

**Resource-saving technologies and technical means for processing raw materials difficult for concentration**



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#### Abstract

The main scientific and practical results of the development and introduction of resource-saving technologies and technical equipment for processing of difficult raw materials based on the study of regularities of copper melting slag destruction taking into account the impact of free flying piece at a high speed with the barrier of selective disintegration of the slag using energy-efficient centrifugal impact crushing to improve the performance of their subsequent flotation concentration were considered. The complex methods of research including the analysis of literary sources, methods of theoretical studies, laboratory studies with the implementation of the results in the development of new technologies and technical means of activating the processes of extraction of target components during the processing of metal-containing tailings in the practice of ore concentration were used. Theoretical studies were performed using classical methods of mathematical and physical modeling, laboratory research and industrial application using conventional techniques and international experience. The mathematical relationship of required speed of rotation of the crusher accelerator of impact action on physical and mechanical characteristics of the material being destroyed was developed. The estimation of effect of crushing slag method on performance of its subsequent processing was given. A higher release rate of grains of metallic copper and copper sulphides by crushing slag in a centrifugal impact crusher DTs compared with the jaw crusher was shown. The flotation concentration of copper slag of CJSC "Karabashmed" crushed in jaw and cone crushers and

using a centrifugal impact crusher DTs-0.63 in the third stage of crushing was carried out for plot and experimental evaluation of the proposed selective disintegration technology of slag. Flotation was performed according to the scheme of direct selective flotation in a laboratory flotation machine with volume of 3 dm<sup>3</sup> using butyl potassium collective agent, the foaming agent T-92 and lime as a medium regulator.

**Key words:** ORE PREPARATION, DISINTEGRATION, INTERGRANULAR FRACTURE, CENTRIFUGAL IMPACT CRUSHER, COPPER SMELTING SLAG, PHYSICAL AND MECHANICAL PROPERTIES

### The relevance of the problem

Development and introduction of resource-saving and energy-saving technologies for processing of difficult natural and technogenic raw materials necessitate efficient destruction of materials at the ore preparation stage. All the processes of disintegration are very energy-intensive, so modern processes must meet not only the requirements of obtaining a product with predetermined size, but also the intergranular fracture of mineral object on the boundaries of phases coalescence without overgrinding. Therefore, the development and introduction of resource-saving technologies and equipment for processing of difficult raw materials by studying patterns of destruction of slag copper smelting taking into account the impact of free flying piece at high speed with barrier selective disintegration of the slag using energy-efficient centrifugal impact crusher to improve the performance of their subsequent flotation concentration are important scientific and practical tasks that require urgent solution [1-5].

A complex method of research including the analysis of literary sources, methods of theoretical studies, laboratory studies with the implementation of the results in the development of new technologies and means of activating processes of extraction of target components during the processing of metal containing tailings in the practice of ore beneficiation were used. Theoretical studies were performed using classical methods of mathematical and physical modeling, laboratory research and industrial application applying conventional techniques and international experience [6-8].

To solve this problem, the fracture patterns of copper smelting slag based on the impact of free flying piece at a high speed with the barrier and at the development of technological solutions for selective disintegration of the slag using energy-efficient centrifugal impact crushing to improve the performance of their subsequent flotation beneficiation were studied.

### Discussion of research results

Thus, thermal power plants (TPP) of Ukraine produce up to 40% of electricity. Locating in the industrial centers or close to them, they pollute the environment

and form technogenic geochemical anomalies. In addition, the TPP have no cleaning systems of gas and dust emissions of particulate matters, sulfur oxides, nitrogen and other harmful gases. In particular, the Krivoy Rog TPP produces in average of more than 500 tons of ash slag per year. As their hydraulic removal is used at this plant, then there is intensive water pollution with heavy metal salts formed during coal combustion. The total annual volume of water discharged into open water bodies ranges from 6.5 to 7.5 mln m<sup>3</sup>. The main negative impacts of the ash dump on the environment consist in the filtration leaks of water from the construction bowl and dusting of the drying sediments occupying an area of about 430 hectares. Disintegration based on a free impact of ore piece with the barrier in comparison with other ways of destruction takes place primarily on the weak directions, which are the boundaries of minerals fusion, natural fault lines with the guidance of a wide network of micro-cracks due to the difference in strength properties of components and various resistance to impact. This provides a higher degree of valuable minerals release in larger size of the crushed product, which is crucial in the further beneficiation and, in some cases, allow starting beneficiation even at crushing stage with the release of final tailings [9].

Moreover, in the slag dumps of Russia more than 800 million tons of slag of ferrous and non-ferrous metals are accumulated including 350 million tons of ferrous metallurgy slag, 125 million tons of copper smelting slag and more than 200 million tons of nickel. Nowadays, copper smelting slag is increasingly considered as a resource of copper and its volumes accumulated in Russia can compete with the volume of mineral deposits that are put onto to the balance. The works on the adaptation of the parameters of the existing on the plants process to the technological features of copper slag flotation in order to maximize possible copper and related metals recovery in to concentrate or middling product are carried out. This allows solving part of the economic, environmental and social problems of city-forming enterprises of small industrial towns. Enrichment of copper smelting

slag by flotation is widely used in overseas plants. [10]

Analysis of disintegration methods applied in domestic and foreign schemes of ore preparation showed that during the destruction in the devices of centrifugal impact crushing the most selective release of the different strength phases of heterogeneous materials took place. The principle of destruction implemented in these devices was determined by L. I. Baron as the destruction of the free hit. [11]. Material accelerates on the surface of the rotating rotor and hits a reflective plates or a layer of the material in the crusher housing. The advantages of these crushers are the ability and ease of setting up the processing of new materials with different properties or the new size of the power [12].

The process of the materials destruction in a centrifugal impact crushers compared with the destruction of the material due to the shear stresses in the cone and jaw crushers has several other advantages: a high degree of mechanical activation of crushed material; high power density in the crushing area, which ensures a high degree of crushing; obtaining a more uniform grain size distribution of crushing products, which is practically independent of the working bodies wear; low power and metal consumption; low levels of capital and operating costs due to the absence of foundations of crushers and their ease of maintenance. This method of disintegration will provide intergranular destruction of copper smelting slag, the disclosure of complex mineral assemblages in the slag composition and higher rates of subsequent flotation of the techno-

genic materials.

The object of the study was CJSC “Karabashmed” copper smelting slag. According to aggregation state, copper smelting slags are pieces of solidified melt with fairly homogeneous composition of size  $-100 + 10\text{mm}$ . Slags contain an average of up to 1.5% of copper, 0.3 g/t of gold and 10 g/t of silver. For evaluation of the slag behavior under the influence of external loads, the study of the phase composition, structural and technological, physical and mechanical properties of the slag was carried out. Electron microscopic study of slag was performed using the scanning electron microscope Leo 1420 VP, qualitative elemental analysis of the samples was carried out with energy dispersive spectrometer INCA-300 set on the X-ray microscope. Morphostructural parameters of slag ore minerals (mass granular composition, form factor) were defined by optical-geometrical method using image analysis system SIAMS-600.

The strength properties of basic slag phases were evaluated by indicators of “microfragility” and “microhardness” determined by semiautomatic micro durometer PTM-3 [13]. Microhardness of the main phases of the investigated slag was determined by the method of the restored print after indentation of indenter, which has shape of four-sided pyramid with a square base (Vickers method) [14]. The fragility was evaluated according to the number of prints with cracks of the same type and to the nature of cracks. Total score of fragility was calculated using the following formula:

$$Z_p = 0 * n_0 + 1 * n_1 + 2 * n_2 + 3 * n_3 + 4 * n_4 + 5 * n_5, \quad (1)$$

Where 1–5 –score of fragility depending on the nature of the print ;  $n_0, n_1, n_2, \dots$  – number of prints with this score of fragility, respectively.

Analysis of slag release at the different methods of destruction was carried out by the number of free grains of ore minerals and their intergrowths with fayalite in the crushing products using industrial image analysis system SIAMS-600 and the automated analyzer of optical-mineralogical studies of rocks, ores and ore concentrates Mineral C7.

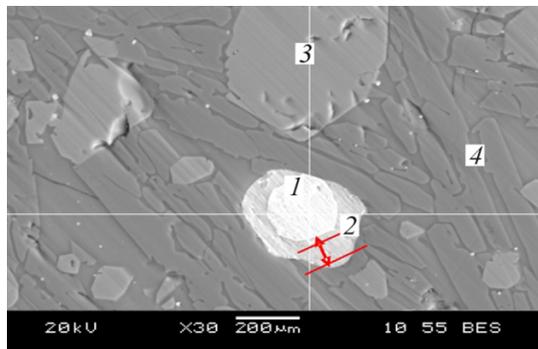
Flotation concentration of CJSC “Karabashmed” copper slag crushed in jaw and cone crushers using a centrifugal impact crusher DC-0.63 in the third stage of crushing was carried out for pilot and experimental evaluation of the proposed selective disintegration technology of slag. Flotation was performed according to the scheme of direct selective flotation in a laboratory flotation machine of 3 dm<sup>3</sup> capacity using butyl potassium collector, foaming agent T-92 and lime as the medium regulator.

### The results of research

The mineral composition of slag as rocks includes mainly silicates and oxides. Specific features of the slag formation are different from the natural ores on material composition and properties, the presence of unusual technological phases, which are not found in nature. [15] In turn, basicity factor depends on the phase of the slag composition. The conditions of formation, as well as their rate of cooling influence on the specifics of the mineral composition of slag.

The improvement of experimental technique and the introduction of innovative technologies of studying technogenic materials using a scanning electron microscope have allowed diagnosing basic slag phases. It was found that the smelter slags of CJSC “Karabashmed” are formed in  $2\text{FeO} \cdot \text{SiO}_2$ , the structure of which may include isomorphic zinc. Also in the slag, forming matrix zinc silicate ( $\text{Zn}_2\text{SiO}_4$ ) is identified. Copper is present in the form of native copper and copper sulfide minerals (chalcopyrite  $\text{CuFeS}_2$ , bornite

$\text{Cu}_3\text{FeS}_4$ ). Native copper has a shape, release size is 200 microns in diameter, the granite edges are often observed around. Stake of sulfide minerals falls to 20% of copper from the total amount of metal in the slag. They are present in the form of rounded grains of 1 micron or less (Fig. 1).



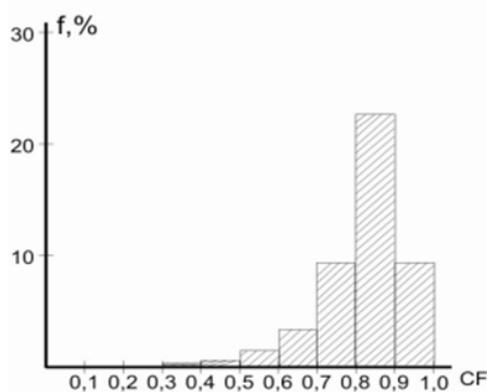
**Figure 1.** The microphotographs and phase composition of copper slag of CJSC “Karabashmed”: 1 - metallic copper; 2 - zinc spinel  $\text{ZnO} \cdot \text{Al}_2\text{O}_3$ ; 3 - matrix – fayalite  $\text{FeO} \cdot \text{SiO}_2$  with impurities  $2\text{ZnO} \cdot \text{SiO}_2$ ; 4 - wustite  $\text{FeO}$  with impurities Zn, Cr, Al

Study of the phase composition showed that slag was formed in the main by silicate and aluminosilicate phases. The copper smelting slag matrix was presented by ferrous olivine – fayalite. A distinctive feature of

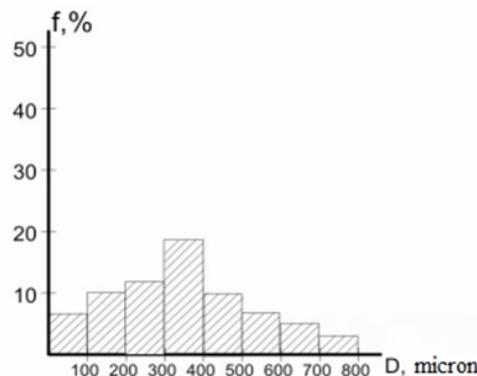
non-ferrous metals slag recycling is the presence of eutectic structures and the presence of granite, which formation mechanism is not clear. Availability of individualized ore phases with clear boundaries favorably affects their release from the slag forming matrix during the disintegration.

In the study of morphostructural parameters of ore minerals of slag by optic-geometrical method (Fig. 2), it was established that the inclusion of metallic copper have form factor 0.92 close to unity indicating an isometric (round) shape of the ore release with clear smooth boundaries [15].

Therefore, when the destruction of slag in the centrifugal impact the destruction of prismatic and needle fayalite grains, iron-magnesium oxide and irregularly shaped grains of melilite will take place firstly and destruction of metallic impurities will have only shear nature. The average size (mass granular composition) of ore phases is 352 microns. In centrifugal impact crushing devices, there is selective destruction of the material components having a different impact resistance – hardness and fragility. The significant differences in microhardness and microfragility of basic slag phases were established when studying the physical and mechanical properties of the basic slag phases (Table 1).



a)



b)

**Figure 2.** Morphostructural parameters of slag: a– form factor of ore minerals  $CF = 0.92$ ; b– size distribution of ore minerals  $D_{av} = 352$  micron

**Table 1.** Microhardness and microfragility of basic slag phases

Slag type	Phases	Total score of fragility	Microhardness, $\text{kg/mm}^2$
Copper slag of CJSC "Karabashmed"	metallic copper	19	148
	fayalite with impurities $2\text{ZnO} \cdot \text{SiO}_2$	35	293
	zinc spinel	102	754
	wustite with impurities Zn, Cr, Al	39	265

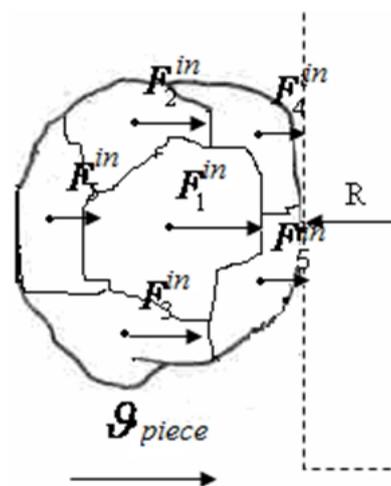
The value of the microhardness of silicate matrix of the test slag is significantly higher than microhardness of metal inclusions. Reduced microhardness of fayalite occurring in CJSC “Karabashmed” slags, which amounted to 293 kg/mm<sup>2</sup> is due to long-term presence of this slag in dumps, related hypergenesis processes and the presence of ZnO in its composition. The microhardness was 265 kg/mm<sup>2</sup>, which is also due to technogenic peculiarities of the composition of this mineral.

The least fragile ore phase is a metallic phase of the slag, which total score of fragility was 19, slag phases minerals have high fragility (the total score of fragility is 35). Metals have greater plastic deformation zone prior destruction compared with the slag phase and are not prone to fragile destruction. The most fragility in the investigated slags have those phases, which total score of fragility is in the range of 100 - 106. Thus, the edges in slags have not only a lower hardness, but also susceptibility to fragile destruction. The structural heterogeneity of metallurgical slag, the differences of grains shapes and sizes of ore minerals and silicate matrix, the presence of structures of substitution in the form of edges, and the difference in hardness and fragility of the individual slag phases create the preconditions for the stress concentration, the conditions for the emergence and development of cracks under impact loading implemented in devices of centrifugal impact crushing. The destruction of the material piece with the free hit will occur more selectively along the planes of phases fusion with the guidance of a wide network of microcracks.

As a criterion of selectivity of the slag disintegration in the devices of centrifugal impact crushing, it has been proposed to use a ratio of microhardness of the silicate phase  $H_m$  and slag metallic inclusions  $H_{in}$ . Theoretical analysis has shown that when  $H_m / H_{in} > 0.83$ , inter granular destruction of the mineral phases along the boundaries of their fusion is provided [16]. For CJSC “Karabashmed”, slag ratio of matrix microhardness and metal inclusions was 5.09, which is significantly more than the set limit value of 0.83 and indicates the possibility of selective destruction of slag in the devices of centrifugal impact crushing along the boundaries of the grains fusion of metallic inclusions and silicate matrix.

The process of disintegration of the materials in the devices of centrifugal impact crushing is determined by the nature of the force interaction of the piece and impact plates. It is necessary to take into account the heterogeneity of the structure and mechanical properties within each piece. The data obtained on the phase composition, physical and mechanical pro-

perties and structural parameters of slag allowed us to present slag piece as a set of fragments having a different density, size, and form factors, physical and mechanical properties. When crushing in a centrifugal impact crushers slag is fed through the drawbell to a separation accelerator cone and spread evenly over the channels of the accelerator. After receiving the required peripheral speed for discharging a piece with a high velocity is directed to impingement surface of the crushing chamber and, it is crushed as a result of a free kick. The crushed product is showered on special chutes down to the crusher for unloading of the finished product (Fig. 3).



**Figure 3.** Scheme of slag piece loading to the chamber of centrifugal impact crusher (designations in text)

In a piece of material, the distributed forces of inertia are occurred due to its sharp deceleration on the plate and directed along the vector velocities in the final phase of the movement. We believe that the velocity vector is perpendicular to the surface of the plate. Considering the significant difference of constituting piece fragments densities, the force of inertia should represent a set of elementary inertia forces applied to masses of isolated fragments centers. The value of the elementary forces of inertia is defined by the following formula:

$$F_i^{in} = V_i \cdot \rho_i \cdot a_{st}, \quad (2)$$

where  $V_i$  – fragment volume, m<sup>3</sup>;  $\rho_i$  – density, kg/m<sup>3</sup>;  $a_{st}$  – acceleration at deceleration, m/s<sup>2</sup>.

Thus, the greater the differences in density and volume of the individual phases in a rupturable material, the greater the difference of inertia forces generated in the phases. In CJSC “Karabashmed” copper slag density of copper inclusions is 8.3 kg/m<sup>3</sup>, and fayalite – 4.39 kg/m<sup>3</sup>. The dimensions of the metallic grains and fayalite grains are 352 and 200 microns, respectively. This difference of magnitudes of inertia

forces and the distributed nature of these forces contribute to the fact that in the process of centrifugal impact crushing as normal stresses due to compression  $\sigma_c$ , and normal stresses caused by bending  $\sigma_b$ , the intensity of latter exceeds  $\sigma_c$  are occurred in a piece of slag. Stresses zone widens considerably compared to the local loading. Such a scheme of loading a piece in a crusher of impact action provides a breakdown of the material along the boundaries of grains fusion at lower values of acceleration and, consequently, lower energy costs allowing disclose the metallic inclusions fusions even at crushing stage.

Character of fracture of smelter slags in inertial devices will also be determined as well as the geometry of the individual phases of grains [17]. In the studied copper smelting slags, it has been found that ore minerals, in particular, metallic copper inclusions have the form factor close to unity (0.7-0.92) indicating an isometric (round) shape of the ore discharge with clear even boundaries. Consequently, in the centrifugal impact devices, the destruction of prismatic and needle fayalite grains, iron-magnesium oxide grains and irregularly shaped melilite will occur firstly, while destruction of metallic impurities will be only

of the shear nature.

To determine the mutual influence of the design parameters of the device and technological properties of crushed material, a mathematical model of motion of the piece of material in the working space of centrifugal-impact device was considered [18].

$$v = 3,19 \cdot \sigma_c^{5/6} \sqrt[3]{\frac{(1-\mu^2)}{E}} \cdot \sqrt{\frac{3}{4\pi\rho}}, \quad (3)$$

where  $v$  – linear velocity of the piece at the escape from the crusher accelerator, m/s,  $\sigma_c$  – compressive strength limit, Pa;  $E$  – modulus of elasticity of crushed material, Pa;  $\mu$  – Poisson's ratio;  $\rho$  – density of material, kg /m<sup>3</sup>, 3.19 – empirical coefficient.

The release of CJSC “Karabashmed” copper slag crushed to a particle size less than 5 mm in a laboratory jaw crusher and centrifugal impact crusher DTs - 0.63 was studied. The finest product was obtained by crushing the slag in DTs crusher at an accelerator rotational speed of 90 m/s. The nominal grain size of the crushed product was 3.5 mm at the output of the size less than 0.071 mm 10.5%. Contents of floating grain size of less than 0.074 mm in a jaw crusher product was only 4.42% (Table 2).

**Table 2.** Copper slag release

Crushing product	Grain size class, mm	Yeild%	Mass fraction Cu, %	Extraction Cu, %	Copper, %		Sulphides, %	
					Free grains	Fusions	Free grains	Fusions
Jaw crusher $\beta_{-0.071}=4.42\%$	+0.56	81.84	6.76	84.30	0.45	9.11	0.26	6.88
	+0.28	5.43	7.39	6.11	0.49	11.64	0.67	4.96
	+0.14	6.45	6.25	6.14	0.87	8.75	0.59	3.13
	+0.1	0.30	6.33	0.29	2.30	6.93	0.85	1.32
	+0.071	1.56	5.44	1.29	6.06	3.15	3.22	0.66
	+0.045	2.03	3.17	0.98	8.73	1.58	2.78	0.51
	-0.045	2.39	2.42	0.88	11.70	0.64	1.64	0.13
	Total:	100	6.56	100.00	30.60	41.80	10.01	17.59
DTs, 90 m/s $\beta_{-0.071}=10.5\%$	+0.56	58.9	6.26	56.15	0.38	5.87	0.26	6.77
	+0.28	12.70	6.94	13.42	0.42	9.13	0.54	3.08
	+0.14	14.20	6.68	14.45	0.55	8.65	0.53	1.69
	+0.1	0.60	7.11	0.65	4.78	5.65	1.75	0.76
	+0.071	3.10	7.34	3.47	9.09	2.57	4.02	0.54
	+0.045	4.70	7.48	5.35	11.67	1.49	2.44	0.21
	-0.045	5.80	7.37	6.51	14.13	0.14	2.78	0.11
	Total:	100	6.57	100.00	41.02	33.50	12.32	13.16

Mineralogical analysis has shown that the release of grains of copper slag components is higher at crushing in devices of centrifugal impact crusher in comparison with a jaw crusher. The content of free grains of metallic copper at crushing the slag in DTs crusher at a speed of rotation of the accelerator of 90 m/s

is 41.02%, that is significantly higher than the content of grains in the jaw crusher product – 30.6%. The total amount of the released grains of metallic copper and copper sulfides at copper slag disintegration in DTs devices was 53.34%, while at the conventional process of ore preparation it was 40.61%.

When centrifugal impact crushing at the same time with accumulation of fine floating grain size class of less than 0.071 mm, its enrichment with copper-containing grains takes place. Extraction of copper in this class increased from 1.86% at crushing in a jaw crusher to 11.86% at DTs crushing, the number of released free grains of metallic copper and copper sulphides in this class increased from 24.85 to 30.24%. It allowed recommending the use of centrifugal-impact crushers in the ore preparation schemes of copper slag in order to increase the number of released grains of the valuable components prior to subsequent flotation concentration, as well as for the transfer of part of the work on grinding to crushing and thereby reducing the amount of energy expended. For the processing of copper slag, it is recommended to carry out a third step of crushing in a centrifugal impact crusher DTs-1.6.

Flotation is the main method of additional recovery

of copper when involving in the recycling the stale slag from the dumps. The flotation concentration of CJSC “Karabashmed” copper slag crushed in jaw and cone crushers and using DTs-0.63 in the third stage of crushing was carried out. Technological scheme for processing copper slag included the following operations: crushing, classification, grinding, copper head, regrinding, basic copper flotation. Technological parameters of the slag flotation, which ore preparation consisted in selective disintegration in centrifugal impact crusher, were higher than those obtained during the processing of slag crushed using conventional crushers. Mass fraction of copper in copper concentrate amounted to 27.04%, at recovery of 96.27% (mass fraction of copper in the initial slag was 6.35%). When the concentration of slag prepared for flotation in a standard way, the mass fraction of copper in copper concentrate did not exceed 21.58% at copper recovery of 76.86% (Table. 3).

**Table 3.** Results of copper slag flotation

Variants of ore preparation	Product	Yield, %	Mass fraction of copper, %	Copper extraction, %
Crushing in a jaw crusher	concentrate	22.62	21.58	76.86
	tailings	77.38	1.90	23.14
Crushing in DTs, accelerator rotation speed of 50 m/s	concentrate	22.90	24.62	88.80
	tailings	77.10	0.92	11.20
Crushing in DTs, accelerator rotation speed of 70 m/s	concentrate	22.34	25.72	90.49
	tailings	77.66	0.78	9.51
Crushing in DTs, accelerator rotation speed of 90 m/s	concentrate	22.61	27.04	96.27
	tailings	77.39	0.31	3.73

Thus, at increase in the centrifugal crusher accelerator rotational speed, the quality of the obtained copper concentrate is improved and the extraction of copper in concentrate increases. The best technological parameters of copper slag flotation are achieved when the rotation speed of the accelerator crusher of 90 m/s.

### Conclusion

The theoretical study and pilot and experimental verification showed that the use of intergranular fracture in the processing schemes of structurally inhomogeneous raw materials of technogenic origin (metallurgical slag) is promising. Based on the data obtained on the phase composition, structural heterogeneity of copper smelting slag, the presence of structures of substitution in the form of edges at the periphery of the ore inclusions grains, a significant difference in the hardness and friability of the indivi-

dual phases of slag, it is concluded that it is possible to release slag intergranularly in devices of centrifugal impact crushing.

The use of the proposed technology for recycling of ash slags in the conditions of the Krivoy Rog TPP will allow obtaining commercial products in the form of scrap metal (50 - 70 thousand tons /year), ensure environmental safety in the location of the ash slag dump area, reduce environment pollution and payments for damage caused as a result of the plant operation and save the capital cost of construction (extension) of the dump and energy resources spent on hydraulic transport of ash slags and water clarification returned to the working cycle of TPP.

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