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Study and justification of the combination of beneficiation processes for obtaining flake graphite from technogenic carbon-containing dusts

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Abstract. The most important task of modern production development is to provide the mineral and raw materials sector of the economy with resources included in the list of strategic raw materials, including flake graphite. In addition to natural raw materials, the source of its obtaining can be metallurgical production wastes not involved in processing. Development of metallurgical dust beneficiation technology will solve the problem of obtaining high-purity flake graphite with a crystal structure close to ideal and in demand in the production of high-tech materials. It will allow creating a renewable raw material base of graphite and utilising metallurgical production wastes. The research included the study of dust beneficiation by coarseness, magnetic and flotation methods, the influence of dust disintegration processes on beneficiation indicators. Based on the established technological properties of the components of dusts, magnetic, flotation and gravity beneficiation methods can be applied for their separation in different sequence. It is shown that dusts from different sites have different enrichability by these methods, and it should be taken into account when developing a complex technology of their processing. The degree of beneficiation increases in a row of dusts from the blast furnace shop (BF) – electric steel smelting shop (ESS) – oxygen-converter shop (OCS). The method of grinding has a significant influence on the separation indicators – at dry grinding in a centrifugal-impact mill with subsequent pneumatic classification the quality of graphite concentrates increases by 22.7 % of carbon for BF dust and by 13.48 % of carbon for ESS dust. OCS dust beneficiation indicators are high at coarse grinding with steel medium – mass fraction of carbon 96.1 %.

***Keywords*:** flake graphite; iron-graphite dust; disperse composition; material composition; disintegration method; centrifugal-impact mill; pneumatic classification; magnetic separation; flotation; carbon content

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Introduction. The mineral resource base depletion of strategic ores is a real challenge for the Russian economy and stimulates research on the development of technological solutions for the involvement of complex, poor and unconventional mineral raw materials in processing [1, 2]. By 2025, a significant, more than 700 %, increase in the global demand for graphite is expected [3], associated with the global transition to clean energy sources and the use of electric vehicles [4]. The growing demand for mineral graphite resources will require significant reserves of high-quality raw materials. The most valuable graphite raw material used for the production of spherical graphite for lithium-ion batteries and graphite for super composites is flake large-crystalline graphite [5]. The share of such raw materials in the total reserves of graphite ores in Russia is small [6] and requires significant investments in the exploration of new deposits and development of proven reserves. It becomes promising to develop technologies for obtaining high-purity flake graphite from metallurgical dusts, which will make it possible to obtain a constantly renewable source of valuable, high-quality graphite with a crystal lattice close to ideal, and, in addition to the resource issue, to solve environmental problems of metallurgical production.

Annual formation of graphitised dusts at metallurgical enterprises in the Urals is estimated at10^5 t [7] and is associated with the conversion of pig iron into steel. The yield of dispersed iron-graphite waste is up to 600 g/t pig iron [8]. Graphite is formed during cooling of pig iron as a growth result of graphite inclusions due to carbon atoms of austenite or as a result of direct decomposition of cementite [9]. Since graphite dust is not wetted by the metal, it is picked up from its surface by the convective air flow and carried away. Typical blast furnace graphite dusts contain carbon 15-25 wt.%, iron 25-50 wt.% and zinc 1-5 wt.% [10], in converter dust – carbon from 27.99 wt.% [9], and in dusts from electric arc furnace melting – iron 30-45 wt.%, zinc 3-17 wt.% and lead 1-7 wt.%. Compared to the carbon content in domestic flake graphite deposits, graphite dusts from metallurgical production appear to be a richer source.

During the last decade, the most significant studies of metallurgical kish have been carried out at Donetsk National University. A significant part of them is on the dusts of the mixer department of the converter shop of the metallurgical plant "Azovstal". Mineralogical and structural features of dusts [11-13], conditions of graphite emission reduction [14, 15], ecological problems [16], possibilities of obtaining flake graphite [11] and thermographenite with magnetic properties [17] were studied.

The most comprehensive studies of metallurgical graphitised dusts are carried out in China, where the production capacity of kish-graphite (KG) formation is relatively large [18]. Kish-graphite in China is not utilised efficiently, resulting in enormous waste of resources and environmental pollution. The recycling and utilisation of KG has attracted increasing attention from researchers. Studies have shown that KG has many applications. The authors of the paper [19] obtained KG flakes with 97 % carbon content by a process of screening, flotation, crushing, magnetic separation and hydrochloric acid etching. The KG flakes were used to successfully produce graphene under microwave irradiation. In [20, 21], high purity KG flakes were extracted using an integrated process of air separation, flotation, ultrasound and magnetic separation, and the prepared KG-based blown graphite showed excellent adsorption properties towards oil. In [18], KG was beneficiated and purified using complex separation processes including water washing, dust removal, magnetic separation, and acid leaching. This product can be used as cathode material of aluminium-ion battery [22]. Using mechanochemical ball milling, iodinated KG was obtained, which showed excellent electrocatalytic activity for oxygen reduction reaction [23]. By examining blast furnace dust, KG with a high degree of graphitisation, complex processing by flotation-acid leaching extracted with small particle size and obtained graphite with purity of 95.00 % [21]. However, obtaining KG with high carbon content (>99.00 %) remains a serious problem.

For chemical beneficiation of graphite concentrate with ash content of 10-14 %, obtained from graphite-containing dust of Krivoy Rog metallurgical plant, the thermochemical method of flotation concentrate finishing was applied [24]. The obtained product has ash content up to 1 %. Thus, the combination of various methods of ore preparation and beneficiation is a key aspect of the process of beneficiation of technogenic graphite-containing raw materials. The aim of the study is to establish the regularities of separation of iron-graphite dust from different areas of metallurgical production by beneficiation methods and to determine their rational combination for obtaining flake graphite.

Methods. The iron-graphite dust sampled at different sites of formation at a metallurgical plant with a full cycle of processing of iron ore raw materials into steel was studied: in blast furnace (BF), oxygen-converter (OCS) and electric steelmaking (ESS) shops. The selected samples have visual differences and differences in material and disperse compositions, established by methods of sieve and laser granulometric analysis (Mastersizer 2000), magnetic analysis by size classes (by hand magnet of 42.8 kA/m intensity), carbon distribution by size classes (on CS-144DR analyser), optical analysis (Mineral C7 SIAMS Photolab in reflected light), chemical analysis, electron microscopy (scanning electron microscope (SEM) JEOL JSM-6490 LV in secondary electrons), X-ray phase (using a special attachment to SEM – energy dispersive spectrometer INCA Energy) and X-ray spectral analyses (diffractometer XRD-7000 (Shimadzu)) [25]. Comparative characterisation of the selected samples is presented in Table 1, 2. Fig.1 shows the characteristics of coarseness of the studied dusts and particle size distribution in them, determined by laser diffraction method. Optical study of samples showed that graphite particles have flat irregular rounded or close to hexagonal shape, with uneven or straight edges. Graphite particles with smooth, up to mirror-clear surface are rare. The surface of the majority of particles contains a significant number of spherical inclusions from smallest to rather large. There are also flakes with spherical particles included in the plate structure. Besides flat graphite particles and spherical iron-containing particles there is an insignificant amount of irregularly shaped particles of predominantly silicate composition.

Based on the technological properties of the components that make up the dusts and materials of various reviews on methods of beneficiation of graphitised raw materials [21, 23, 24], magnetic separation, air and hydraulic classification, and flotation are most often used to separate ores and dusts containing graphite. Despite the high natural hydrophobicity of coarse flake graphite, a collector (paraffin) and a blowing agent (MIBK) are used to improve the flotation process, increase the mass fraction and carbon recovery [26-28]. Electroflotation is used for raising superfine graphite into foam, ultrasonic flotation – for simultaneous cleaning of flake surface [4]. The difference between flotation of flakes smaller and larger than 150 μm is indicated. It is emphasised that large particles of flake graphite are poorly flotated after damage to their structure and it is important to separate large from small flakes during processing. However, there are several problems associated with the flotation of fine graphite, including high collector consumption and entrainment. Hydraulic classification is used to classify KG after disintegration operation before flotation, which can be not only a preparatory but also a beneficiation operation. Classification leads to additional effects that favour graphite beneficiation. It is noted that graphite particles less than 150 μm after hydraulic classification consume 34 % less acid in the leaching process [4].

Table 1

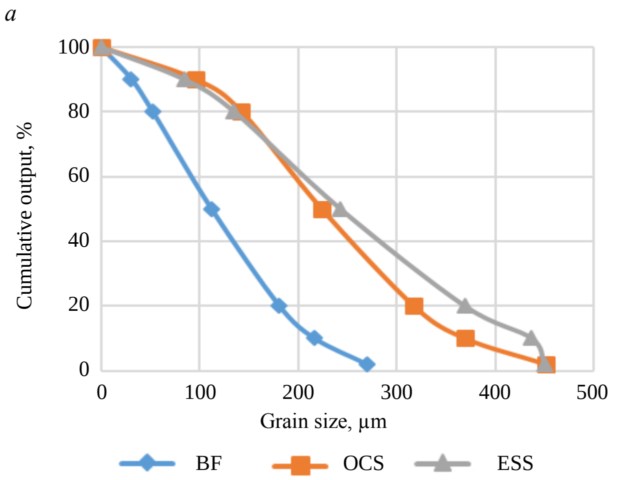
Substantial composition of investigated samples and technological properties of dust components

Samples charcteristics	Sampling site		
	BF (2022)	OCS	ESS
Colour	Brownish-black	Shiny, graphite black	Shiny, graphite black
Chemical composition, wt.%			
Carbon	10.17	>30.0 (32.09)	>30.0 (38.05)
Iron	62.9	46.8	53.9
Harmful impurities (P, S, Zn)	0.036, 0.178, 0.119	<0.005, 0.041, 0.026	<0.005, 0.042, 0.027
TEP	10.4	31.0	30.3
Content of highly magnetic fraction, %	91.06	58.04	46.86
Mineral composition of iron-oxygen inclusions	Magnetite, haematite, graphite	Graphite, magnetite	Graphite, wustite
Particle size distribution			
D_{max}, mm	6-8	12-15	8-10
Class –0.071 mm, %	50.6	11.7	18.1
Graphite unit cell			
Ideal: a = 2.4612, c = 6.7079, z = 4	a = 2.456, c = 10.044, z = 6	a = 2.462, c = 6.711, z = 4	a = 2.465, c = 6.721, z = 4
Type of crystal lattice	Non-centrosymmetric rhombic	Centrosymmetric hexagonal and rhombic	Centrosymmetric hexagonal
Fraction of rhombic graphite	>	>	>

Table 2

Reference properties of minerals

Minerals	Density, g/cm^3	Specific magnetic susceptibility, 10^{-6} cm^3/g	Specific resistivity, Ohm/cm	Flotation properties according to M.A.Eigeles
Graphite	2.08-2.23	–2 to –10	$0.5\cdot10^{-4}$-$0.5\cdot10^{-2}$	High natural hydrophobicity
Magnetite	5.0-5.2	>20,000, ferrimagnetic	$0.5\cdot10^{-2}$-$0.5\cdot10^{-1}$	Flotate with cationic collectors, carboxylic acids and soaps; activation is sometimes necessary
Hematite	4.9-5.3	70-300	$0.5\cdot10$-$1\cdot10^{3}$	
Wüstite	5.88-5.97	Antiferromagnetic [29]		



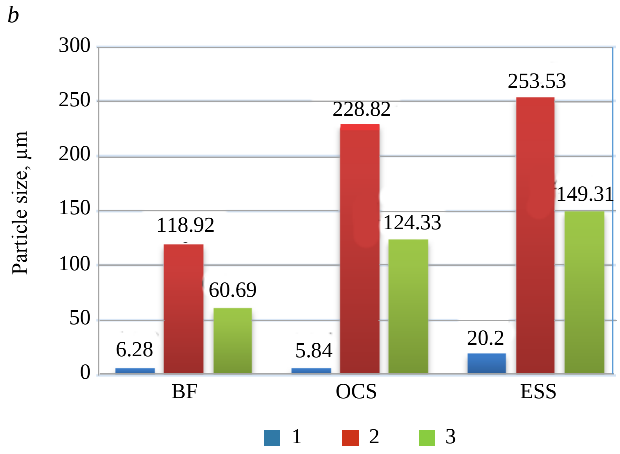


Fig.1. Characteristics of coarseness according to the results of analysis on the laser analyser:
a – total characteristic of coarseness; *b* – numerical characteristics of particle size distribution
1 – arithmetic mean diameter; 2 – weighted average diameter per mass and volume – De Brooker mean diameter;
3 – weighted average diameter per surface area – average Sauter diameter

Electroseparation, which is based on the difference in the acquired charge of particles with different conductivity and dielectric properties as a result of friction or in the corona discharge field, is rarely used. Since static electricity is directly proportional to the magnitude of the particle surface charge and the strength of the force field, it has a more significant effect on thin light graphite particles in the form of chips (thin rectangular plates with an area of fractions to several square centimetres). Consequently, the particles can be effectively separated [30].

Studies on enrichability of samples by different methods were carried out in the laboratories of ore preparation and mineral beneficiation of Nosov Magnitogorsk State Technical University and at the experimental site of CJSC UralOmega with grinding complex GC-0,36. The programme included the study of the processes of dust disintegration, dynamic pneumatic classification, magnetic separation, and foam flotation of dust ground under different conditions and to different sizes. Dust grinding was carried out in metal and porcelain ball mills on a roller conveyor and in centrifugal mills of the grinding complex GC-0,36 (CJSC UralOmega). Regime parameters of ball grinding are ball size, solid-liquid phase ratio, grinding time. In the centrifugal-impact mill the adjustment parameters are the mill rotor speed, the position of blades in the upper part of the mill, the air flow rate (by changing the position of the damper on the air duct). The operating mode of the complex is adjusted for obtaining three products with the coarseness of 0.5 mm, 0.315 mm and 0.1 mm. In the dynamic classifier included in the grinding complex GC-0.36, the crushed product was separated by the grain boundary of 0.071 mm. The rotor speed of the dynamic classifier is 3,000 rpm. The wheel diameter is 0.4 m.

Regularities of the crushed dust separation by magnetic method were investigated on the electromagnetic tube analyser 298 SE-00.000PS. Variable parameters are the method of grinding, feed size and magnetic field strength. The study of patterns of froth flotation was carried out on a laboratory flotation machine of mechanical type under the reagent regime, including feeding of the collector illuminating paraffin and foaming agent VKP or T-80. The quality of separation products was evaluated by the content of carbon and highly magnetic fraction in the products. The carbon content was determined on the analyser SC-144DR by combustion of carbon in the atmosphere of oxygen to CO_2, strongly magnetic particles – by a hand magnet, creating field strength of 42.8 kA/m.

Discussion of results. The studied samples are in a dispersed state, which allows us to consider the possibility of their beneficiation by size without additional disintegration. The granulometric composition of the studied samples and the distribution of carbon and highly magnetic fraction by size classes were analysed (Fig.2). It was found that in the BF sample half of the material consists of particles of size less than 0.071 mm and in all size classes strongly magnetic particles prevail over graphite particles; carbon recovery does not exceed 28 %, and the strongly magnetic fraction 50 %. Thus more than 51 % of carbon and more than 72 % of strongly magnetic particles have the size less than 0,1 mm. The obtained data indicate a close association of the main components in this dust sample and the absence of a noticeable beneficiation of sieving products in carbon and iron at sieving of any class.

In the OCS sample, graphite predominates in the largest class (coarser than 1 mm), and there is a pattern of increasing magnetic fraction content and decreasing carbon content from large to small classes. Carbon extraction in classes of coarseness less than 0.25 mm does not exceed 5 %. In small classes strongly magnetic particles are concentrated, and for this sample in the construction of the technological scheme it may be appropriate operation of screening of small classes. By screening of particles less than 0.071 mm, an iron-containing product with a yield of about 11 % can be obtained, with iron content in it about 71.5 % in terms of magnetite suitable for recycling. The carbon loss with this product will not exceed 2 %.

In the ESS sample strongly magnetic particles prevail in the classes larger than 1 mm and smaller than 0.1 mm, in the intermediate classes – graphite. Screening of the largest class will result in a low quality product in terms of iron (~40 %) and with a loss of 18 % of graphite. In case of –0.071 mm class

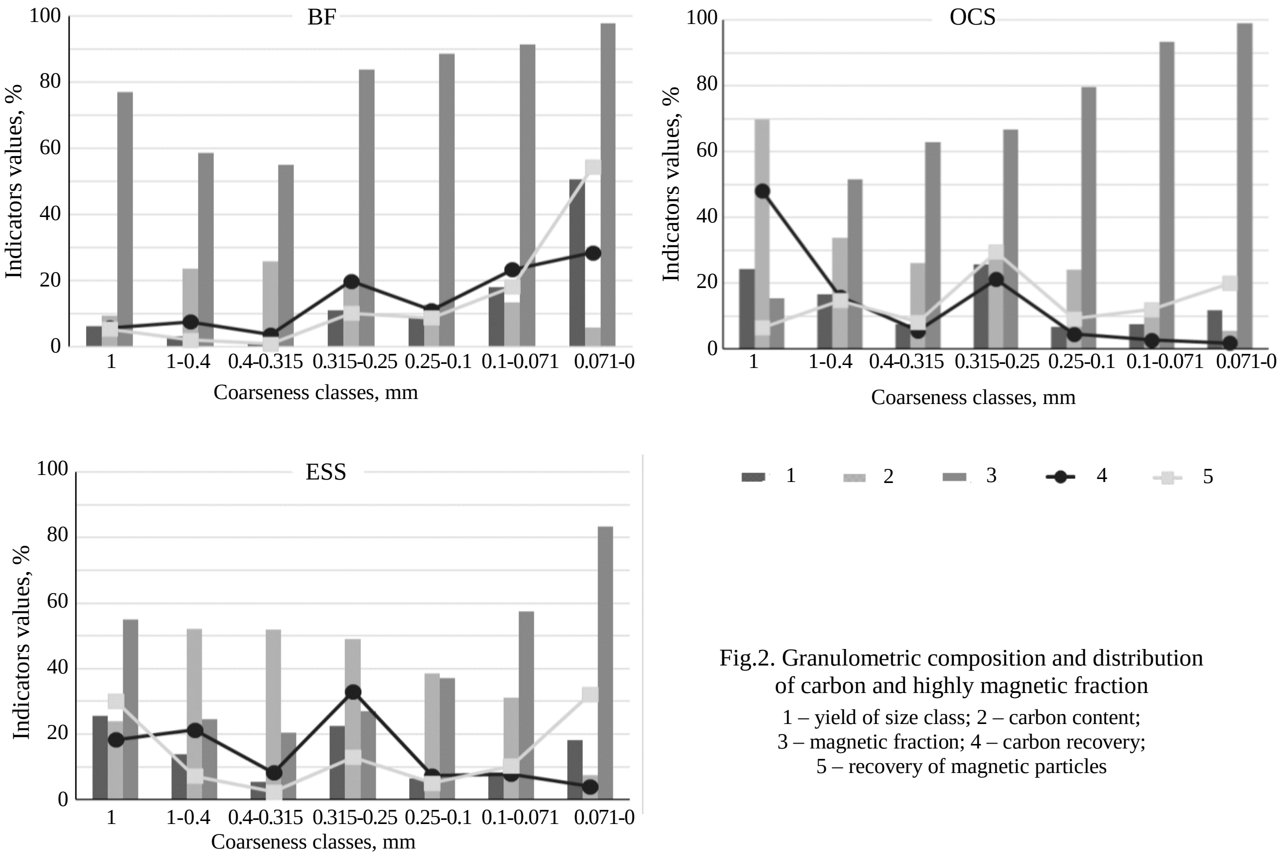


Fig.2. Granulometric composition and distribution of carbon and highly magnetic fraction

1 – yield of size class; 2 – carbon content; 3 – magnetic fraction; 4 – carbon recovery; 5 – recovery of magnetic particles

screening, the quality of the obtained product will be lower than the requirements for the quality of iron concentrates when processing magnetite skarn ores.

Optical-microscopic and electron-microscopic analyses of samples have shown [11, 31] that in the free state in the sample there are mainly spherical particles and irregularly shaped particles of carbon-free composition. Graphite flakes are rarely free of foreign impurities, and the main contaminants are spherical particles located both on the surface and in the space between the flakes. X-ray spectral analysis of the spherical particles has established their iron-oxygen composition. The size of spheres varies in a wide range. The fact of contamination of graphite flakes with iron-containing spherical particles determines the presence of weakly magnetic properties of graphite particles and their attraction to a strong neodymium magnet N30 (H = 725 kA/m). Removal of contaminating impurities is possible only after grinding the material. Considering the value of large graphite flakes, it is important to strike a balance between preserving the flake structure of graphite particles and separating particles of other phases from them. Taking into account the differences in the graphite and iron content in the initial samples (Table 1, 2), the character of distribution of large and small particles in the samples (see Fig.1), it is necessary to study the regularities of grinding of samples of different areas of their formation in standard laboratory roller conveyor mills.

Table 3

Influence of grinding time on coarseness

Grinding time, min	Class content –0.071 mm, %		
	BF	OCS	ESS
0	50.6	11.7	18.1
5	63.48	15.44	19.1
10	70.88	19.68	25.22
20	81.16	20.23	26.15

Modes of ball grinding of iron-graphite dust – ball size, ratio of solid and liquid phases – were selected in the course of prospecting studies on the modes of graphite ore grinding. The grinding medium was a mixture of metal balls of 5, 7, 15 mm in size, the ratio of phases in the mill at grinding of dust BF S:L:B = 1:1:6, at grinding of dust OCS and ESS, because of the greater amount of graphite flakes in them, S:L:B = 1:1:12. Table 3 shows data on the effect of grinding time on the content of 0.071 mm size class in the ground products. With the increase of grinding time in the BF sample the increase of fine particles is more significant than in the OCS and ESS samples. Macroscopically these samples contain very large flakes of graphite and in greater quantity than in the BF sample, which is evidenced by the greater weight of the BF sample. The grindability of graphite by grinding bodies is also important. When processing flake graphite ores and using rod and ball mills in grinding, graphite is concentrated in large size classes [32]. This is due to the fact that in this type of grinding equipment the main destructive force of falling or rolling grinding bodies in relation to graphite flakes will be directed mainly on the plane of the flakes, in which strong covalent bonds act, and not on the faces of the flakes bound together by weak molecular forces. Rod mills are chosen over other types of grinding when the ore is prone to sticking. Compared to ball milling, rod mills generally do less damage to flake size and shape. Agitated grinding [33, 34] and jet grinding [4] are used in order to preserve flake size and the layered structure of graphite. A promising direction of modernisation of grinding processes is the use of technologies based on selective disintegration [35].

The main parameter in selecting a beneficiation method for any raw material, except for the technological properties and the size of the recoverable particles, is the content of recoverable components or removable contaminants. Other things being equal, the method that extracts components contained in smaller quantities is used. On this basis, magnetic separation is preferred for the OCS sample and flotation is preferred for the BF and ESS samples. The results of the study are summarised in Table 4. The background highlights the highest achieved technological indicators and beneficiation efficiency of wet magnetic separation of the studied samples. The following rational parameters correspond to these indicators: for dusts of BF – ball size reduction up to 81.16 % of –0.071 mm class and magnetic field strength of 88 kA/m; for OCS the ball size reduction up to

15.44 % of –0.071 mm class and separation at magnetic field strength of 88 kA/m; for ESS – ball size reduction up to 25.22 % of –0.071 mm class and magnetic field strength of 88 kA/m. Under these conditions it is possible to obtain graphite product of high purity 96.1 % by wet magnetic separation only from OCS sample at coarse grinding. The indicators of magnetic beneficiation of samples of iron-graphite dust of BF and ESS are low, the mass fraction of carbon is not higher than 22 % for BF sample and 78 % for ESS sample. The content of magnetic fraction in non-magnetic products decreases to 0.56 % and 1.1 %, respectively. The most complete separation of free strongly magnetic particles into the magnetic product occurs at a magnetic field strength of 88 kA/m.

Table 4

Influence of grinding size and magnetic field strength on the parameters of non-magnetic (graphite) product

Grinding time, min	Tension, kA/m	BF-2019*					OCS					ESS				
		γ, %	β_C, %	ε_C, %	β_{magn}, %	E, %	γ, %	β_C, %	ε_C, %	β_{magn}, %	E, %	γ, %	β_C, %	ε_C, %	β_{magn}, %	E, %
5	56						39.9	85.7	81.5	4.34	71.7	68.2	58.0	81.2	20.07	25.3
	80						40.6	88.5	85.6	2.18	77.6	51.6	70.5	74.8	5.56	45.2
	88						43.4	96.1	99.2	0.7	96.2	42.0	78.4	67.7	1.1	50.1
10	56	41	9.23	74.0	6.31	34.8	42.4	86.3	87.0	2.24	76.9	60.6	66.4	82.6	12.72	42.9
	80	13.7	18.4	49.2	2.64	37.4	42.3	88.8	89.5	0.52	81.4	57.1	73.3	85.9	6.03	56.1
	88	14.6	22.2	63.3	0.56	51.3	33.9	89.6	72.4	0.3	66.4	53.7	78.7	86.8	2.02	64.5
20	56	36.4	11.3	80.5	15.8	46.5	42.4	78.8	79.5	5.17	64	62.9	70.0	90.5	27.04	53.8
	80	15.2	21.5	63.8	1.63	51.2	36.2	87.0	75.0	1.0	66.9	54.9	74.8	84.3	11.78	57.3
	88	16.9	20.4	67.5	0.78	53.3	36.0	88.7	76.0	0.34	69	46.5	76.3	72.8	2.51	51.3
Source product		100	5.11	100	87.5		100	42	100	58.0		100	48.7	100	46.9	

* BF has been sampled twice, in 2019 and 2022; the samples differ slightly in their mass fraction of carbon and the highly magnetic fraction.

The study of flotation was carried out at grinding of samples for 10 min and at different ratio of solid and liquid phases. The conditions of graphite dust flotation by the amount of contained graphite can be regarded as the conditions of recleaning operations of graphite ore flotation, so flotation was carried out in diluted slurries. The results of flotation of the studied samples are given in Table 5. Higher results on mass fraction of carbon were obtained at flotation of graphite from samples of BF and ESS. Compared to wet magnetic separation, the quality of graphite products is twice as high for BF, slightly lower for OCS and approximately at the same level for ESS with a higher content of highly magnetic fraction. Lower performance of flotation compared to magnetic separation led to the rejection of this method for OCS dust.

Table 5

Influence of pulp density on foam (graphite) product performance

Solid content in flotation, %	BF-2022					OCS					ESS				
	γ, %	β_C, %	ε_C, %	β_{magn}, %	E, %	γ, %	β_C, %	ε_C, %	β_{magn}, %	E, %	γ, %	β_C, %	ε_C, %	β_{magn}, %	E, %
5	18.09	49.02	88.23	48.6	78	42.15	74.94	75.21	14.17	57	46.48	80.52	76.38	21.19	58.6
7.5	20.75	47.01	97.04	42.8	84.8	41.71	74.65	74.14	8.86	55.91	53.46	69.73	76.07	23.58	44.3
10	21.31	43.78	92.82	54.01	79.5	42.55	73.63	74.60	19.08	55.26	50.91	72.37	75.18	27.10	47.6
Source	100	10.05	100	91.06		100	42	100	58.04		100	49	100	46.86	

The quality of flotation concentrates is improved by re-cleaning of froth products. However, as the experience of processing flake graphite ores at Taiga concentrator shows, the quality increase from re-cleaning to re-cleaning is small, and even in diluted slurries high hydrophobic properties of graphite cause mechanical capture of non-flotation particles and their contamination of concentrate. In addition, in the re-cleaning cycle there are additional grinding operations, which cause an increase in energy consumption.

The reserve of increase of technological indicators of flotation and magnetic separation of kish by BF and ESS is the use of equipment in preparatory operations, providing selective separation of spherical particles contaminating them from the flakes. Some types of grinding equipment can lead to graphite amorphisation [31]. Differences in physical and mechanical properties of iron-oxygen compounds and graphite flakes, as well as the nature of their interrelation [36] allowed us to assume the possibility of their opening between each other due to the destruction of accelerated particles by free impact. Such a method of destruction is realised at centrifugal-impact grinding in a mill with a vertical shaft, which is a part of the grinding complex GC-0.36 of CJSC UralOmega. In [37] it is shown that due to mechanoactivation and change of structural and morphological state of obtained particles the use of such equipment in processing of technogenic raw materials will give higher indicators than traditional [31, 38]. The grinding complex has a dynamic classifier, the work of which was adjusted to the separation by the boundary grain of 0.071 mm with obtaining coarse and fine classification products. It is shown that the separation in the classifier occurs not only by coarseness, but also by material composition [39], and the obtained classification products are characterised by a narrower particle size distribution in comparison with grinding with steel and porcelain grinding bodies [36].

BF and ESS dusts were subjected to grinding and classification in the grinding complex GC-0.36. Coarse and fine classification products were intended for beneficiation study by magnetic separation and flotation. When preparing samples for magnetic separation, the suspensions of dry products were mixed with water in a beaker for uniform feeding of the material into the tubular analyser. In the process of sample preparation it was found that the obtained products have different wettability with water. Products of grinding and classification of BF dust are wetted with water better than ESS dust products. This is due to the lower content of graphite in the BF sample and, accordingly, lower aggregation of dust classification particles. Particles of grinding and classification products of ESS dust were not wetted by water at any long mixing time and remained floating on the surface. Fig.3 shows photos of ESS dust ground by different methods and classified by coarseness. It can be seen that the dust particles ground in centrifugal mill and classified in dynamic classifier (Fig.3, *b*, *c*) remain dry compared to the dust ground in ball mill (Fig.3, *a*). With such poor wettability and no stirring conditions in the magnetic analyser or any other magnetic separator, due to the strong dry aggregation of particles, the magnetic separation process will not proceed selectively. That is why it was decided to abandon the study of wet magnetic separation for ESS dust after its grinding and classification in the complex GC-0,36. The change of technological parameters of wet magnetic separation of BF dust,

Fig.3. Photographs of interaction of ESS dust ground in a ball mill (*a*), from coarse (*b*) and fine (*c*) classification products in the GC-0.36 complex with water

ground in a centrifugal mill to a coarseness of 0.1 mm and classified by a coarseness class of 0.071 mm was investigated (Table 6). Comparison of the results with the data in Table 4 shows that the indicators of wet magnetic separation on the classification products of the grinding complex GC-0.36 are comparable with the results of separation after ball milling. Low selectivity of magnetic separation is caused by a higher content of strongly magnetic iron-oxygen phases, contamination of graphite flakes with magnetic spheres in the BF sample, which leads to non-selective magnetic flocculation of particles. For the same classification products beneficiation by flotation allows obtaining graphite products of higher quality: mass fraction of carbon is higher by 4.4-22.7 % (Table 7). One of the factors of flotation performance increase is flotation in narrow size classes, which is achieved by pneumatic classification. Thus, for BF dust it is more reasonable to separate by flotation after centrifugal-impact grinding and pneumoclassification of the crushed product. From the given results it is obvious that preparation of ESS dust for flotation in the grinding complex GC-0.36 allows obtaining higher indicators than in the ball mill (Table 7). From ESS dust it is possible to obtain graphite concentrate of high quality (94 % of carbon) with high carbon recovery and absence of free highly magnetic particles in the product.

Table 6

Comparison of technological parameters of wet magnetic separation on products of ball and centrifugal grinding of BF dust

Tension, kA/m	Classification products									
	Large-sized, the output 27.3 %					Fine product, the output 72.7 %				
	Non-magnetic (graphite) product indicators									
	γ, %	β_C, %	ε_C, %	β_{magn}, %	E, %	γ, %	β_C, %	ε_C, %	β_{magn}, %	E, %
56	17.24	15.9	66.8	2.56	51.7	42.6	11.7	69.3	78.64	28.8
80	19.1	17.32	80.9	4.43	64.4	34.4	19.8	94.6	37.53	64.9
88	17.5	19.15	81.9	0.23	67.1	28.4	22.68	89.5	2.47	65.8
Source product	100	4.09	100	98.35		100	7.19	100	71.1	

Table 7

Influence of grinding method on foam (graphite) product parameters

Grinding method	$\beta^{-0,074\ mm}$, % ($\beta^{-0,04\ mm}$, %)	Output, %	Carbon mass fraction, %	Carbon extraction, %	Mass proportion of magnetic fraction, %
BF					
Metal balls, 20 % sol.	81.16	17.27	28.7	97.02	27.1
Metal balls 7.5 % sol.	81.16	20.75	47.01	97.04	42.8
Large product GC-0.36, 20 % sol.	98.9 (89.35)	7.84	46.2	88.61	5.27
Fine product GC-0.36, 20 % sol.	95.38 (91.3)	12.43	51.4	88.89	4.71
ESS					
Metal balls, 5 % sol.	19.1	46.48	80.52	76.38	21.19
Large product GC-0.36, 5 % sol.	79.0	50.76	75.5	98.98	5.8
Fine product GC-0.36, 2 % sol.	95.3	62.13	94	99.56	0

The conducted studies show that dusts formed at different sites of metallurgical processing require individual technological solutions for obtaining flake graphite from them. Studies of dust beneficiation by size, magnetic and flotation methods have proved the possibility of obtaining products of a quality suitable for utilitarian purposes (lubricating, foundry, pencil graphite). In order to obtain concentrates of a quality that meet the requirements of high-tech materials, they can be sent for finishing by chemical and physicochemical methods.

Conclusion. It is established that different conditions of iron-graphite dust formation cause specific technological properties of dust components – differences in granulometric and chemical composition, content and phase composition of iron-oxygen components, crystalline structure of graphite. The revealed peculiarities cause different beneficiation of iron-graphite dust from different areas of formation by separation by size, magnetic and flotation methods.

The different character of dust components distribution by size distribution was revealed, which consists in concentration of iron-oxygen component in the size class less than 0.071 mm in OCS dust in comparison with dusts of BF and ESS. For OCS dust the use of preliminary beneficiation of the initial material by size in the technological scheme will allow to obtain about 11 % of iron-conditioned concentrate (with iron content of about 71.5 % in terms of magnetite) suitable for recycling. In other samples the character of distribution of components testifies to close interrelation of components with each other and disintegration is necessary for their separation.

The better beneficiation of graphite dust of OCS site by wet magnetic separation in comparison with dusts of BF and OCS and beneficiation by flotation at coarse grinding of dust by metal ball grinding medium is established. The rational parameters of wet magnetic separation are the size reduction of 15 % of –0.071 mm class and separation at magnetic field strength of 88 kA/m. A graphite concentrate of 96.1 % carbon purity with 99.2 % recovery was obtained.

Samples of iron-graphite dust of BF and OCS sections are better beneficiated by flotation in comparison with beneficiation by wet magnetic separation. At the same time, graphite from ESS sample is better beneficiated by flotation – the difference in the quality of concentrates is 33.5 %, while the difference in the content of highly magnetic fraction is 27.41 %. Better beneficiation by flotation of ESS dust is due to the high graphite content and centrosymmetric hexagonal structure of graphite flakes in this sample. In the BF sample the share of graphite with rhombic structure, which characterises defective structure of flakes and has lower flotation properties, increases.

The quality of obtained flotation graphite concentrates depends on the method of their preliminary grinding and the use of coarse classification before flotation. To a greater extent it is manifested at flotation of ESS dust. It is established that dry grinding of iron-graphite dust in mills of centrifugal-impact grinding and subsequent pneumoclassification of ground products provide obtaining of products with narrow particle size distribution and cause increase of flotation activity of graphite particles in comparison with grinding with metal balls. Close sizes of graphite particles in the flotation feed provide closeness of flotation properties of particles having different wettability on planes and faces and ratio of areas of planes and faces at different scale size. Narrow range of graphite dust classification product size provides higher and more stable beneficiation parameters – flotation of ESS dust yielded a product with purity of 94 % of carbon, with recovery of 99.56 %. Optical analysis of the product showed that there are no free particles of strongly magnetic iron-containing impurities in it.

The studies of graphite dust beneficiation at different sites allow us to classify the samples as easily beneficiated (OCS), medium beneficiated (ESS) and hard beneficiated (BF).

Further studies of dust properties of different metallurgical sites and their processing will be aimed at improving the quality of graphite concentrates that meet the requirements for the production of carbon graphite materials for high-tech applications.

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