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THE STUDY OF THE MINERALOGICAL COMPOSITION AND FLOTATION PARAMETERS OF QUARTZ-GRAPHITIZED SCHIST

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Abstract: Exploration studies in Uzbekistan revealed one graphite deposit (Taskazgan) and about 25 sites with varying perspective degree. In order to obtain the graphite for refractory industry uses insufficiently known Rupert, Zauchak and Zahchahona sites were studied. According to the research, Zahchahona site can be classified as a medium-sized field; the refined graphite content in the ore deposit is 3 to 15 %, which meets the requirements of the industry for this type of raw material. Graphite was refined by flotation and leaching process, brought to grade of 75 % carbon.

Keywords: graphite, crystalline schist, concentrate, flotation.

1. Introduction

The issue of development of new graphite deposits is particularly acute in connection with the further development of mechanical engineering, mining and minerals processing, chemical and metallurgical industries that are major consumers of graphite-ceramic refractory materials.

The estimated amount of graphite deposits in the world exceeds 800 million tones. China tops the list of countries that produce graphite by providing over 70 % of the worldwide production. Brazil, Canada and Madagascar are also major suppliers of graphite, specifically its flake form, and Sri Lanka is the main exporter of lump graphite. With the constantly increasing demand for large flake graphite, it has been estimated that at least 25 new graphite pits will be required by 2020 to cope with the world demand.

The largest graphite deposit in Central Asia is located in Uzbekistan. It is Taskazgan deposit and more than 25 sites of varying perspectives, but all of them are

studied rather poorly. Therefore, the aim of our work was to study the chemical and mineralogical composition of graphitic schists of Uzbekistan and to determine the possibility to enrich them.

2. Experimental

As a source of graphite graphitic schists of Rupert, Zauchak and Zahchahona (Uzbekistan) sites were used. The studies of the phase composition of raw materials were performed using modern methods of physical and chemical analysis. The crystalline phase identification was performed by means of X-ray diffraction (XRD; Bruker AXS D8 Advance, Bruker, Germany), supported by data from Match! program package (Crystal Impact GbR, Bonn, Germany). Total carbon analyses were carried out according to ASTM C562-91 [1] and C561-91 [2] designations. Graphitic carbon content was determined by semi-quantitative X-ray analysis using the data of Match! program package: for hexagonal graphite PDF #00-04101487; calcite PDF #00-072-1937; quartz PDF #00-087-2096. Optical analysis in transmitted and reflected light was carried out by immersion method using a polarizing microscope Motic, MIN-8 and POLAM P-312.

The quartz-graphitic schist samples were dry crushed and ground in a ball mill. For enrichment of graphite flotation method was used. The optimal size of the graphite ore grinding prior to flotation was 0.074 mm. Deflocculating of the smeared graphite was carried out with sodium silicate in an alkaline solution. To suppress easy floatable minerals (calcite) soda ash, caustic soda, and sodium silicate were used. Froth flotation of the graphite rock was carried out using kerosene, pine and diesel oil, using sodium silicate, acidic and alkaline medium. To increase the graphite content the method of chemical purification by means of acid leaching (HCl) after flotation was used.

3. Results and Discussion

Search and exploration studies in Uzbekistan revealed one graphite deposit (Taskazgan) and about 25 sites [3]. The Taskazgan graphite deposit (not currently under development) is located in Kuldzhuktau mineragenous area and is represented by lump graphite equivalent in quality to the world famous Ceylon graphite. Graphite reserves suitable for development according to the Soviet reserve classification system (balance reserve) were reportedly 6.135 Mt of ore containing 1.115 Mt of graphite, 500 t of cobalt, 3,000 t of copper, and 10,000 t of nickel [4]. But due to its fineness and amorphousness it is not suitable for use in the production of refractory materials.

In order to obtain the graphite for refractory industry uses insufficiently known Rupert, Zauchak and Zahchahona sites were studied. Geologically, by almost 50 % of the described area is composed of highly dislocated and intruded metamorphic and volcanic-sedimentary formations, which gives reason to include this part of the territory to the very complex geological structure of categories.

3.1. Rupert Graphite Deposit Investigations

Rupert graphite deposit is on the east-south-east slopes of the Surkhantau ridge in the area of high mountains (absolute mark is 2800–3000 m) with a dissected terrain; the relative differences of elevation 200–500 m. It is located in Sariasiya administrative district of Surkhandarya region, 6.5 km to the north of the village Sangardak.

In the areas of Rupert and Zauchak graphite mineralizations the following suites were highlighted by lithological composition and structure: Karatash and Malyand (Rupert) and Handiza (Zauchak) suites. In the Karatash suite the graphite mineralization is low-power, unrestrained and is confined to the upper sub-suite of the Karatash suite, folded in micaceous quartzites with the capacity of 0.2–0.3 m. In the upper Malyand suite the graphite mineralization is associated with its lower sub-suite and is represented by two horizons of graphitic schist with power of 0.25–0.44 m.

The mineral composition of rocks of the metamorphic complex of the Malyand suite is not very diverse. Quartz has the maximum spread of (in wt %) 20–90, followed by feldspar (plagioclase) 25–80, biotite 10–37, sericite 2–60, muscovite 1–10, garnet rarely to 5, graphite 1–3; accessory – apatite, rutile, zircon, pyrite, and magnetite.

The study of quartz-graphitic schist with electron microprobe analysis showed that the rock is mainly composed from spliced quartz aggregates sizes from 25×25 to 38×50 mm and massive dolomite crystals. Areas of dolomite rocks are intersected with whitish streaks of glandular dolomite – ankerite. The composition of the dolomite can change: MgO from 20.48 to 23.58 %, CaO from 24.93 to 25.69 %, and FeO from 0 to 3.55 %. The potassium aluminosilicates are distributed in the pores between the crystals of quartz and dolomite. The study of ore showed the presence of 0.001–0.1 mm sized graphite aggregates and plates.

The chemical composition of Rupert quartz-graphitic schist is defined in the Central Laboratory of Government Committee for Geology and Mineral Resources of the Republic of Uzbekistan as the following: (in wt %): SiO₂ 48.95–60.24; TiO₂ 0.02–0.95; Al₂O₃ 0.79–17.50; Fe₂O₃+FeO 2.92–4.78; MgO 2.92–8.26; MnO 0.06–0.32; CaO 1.68–12.20; Na₂O 0.03–0.98; K₂O 0.12–4.62; P₂O₅ 0.097–0.20; SO₃ (total) 0.48–2.28; LOI 6.24–26.26; H₂O (333 K) 0.15–0.80; CO₂ 1.10–8.96; C graphite 3.06–15.85; and ash (1123 K) 74.54–94.32.

The semi-quantitative spectral analysis method of Rupert schist shows the following elements: Sb, V, Sn, Cr, Mn, Zn, Ta, and Pb. The first two elements exceed the Clarke concentration by 6 times, the value of third and fourth elements – by 3 times, and the remaining – by 2 times. Given the low and very low contents of Ag, Bi, Cd, and As, they are of no practical value. A relatively higher level of thallium draws attention; all analyzed samples contain equal amount of thallium (10·10⁻³ %). The reasons for increased content of thallium are not discovered. The Clarke concentrations values are Li, Ti, Co, Ge, and Mo. Contents less than Clarke are inherent in Be, Cu, Nb, Ni, and Ba.

In accordance with the mineralogical composition of Rupert graphitic schist the gravity-flotation method is selected for their enrichment. Froth flotation of Rupats graphite rocks was carried out using kerosene, pine oil, and sodium silicates, in weak and strong alkaline medium. The output of the main flotation concentrates ranged from 2.1 to 8.4 %. Starting concentrates has high ash content (56–69 % of ash). Total carbon content in final concentrate is 45–30 % and total carbon recovery is 15–10 %.

3.2. Zauchak Graphite Deposit Investigations

Zauchak graphite deposit is located 9 km north of the village Degibadam. In geological terms its structure is similar to the deposit of Rupert. It is represented by a thick layer of metamorphic rocks of Cambrian age, being a part of the Handiza schist that lies without apparent dissent on the rocks of the upper member Malyand suite. In the

Handiza suite section there are two sub-suites: lower and upper. The lower sub-suite is characterized by intense silicification process and the formation of varieties of mica gneiss and secondary quartzites.

The upper sub suite, when slicing the top by overlying carbonate deposits is shown in the area of research as an incomplete cut, folded with alternating schist coarse sedimentary rocks, phyllites, phyllicortoschists, biotite gneisses mineralization, and quartzite. In terms of composition there are the following varieties of quartzite: graphitic dark gray or black and gray quartzite not containing graphite. The graphite quartzite composition (in wt %) is quartz (70–95), plagioclase (15), graphite (5–7) mineralization, and sericite-chlorite cement (1–10). Composition of gray quartzite without graphite: quartz (40–65), plagioclase (20–40), muscovite (2–3), biotite (4), and chlorite (2). A layer of black quartz-graphitic schist lies at the base of a powerful pack of quartzites and quartzite gneiss.

Spectral analysis found a relatively high content of base metals. Thus, in the middle of the upper sub-suite in the field of coarse formations the content of lead is 3–5 times higher than Clarke, and in the middle part, its lower subsuite, where are graphite quartzite, biotite gneisses mineralization and phyllites, concentration of Pb (up to 0.02 %) exceeds the Clarke concentration by 10–12 times. However, the average content of lead in the entire thickness of Handiza schist is the Clarke, or slightly below the Clarke. Zinc mineralization, as lead mineralization, is ambiguous. In the lower part of the sub-suite the amount of it is Clarke, and in the upper subsuite, it is below Clark. In the middle of the lower sub-suite in stationed quartzite gneisses the zinc content increases to 0.03 % and reaches the same amount as copper values. In general, the concentration of suite copper, beryllium, zinc and ytterbium are below Clarke, and graphite-containing stratum increases to 1.5 times higher than the Clarke.

The increased confinement of yttrium and beryllium to the layers of graphitic rocks: quartzite, schist mineralization, conglomerates, gives a reason to consider them as elements of syngenetic origin. The relatively high concentrations are typical of Cr, Ga, Ge, Co, and Sn. Thus, the Cr content ranges within 0.02–0.003 %, Ga 0.03–0.005 %, Ge 0.003–0.005 %, Co 0.001–0.002 %, and Sn 0.001–0.003 %. The content of other elements varies as follows: Ba 0.07–0.0007 %, V 0.07–0.02 %; Mn 0.05–0.015 %, Ti maximum 0.05 % in the fixed half of the samples, and the remaining 0.3 %: Bi – < 0.0002 %, Au – < 0.0003 %, Ta – < 0.01 %, Nb – 0.0004 %, Li – 0.003 %, Ni – 0.001–0.00006 % and Ag – 0.00001 %.

Graphite is presented as fine-crystallized variety. For graphite flotation kerosene and diesel oil were used as collector and pine oil as frother, in acidic medium

pH = 2–3 (H₂SO₄). Output of the main flotation concentrates ranged from 5 to 10 %. Total carbon content in final concentrate was 57 % and total carbon recovery – 11.4 %.

As a result of Zauchak quartz-graphitic schists enrichment a large amount of the waste rock is produced. The mineral composition of waste products is the following (in %): quartz – 31.9; plagioclase – 11.5; calcite – 3.6; dolomite – 7.8; chlorite – 2.6; pyrite – 1.1, and the amount of clay (chlorite, hydro mica) – 41.5. Given the predominantly quartz-plagioclase composition the waste product can be recommended for use in the preparation of building materials (ceramic bricks, tiles) [5].

Since the task of the research was to identify quality graphite materials with relatively large resources and relatively easy concentrability, the authors have studied the site of Zahchahona having greater resources, conditioning useful content and favorable geological conditions.

3.3. Zahchahona Graphite Deposit Investigations

Zahchahona deposit of graphite is located on the territory of Shahrissabz district of Kashkadarya region and is situated on the southern slopes of Zahchahona (north-western spurs of the Gissar ridge) at the altitude with absolute marks of 2700 to 3400 m.

Zahchahona deposit was investigated repeatedly by geological prospecting teams [6]. According to the research, it can be classified as a medium-sized field; the refined graphite content in the ore deposit is 3.95 %, which meets the requirements of the industry for this type of raw material.

Structurally, the deposit is placed in the south wing of Zahchahona syncline. The shape of the deposit site is of a lenticular body, composed of graphitized marbles of up to 2.2 km with an average capacity of 145 m. The maximum capacity of the productive formation, reaching up to 350 m, is confined to the central part and in the eastern the capacity is reduced to 40 m. A complex of geological prospecting was produced for detailed delineation of exit productive strata to the surface, drawing a schematic geological map scale of 1:10.000, geological sections with sampling, piece and channel samples, as well as technological samples weighing 91 kg. The total distance of the route was 7240 m.

The maximum areal development of formations are the manifests of suites of Siomin presented intensively in metamorphosed marble, slate, aleurolites, argillites, and metamorphosed tuffaceous rocks. It is split into five distinctly different packs. Productive stratum, composed of massive streaky marbles of gray and dark gray, is often

intensely graphitized. The productive stratum with a capacity of 10–20 m on the flanks of the ore body to 320 m average grade of graphite is 3.95 % with fluctuations from 0.3 to 12–14 % and extends to a distance of 2200 m. The inferred resources are of 8.5 million tons of graphite.

Our research has shown that the mineral composition of productive strata and its nature changes along power capacity. An unclearly expressed trend of the content of graphite decreasing along strike in the direction from west to east was marked. According to the power of other useful strata, another pattern is fixed: the less apparent the ore power, the higher the carbon content and vice versa, the larger the apparent power, the lower the carbon content. In the direction from south to north the recorded tendency is an overall increase in the content of graphite. Nature of the change of the graphite mineraliza-

tion from apparent capacity of productive strata of the central and western parts of the sites of graphite in Zahchahona is shown in Fig. 1.

The elements of the high concentration were Ba, Ge, Cd, Co, Mo, Sb, Nb, and Ag, of which the elements which contents exceeds Clarke concentration by 5–10 times are Ge, Ag and by 10–15 times – Ba, Co, Cd, Mo, Sb, and Nb. Clarke high content of Ba and Ag are recorded at the base of the productive horizon, at the contact of light gray marble Karakul suite with graphitized marbles of Siomin suite. Some of these elements form a proper mineralization in areas of maximum metamorphic graphitized marbles. Of practical interest are such elements as cobalt, niobium, cadmium, molybdenum, and antimony, the concentration of which exceed the Clarke value by 10–15 times. The mineralogical composition of the investigated graphitic sample is shown in Table 1.

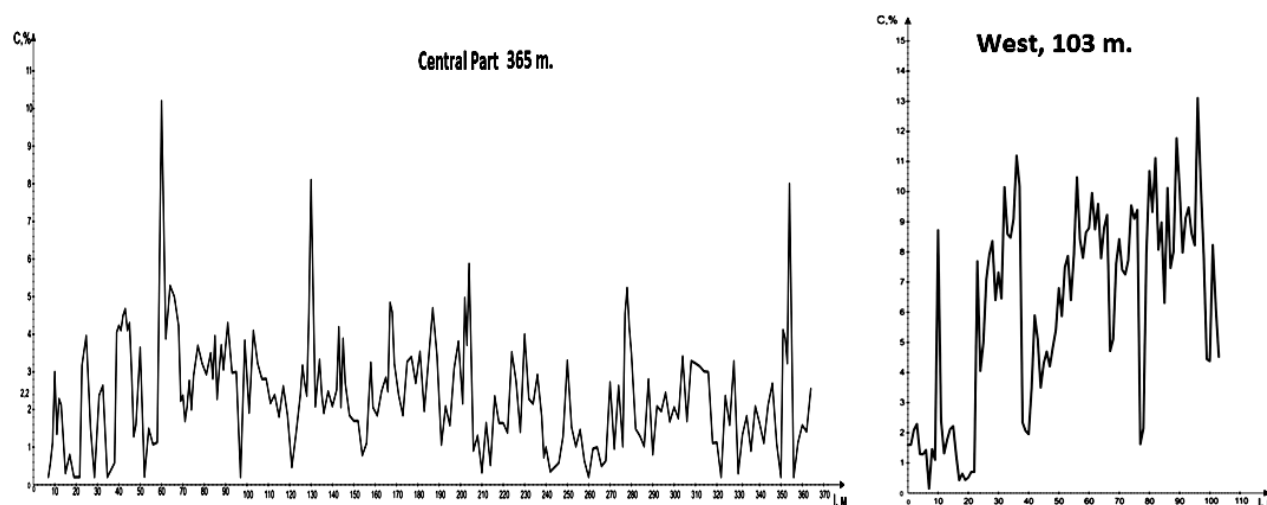


Fig. 1. Nature of the change of graphite mineralization in Central and Western parts of Zahchahona graphite deposit

Table 1

The mineral composition of Zahchahona graphitic schist

Minerals	Content, wt %	Size, mm	Description of minerals
Calcite	80–89	< 0.03–0.2	Rhombic shape of the crystals, xenomorphic, elongated
Quartz	5–12.5	0.02–0.04	Gray color, the shape of the crystals is irregular
Goethite	0.3	0.2–0.4	Color brown, opaque grains, cubic shape
Sericite	0.6	< 0.01	Found in the rock in the form of single sheets, often in conjunction with clay accumulations
Graphite	< 15	< 0.005–0.05	In the rock found in the form of films, thin-sheeted clusters in calcite rocks. Color silver gray, gray. The thickness of the films of < 0.005 mm
Clay mineral kaolin	< 1.6	< 0.001	Forms fine-grained clusters in the intergranular spaces. Contains splices sericite, graphite particles

3.4. Flotation Enrichment of Quartz-Graphitized Schists

In accordance with the mineralogical composition of quartz-graphitic schists of Zahchahona the gravity-flotation method was chosen for its enrichment.

An uneven-clastic sample of quartz-graphitic schists has been technologically researched (particles from 40x60 to 10x16 mm) with a total weight of 91 kg. The samples were dry crushed and ground in a ball mill. The optimal size of the graphite ore grinding prior to flotation is 0.074 mm. As of the full disclosure of the graphite component in the ore and reducing the size, it is implemented gradually, during the stage of regrinding.

When grinding the graphite, particles are coated with waste minerals (clay, quartz, calcite), and therefore it is difficult to suppress them. Deflocculating of the smeared graphite is carried out with sodium silicate in an alkaline solution. To suppress easy floatable minerals (calcite) soda ash, caustic soda, and sodium silicate were used.

Froth flotation of the graphite rock was carried out using kerosene, pine and diesel oil, using sodium silicate acidic and alkaline medium. Solid to water ratio (w/w) was 10 %. Output of the main flotation concentrates ranged from 2.1 to 10 %. As a result of the primary flotation using pine oil (100 g/t) and T- 80 (200 g/t) as a foaming agent, kerosene (500–1000 g/t) as collector, and sodium silicate (500 g/t) as suppressor roughing tailings and graphite concentrate were obtained. Flotation time was 10–16 min. Since the production of crude (starting) concentrates has high ash content (43 % of ash), they were subjected to further enrichment in five successive stages with two intermediate regrinding.

Total carbon content in final concentrate was 60 % and total carbon recovery – 15.2 %. To increase the graphite content the method of chemical purification by means of acid leaching after flotation was used. The flo-

tation concentrate was treated with HCl; as a result the ready concentrate had the ash content of 25 %. Total carbon content in the Zahchahona ore was increased from 3.95 to 75 %. According to the results of X-ray studies, the results of which are shown in Fig. 2, the graphite concentrate consists of graphite and calcite. P. Walker *et al.* [7] showed that X-ray analysis may be used for determination of graphitic carbon in concentrate. For determination of the crystalline graphite in ready concentrate we investigated (002) region in the diffraction patterns of graphite concentrate corresponding to the angle of X-rays reflection $2\Theta = 26\text{--}27$ in Fig. 2. The (002) region contains sharp and strong peak, indicating the presence of crystalline graphite. Calculated unit cell parameters for enriched graphite (hexagonal system) $a = 0.2467$ nm; $c = 0.6749$ nm agree well with the reference data for hexagonal graphite PDF#00-04101487 in Match! program package: $a = 0.2470$ nm; $c = 0.6724$ nm.

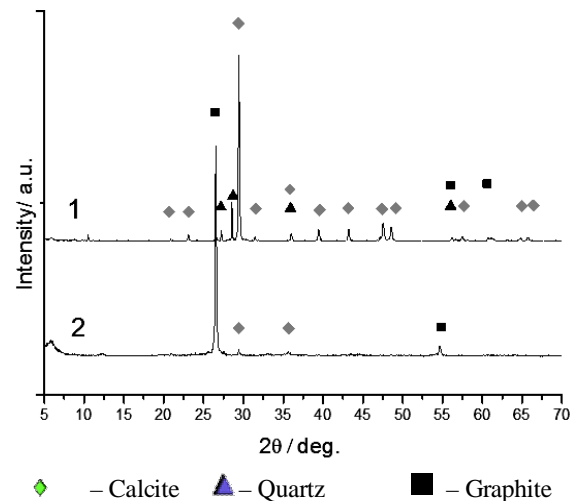


Fig. 2. The diffraction patterns of the samples of the graphitic schist Zahchahona (1) and graphite concentrate (2)

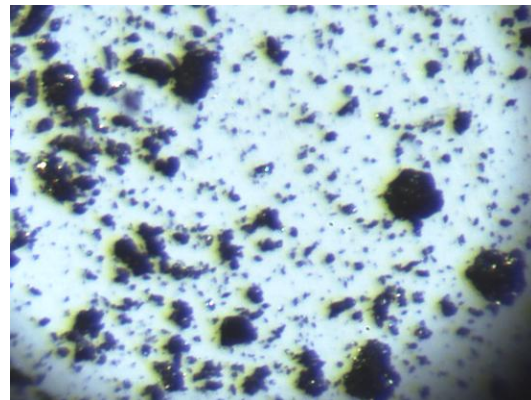
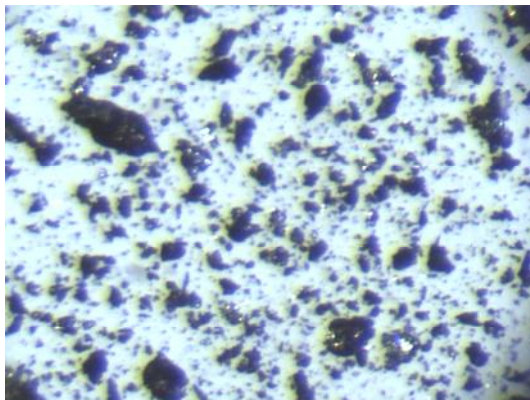


Fig. 3. The microscopic images of particles of graphite concentrate G-1 (magnification of 80x, MOTIC microscope, France)

The microscopic examination of the structure of the particles was carried out using a polarizing microscope MOTIC, France. Crystal size in a graphite concentrate (Fig. 3) is from 0.00015 to 0.05 mm. The form of individual units (crystals) is irregular, close to the hexagonal, round or other. A particle size distribution was conducted on graphite concentrate G-1 (size fraction–weight): +300 μm – 4.4 %; +90 μm – 19 %; +63 μm – 25 %; -63 μm – 51 %.

4. Conclusions

As a result of comprehensive research of Uzbekistan graphite schists of Rupert, Zauchak and Zahchahona deposits it was found that the best technological parameters (degree of enrichment, the quality of the resulting graphite concentrate) and geological location (availability of raw materials) are in the Zahchahona deposit. Complex geological conditions, low power graphitized layers, intensive crumpling and crushing of productive strata of Zauchak deposit, as well as low levels of graphite makes this deposit not promising for development.

Results of enrichment of Rupert samples are positive, but these results are preliminary, since the graphite mineralization of the middle and upper subformations of Malyand suites remain untested, and further study of this manifestation is required.

Zahchahona deposit of graphite is promising and deserves posing exploration work in order to obtain reliable data for a reliable geological, technological and economic assessment of the significance of the object. The inferred resources of Zahchahona deposit are 8.5 million tons of graphite. Enrichment of Zahchahona graphite ore by flotation and chemical leaching has been done, as a result total carbon content was increased from 3.95 to 75 %. The obtained graphite concentrate can be

recommended for use in carbon-ceramic refractory materials production. The schists also contain high concentrations of rare metals such as cobalt, niobium, cadmium, molybdenum, and antimony, which create areas of maximum metamorphic graphitized marbles due to proper mineralization. Further studies of the possibility to enrich graphitic schists should be conducted in Zahchahona to extract rare metals.

References

- [1] ASTM Designation: C 561-91, Standart Test Method for Ash in Graphite Sample.
- [2] ASTM Designation: C 562-91, Standart Test Method for Moisture in Graphite Sample.
- [3] Khamidov R.: *Geologia i Mineral. Res.*, 2011, **2**, 34.
- [4] <http://www.total.net/~bogdan/graphite.html>.
- [5] Babakhanova Z. and Aripova M.: *Khim. Prom.*, 2015, **1**, 12.
- [6] Bezuglov E.: Report on the Results of the GSP Surhantauskoy Geological Survey Scale of 1: 50,000 in the 1966-68 Biennium, Funds of Goscomgeology of Uzbekistan. Tashkent 1969, 352.
- [7] Walker P., Rakszawski J. and Amington A.: *ASTM Bulletin*, 1955, **208**, 52.

ДОСЛІДЖЕННЯ МІНЕРАЛОГІЧНОГО СКЛАДУ ТА ФЛОТАЦІЙНИХ ПАРАМЕТРІВ КВАРЦ- ГРАФІТОВОГО СЛАНЦЮ

Анотація. Показано, що за даними геологорозвідки в Узбекистані існує один графітовий поклад (Taskazgan) і близько 25 ділянок різної перспективи. Проведені дослідження нових покладів Rupert, Zauchak і Zahchahona для одержання графіту для вогнетривкої промисловості. Визначено, що поклад Zahchahona може бути класифікований як середній за розміром; вміст очищеного графіту в родовищі руди становить від 3 до 15 %, що відповідає вимогам галузі для даного виду сировини. Проведено очищення графіту флотацією та вилуговуванням, що привело до вмісту вуглецю 75 %.

Ключові слова: графіт, кристалічний сланець, концентрат, флотація.