

Engineering of experiment

Molchanov¹ V.P., Medkov² M.A. Principal technological scheme of cleaning natural graphite of Russia from impurities using hydrometallurgy methods. UDC 553.22+551.2

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Abstract. The experimental study of graphites from deposits in the south of the Far East of Russia was carried out. As is known, it is among the most sought after types of solid minerals by modern technologies. In particular, low-ash graphite can be used as a structural material in nuclear power engineering, heat engineering, etc., and also as a raw material for colloidal graphite, graphite oxide (compound of carbon, hydrogen and oxygen in various ratios, which is formed during processing graphite strong oxidizing agents) and expanded graphite. A process flow diagram for the purification of natural graphite concentrate has been developed and laboratory modes have been developed to obtain enrichment products with a carbon content of at least 99,5%. The scheme includes the stages of purification of high-ash graphite concentrate with ammonium difluoride and leaching of impurities of soluble fluorides.

Keywords: *natural graphite, ammonium hydrofluoride, fluoridation, leaching.*

Many science-intensive technologies, which are indicators of the level of development of industrial production in advanced countries, are unthinkable without the use of graphite. The unique properties of this mineral together with the latest discoveries in the field of nuclear power, electronics and nanotechnology have completely changed our understanding of the possibilities of its use. Low-ash crystalline graphite is widely used in various industries. In metallurgy, graphite is an additive to increase the refractory properties of the material. Due to the high electrical conductivity, plasticity and mechanical strength in electrical graphite is used to obtain galvanic cells, electrodes, alkaline batteries, etc. high-Quality graphite is used as a moderator of nuclear reactions in nuclear boilers, used in reactive technology, where it is used for the manufacture of blade turbines and missiles, used to produce colloidal

graphite, oxidized and thermally expanded graphite (Marmer, 1973; Violets, 1997). In the European Union and China graphite is included in the list of critical minerals. The main deposits of high-quality crystalline graphite are located in China, India, Brazil, the Czech Republic, Canada and Mexico. At the same time, the main producer and exporter of graphite raw materials is China. The few Russian enterprises specializing in graphite mining only to a small extent meet the needs of our country in graphite products. The main part of crystalline graphite is imported from abroad. One of the areas of national security of Russia is the creation of new centers of production and processing of graphite ores of high quality.

High-carbon rocks occupy vast territories within the Far East of the Russian Federation. Only in Primorsky Krai they form a broad zone that is elongated in n-s direction for tens of kilometers on the neighboring territories of Russia and China from the city of Dalnerechensk in the North through the city of Lesozavodsk. One of the most important results of geological studies of recent decades within this zone is the discovery (hanchuk et al., 2004) of manifestations of noble-rare-earth mineralization. In its Northern part (Dalnerechensk) identified five fields (the largest of them Filinskoe), and in the South (Lesozavodsk) there are over thirty objects (including known deposits of graphite Tamga and Turgenev). Given the wide area manifestation of metal-bearing graphitized rocks with their considerable vertical power (up to 3000 m), it can be assumed that they, in addition to graphite, accumulate significant resources of precious metals and rare earth elements. The quantity and quality of useful components concentrated in the Primorsky graphite ores indicate that in the near future they will determine the prospects for the development of the mineral resource base of the far Eastern region of Russia.

Application conditions dictate different requirements for purity and crystal structure of graphite. All known methods of graphite purification can be attributed to three types – chemical cleaning, thermal and thermal refining. Thermal purification of graphite is the most common method, although the refining processes are very energy-intensive, since they are carried out at a temperature of 2500-3000 °C (Avdeev et al., 2011). Chemical cleaning involves sintering graphite powder with an aqueous solution of an alkaline agent, followed by washing with water and dilute acid (Lu X. J. et al., 2002; Li Yu-feng et al., 2012). Gas-thermal refining is based on the production of low-ash crystalline graphite by

chemical treatment of high-carbon mineral raw materials with ammonium hydrodifluoride (Epov et al., 2016). The physico-chemical basis of the process of ammonium hydrodifluoride fluorination is the ability of oxygen-containing compounds of transition and many non-transition elements in interaction with NH_4HF_2 to form very convenient for the processing of ammonium fluorometallates. We have studied the possibility of using hydrodifluoride purification processes on the example of coastal graphite.

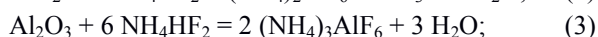
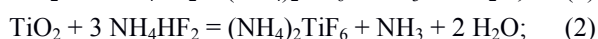
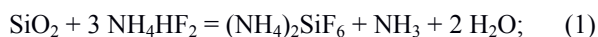
Research areas were selected batch of graphite concentrate, obtained by enrichment graficheskikh rocks Ruginski square flotation method. At the same time, pine oil was used as a foaming agent, and long – chain amine was used as a collector. Under flotation conditions, the bulk of graphite (~90 %) and some impurities are concentrated in the foam product. Ammonium hydrodifluoride grade “chd” was used as a reagent for cleaning the concentrate.

The changes occurring with the substance during heating and leaching were controlled by the decrease in the mass of the initial mixture and x-ray phase analysis of products obtained at various stages of hydrodifluoride processing of graphite concentrate.

X-rays of the samples were taken on the d-8 ADVANCE automatic diffractometer with the sample rotation in $\text{Cu } K_\alpha$ -radiation. X-ray phase analysis was performed using EVA search program with PDF-2 powder data Bank.

The contents of the elements in the filtrates obtained in the leaching water protonirovanie concentrate, determined by atomic absorption spectrometry (spectrometer Solaar 6M) on the analytical lines of the above - mentioned elements-admixtures of graphite.

Among the elements - admixtures of the investigated graphite concentrate after beneficiation flotation method is marked by the presence of Si, Ti, Al, Fe, Mg, Ca, Na, K. When it is processed with ammonium hydrodifluoride with the formation of complex salts may following reactions:



The interaction of oxides of calcium, magnesium, sodium and potassium with NH_4HF_2 proceeds with the formation of simple fluorides:

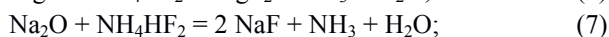


Table. The content of elements in the combined wash water ($V = 400 \text{ ml}$) in terms of their phases.

Element	Phase	Element	Phase	Content, mg F ⁻ - ion
Si	$(\text{NH}_4)_2\text{SiF}_6$	144,307	917,78	587,79
Fe	$(\text{NH}_4)_2\text{FeF}_6$	44,933	179,73	91,47
Al	$(\text{NH}_4)_3\text{AlF}_6$	46,738	37,55	197,34
Mg	MgF_2	4,826	12,47	7,64
Ca	CaF_2	1,659	3,24	1,58
K	KF	19,186	28,53	8,86
Na	NaF	0,834	1,52	0,69
Total			1180,82	895,37

It should be noted that the simple fluorides of alkali metals, as complex formoney salt, given in equations (1)-(4), readily soluble in water.

Chemical treatment of graphite concentrate with ammonium hydrodifluoride was carried out at a mass ratio of the concentrate to the fluorinating agent 5:1 in a glass-carbon container, which was placed in a reactor with electric heating and two sequentially arranged capacitors – Nickel and fluoroplastic. The temperature of the electric furnace was set using a high-precision temperature controller VRT-2. The sample size of the concentrate was 20-40 g. For uniform distribution and close contact with the reagent, the graphite concentrate was mixed with an

ammonium hydrodifluoride solution obtained by dissolving the calculated amount of NH_4HF_2 in 20-30 ml H_2O . The resulting thick homogeneous mass was slowly (~1,5 deg/min) heated to a temperature of 170-180 °C and kept at this temperature for 2 hours.

The process of leaching of the profluorinated graphite concentrate was carried out at room temperature by 4-fold dissolution of 10 g of the product in 100 ml of water (T:W=1:10) in glass cups for 15 minutes and subsequent filtration through the filter "blue tape". The obtained filtrates were evaporated to dry salts for analysis. The dry weight of the residue was 1,44 g. According to x-ray phase analysis in the solution in the leaching water passed

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formoney salts of silicon, aluminum and iron and fluorides of sodium and potassium. In addition, as shown by atomic absorption analysis, with water leaching, a partial transition to a solution of magnesium and calcium ions is observed, due to the insignificant solubility of their fluorides. The table presents the results of atomic absorption determination of the content of elements in leaching solutions in terms of the form of their location.

It was established that the content of elements in wash water is consistent with the mass of dry residue (1,44 g) obtained by evaporation of wash water. The content of fluoride ion in 400 ml of wash water is 895,37 mg, which corresponds to a concentration of ~ 0,22%. Free fluoride ion in wash water is practically absent (the content of free fluoride ion is 9,55 mg, which corresponds to a concentration of 0,0024%). All of the fluorine present in the wash water is included in the composition of the compounds from which it can be separated by ammonia hydrolysis as the starting fluorinating agent and used in circulation. The ash content of graphite obtained after the stages of fluorination and water

the interaction of the elements-impurities of the concentrate with NH_4HF_2 occurs with the formation of a mixture of complex fluoroammonium salts and simple fluorides. It is shown that the fluorination process at a temperature of 170-180 ° C and subsequent aqueous leaching of the profluorinated product leads to the purification of natural graphite and the preparation of enrichment products with a carbon content of at least 99.5 %.

The work was supported by RFBR grant № 17-05-00910.

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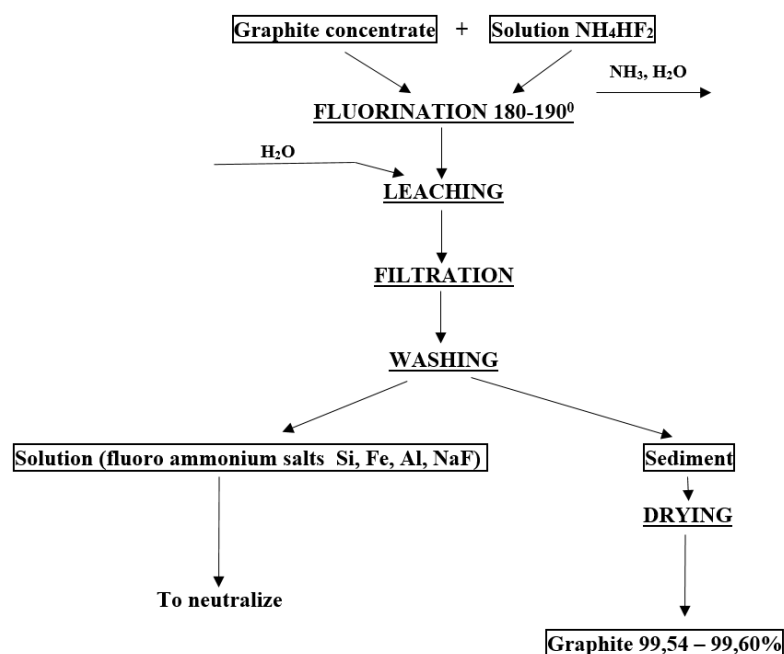


Fig. The basic technological scheme of cleaning graphite concentrates Ruzhinskaya area

leaching of the profluorinated product was 0.40-0.46%, and its purity, respectively, 99,60-99,54%.

On the basis of the research conducted, a process flow diagram for the purification of the initial graphite concentrate has been developed to obtain enrichment products with a carbon content of at least 99,5%, presented in the figure.

Thus, the studied conditions for clearing the seaside graphite using processes hydrovhloride processing flotation concentrates. It was found that

Zharikov A.V.¹, Malkovsky V.I.^{1,2} Transport properties of the HLW depository near field rocks – a forecast based on the experimental data UDC 621.39: 754.716

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Abstract. On the base of the experimental data a forecast of transport properties changes for the main type of rock of the Eniseiskiy site was developed.

Keywords: rock permeability, HLW underground disposal

Groundwater is the main agent carrying out the transfer of radionuclides in the geological environment. Therefore, the main requirement for the site selected for the underground disposal of radioactive waste is to minimize the risk radionuclide transport by groundwater flow into the biosphere. In this regard, it is obvious to focus the studies on the rock transport properties, and primarily on their permeability - one of the main factors determining the flow dynamics of both natural and tectogenic fluids in the geological environment.

It was found that gneisses and dolerites, which compose a large part of the section, of the Enisseyskiy site, where it is supposed to build the underground HLW repository (Fig. 1.) are characterized by sufficiently high strength (average uniaxial strength ~ 120 MPa, low porosity (average value ~ 0.4 %). The values of true permeability have to be clarified, but taking into account the data obtained for the analogues sites and rocks [Petrov et al., 2005; Zharikov et al., 2003, 2014], obviously, are also low ($\sim 10^{-20}$ - 10^{-18} m²). The contrasting differences in permeability (preliminary estimates ~ 50 %, possibly more) and in strength (average ~ 70 % for compressive strength) between gneisses and dolerites is the main feature of the section. It should be noted that the most part of the rocks are layered

anisotropic and this is manifested for permeability and physico-mechanical properties, as well. As the dip of the rocks in this area is relatively shallow, their anisotropy lead to significant differences between the rock physical properties in lateral and vertical directions. The permeability of rocks normally to bedding is much lower that almost eliminates upward filtration, and the compressive strength, on the contrary, is higher. This is a very favorable factor for the safe HLW isolation. However, the compressive strength in the rocks dip direction is much lower and that, on the contrary, is an unfavorable factor for the stability of mining excavation.

The decompacted rocks related to the contacts with the dikes, the dikes of the second phase with porphyry structures, as well as zones of alterations may occur on the general background of massive and strong rocks. In order to characterize such zones, to refine the true permeability values of occurring rocks, and to establish the spatial distribution of reservoir properties nearby the HLW disposal site it is necessary to conduct further detailed laboratory studies. Thus, to avoid significant systematic errors, it is necessary to use special methods for measurements of low- permeability and techniques for sample preparation [Malkovsky et al., 2013].

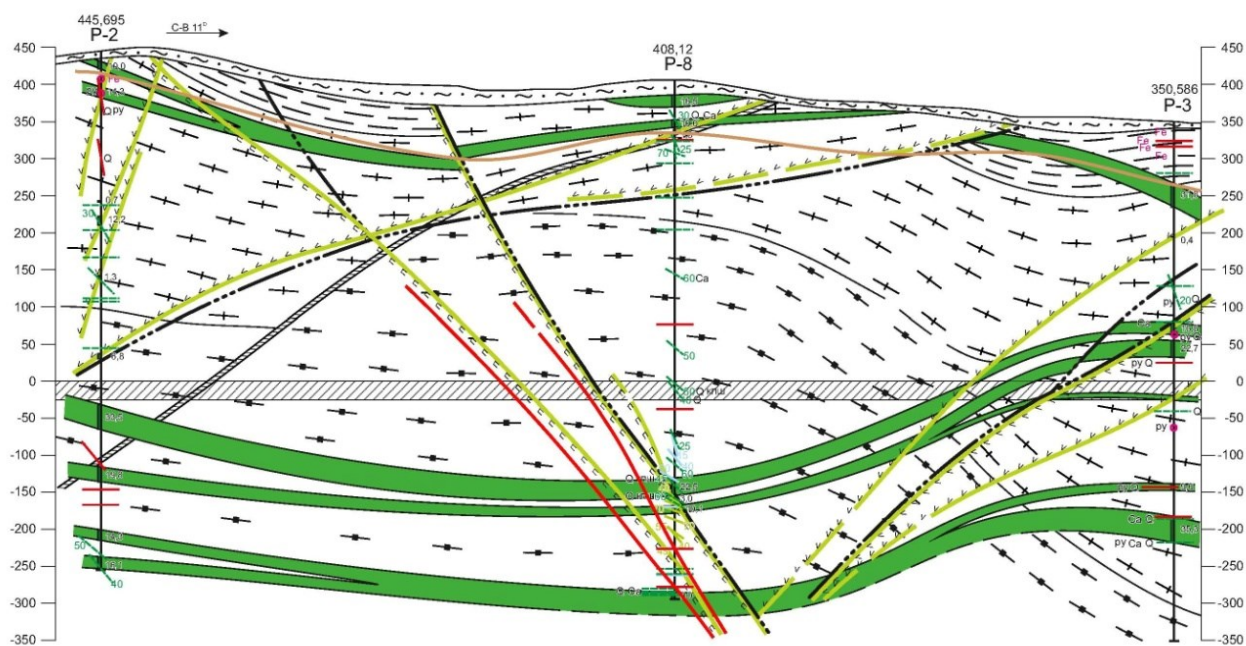


Fig. 1. Geological section of the target interval (Kochkin et al., 2017).

Basing on the results of determinations of the filtration properties of the rocks from the Enisseyskiy site and the analysis of the experimental data obtained for analogues samples at ambient and at high temperatures [Zaraisky & Balashov, 1995, Zharikov et al., 2003, 2014], a prediction of their

changes with heating is made. The most conservative estimate is taken into account: heating up to maximum temperatures of 600 – 700°C not only in dry conditions but also in conditions of water saturation. Moreover, in the last case the processes of pressure solution, which can lead to microcrack

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sealing and pores colmatation, are not active. It is found that changes in transport and physico-mechanical properties of rocks are caused by their composition (the higher quartz content leads to the more intensive decompression) and by their microstructure changes under heating (opening of intergranular boundaries).

The intensity of changes in physical properties of rocks varies with temperature increase and depends on fluid saturation. The same factors characterize the reversibility of the changes in physical properties under heating.

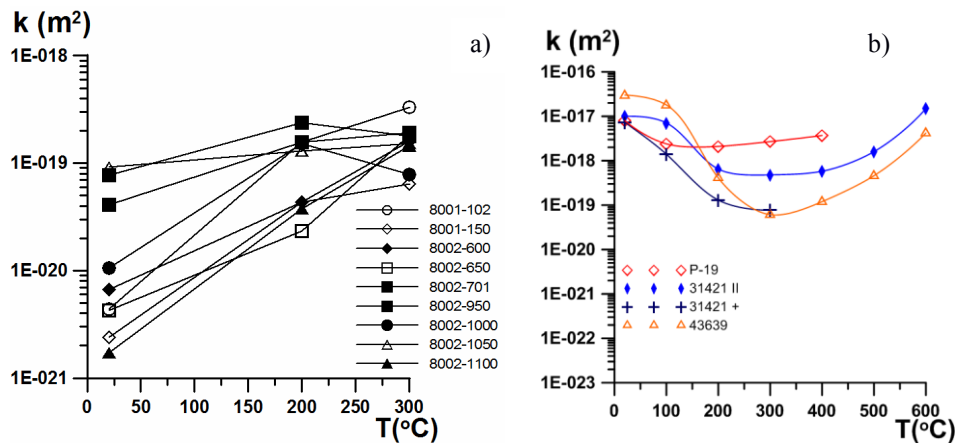
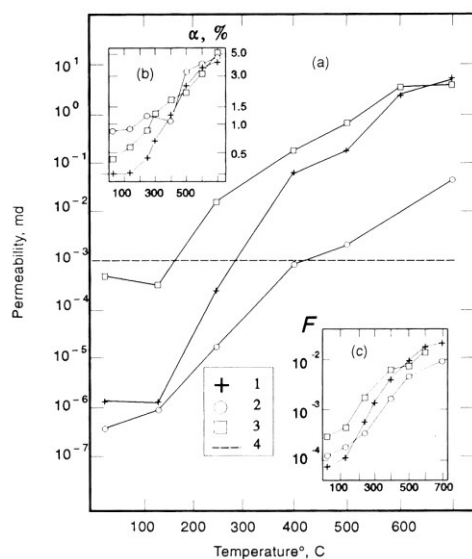
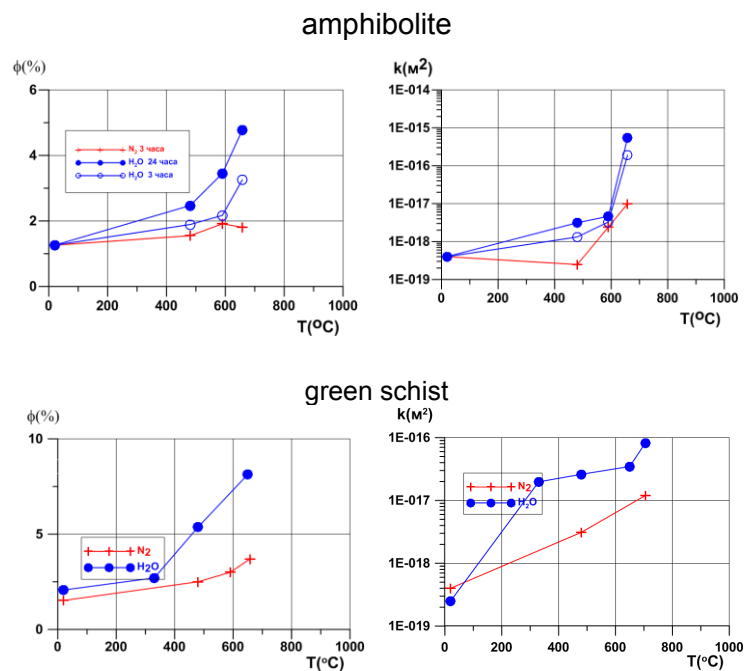


Fig. 2. Dependences of permeability of metavolcanites from PA Mayak – a and gneisses of the Kola series – b on temperature at constant pressure (dry conditions).



a



b

Fig. 3. Porosity, permeability and form factor of granite and gabbro-dolerite with heating [Zaraisky & Balashov, 1994].

Fig. 4. The porosity (ϕ) and permeability (k) of amphibolite and green schist with heating.

Heating of the near field rocks in the first decades, after the heat-generating HLW will be loaded, will lead to an increase in their permeability and porosity. The permeability of the basic rocks will obviously increase monotonously (Fig. 2 a), while the permeability of gneisses may firstly decrease, reach a minimum, then to increase (Fig. 2 b). Taking into account that the average initial permeability of the dolerites is lesser by a decimal order than the

permeability of gneisses, it can be assumed that at temperatures of about 200°C the difference in permeability between the main types of rocks will decrease, heating to higher temperatures will lead to permeability increase for the rocks of both lithological types. Permeability of acidic rocks, obviously, will increase faster than the basic ones. At temperatures > 400°C, porosity and permeability will reach the maximum values. Obviously, one can

expect the increases of porosity by several times, and permeability by several orders of magnitude compared to the original.

Under heating in dry conditions to temperatures $< 250^{\circ}\text{C}$, the properties of rocks after cooling can return to their original values. Under heating up to $250 - 500^{\circ}\text{C}$ after cooling residual decompression will be observed only in gneisses, and under heating to higher temperatures, all rocks except gabbro after cooling will not return to their original state.

The work was performed within the framework of the research plan of IGEM and with the financial support of RFBR (grant No. 19-05-00466).

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