rock are a carbon mineral composition and it was decided, as mentioned above, to test them not as a reductant, but as a complex шихты for electric sublimation of yellow phosphorus. In this work, concentrates with the chemical composition presented in Table 47 were used.

Table 47

Chemical composition of the shungite concentrates

№ sample	Content of mineral part*, % mass.					
	C	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	K ₂ O
1	30,9	52,2	8,3	2,8	1,8	2,4
2	50,3	30,1	8,1	2,0	2,5	1,5
* – the sum of up to 100% are microimpurities that do not affect the course of the experiment						

On the basis of concentrates, carbon-quartzite briquettes were prepared without mineral additives, the technological scheme for preparation of which is shown in Figure 61.

The initial material was the concentrate obtained by enriching on an air classifier (further – briquette sample 1), and the same rock after flotation enrichment (further – sample 2); as a binding material, coal tar pitch with an optimal percentage of 8% was used.

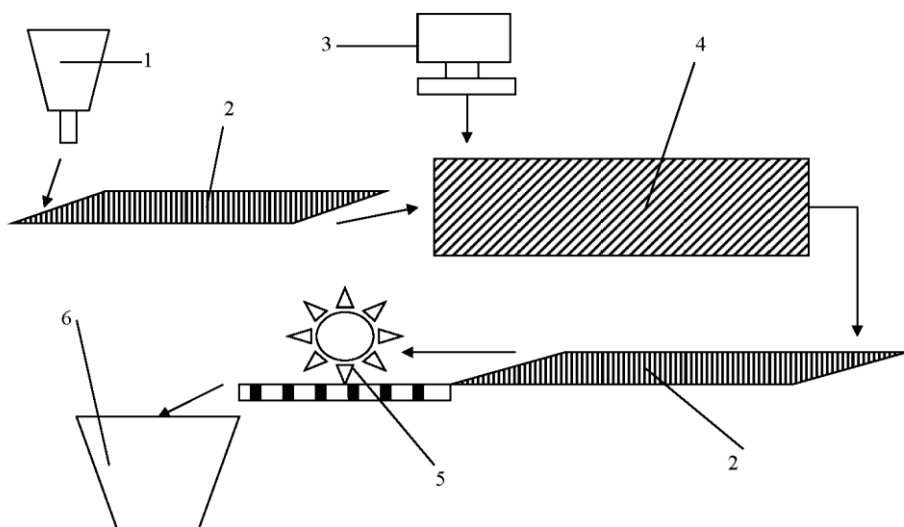


Figure 61 – The technological scheme for preparation of shungite briquettes (1 – hopper with concentrate; 2 – feeder screw; 3 – coal tar pitch hopper with a dispenser; 4 – heated tubular mixer; 5 – rotary tablet machine; 6 – receiving briquette hopper)

The briquettes were pressed under the pressure of 7,84 MPa in a heated form at 120 °C (melting temperature of coal tar pitch).

The obtained briquettes had tablet like shape with a diameter of 15 mm. The physico-mechanical characteristics of industrial coke and experimental carbon-quartzite briquettes obtained experimentally from shungite material are presented in Table 48.

Figure 48

Physical and mechanical characteristics of industrial coke and briquettes based on shungite concentrate

Name of indicators	Shungite briquettes		Metallurgical coke	Foundry coke
	1	2		
Moisture in analytical sample, % mass.	4,1	7,1	1,5	-
Moisture in working sample, % mass.	4,2	7,1	1,5	5,0
Ash in working sample, % mass.	14,3	9,2	11,0	11,0
Ash in absolute dry sample, % mass.	15,4	12,3	11,2	-
Content of volatile substances, % mass.	3,3	4,2	3,1	-
Total sulfur content, % mass.	0,6	0,6	0,6	2,0
Strength M_{25} , %	72,0	87,4	-	-
M_{10} , %	6,0	9,2	-	8,0
M_{40} , %	-	-	-	67,0

Reactivity, heat of combustion and electrical resistivity of carbon-quartzite briquettes were determined using the methodology described in Chapter 2 of this book.

For shungite briquettes these indicators are low, like the coals of high stages of metamorphism. Most likely, this is due to the relatively high degree of structural ordering of shungite. In this case, although samples of various degrees of enrichment were analyzed, it is nevertheless evident that with an increase in the amount of carbon, a slight increase in the numerical values of the content of volatile substances is observed. This fact is most likely associated with an increased content of volatile substances in coal tar pitch. It should be noted that the content of volatile substances in the carbon material is limited by the operation mode of the furnaces [165]. Thus, for open-type furnaces, a high content of volatile substances will cause increased gas emission and complicate the maintenance of the колошника. Limitations on the volatile content of closed-type furnaces are due to the formation of hydrogen, the presence of which in exhaust gases is undesirable in terms of safety.

Mechanical strength is an important characteristic of cokes. It is characterized by crushability and abrasion. Crushability (M_{25}) determines mainly the loss of coke in preparation for smelting. Abrasion (M_{10}) to a large extent determines the rate of formation of coke fines in the furnace and characterizes the resistance of coke to abrasion. Data on the crushability of M_{25} and abrasion resistance of M_{10} , which characterize the mechanical strength of shungite briquettes of both series are presented in Table 49.

As the measurements showed (Figure 62), the strength of briquettes of the series II is higher than the strength of briquettes of the same composition, but not containing coal tar pitch. Moreover, a decrease in the strength of briquettes is observed with an increase in the amount of quartzite in the composition of the шихтового material. However, it is valuable that prepared briquettes with a high content of quartzite, however, have relatively high strength indices. Thus, the strength of the briquette of the series I is comparable to and even exceeds the series II, and also the strength of the metallurgical coke.

Thus, the data in Table 48, in general, allow to conclude that it is possible to use shungite briquettes as a reducing agent for ore thermal production.

Based on the studies and data in Table 49, it could be concluded that the obtained indices both by reactive and electrical resistivity characterize shungite briquettes of a strictly defined composition, which in no case could be identified as an ordinary shungite.

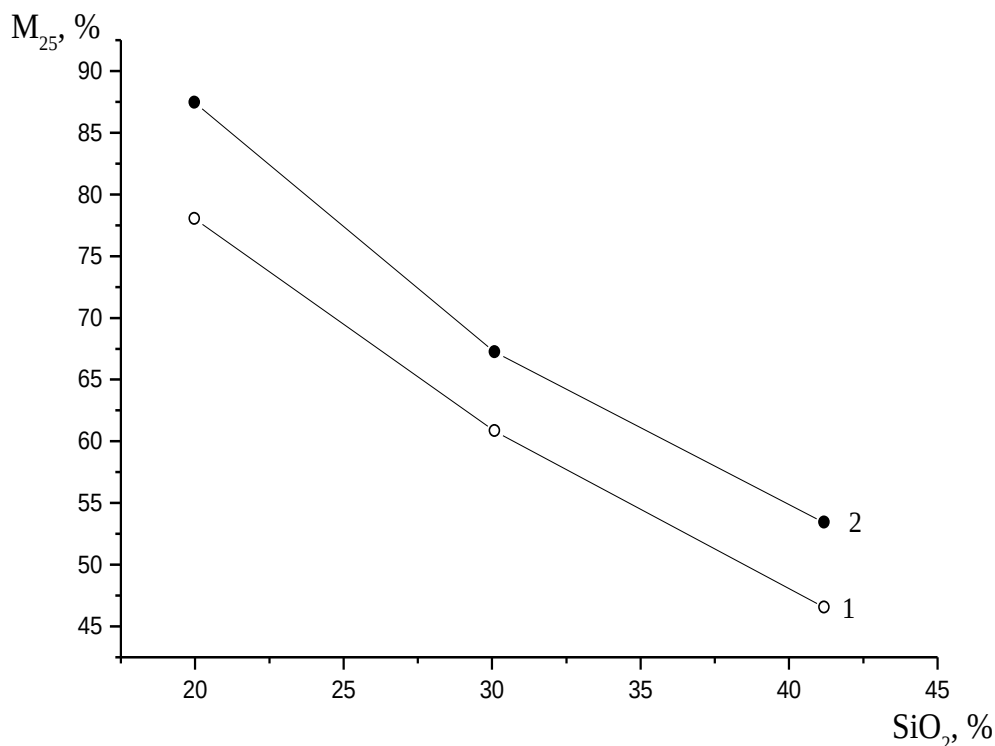


Figure 62 – The dependence of the strength of shungite briquettes on quartzite content in the шихте briquettes of the series I; 2 – briquettes of the series II.

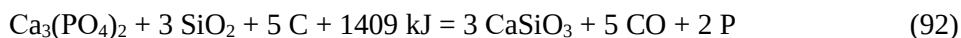
Regarding the obtained shungite briquettes, it could be noted that they have a reactivity similar to metallurgical coke, and the resistance is one to two orders of magnitude higher compared to coke. Such result guarantees a good quality of shungite briquettes in the reaction of phosphorus recovery.

8.2. Recovery of phosphorite using carbon-quartzite briquettes based on the concentrate of shungite rocks

The team of authors of the book carried out enlarged laboratory tests to prepare an experimental batch of briquettes of the series II on an installation with a capacity of 25 kg/day while maintaining the conditions for the briquetting process as described above. The total mass of the test sample of briquette was 20 kg and the physicochemical properties are presented in Table 49. It should be noted that the results of determining the physicochemical properties of shungite briquettes obtained in the course of enlarged laboratory tests are in good agreement with the laboratory data.

Tests for the recovery of Karatau phosphorites (averaged composition of P₂O₅ – 18%, CaO – 35%, SiO₂ – 19% mass.) were carried out using shungite briquette of the series II. This sample was chosen because it had a constant composition similar to the stoichiometric by equation of phosphorus reduction reaction.

The electrothermal process of preparation of phosphorus is based on the reduction of phosphorus-containing raw materials (phosphorites) with carbon by the reaction with subsequent condensation of phosphorus:



In this case, it should be considered that during the phosphorus reduction process, partial replacement of SiO_2 by Al_2O_3 in the шихте is allowed, since the influence of the latter on the шихты melting and the reduction process are close to the effect of silicon dioxide [171]. Moreover, it is characterized by high indices of electrical resistivity and reactivity with reasonable mechanical strength.

Table 49

Physical and mechanical properties of shungite briquettes

Content of volatile substances, % mass.	Mechanical strength		Electrical resistivity, $\Omega \cdot \text{cm}$	Reactivity, $\text{cm}^3/(\text{g} \cdot \text{s})$
	$M_{25}, \%$	$M_{10}, \%$		
4,3	87,4	9,2	5,5	0,72

The completeness of phosphorus extraction from raw materials is determined by the amount of carbon in the шихте. With a lack of the reducing agent, the residual content of P_2O_5 in the slag increases, and, consequently, the degree of phosphorus extraction decreases. The increased content of the reducing agent leads to the “carburation” of the furnace bath. Excessive coke accumulates in the area of slag tap holes and prevents slag discharge. Due to the low specific electrical resistance of coke, its excessive accumulation in the furnace leads to a sharp decrease in the resistance of the bathtub and a decrease in the depth of the electrode seating. This causes a disruption to the normal operating mode of the furnace, an increase in the role of the arc and a sharp increase in temperature in individual zones. As a result, the proportion of undesirable energy-intensive side reactions of phosphide and carbide formation increases. The dustiness of the outgoing gases also increases, the quality of commodity phosphorus deteriorates, and the overheating of the electric furnace arch occurs. Usually, coke in excess of 3-5% mass. is used for full recovery. relative to stoichiometric amount.

It is also important to chose the optimum amount of flux. Its disadvantage in the шихте contributes to an increase in the temperature of smelting of the formed slag. The presence of refractory slag in the furnace leads to the emergence of deposits and can cause the bath to freeze. At the same time, with an excess of flux, the concentration of phosphorus in the шихте decreases. While, the number of remelted materials per ton of product increases, which causes an increase in the specific consumption of electricity and, consequently, a decrease in unit productivity. The amount of quartzite in the mixture is determined taking into account the acidity modulus (the ratio of the mass of silicon oxide to the mass of calcium oxide). The value of the latter is maintained within the limits of 0,8-0,9. Therefore, upon preparing the шихты, it is necessary to accurately calculate not only the optimal amount of reducing agent, but also the flux.

Since shungite briquette has a rather high value of electrical resistivity, it could be assumed that its excess leads to the same disruptions in the operation of the furnace, as indicated above for coke. However, it is believed that the situation will be much worse in the case of a lack of flux, which will affect the disruption of the normal liquid mobility of the melt, the discharge of slag from the furnace, and, no less important, the incomplete binding of calcium oxide, due to which P_2O_5 activity decreases. Therefore, upon preparing the шихты, shungite reducing agent with a larger excess of carbon (105

g per 250 g of phosphorite) was used at a normal SiO_2/CaO ratio equal to 0,9 (considering SiO_2 content in phosphorite).

In parallel, for comparison, the phosphate-containing raw material was recovered with coke in the following шихты composition: 250 g phosphorite, 24 g coke, 30 g quartzite. Thus, the content of shungite carbon in the experimental шихте was ~2 times higher compared to the content of the standard carbon reducing agent in the control шихте.

Reagents of 3-5 mm fraction were loaded into an alundum crucible heated in an electric furnace (in the course of experiments it was established that the crucible material does not practically affect the results). Phosphorus was reduced in a furnace (VEB ELEKTRO INDUSTRIEOFENBAN, 24 kVA) at 1500 °C of industrial process.

Figure 63 presents the results of experiments in the form of curves for the recovery of phosphate by shungite and coke (for greater objectivity, the dependence is not on the dissipation of P_2O_5 in time, but the change in the ratio of $\text{P}_2\text{O}_5/\text{CaO}$; the content of CaO in phosphorite is ~ 35% mass.) [165]. Both curves have the same character: at the beginning of the reaction (at high P_2O_5 values), the recovery process is much more intensive and the activity of the shungite reducing agent is higher than the activity of coke, possibly due to the higher carbon content. As the amount of P_2O_5 decreases, the process speed sharply slows down. Moreover, the process in the control шихте (curve 2) by intensity begins to exceed the process in the experimental шихте (curve 1). In 1 hour, the degree of extraction of phosphorus from phosphorite using shungite is 72,8%, and using coke – 82,2%. For comparison, it could be noted that the degree of reduction of P_2O_5 by domain coke at 1400 °C is 65,9% (in the absence of SiO_2) and 79,0% (in the presence of SiO_2). As it turned out, in our case the degree of phosphorus extraction using shungite was slightly lower compared to coke (the obtained data is in good agreement with the reactivity of shungite briquettes, determined by the interaction with CO_2).

However, there was reason to believe that shungite would exhibit higher activity compared to coke in an industrial furnace. The fact is that under the conditions of the experiment between the reducing agent and the recovered rock, due to the fact that the reducing agent is located on the surface of the latter, the interaction occurs only at the boundary layer. The top layer of the reductant turns out to be inactive during the recovery process. In the furnace, a phosphorite melt as a result of the so-called “filtration” [167] breaks through a layer of carbon reducing agent.

Thus, in the furnace, the interaction between the carbon material and the phosphorite rock occurs in volume, and each piece (briquette) of the reducing agent by its surface reacts with the phosphorite melt. Due to the fact that shungite reducing agent is made in the form of carbon-quartzite briquettes (assuming equal quantitative content of elemental carbon and close granulometry), the contact surface of the phosphorite melt with shungite carbon will be larger than with coke, which will positively affect the degree of phosphorus reduction by shungite.

In addition, the high electrical resistivity of shungite briquettes upon using them as complex raw materials for the electrothermal sublimation of phosphorus will significantly improve the technological parameters of the industrial furnace. This is due to the fact that the high specific resistance of carbon-quartzite briquettes the resistance of the шихты increases and more importantly, the sub-electrode space of the furnace will increase in comparison with conventional work on coke. The latter will affect a deeper fit of the electrodes, will lead to an increase in the filter layer of solid materials

in the reaction zone. However, a deep seating of the electrodes will contribute to an increase in the consumption of electrodes, which is not desirable. In order to eliminate this effect, an excess amount of the reducing agent could be used, which, in turn, will involve a more complete extraction of phosphorus from the ore, i.e. will increase the degree of its recovery. The use of shungite briquettes, in our opinion, will increase the voltage on the electrodes and, accordingly, the electrical efficiency of the furnace installation, reduce the temperature and dustiness of the exhaust gases. However, this statement requires verification, but during industrial testing.

Furthermore, it should be noted that, due to the increase in strength properties (with a high content of quartzite) and high electrical resistivity, briquetting of shungite rocks should become more economical than using coke and quartzite separately as a шихты or preparation of carbon-quartzite briquettes from coal and sand followed by coking.

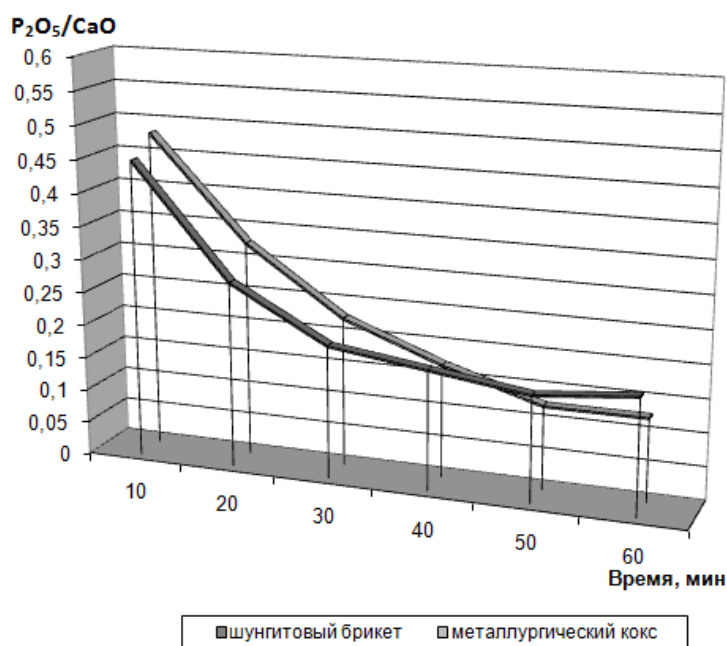


Figure 63 – Kinetics of phosphorite recovery

In general, it could be concluded that shungite briquettes possess reasonable strength and reactivity comparable to that of coke, while at the same time high numerical values of the electrical resistivity index relative to the latter. This positively characterizes shungite material as the reducing agent, moreover, as a complex raw material for the production of yellow phosphorus, and allows to recommend shungite briquettes to use in industrial scales.

8.3. Material balance and calculation of the economic efficiency of the preparation of carbon-quartzite briquettes

The implementation of any technological process is impossible without the calculation of the major stages and flows. In this regard, the material balance of the process of preparation of carbon-quartzite briquettes was calculated.

The calculation of the material balance was made for 1 ton of the finished product with the chemical composition shown in Table 50.

Table 50

The chemical composition of carbon-quartzite briquettes

Content of mineral part*, % mass.					
C	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	K ₂ O
30,9	52,2	8,3	2,8	1,8	2,4

Consolidated material balance of the process for production of carbon-quartzite briquettes is given in Table 51.

Таблица 51

Consolidated material balance of the process of production of carbon-quartzite briquettes

Income			Consumption		
Name of the article	kg	Mass fraction, %	Name of the article	кг	Mass fraction, %
Circulating water	3000,0	54,0	Carbon-quartz briquettes	1000,0	18,1
Coal tar pitch	120,0	2,1	tailings	1640,0	29,5
Shungite rock	2429,5	43,8	Circulating water	2910,0	52,4
flotation reagents	0,5	0,1			
Total	5550,0	100,0	Total	5550,0	100,0

The recommendation for the use of shungite briquettes as the complex raw material for electrothermal processes requires calculating the economic effect. The calculation of the economic effect is usually done by comparing the cost of manufactured or exploited products before and after the start of the use of the invention. In this case, only those costs that vary in connection with the use of the invention should be considered. The cost of production is a combination of all material, labor and monetary costs expressed in terms of money incurred by the enterprise in the course of its activities. Cost is characterized by the composition and ratio of the individual elements of costs and cost items to total costs of production.

Usually, the structure of production cost is considered in two aspects (Table 52): by cost elements, reflecting the expenses of the enterprise for primary and auxiliary materials, fuel, depreciation, wages, etc., and by article of calculation, which characterize the direction of cost-expenses directly related to the production of this type of product, equipment maintenance, workshop management, etc.

The cost of production is a synthetic indicator that characterizes the success of the entire production work of the enterprise. The cost of production is affected by the expenditure of materials, fuel and energy, the use of advanced, rational processing techniques, the organization of labor, the prevention of unproductive losses and expenses, i.e. essentially all the moments that characterize the organization of this production. Therefore, the reduction the cost of production with all sorts of unproductive losses and expenses is one of the most important tasks of economic policy.

Table 52

Grouping of production costs

By items	By articles (calculation)
Raw materials and basic materials (net of waste), including purchased materials and products. The main and additional wages of industrial production personnel. Deductions for social insurance. Depreciation of fixed assets. Wear out of purchased, low-value, and fast-wearing tools and items. Other cash costs. Total production costs Costs of products and labor, not included in gross production (excluded). Change in the balance of future years. Cost of gross output. Cost of change in the balance of semi-finished products and work in progress. Factory production cost of commodity products. The total cost of goods.	Внепроизводственные расходы. Полная себестоимость товарной продукции. Raw materials and basic materials. Semi-finished products purchased. Fuel. Electricity. The basic salary of production labor. Workshop costs for the maintenance and operation of equipment. General workshop expenses, including additional wages for employees and social security contributions. General factory expenses. Total: factory production cost, commodity production. Non-manufacturing expenses. The total cost of commodity products.

The calculation of the annual economic effect was carried out by comparing the given costs before and after the start of the use of the invention or rationalization proposal.

The above costs are the sum of the cost and normative profit:

$$3 = C + E_n K, \quad (93)$$

where 3 – reduced unit costs of production (work), tenge; C – the cost of a unit of production (work), tenge; K – specific capital investments in production assets, tenge; E_n – the normative coefficient of capital investments.

Savings calculated using the equation:

$$\mathfrak{D} = (3_1 - 3_2) \cdot A_2, \quad (94)$$

where $\mathfrak{D}$ – annual economic effect, tenge; 3_1 and 3_2 are the unit costs of production before and after the start of the use of the invention; A_2 – the annual volume of production after the start of the use of the invention.

By substituting the value of the equation (93) into equation (94):

$$\mathfrak{D} = [(C_1 - C_2) - E_n(K_2 - K_1)] \cdot A_2, \quad (95)$$

Where C_1 and C_2 – the cost of a unit of production (work) before and after the start of the use of the invention, tenge; K_1 и K_2 – specific capital investments in production assets before and after the start of the invention.

The unit cost of production (work) in the specified equation is the sum of the changing cost of items, and not such a workshop, factory, plant or full cost, and even more the wholesale price of the enterprise.

Therefore, if as a result of the use of the invention costs are changed: on materials (C_M) (in our case), wages (C_3), electricity (C_5), etc., C_{Π} – other costs, and the cost price will be the sum of the changing cost items.

$$C = C_M + C_3 + C_{\mathfrak{A}} + \dots + C_{\Pi} \quad (96)$$

$$\text{or } C = \sum_M^{\Pi} C. \quad (97)$$

By substituting this value into the equation (96):

$$\mathfrak{A} = \left[\sum_M^{\Pi} (C_1 - C_2) - E_{\mathfrak{H}} (K_2 - K_1) \right] \cdot A_2. \quad (98)$$

Because in our case (i.e. before replacing the шихтовых materials of coke and quartzite with carbon briquettes and after transferring the work to briquettes), new capital investments are not required, then in equation (99) one can neglect the index $-E_{\mathfrak{H}}(K_2 - K_1)$. Moreover, since using the invention in equation (98), only C_M index will change, and upon calculating the cost of finished items and further economic effect, then only this indicator will be considered.

The costs of materials prior to introduction of the invention, on average:

the cost of 1 ton of coke – 11600 tenge;

the cost of 1 ton of quartzite – 2900 tenge.

The costs of materials after introduction of the invention, on average:

the estimated cost of 1 ton of carbon-quartzite briquettes – 11455 tenge.

Consequently, the annual economic effect at $A_2 = 10000$ tons, tenge:

$$\mathfrak{A} = (11600+2900)-11455 \cdot 10000 = 30450000 \quad (99)$$

CHAPTER 9 PILOT INDUSTRIAL PRODUCTION OF CARBON POWDERS BASED ON SHUNGITE ROCKS OF EAST KAZAKHSTAN

9.1. Creation of production. Architectural and planning decisions. General explanatory note

On the basis of the fundamental, applied and research works, the authors of the book implemented a project for the commercialization of scientific and technical works. The grant was provided by the Ministry of Education and Science of the Republic of Kazakhstan, with the support of the World Bank for Reconstruction and Development (Agreement No. 586 of November 9, 2011). Upon implementation of the project, a pilot-industrial production of shungite concentrates with a capacity of 2000 tons of carbon nanostructured materials was created. All sections of information passed the agreement and approval in the relevant structures. The State Act of Operational Acceptance Certificate of the enterprise was received (Appendix D). Below is the scientific and technical documentation, the production design and the section “Environmental Impact Assessment (EIA)”.



«Georesource Engineering» LLP

APPROVED:
**Director of SSE «CENTER OF PHYSICO-
CHEMICAL METHODS OF RESEARCH AND ANALYSIS»**
_____ **M.K. Nauryzbayev**
«____» _____ **2014**

**Проект «Временная опытно-промышленная дробильно-сортировочная
установка по выпуску углеродных порошков»**

Volume 1

Book 2

General explanatory note

29.03.2013-GEN

Agreement: **№ 7 from 06.09.2013**

**City of Oskemen
2014.**



«Georesource Engineering» LLP

Project «Временная опытно-промышленная дробильно-сортировочная установка по выпуску углеродных порошков»

**General explanatory note
29.03.2013-GEN**

Agreement: № 7 from 06.09.2013

Deveopers:

Director of «Georesource Engineering» LLP

B.A. Nurtazinov

Chief Project Engineer

S.A. Zhdanov

**City of Oskemen
2014**

The project “Временная опытно-промышленная дробильно-сортировочная установка по выпуску углеродных порошков” was developed by “Georesource Engineering” LLP (ГСЛ license No.013992 dated 02.26.2004, Appendix 2) in accordance with the state normatives, regulations, and standards operating in the territory of the Republic of Kazakhstan.

Chief Project Engineer

S.A. Zhdanov

PROJECT CONTENT

Volume	Book	Обозначение	Name	Note
1	2	3	4	5
1	1	29.03.2013-П	Project passport	not secret
	2	29.03.2013-ОПЗ	General explanatory note	-«-
2	1	29.03.2013-TX	Technological Drawings	-«-
	2	29.03.2013-AC, KM	Construction (architectural and construction decision, metal structures). Drawings	-«-
	3	29.03.2013-ЭС, ЭО, ЭМ	Power supply, electric lighting, power electrical equipment, electrical substation. Drawings	-«-
3	1	29.03.2013-ОВОС	Environmental impact assessment (EIA)	-«-
	2		Environmental Impact Statement (EPA)	-«-
4	1	-CC	Consolidated, object cost estimates	-«-
	2	-ЛС	Local cost estimates	-«-

List of drawings

№ sheet	Name of drawings	Number of drawings	Note
1	2	3	4
Architectural and construction decisions			
1	Общие данные	29.03.2013-АС	не секретно
2	Ситуационная схема участка	29.03.2013-АС	-//-
3	Фасады. План цеха на отм.0.000, -2.000	29.03.2013-АС	-//-
4	Схема расположения фундаментных балок, прямиков	29.03.2013-АС	
Metal structures			
1	Общие данные	29.03.2013-КМ	-//-
2	Схема расположения лестниц, ограждения прямиков.	29.03.2013-КМ	-//-
3	Схема расположения площадок на отм. +4.925 и +6.250	29.03.2013-КМ	-//-
Power supply			
1	Электроснабжение. Общие данные.	29.03.2013-ЭС	-//-
2	Электроснабжение. Схема однолинейная силовой сети	29.03.2013-ЭС	-//-
3	План прокладки воздушной и кабельной линии бкв.	29.03.2013-ЭС	-//-
	Заказная спецификация оборудования и материалов (2 листа)	29.03.2013-ЭС.С1	-//-
Power electrical equipment			
1	Силовое электрооборудование. Общие данные.	29.03.2013-ЭМ	-//-
2	Структурно-технологическая схема с присвоением электрических обозначений.	29.03.2013-ЭМ	-//-
3	Щит Щ1. Схема однолинейная силовой сети (начало)	29.03.2013-ЭМ	-//-
4	Щит Щ1. Схема однолинейная силовой сети (окончание)	29.03.2013-ЭМ	-//-
5	ПР1. Схема однолинейная силовой сети.	29.03.2013-ЭМ	-//-
6	ПР2. Схема однолинейная силовой сети.	29.03.2013-ЭМ	-//-
7	Транспортировка материала. Схемы электрические принципиальные	29.03.2013-ЭМ	-//-
8	Транспортировка материала. Схемы электрические принципиальные	29.03.2013-ЭМ	-//-
9	Кабельный журнал	29.03.2013-ЭМ	-//-
10	Кабельный журнал	29.03.2013-ЭМ	-//-
11	План расположения электрооборудования и разводки кабелей (начало)	29.03.2013-ЭМ	-//-
12	План расположения электрооборудования и разводки кабелей (окончание)	29.03.2013-ЭМ	-//-
13	План прокладки наружных кабельных сетей	29.03.2013-ЭМ	-//-

14	Внутреннее заземляющее устройство цеха	29.03.2013-ЭМ	-/-
	Заказная спецификация оборудования и материалов	29.03.2013-ЭМ.С1	-/-
Electrical substation			
1	Подстанция. Электрощитовая. Общие данные	29.03.2013-ЭП	-/-
2	Подстанция КТПН. Схема однолинейная силовой сети	29.03.2013-ЭП	-/-
3	Подстанция КТПН. Щитовая. План установки.	29.03.2013-ЭП	-/-
4	Установка фундаментных блоков под КТПН и щитовую	29.03.2013-ЭП	-/-
5	Заземляющее устройство подстанции и щитовой	29.03.2013-ЭП	-/-
	Щитовая N1 в комплекте со щитом Щ1	29.03.2013-ЭП.Н1	-/-
	Заказная спецификация оборудования и материалов	29.03.2013-ЭП.С1	-/-
	Заказная спецификация нетиповых щитов	29.03.2013-ЭП.С2	-/-
electric lighting			
1	Электроосвещение. Общие данные	29.03.2013-ЭО	-/-
2	Цех и подача руды. Электроосвещение.	29.03.2013-ЭО	-/-
3	АБК, КПП. Наружное электроосвещение.	29.03.2013-ЭО	-/-
	Заказная спецификация оборудования и материалов	29.03.2013-ЭО.С1	
Technological solutions			
1	Общие данные	29.03.2013-ТХ	-/-
2	Аппаратурно-технологическая схема	29.03.2013-ТХ	-/-
3	Погрузочно-дробильный узел	29.03.2013-ТХ	-/-
4	Цех по получению углеродных порошков	29.03.2013-ТХ	-/-
5	Насыпной пандус	29.03.2013-ТХ	-/-
6	Поз. 1-1 .Сварная стенка пандуса	29.03.2013-ТХ	-/-
7	Поз. 1-5. Упор для погрузчика	29.03.2013-ТХ	-/-
8	Нестандартное оборудование. затворы-мигалки ЗМО и ЗМД		-/-



Public hearings with activists and residents of Auezov village for the construction of the factory



Installation of the technological equipment of CJSC “Ural-Omega”, complex КИ-0,63

9.2 Environmental impact assessment (EIA)



«Georesource Engineering» LLP



«ECOLIRA» LLP

APPROVED:
Commercial Director
«AimLab» LLP

Nauryzbayev M.K.
« ____ » _____ 2014

ПРОЕКТ
«ВРЕМЕННАЯ ОПЫТНО-ПРОМЫШЛЕННАЯ
ДРОБИЛЬНО-СОРТИРОВОЧНАЯ УСТАНОВКА ПО ВЫПУСКУ
УГЛЕРОДНЫХ ПОРОШКОВ»

ENVIRONMENTAL IMPACT ASSESSMENT (EIA)

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**City of Oskemen,
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Environmental Impact Assessment (EIA) for the project “Временная опытно-промышленная дробильно-сортировочная установка (ВОПДСУ) по выпуску углеродных порошков” was carried out by the Limited Liability Partnership “ECOLIRA” (state license of the Ministry of Environmental Protection of the Republic of Kazakhstan No.01140P 03.12.12) in accordance with the normative and technical documentation operating in the territory of the Republic of Kazakhstan.

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Annotation

“Environmental Impact Assessment (EIA)” to the project “Временная опытно-промышленная дробильно-сортировочная установка (ВОПДСУ) по выпуску углеродных порошков” was carried out to comprehensively consider the possible environmental impact (impact on atmosphere air, underground and surface waters, subsoil, soil, flora and fauna), economic and social nature associated with geological exploration.

The technical solutions of the project comply with the modern requirements of regulatory documents in terms of environmental protection, industrial hygiene, fire-fighting measures and recommendations of scientific-research organizations.

Currently, shungite carbon powders are used practically in all industrial sectors (metallurgy, construction, etc.), in medicine, ecology, and agriculture. Moreover, the finer the shungite powders, the wider the range of their application.

The temporary pilot-industrial crushing-sorting plant (ВОПДСУ) is intended for testing and processing, in industrial conditions developed by “AimLab” LLP, the technology for production of high-quality carbon powder from dump shungite rocks of “Bolshevik” gold deposit of “Bakyrchik mining enterprise” LLP.

The applied technology and materials – fire and explosion safe.

The study of the impact on the components of the environment provides to make conclusions:

Exposure to the air is permissible.

Exposure to surface water is permissible.

Exposure to groundwater is permissible.

The impact on the soil layer and soil is permissible.

The impact on the biological system is assessed as acceptable.

Based on the foregoing, it is concluded that the envisaged environmental protection measures ensure compliance of the parameters of the planned work with acceptable sanitary, hygienic and environmental standards.

In accordance with the foregoing, the planned construction of a temporary pilot industrial crushing and sorting installation (VOPSU) for the production of carbon powders is accepted as appropriate.

CONTENT

ВВЕДЕНИЕ

1. ОБЩИЕ СВЕДЕНИЯ О ПРЕДПРИЯТИИ

- 1.1. Характеристика объектов проектируемых работ
- 1.2. Характеристика проектируемых работ
- 1.3. Описание технологического процесса
- 1.4. Монтаж установки.
- 1.5. Архитектурно – строительные решения.

2. ОЦЕНКА ВОЗДЕЙСТВИЯ НА АТМОСФЕРНЫЙ ВОЗДУХ

- 2.1. Условия района
- 2.2. Оценка воздействия намечаемой деятельности на воздушную среду
 - 2.2.1. Строительные работы
 - 2.2.1.1 Выбросы загрязняющих веществ при срезки и складировании ПСП (Неорганизованный источник 6001-01)
 - 2.2.1.2 Выбросы загрязняющих веществ при работе сварочного поста (Неорганизованный источник 6001-02)
 - 2.2.1.3 Выбросы загрязняющих веществ при движении строительной техники и механизмов. Неорганизованный источник (6001-03)
 - 2.2.2. Выбросы загрязняющих веществ при эксплуатации объекта
 - 2.2.1.4 Выбросы загрязняющих веществ при выемки породы с отвала (Неорганизованный источник 6010-01)
 - 2.2.1.5 Выбросы загрязняющих веществ при формировании склада (Неорганизованный источник 6020)
 - 2.2.1.6 Ленточный конвейер (источник 6023)
 - 2.2.1.7 Дробилка роторная (источник 6024)
 - 2.2.1.8 Ленточный конвейер (источник 6025)
 - 2.2.1.9 Пересыпка с конвейера в бункер (источник 6026-01)
 - 2.2.1.10 Пересыпка материала с ленточного конвейера в ковшевой элеватор (источник 6026-02)
 - 2.2.1.11 Пересыпка материала после сушки на ленточный конвейер (источник 6026-03)
 - 2.2.1.12 Пересыпка материала после сушки с ленточного конвейера в ковшевой элеватор (источник 6026-04)
 - 2.2.1.13 Пересыпка материала с ковшевого элеватора в устройство комплекса измельчения (источник 6026-05)
 - 2.2.1.14 Выброс загрязняющих веществ после улавливания (источник 0002)
 - 2.2.1.15 Расчет выделения и выбросов в атмосферу загрязняющих веществ от барабанной сушке на мазуте (источник 0001)
 - 2.2.3. Метеорологические коэффициенты и характеристики, определяющие условия рассеивания загрязняющих веществ
 - 2.2.4. Расчеты ожидаемого загрязнения атмосферного воздуха.
 - 2.2.5. Реализация мероприятий по предотвращению выбросов в атмосферный воздух на уровне, соответствующем передовому мировому опыту
 - 2.2.6. Предложения по этапам нормирования с установлением предельно-допустимых выбросов (ПДВ)
 - 2.2.7. Обоснование принятого размера санитарно-защитной зоны (СЗЗ)
 - 2.2.8. . Оценка последствий загрязнения атмосферного воздуха и мероприятия по снижению на него отрицательного воздействия
- 2.3. Организация мониторинга и контроля за состоянием атмосферного воздуха

- 2.4. Мероприятия по регулированию выбросов в периоды НМУ
3. ОЦЕНКА ВОЗДЕЙСТВИЯ НА ВОДНЫЕ РЕСУРСЫ
 - 3.1. Гидрогеологические условия
 - 3.2. Потребность в водных ресурсах на период проведения работ
 - 3.2.1. Оценка воздействия намечаемой деятельности на поверхностные воды района
 - 3.3. Оценка воздействия намечаемой деятельности на подземные воды
4. ОЦЕНКА ВОЗДЕЙСТВИЯ НА НЕДРА
5. ОБРАЩЕНИЕ С ОТХОДАМИ ПРОИЗВОДСТВА И ПОТРЕБЛЕНИЯ
 - 5.1. Виды и объемы образования отходов
 - 5.1.1. Перечень образующихся отходов производства и потребления
 - 5.1.2. Классификация отходов производства и потребления
 - 5.2. Особенности предотвращения загрязнения территории отходами
6. ОЦЕНКА ФИЗИЧЕСКИХ ВОЗДЕЙСТВИЙ
 - 6.1. Оценка возможных физических воздействия и их последствий
 - 6.1.1. Оценка возможного шумового воздействия
 - 6.1.2. Оценка вибрационного воздействия
 - 6.1.3. Оценка электромагнитного воздействия
 - 6.1.4. Оценка теплового воздействия
 - 6.2. Оценка возможного радиационного загрязнения района
 - 6.2.1. Характеристика радиационной обстановки в районе намечаемой деятельности
 - 6.2.2. Оценка потенциального радиационного воздействия
 - 6.3. Оценка значимости физических факторов воздействия
7. ОЦЕНКА ВОЗДЕЙСТВИЯ НА ЗЕМЕЛЬНЫЕ РЕСУРСЫ И ПОЧВЫ
 - 7.1. Состояние и условия землепользования района
 - 7.2. Характеристика ожидаемого воздействия на почвенный покров
 - 7.3. Мероприятия по охране почвенного покрова
 - 7.4. Организация экологического мониторинга почв
8. ОЦЕНКА ВОЗДЕЙСТВИЯ НА РАСТИТЕЛЬНОСТЬ
 - 8.1. Характеристика растительного мира района
 - 8.2. Оценка воздействия намечаемой деятельности на флору района
9. ОЦЕНКА ВОЗДЕЙСТВИЯ НА ЖИВОТНЫЙ МИР
 - 9.1. Характеристика животного мира района
 - 9.2. Оценка воздействия намечаемой деятельности на фауну района
10. ОЦЕНКА ВОЗДЕЙСТВИЯ НА СОЦИАЛЬНО-ЭКОНОМИЧЕСКУЮ СРЕДУ
 - 10.1. Социально-экономическая характеристика района
 - 10.2. Оценка влияния намечаемой деятельности на социально-экономические условия
 - 10.2.1. Методология оценки воздействия на социально-экономическую среду
 - 10.2.2. Интегральная оценка воздействия на конкретные компоненты социально-экономической среды
 - 10.3. Оценка санитарно-эпидемиологического состояния территории и прогноз его изменения
11. ОЦЕНКА ЭКОЛОГИЧЕСКОГО РИСКА РЕАЛИЗАЦИИ НАМЕЧАЕМОЙ ДЕЯТЕЛЬНОСТИ

- 11.1. Ценность природных комплексов
 - 11.2. Комплексная оценка последствий воздействия на окружающую среду при нормальном (без аварий) режиме эксплуатации объекта
 - 11.3. Анализ возможных аварийных ситуаций. Рекомендации по предупреждению аварийных ситуаций и ликвидации их последствий
 - 12. ВЫВОДЫ ПО ОВОС
 - 13. СПИСОК ИСПОЛЬЗОВАННЫХ ЗАКОНОДАТЕЛЬНЫХ И НОРМАТИВНО-ПРАВОВЫХ АКТОВ, ЛИТЕРАТУРНЫХ ИСТОЧНИКОВ
 - 13.1. Законодательная база процедуры ОВОС
 - 13.2. Справочные, нормативно-технические и литературные источники
- ЗАЯВЛЕНИЕ ОБ ЭКОЛОГИЧЕСКИХ ПОСЛЕДСТВИЯХ (ЗЭП)
- ПРИЛОЖЕНИЯ



Landscape of the construction site, East Kazakhstan шидфые, Zharma district, Auezov village

INTRODUCTION

The obligation to carry out an environmental impact assessment for any types of economic and other activities that may have a direct or indirect impact on the environment and population health is regulated by Article 36 of the Environmental Code of the Republic of Kazakhstan.

Environmental Impact Assessment (EIA) is a procedure in the framework of which the possible consequences of economic and other activities for the environment and human health are assessed, measures are being developed to prevent adverse effects (destruction, degradation, damage and depletion of natural ecological systems and natural resources) improving the environment considering the requirements of the environmental legislation of the Republic of Kazakhstan.

Thus, the objectives of the environmental impact assessment are:

- determination of the economic, environmental and social consequences of the considered options for economic and management decisions;
- development of recommendations for the elimination of environmental degradation, or the maximum possible reduction of adverse effects on it.

In accordance with Article 37 of the Environmental Code of the Republic of Kazakhstan, environmental impact assessment is carried out sequentially taking into account the stages of urban planning and construction design provided for by the legislation of the Republic of Kazakhstan. In accordance with the stages of development of the documentation substantiating economic and other activities, the stages of EIA, providing for their consistent detailing and concretization, the following names are assigned:

Stage 1 – Preliminary Environmental Impact Assessment (PEIA);

Stage 2 – Environmental Impact Assessment (EIA);

Stage 3 – Section “Environmental Protection” (EP).

The second stage of EIA procedure is carried out in order to fully and comprehensively analyze the possible effects of the implementation of the project or the further implementation of economic and other activities, justification of alternative options and the development of an environmental management plan (program).

The environmental impact assessment was carried out on the basis of the normative-legal and instructive-methodological documents, that in force in the Republic of Kazakhstan, regulating the implementation of work on the assessment of the impact of economic activity on the environment, the basis of which are:

- Environmental Code of the Republic of Kazakhstan. Code of RK dated January 9, 2007 No.212-III.

- Water Code of the Republic of Kazakhstan. Code of RK dated July 9, 2003 No.481-III.

- Land Code of the Republic of Kazakhstan. Code of RK dated June 20, 2003 No.442-III.

- «Инструкция по проведению оценки воздействия намечаемой хозяйственной и иной деятельности на окружающую среду при разработке предплановой, предпроектной и проектной документации» (утверждена приказом МОС РК от 28 июня 2007 года № 204-п).

- «Методические указания по проведению оценки воздействия хозяйственной деятельности на окружающую среду» (утверждены приказом МООН РК 29 октября 2010 года № 270-п).

- Методика определения нормативов эмиссий в окружающую среду (утверждена приказом МООН РК от 21 мая 2007 года № 158-п).

- РНД 01.01.03-94. Правила охраны поверхностных вод РК (утверждены приказом Министерства экологии и биоресурсов РК от 27.06.94 г.).

- СНИП РК 1.02-01-2007. Инструкция о порядке разработки согласования, утверждения и составе проектной документации на строительство.

- СП «Санитарно-эпидемиологические требования по установлению санитарно-защитной зоны производственных объектов» (утверждены ПП РК от 17 января 2012 года № 93).

- SanPiN “Sanitary and Epidemiological Requirements for the Surface Waters Protection Against the Pollution” (approved by the Order of the Ministry of Health of the RK from 28th June 2004, No. 506)

- Указания по составлению проектов рекультивации нарушенных и нарушаемых земель в Республике Казахстан (утверждены ГосКомземом Республики Казахстан 5 мая 1993 г.).

- GOST 17.8.1.01-86. Nature protection. Landscapes. Terms and definitions.

- GOST 17.5.1.01-83. Nature protection. Land reclamation.

- Terms and definitions.

- GOST 17.4.3.02-85. Nature protection. Soils. Requirement for fertile layer conservation in performing earth-moving.

- GOST 17.5.3.04-83. Nature protection. Lands. Reclamation general requirements.

- GOST 17.5.3.06-85. Nature protection. Lands. Requirements for determination of the fertile soil layer standard disposal while performing earth-moving.

- GOST 17.5.1.03-86. Nature protection. Lands. Classification of overburden and enclosing rocks for biological recultivation of lands.

В соответствии с требованиями «Инструкции по проведению оценки воздействия намечаемой хозяйственной и иной деятельности на окружающую среду при разработке предплановой, предпроектной и проектной документации» (утверждена приказом Министра охраны окружающей среды Республики Казахстан от 28 июня 2007 года № 204-п) Оценка воздействия на окружающую среду» – включает в себя материалы оценки по компоненты окружающей среды:

- air environment (section 2 EIA);

- water resources (section 3 EIA);

- subsoil (section 4 EIA);

- production and consumption wastes (section 5 EIA);

- physical effects (section 6 EIA);

- land resources and soils (section 7 EIA);

- vegetation (section 8 EIA);

- fauna (section 9 EIA);

- socio-economic environment (section 10 EIA);

- assessment of the environmental risk of the implementation of the proposed activity (section 11 EIA).

Методология подхода к оценке воздействия намечаемой хозяйственной деятельности на окружающую среду, включая ее природную и социальную составляющие, принята в соответствии с рекомендациями «Методических указаний по проведению оценки воздействия хозяйственной деятельности на окружающую среду» (утверждены приказом МООС РК 29 октября 2010 года № 270-п). The proposed methodological approach is based on the determination of three exposure parameters: spatial, temporal and intensity of impact. Each of the three parameters is evaluated according to a special scale using the criteria developed for the respective gradations of scale. Due to the fact that the effect of numerous factors affecting the natural and socio-economic environment could not be quantified, a semi-quantitative (score based) method of impact assessment which allows to compare types of impacts that are different in nature, with the additional use of a personal method to assess the risk. Impact assessment is carried out on the individual components of the natural environment. The assessment of the magnitude and significance of the impacts on the components of the environment is usually carried out in three stages:

Stage 1: identification of initial impacts (screening);

Stage 2: development of a set of mitigating measures;

Stage 3: assessment of the magnitude and significance of residual impacts.

EIA CONCLUSIONS

An environmental impact assessment (EIA) was carried out for the project “Временная опытно-промышленная дробильно-сортировочная установка (ВОПДСУ) по выпуску углеродных порошков”.

Based on the materials presented in this work, the following conclusions can be drawn:

1. Impact on the air is assessed as permissible.
2. Impact on groundwater and surface water is assessed as permissible.
3. The impact on the state of the subsoil is assessed as permissible.
4. The impact on the soil cover is assessed as permissible.
5. The impact on the plant kingdom is assessed as permissible.
6. The impact on the animal kingdom is assessed as permissible.
7. The impact of the intended activity on the socio-economic living conditions of the population is assessed as permissible.

Based on the foregoing, it is concluded that the envisaged environmental protection measures ensure compliance of the parameters of the planned work in the region with acceptable sanitary, hygienic and environmental standards. The planned work, considering the reclamation of disturbed lands, determines the permissible impact on the components of the environment and on the socio-economic conditions of the region.

According to the foregoing, the planned construction and operation of the “Временная опытно-промышленная дробильно-сортировочная установка (ВОПДСУ) по выпуску углеродных порошков” is adopted as appropriate.

CONCLUSION

The book “Shungite minerals of Kazakhstan: properties and applications” contains important information about shungite, its physicochemical properties, features of modification and the possibility of practical application with the commissioning of the plant for the production of shungite powders.

The team of authors found that the studied carbon mineral belongs to the group of shungites. The black shale rocks of “Bolshevik” deposit are a multiphase system that contains carbonaceous substance in the amorphous state and mineral components. The mineral part of shungite rocks is mainly represented by oxides of silicon, aluminum, as well as calcium, magnesium, potassium and sodium, iron and titanium. Among the mineral components, the following minerals were identified: quartzite, hydromica, chlorite, carbonates (siderite, dolomite); pyrite and feldspar in smaller amounts.

Adsorption and electrokinetic characteristics of shungite ore were determined (for example, БКс). It was shown that with an increase in the pH of the medium, the adsorption of БКс decreases due to the hydrophilization of the shungite surface with hydroxyl ions. With an increase in the concentration of БКс, the negative charge on the surface of shungites increases. The established fact makes it possible to simulate the flotation process, to determine the optimal ratio of flotation agents upon enriching shungite rocks.

For the first time, the technology of flotation enrichment of shungite rocks of “Bolshevik” deposit in the East Kazakhstan oblast was developed. The technological parameters of the enrichment process are determined: the optimal fractional composition of the initial shungite ore is determined to obtain the enrichment pulp, the conditions for the supply of flotation reagents. It was shown that upon using the collector – kerosene (250 g/t) and the foaming agent – Flotol B (300 g/t) in the process of flotation enrichment, it is possible to increase the carbon content up to 40.0% in one stage without purification regardless of the composition of the initial shungite ore. A carbon concentrate of a given chemical composition was obtained.

For the first time, the structure of shungite carbon was determined, the diffraction pattern of which is characteristic of a turbostratic carbon structure consisting of polycondensed aromatic networks of small size, stacked parallel to the packages and not azimuthally oriented relative to each other. X-ray analysis revealed that one graphite-like phase ($d_{002} = 0,357$ nm) and three hydrocarbon ($d_{002} = 0,47; 0,8; 2,2$ nm) are present in the organic matter of shungites. Shungites, unlike coals of low stages of metamorphism, are characterized by the absence of the intermediate phase. By the quantitative content of graphite-like and polynaphthenic phases, as well as their ratio, shungites are similar to coals of the VI – VII stage of metamorphism. It was established that upon enrichment of shungite rocks by carbon, oxygen-containing carboxyl groups appear as a result of oxidation. Using electron microscopy technique, it was shown that shungite carbon is a spherical formation of isometric and dendritic forms. The value of the interplanar spacing for the first ring varies depending on the size and density of the cluster in the range from 0,34 to 0,36 nm. Teat shungite composites have the nanostructured size formed by carbon nanoparticles (~ 500 Å), the diameters and length of which depend on changes in the carbonization conditions.

For the first time, the kinetic characteristics of the process of combustion of shungite carbon have been determined by chemical and physico-chemical analysis

methods. It was shown that the effective energy activation of the combustion in the series of “low-carbon – high-carbon shungite rocks” falls and, in general, it is lower than the energy activation of the combustion of various types of coke. The values of the reduced effective activation energy ($E_{o\text{эф}}$) of shungite rocks (15,3 kJ/mol) and shungite concentrates (17,6 kJ/mol) were determined, with the dependence of the growth of the values of this indicator being preserved upon transition from rocks with a high carbon content to highly mineralized rocks.

Using the Raman scattering technique, the structural proximity of shungite carbon with coke and charcoal was revealed. Using electron microscopy, the identity of the supramolecular cluster-like (dendritic) structure of shungite and the supramolecular chain structure of carbon black was established.

Theoretically substantiated and experimentally proved the scientific basis of the use of natural carbon and mineral raw materials of Kazakhstan – shungite rocks in technological processes as substitutes for traditional carbon materials (carbon black, coke, adsorbents).

The technological scheme of preparation of the reinforcing filler of composite materials as a substitute for carbon black in the production of composite materials (for example, rubber compounds) without changing the technology of their manufacture and with the prospect of improving the physical and mechanical properties of finished products is proposed. It was established that shungite rocks with the high carbon content (40–50%) are more active fillers of elastomeric compositions compared to low-carbonaceous rocks and even industrial soot, which corresponds to low- and medium-active grades of carbon black. This is explained by the low degree of ordering of the graphite-like layers of shungite and the high dispersity of the shungite carbon particles compared to soot. The model is proposed that explains the enhancing properties of shungite filler by the formation of chemical links between of elastomer macromolecules and the solid surface of shungite particles.

On the basis of Almaty Technological Park, an enlarged technological line for the production of reinforcing filler with a capacity of up to 50 kg/shift has been created. The prepared carbon material passed industrial testing in the technological cycle of the plant for the production of rubber products “Rezina” LLP (Esik). The technological regulations for the production of reinforcing fillers with a capacity of up to 3 thousand tons/year have been developed; hygienic and radiological conclusions of PCЭC on product safety have been obtained.

Carbon-mineral sorbents (MCMS) modified with ions of iron (III) and manganese (IV) were first obtained with the following characteristics: strength 38–41%, total porosity 0,30–0,35 g/cm³, sorption capacity 28–32 mg/g for soil decontamination processes from components of rocket fuel. (rocket kerosene, UDMH and products of their transformation) by modified carbon-mineral sorbents are determined. The conditions for detoxification of rocket fuel (rocket kerosene, UDMH and products of their transformation) by modified carbon-mineral sorbents are determined. The optimal conditions for conducting the process are the ratio of soil:MCMS = 5: 1 and contact time 24 hours, with the concentration of CLRF products from 1 mg/kg to 200 mg/kg. It was established that during the accumulation of UDMH and its decomposition products in MCMS, oxidation of CLRF occurs, which is associated with the catalytic effect of manganese and iron ions. The adsorption technology for the detoxification of soils contaminated with rocket fuel components using the modified sorbent based on shungite rocks was developed. Field tests of the effectiveness of the MCMS for soil

decontamination in the places of fall of the separable parts of “Proton” carrier rocket showed their complete consistency.

For the first time, carbon-mineral sorbents based on carbon concentrate of shungite rocks were prepared. The sorption parameters of carbon-containing sorbents were determined. It was established that an increase in sorption characteristics occurs as a result of the steam-gas activation of carbon-mineral sorbents, due to the formation of a large amount of macro-, micro-, mesopores, as well as due to the result of chemical sorption, which is caused by the interaction with surface functional groups. The effectiveness of the carbon-mineral sorbent in the treatment of industrial wastewater from heavy metal ions (Pb, Cu, Co, Ni, Cd) was determined. The course of physical sorption due to Van der Waals forces during the adsorption of heavy metal ions was proved experimentally.

The material balance of the processes and the technical and economic calculations of the production of carbon-mineral sorbent are quantified. The technological regulation for the production of carbon-mineral sorbents (for the absorption of ions of heavy and non-ferrous metals) based on shungite rocks of Kazakhstan has been developed.

The PCЭC Sanitary and Hygienic Conclusions on the effectiveness of household water *эксплуатации* with a carbon-mineral sorbent were received, the technical conditions for these products and the quality certificate were developed and approved. Industrial production of household filters for purification of drinking water using carbon-mineral sorbents based on shungite rock concentrate is in progress.

The technology for production of carbon-quartzite briquettes based on shungite rocks with the use of coal tar pitch as the binder has been developed. It was shown that shungite briquettes, which are complex raw materials, have reasonable strength at sufficiently high quartzite content, reactivity that comparable to that for coke, and at the same time significantly higher indicator of electrical resistivity compared to coke. A slight increase in the reactivity of shungite briquettes with an increase in the quantitative content of the carbon part in their composition has been established. It was determined that the reason for the increase in the resistivity of the briquettes and the decrease in their strength with an increase in the quantitative quartzite content is a break in the integrity of the briquette due to the formation of microcracks during the heating period. The material balance of the processes and the technical and economic calculations of the production of carbon-quartzite briquettes are quantified. During pilot tests using the example of phosphate recovery, the possibility of using carbon briquettes from shungite concentrate as a complex raw material for electrothermal production was shown, while the degree of phosphorus extraction from phosphorite by shungite briquette is 72,8%.

Therefore, on the basis of the “expanded” synton approach and a retrospective analysis of the production schemes, new directions for the use of carbon-mineral raw materials theoretically are discussed and experimentally confirmed – shungite rocks in technological processes. The scientific data obtained by the team of authors reflect the successful solution of a number of tasks in the field of chemical technology of inorganic substances and make a certain contribution to the development of the scientific direction of carbon materials, in particular the expansion of their raw material base. The obtained scientific results could be applied in many areas of the chemical, food and petrochemical industries. Upon implementation of the proposed technology, the raw material base of carbon materials is significantly expands, and the possibility of import substitution of similar types of products increases. The technical and economic efficiency of the developed technologies is competitive, since until now there are no similar plants for the processing of shungite rocks. Currently, carbon-mineral sorbent and household

filters for purification of drinking water are already being produced. The introduction of a new type of carbon-containing products into the technological scheme will reduce the cost of finished products. Moreover, the annual profit could be in the production of carbon-mineral sorbents, with an annual sale of 100 tons, - 8 931 385 tenge; the production of carbon-quartzite reducing agents, in the production of 10000 tons, - 30450000 tenge. The proposed technological methods for production of carbon-containing products technologically, economically and environmentally justify their implementation.

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APPENDIX A

Table 1

Composition No.1 of the standard rubber compound for the sole rubber of women's shoes

Ingredients	Estimated recipe wt. p per 100 wt. p rubber	Working recipe: mass of the ingredients of the mixture, g
CKMC-30П	100,0	360
Regenerate	55,6	200
П 803	44,4	160
БС – 100	38,9	140
Coumarone resin	12,2	44
Vaseline oil	13,9	50
Zinc oxide	6,4	23
Stearin technical	3,1	11
Каптакс	2,8	10
Diphenylguanidine	1,1	4
Sulfur	4,2	15
Крошка	16,7	60
Phthalic anhydride	0,8	8
Kaoline	44,4	160
Total	344,5	1240

Table 2

Composition No.4 of the experimental rubber compound for children's shoes

Ingredients	Estimated composition, wt. %				Working recipe: mass of the ingredients of the mixture, g			
	1 composition		2 composition		1 composition		2 composition	
	sole	children 's tape	sole	children 's tape	sole	children 's tape	sole	children 's tape
Rubber CKMC-30П	27,7 8	41,60	27,7 8	41,60	416,0 0	624,00	416,0 0	624,00
Rubber KP-50 наирит	-	10,40	-	10,40	-	156,00	-	156,00
Regenerate ПИИ	15,7 0	-	15,7 0	-	236,0 0	-	236,0 0	-
Kaoline white	15,7 0	17,30	-	-	236,0 0	260,00	-	-
Soot БС-100	10,6 7	8,70	10,6 7	8,70	160,0 0	131,00	160,0 0	131,00
Shungite	11,7 4	1,80	27,4 4	19,10	176,0 0	27,00	412,0 0	287,00
Coumarone resin	3,45	5,20	3,45	5,20	51,65	78,00	51,65	78,00
Канифоль	0,78	1,70	0,78	1,70	11,70	25,00	11,70	25,00
Vaseline oil	3,45	4,80	3,45	4,80	51,65	72,00	51,65	72,00
Zinc White	1,78	2,80	1,78	2,80	26,70	42,00	26,70	42,00
Stearin technical	0,86	0,70	0,86	0,70	12,90	10,00	12,90	10,00

Каптакс	0,78	1,00	0,78	1,00	11,70	15,00	11,70	15,00
Diphenylguanidine	0,38	0,80	0,38	0,80	5,70	12,00	5,70	12,00
Phthalic anhydride	0,23	0,50	0,23	0,50	3,50	7,50	3,50	7,50
Sulfur	2,00	1,30	2,00	1,30	3,00	19,50	3,00	19,50
Modifier KM-2	-	1,40	-	1,40	-	21,00	-	21,00
Rubber flour	4,70	-	4,70	-	70,50	-	70,50	-
Total	100,0	100,0	100,0	100,0	1500	1500	1500	1500

Table 3

Composition No.6 of the experimental бурочной rubber compound

Ingredients	Estimated composition, wt. %		Working recipe: mass of the ingredients of the mixture, g	
	1 composition	2 composition	1 composition	2 composition
Rubber СКМС-30ПП	31,30	31,30	469,50	469,50
Regenerate ПИИ	12,54	12,54	188,10	188,10
Kaoline white	15,80	-	237,00	-
Soot БС-100	10,75	10,75	161,25	161,25
Coumarone resin	3,47	3,47	52,05	52,05
Vaseline oil	3,54	3,54	53,10	53,10
Zinc White	1,80	1,80	27,00	27,00
Stearin technical	0,87	0,87	13,05	13,05
Каптакс	0,79	0,79	11,85	11,85
Diphenylguanidine	0,38	0,38	5,70	5,70
Phthalic anhydride	0,23	0,23	3,45	3,45
Sulfur	2,19	2,19	32,85	32,85
Rubber flour	4,70	4,70	70,50	70,50
Shungite filler	11,64	27,44	174,60	411,60
Total	100,00	100,00	1500,00	1500,00

Table 4

Composition No.8 of plantar rubber mixture galoshes of rubber laminated glued

Ingredients	Working recipe: mass of the ingredients of the mixture, kg	
	Standard mixture	Experimental mixture
Rubber СКМС-30 АПКП	48,11	48,11
Rubber СКИ-3	16,70	16,70
Naftam-2	0,80	0,80
Soot П-324	70,00	21,00
Sulfur	2,01	2,01
Тиурам	0,16	0,16
Zinc White	1,60	1,60
Rubber regenerate	15,38	15,38
Stearin technical	0,80	0,80
Канифоль	2,18	2,18
Альтакс	1,60	1,60

Industrial oil	30,46	25,05
Shungite	-	49,00
Total	189,80	184,39

Table 5

Composition No.9 of the standard rubber compound irrigation pipe

Ingredients	Working recipe: mass of the ingredients of the mixture, g
Natural rubber	220
CKC-30 APKM-15	700
Zinc White	18
Каптакс	15
Тиурам	6
Stearin	13
Kaoline	700
Рубракс	130
Dioctyl phthalate	44
Soot II-803	700
Total	2546

Table 6

Composition No.10 of the experimental rubber compound irrigation pipe

Ingredients	Working recipe: mass of the ingredients of the mixture, g	
	1 composition	2 composition
Natural rubber	220	220
CKC-30 APKM-15	700	700
Zinc White	18	18
Каптакс	15	15
Тиурам	6	6
Stearin	13	13
Kaoline	700	100
Shungite	700	1280
Рубракс	130	130
Dioctyl phthalate	44	44
Diphenylguanidine	-	-
Soot II 803	-	20
Total	2546	2546

APPENDIX B

APPENDIX C

The content of HДМА , ДМФА and MTA in the control and in the soil during the detoxification using CMS , $\text{MCMS} - \text{MnO}_2$ and $\text{MCMS} - \text{FeCl}_3$

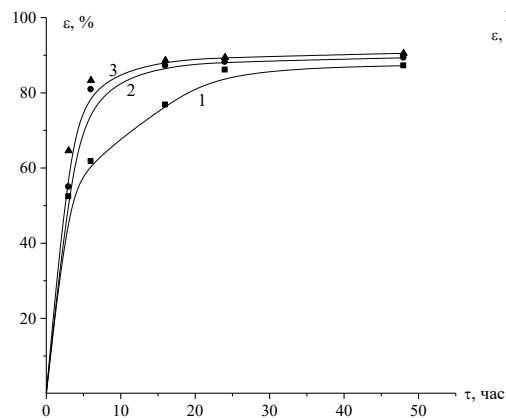
C_0 , mg/kg	Sorbent	C, mg/kg											
		HДМА				ДМФА				MTA			
		time, h				time, h				time, h			
		1	6	16	24	1	6	16	24	1	6	16	24
0,8	$\text{MCMS} - \text{MnO}_2$	0,14	н/о	н/о	н/о	0,13	0,02	н/о	н/о	0,16	0,11	0,08	0,05
	$\text{MCMS} - \text{FeCl}_3$	0,40	0,14	н/о	н/о	0,07	0,05	0,03	0,02	0,11	0,10	0,08	0,07
	CMS	0,34	0,12	0,02	н/о	0,13	0,05	0,05	0,03	0,13	0,11	0,10	0,03
	control	н/о			0,30	н/о			0,15	0,13			0,12
1,2	$\text{MCMS} - \text{MnO}_2$	0,143	0,07	н/о	н/о	0,4	0,2	н/о	н/о	0,13	0,12	0,11	0,04
	$\text{MCMS} - \text{FeCl}_3$	0,25	0,18	0,01	н/о	0,48	0,25	0,04	0,03	0,14	0,12	0,11	0,11
	CMS	0,3	0,2	0,01	н/о	0,50	0,27	0,03	0,01	0,15	0,12	0,11	0,08
	control	0,03			0,15	н/о			0,30	0,14			0,18
3,2	$\text{MCMS} - \text{MnO}_2$	0,27	0,22	0,14	0,01	0,06	0,04	н/о	н/о	0,13	0,12	0,10	0,09
	$\text{MCMS} - \text{FeCl}_3$	0,34	0,09	0,07	0,04	0,05	0,04	0,03	0,02	0,20	0,10	0,09	0,07
	CMS	0,45	0,31	0,17	0,14	0,09	0,06	0,05	0,03	0,17	0,16	0,14	0,13
	control	0,21			0,43	н/о			0,11	0,12			0,17

The content of UDMH decomposition products in the control and in the soil during detoxification using CMS, MCMS – MnO₂ and MCMS – FeCl₃

C ₀ , mg/kg	Sorbent	C, mg/kg											
		DMT				Guanidine				Bis(dimethylgidrason)-ethandiol			
		time, h				time, h				time, h			
		1	6	16	24	1	6	16	24	1	6	16	24
0,8	MCMS – MnO ₂	0,46	0,36	0,16	0,13	н/о	н/о	н/о	н/о	0,03	0,01	н/о	н/о
	MCMS – FeCl ₃	0,36	0,23	0,18	0,16	н/о	н/о	н/о	н/о	0,01	н/о	н/о	н/о
	CMS	0,37	0,28	0,22	0,08	0,10	н/о	н/о	н/о	0,02	н/о	н/о	н/о
	control	0,23			н/о	н/о			н/о	0,07			н/о
1,2	MCMS – MnO ₂	0,25	0,22	0,20	0,09	0,28	н/о	н/о	н/о	0,10	0,08	0,04	0,02
	MCMS – FeCl ₃	0,28	0,27	0,24	0,20	0,17	н/о	н/о	н/о	0,08	0,03	0,02	н/о
	CMS	0,30	0,25	0,21	0,12	0,40	н/о	н/о	н/о	0,12	0,06	0,04	0,03
	control	0,28			0,22	н/о			н/о	0,14			0,04
3,2	MCMS – MnO ₂	0,20	0,18	0,17	0,16	0,60	0,50	0,45	н/о	0,30	0,22	0,15	0,05
	MCMS – FeCl ₃	0,28	0,20	0,15	0,10	0,64	0,60	0,05	н/о	0,26	0,14	0,13	0,12
	CMS	0,30	0,29	0,24	н/о	0,62	0,60	н/о	н/о	0,34	0,33	0,30	0,29
	control	0,34			0,27	н/о			н/о	0,35			0,22

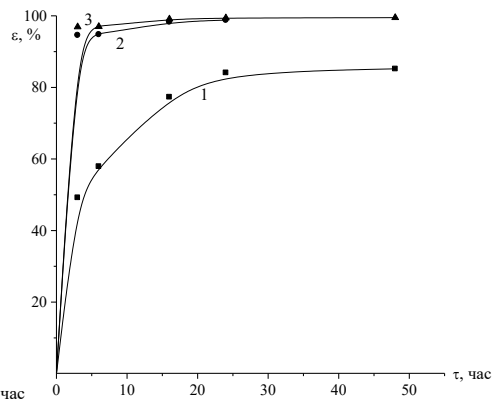
The accumulation of HДМА, ДМФА and МТА in CMS, MCMS – MnO₂ and MCMS – FeCl₃ in the process of detoxification of soils contaminated with UDMH

Initial concentration of UDMH, mg/kg	Ratio of П:С	Content, mg/kg											
		HДМА				ДМФА				МТА			
		time, h				time, h				time, h			
		1	6	16	24	1	6	16	24	1	6	16	24
0,8	CMS	н/о	0,02	0,05	0,14	н/о	0,03	0,04	0,10	0,22	0,32	0,40	0,50
	MCMS – MnO ₂	н/о	н/о	н/о	н/о	н/о	н/о	н/о	н/о	0,07	0,21	0,29	0,33
	MCMS – FeCl ₃	н/о	н/о	н/о	н/о	н/о	н/о	н/о	н/о	0,12	0,25	0,34	0,44
1,2	CMS	н/о	0,27	0,24	0,28	н/о	н/о	0,31	0,58	0,15	0,26	0,29	0,35
	MCMS – MnO ₂	н/о	н/о	н/о	0,15	н/о	н/о	н/о	н/о	0,08	0,12	0,19	0,29
	MCMS – FeCl ₃	н/о	н/о	н/о	0,24	н/о	н/о	н/о	н/о	н/о	0,06	0,17	0,25
3,2	CMS	н/о	н/о	0,06	0,11	н/о	н/о	н/о	0,04	0,06	0,08	0,17	0,24
	MCMS – MnO ₂	н/о	н/о	н/о	0,20	н/о	н/о	н/о	н/о	н/о	0,13	0,18	0,23
	MCMS – FeCl ₃	н/о	н/о	0,40	0,47	н/о	н/о	н/о	н/о	0,17	0,19	0,22	0,25



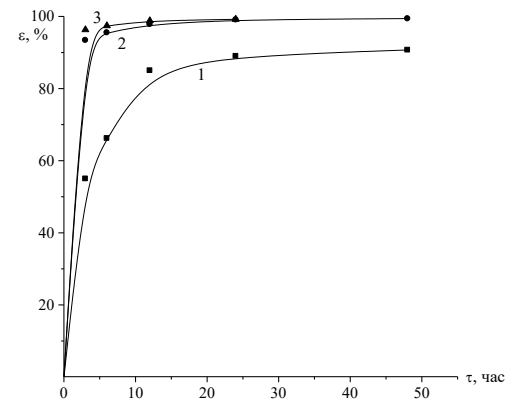
1 – soil : MCMS = 9:1; 2 – soil : MCMS = 5:1; 3 –
soil : MCMS = 3:1;

a)



1 – soil : MCMS = 9:1; 2 – soil : MCMS = 5:1; 3 –
soil : MCMS = 3:1;

б)



1 – soil : MCMS = 9:1; 2 – soil : MCMS = 5:1; 3 –
soil : MCMS = 3:1;

в)

The degree of detoxification of UDMH using CMS modified with Mn^{2+} ions for soils with different concentrations of UDMH: $C_0 = 13,6$ mg/kg (a), $C_0 = 58,9$ mg/kg (b), $C_0 = 115$ mg/kg

APPENDIX D

CONTENTS

C.	
Normative references.....	3
Symbols and abbreviations	4
 INTRODUCTION	 5
Chapter 1. SHUNGITE-CONTAINING MINERALS	7
1.1. Types and properties of shungite-containing minerals	7
1.2. Carbonaceous porous materials, structure and methods of obtaining. Use of carbon-containing materials in adsorption.....	
1.3. Methods of enrichment of carbon-containing rocks	16
1.4. Carbon black, a reinforcing rubber filler.	22
The mechanism of reinforcement of polymers in the highly elastic state with carbon black	25
1.5. Methods of soil detoxification contaminated with liquid rocket fuel components ..	34
1.6. The experience of using novel carbon reducing agents in electrothermal processes	41
1.7. Prospects	49
 Chapter 2. METHODS OF STUDY AND CHARACTERIZATION OF RAW MATERIALS.....	 51
2.1. Characteristics of raw materials and reagents.....	51
2.2. Physico-chemical properties of shungite rocks and concentrates	51
2.2.1. Determination of the composition of shungite rocks	51
2.2.2. Determination of the heat of combustion	53
2.2.3. Determination of the reactivity.....	54
2.2.4. Determination of electrical resistance	55
2.2.5. Determination of density and porosity	56
2.2.6. Determination of the material composition of shungite by thermal analysis.....	57
2.2.7. Analysis of shungite carbon using Raman scattering technique	57
2.2.8. X-ray analysis	58
2.2.9. Study of the structure of shungite using electron microscopy	59
2.3. Determination of fullerene clusters in shungites.....	59
2.4. Determination of physico-chemical characteristics of shungite concentrate used as a filler of composite materials	59
2.4.1. Preparation of rubbers.....	60
2.4.2. Determination of mechanical properties of rubber compounds	61
2.5. Methods of determination of the detoxification conditions of soils polluted with asymmetric 1,1-dimethylhydrazine	62
2.6. The specific surface area of carbon-mineral sorbents based on shungite	63
2.6.1. Determination of the strength of shungite-based briquettes	63
2.6.2. Measurement errors of determination of sorption characteristics of carbon-mineral sorbents.....	64
 Chapter 3. SHUNGITE ROCKS OF KAZAKHSTAN	 66
3.1. Characteristics of shungite rocks of Kazakhstan	66
3.2. Floatation ability and adsorption properties of shungite rocks of “Bolshevik” deposit	71
3.3. Enrichment of shungite rocks of Kazakhstan	79
3.4. Effect of physicochemical factors to the yield and quality of concentrates.....	82

Chapter 4. PHYSICO-CHEMICAL PROPERTIES OF SHUNGITE ROCKS AND CONCENTRATES OF KAZAKHSTAN	89
4.1. Characterization of shungite using Infra-red spectroscopy	89
4.2. Determination of the material composition of shungite by thermal analysis.....	93
4.3. Characterization of shungite carbon using Raman spectroscopy.....	100
4.4. X-ray analysis of shungite rocks	104
4.5. Characterization of the structure of shungite using electron microscopy	115
4.6. EPR spectroscopic characterization of shungite rocks	118
4.7. Determination of fullerene clusters in shungites of Kazakhstan.....	120
Chapter 5. SHUNGITES AS FILLERS OF COMPOSITE MATERIALS	123
5.1. Study of shungite activity as a reinforcing filler of rubber compounds.....	123
5.2. Mechanism for reinforcing elastomers with shungite filler	130
Chapter 6. MODIFIED CARBON-MINERAL SORBENTS FOR SOIL DETOXIFICATION FROM COMPONENTS OF LIQUID ROCKET FUELS	137
6.1. The technology for preparation of modified carbon-mineral sorbents	137
6.2. Investigation of the physicochemical basis of the detoxification processes of soils contaminated with unsymmetric dimethylhydrazine and the products of its transformation using carbon-mineral sorbents modified with Mn^{4+} and Fe^{3+} ions. .	138
6.3. Study of the features of sorption of T-1 rocket fuel from the soil using natural and modified carbon-mineral sorbents	144
6.4. Investigation of the places of fall where the separable parts of a launch vehicle	145
6.5. Field detoxification experiments	150
6.6. Material balance of the processes of preparation of a modified carbon-mineral sorbent and evaluation of their economic activity	153
Chapter 7. CARBON-MINERAL SORBENTS FOR THE DECONTAMINATION OF NATURAL OBJECTS FROM VARIOUS POLLUTANTS	157
7.1. The technological basis of the processes of production of carbon-mineral sorbents based on the concentrate of shungite rocks	157
7.2. Study of physicochemical patterns and features of the sorption processes of metal ions by carbon-mineral sorbents based on shungite	164
7.3. The study of the formation of the porous structure of carbon-mineral sorbents upon steam activation process	168
7.4. The application of sorbents in water treatment processes	172
7.5. Material balance of the preparation process of carbon-mineral sorbent and evaluation of its economic efficiency	177
Chapter 8. THE USE OF CARBON-QUARTZITE BRIQUETTES BASED ON SHUNGITE CONCENTRATE IN ORE THERMAL PROCESSES.....	179
8.1. The technology for preparation of carbon reducing agents for ore-thermal production	179
8.2. Recovery of phosphorite using carbon-quartzite briquettes based on the concentrate of shungite rocks.....	182
8.3. Material balance and calculation of the economic efficiency of the preparation of carbon-quartzite briquettes	186
Chapter 9. PILOT INDUSTRIAL PRODUCTION OF CARBON POWDERS BASED ON SHUNGITE ROCKS OF EAST KAZAKHSTAN	189
9.1. Creation of production. Architectural and planning decisions. General explanatory note.	189
9.2. Environmental impact assessment (EIA).....	205

CONCLUSION 206

REFERENCES 210

APPENDIX A (compositions of rebber compounds) 219

APPENDIX Б (Test acts, conclusions).....222

APPENDIX B (Summary tables of CLRF sorption) 241

APPENDIX Г (The act of commissioning, approvals).....245

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