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Technology of extraction of platinum metals from the wastes of fire-clay lining of glass-melting apparatuses

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Extraction of platinum group metals from the wastes of fire-clay lining of glass-melting apparatuses is carried out using the pyrohydrometallurgical processes, which have a long production cycle and exclude the possibility of waste recycling at waste-forming enterprises. There are known the flotation and gravitational methods of waste treatment. However, the degree of platinum group metals extraction does not exceed 80% at low content in concentrate and significant content in tailings (up to 0.1%). Physical and chemical composition of fire-clay lining, and size and occurrence forms of platinum group metals, were researched for development of resource-saving technology of recycling of fire-clay mass with short production cycle. Concentration of platinum group metals was carried out, using a centrifugal concentrator TsVK-100-2M (ЦВК-100-2М). There were obtained the data on the concentrate yield, according to the L:S ratio, with different size of raw materials' particles. Determination of platinum metals content in tailings was carried out by method of assay and spectral analysis of representative samples. The sampling of wastes was carried out by mechanical pipe sampler. There was developed the technology of concentrating of fire-clay lining wastes with extraction of up to 90% of platinum group metals. The content of platinum group metals in tailings made up 0.04%. The proposed technology can be implemented at the enterprises, which operate the glass-melting apparatuses, or at the regional centers of recycling of scrap and wastes, containing precious metals. Physical and chemical composition of molds and tailings has a high degree of uniformity and guarantees the average sampling possibility.

***Key words*:** platinum metals, wastes, fire-clay lining, glass-melting apparatus, centrifugal concentrator, waste sampling, mechanic pipe sampler, extraction, average sample.

The total content of platinum group metals in fire-clay lining of glass-melting apparatuses is 0.20–0.60%. Traditionally, such wastes are recycled using the pyrohydrometallurgical processes, which have a long production cycle and exclude the possibility of waste treatment at waste-forming enterprises. Because of the heterogeneous physical and chemical composition and high concentration of platinum group metals, original form of wastes sampling causes a significant error in determination of precious metals content in the batch.

The physical and chemical composition of fire-clay lining was researched for the purpose of clarification of the possibility of extraction of platinum group metals from fire-clay lining wastes by the resource-saving methods, which do not require large financial investments. At the same time, there were used the methods of X-ray and atomic emission spectral analysis. The size and occurrence forms of platinum group metals were researched, using a microscope. It is found that the size of platinum metals' particles is 5–100 μm, and their basic amount is aggregated with glass melt and fire-clay (size is 50–500 μm). 20% of platinum group metals from the total content are in the free form, and the grain size is 25–250 μm. Spherical and platelet shapes of free particles of platinum group metals are defined. The density of platinum group metals' particles and fire-clay mass is estimated at 15–18 and 3–4 g/cm^3, respectively. The material is prone to segregation.

On the basis of obtained results, the gravity treatment method was selected for the recycling. There was established the efficiency of vibration type equipment, where the segregation separation of material is realized [1–3]. The closed circulating flows are used during the concentration of finely dispersed particles [4]. The researches were carried out on the segregation type centrifugal vibration concentrator TsVK-100-2M (ЦВК-100-2М) [7], taking into account the previously published data of comparative tests on the concentration of precious metals on various concentrators [5, 6]. The process flow diagram with the projected production capacity of 25–35 kg of wastes per hour included the following equipment: vibratory screen Gr-50 (ГР-50); cone crusher VKMD-10 (ВКМД-10); jaw crusher ShchD-6 (ЩД-6) ("Vibrotekhnik" ("Вибротехник")); pump FGP 3/5 (ФГП 3/5); vibratory mill VM-50 (ВМ-50); electric drive with stirring device; screw lock ShV-350 (ШВ-350); prospecting pan "Gold pan" for the treatment operation quality control; muffle furnace SNOL (СНОЛ); induction furnace ISV (ИСВ); centrifugal vibration concentrator TsVK-100-2M [8]. The closed water rotation was maintained. The occupied area is up to 50 m^2.

For the purpose of determination of optimal conditions of platinum group metals extraction, there was carried out the treatment of fire-clay mass with different grain-size fractions and L:S ratio in concentrator feed.

Table 1 shows the data on the platinum group metals concentrate yield depending on the L:S ratio in feed for the grain-size fraction of –1.6+0.5 mm. It is found that stable concentration conditions for this type of wastes is reached at the ratio of L:S = 6(8):1 in the feed. With the ratio of L:S = = 4:1, the volume of the heavy fraction's concentration zone was significantly reduced and the number of particles of platinum group metals, washed out from the concentrate by the stream, was increased.

Increasing of the ratio to 10:1 and more led to unstable concentration conditions:

Table 1

Results of treatment of fire-clay lining with the size of –1.6+0.5 mm

Batch of fire-clay mass, kg	Concentration mode (L:S)	Yield of platinum group metals concentrate, %
180.56	5:1	2.51
310.84	8:1	1.20
191.76	10:1	1.03

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Table 2
Results of extraction of platinum group metals from experimental batches of fire-clay lining wastes with the ratio of L:S = 8:1 in feed

Weight of recycled batch, kg	Content of platinum group metals in waste, %	Grain-size fraction, mm	Amount of platinum group metals, extracted from the concentrate into the mold of the alloy, containing 98% of platinum group metals, g*	Degree of platinum group metals extraction, %	Content of platinum group metals in tailings, %
77.70	0.42	–1.6+0.5	290.77	89.10	0.0459
77.70	0.42	– 0.8+0.5	293.38	89.90	0.0426
77.70	0.42	–0.5+0.2	294.06	90.11	0.0417
77.70	0.42	–0.2	287.50	88.10	0.0501

*Three-stage treatment without the tailings regrinding.

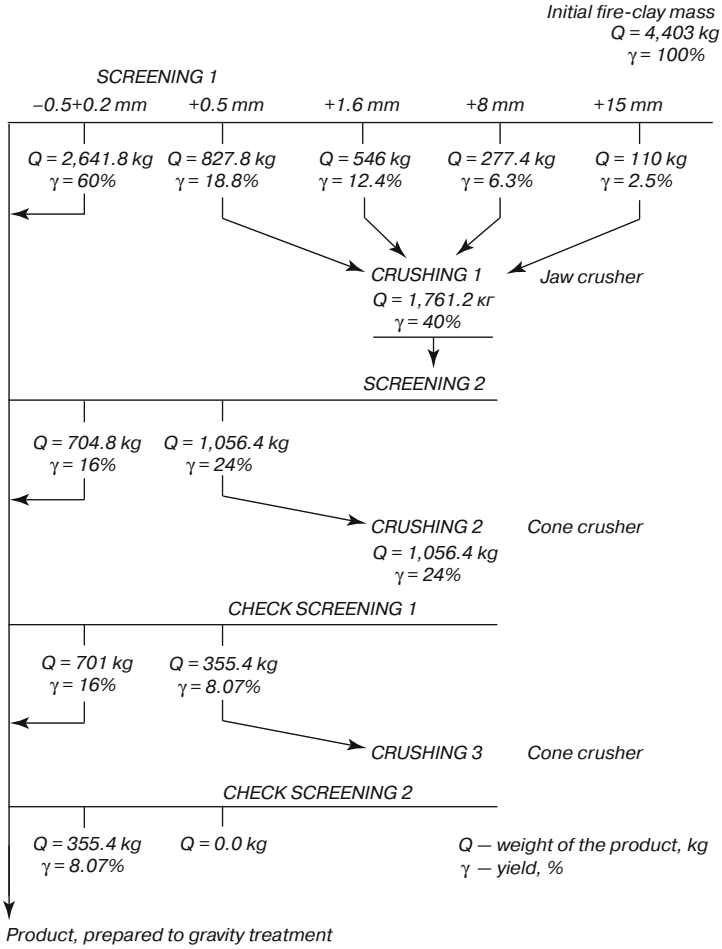

Fig. 1. Scheme of preparation of fire-clay lining wastes to treatment

– the vibration frequency of the bowl was changed spontaneously and temporarily;

– timely removal of the liquid phase from the bowl was not maintained;

– a special mode of the feed and wash water supply was required for the purpose of avoiding of the concentrate outflow from the bowl riffles in the time of stopping.

Table 2 shows the results of the platinum group metals extraction from experimental batches of different-sized fire-clay mass. The maximum degree of platinum group metals extraction was observed at the ratio of L:S = 8:1 in the feed and the size of –0.5±0.2 mm. With the size of –0.2mm, the platinum group metals extraction is minimal and may be connected with particles' overgrinding. The scheme of preparation of the waste batch to gravity treatment is shown in the Fig. 1. The products of screening with the size of +15; +8; +1,6 mm were crushed separately (crushing 1), because, depending on the the physical and chemical composition (the ratio of glass melt and fire clay), each fraction required a different number of crushing stages. Determination of platinum group metals content was carried out by assay and spectral analysis of laboratory samples. The representative sampling was carried out by mechanic pipe sampler Sicon PT-75.

There were established the following parameters of stable technological mode of fire-clay mass concentration:

– L:S ratio = 1:6–1:8;

– the solids feed rate = 36 kg/h;

– the allowable weight load on the funnel = up to 60 g;

– the vibration frequency of the funnel = 9–10 vibrations per one turn of the mechanism shaft.

With maximal fire-clay production capacity of 36 kg of raw material per hour, the units have the following operating life: 4 t of raw materials for funnel; 3.5 t of raw materials for rubber riffle-liner; 3.5 t of raw materials for the shaft and hub, generating the vibration. All works on the platinum group metals concentration were carried out in the circulation concentration mode [6]. The water and slurry transport was carried out by the pump FGP 3/5 (ФГП 3/5). Three stages concentrates, obtained on the centrifugal vibration concentrator, were additionally concentrated on the prospecting pan "Gold pan" and were treated with bromoform. The obtained concentrate was treated with hydrochloric and hydrofluoric acids in a sequential order, which made it possible to reduce the content of iron and glass melt to 1%. The parameters of the fire-clay lining wastes treatment, using the concentrator TsVK-100-2M, are shown in the Fig. 2. Results of upgrading of metal content in the platinum group metals' concentrates, obtained on the concentrator TsVK-100-2M, are given in the Table 3 together with the results of extraction of platinum group metals into the mold.

New design of concentrator's feed pan was developed and tested for the purpose of avoiding of operations of upgrading of concentrate's metal content on the pan and bromoform treatment. At the same time, the sizes of pan were increased with guaranteeing of possibility of its movement in vertical direction for the purpose of intensification of the fractions separating process.

The following conditions were selected:

– the pan slope angle is 25–40°;

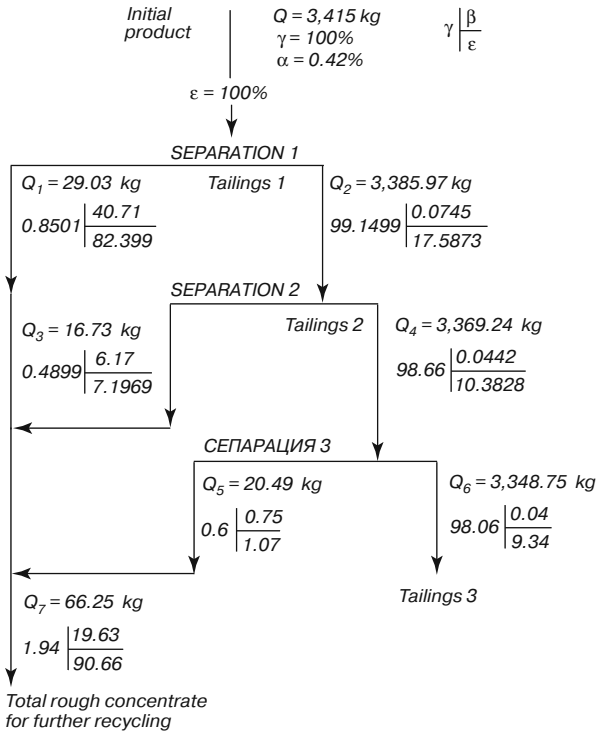

Fig. 2. Treatment of fire-clay lining wastes on the concentrator TsVK-100-2M:
Q – product weight, kg; γ – yield, %; α – content of valuable components in initial product, %; β – content of valuable components in separation products, %; ε – extraction of valuable component into the product, %

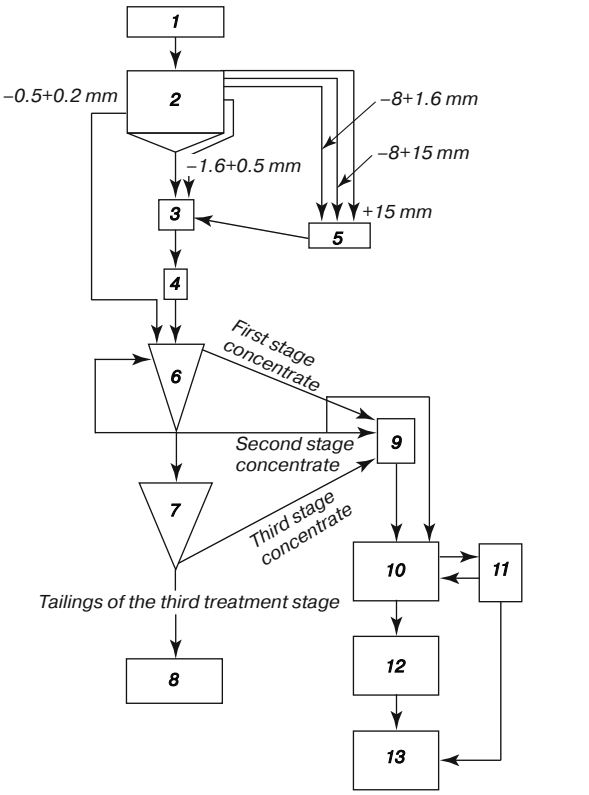

Fig. 3. Process flow diagram of platinum group metals extraction from the fire-clay lining wastes:
1 – ball pulverizer mill; *2* – vibratory screen; *3* – jaw crusher; *4* – vibro-conical mill; *5* – rolling crusher; *6* – concentrator TsVK-100-2M; *7* – Knelson separator KC-MD3; *8* – site for preparation of tailings for recycling at metallurgical enterprise; *9* – unit of concentrate etching in hydrochloric and hydrofluoric acid solutions and upgrading of metal content in the concentrate on the pan; *10* – muffle furnace; *11* – press; *12* – induction furnace (graphite crucible); *13* – induction furnace (electroalumina crucible)

– the wash water supply through the 8 mm nozzle with the laminar flow, reflected from the far wall of the pan, is up to 3 l/min;

– flow layer height is 5–10 mm.

Under the influence of vibration of the operating concentrator, during the manually shaking of pan, there was isolated the fraction with the content of platinum group metals of up to 70%. At the same time, with application of old design of pan, there was isolated the fraction with the content of platinum group metals of up to 40.7% (Table 3).

The consecutive recycling of tailings at the second and third concentration stages on the centrifugal vibration concentrator and then on the Knelson separator KC-MD3 was applied for the purpose of increasing of production capacity and extraction degree of platinum group metals [7, 8]. The process flow diagram of extraction of platinum group metals from the fire-clay lining wastes is given in the Fig. 3. In comparison with three stages of waste treatment, using the concentrator TsVK-100-2M, there was reached the growth of production capacity by 40%. At the same time, the degree of platinum group metals extraction was increased and made up 91% in average (Table 4). Content of platinum group metals in the tailings was decreased to 340 g/t. Melting of platinum group metals concentrate was carried out in an induction furnace ISV-0,01 (ИСВ-0,01) in argon medium. The platinum group metals concentrate was preliminary annealed in a muffle furnace at 1,100 °C in reducing atmosphere. The annealed concentrate was compressed in a pressing tool at the 50 tons force with following re-annealing and melting in graphite crucible under a shielding atmosphere. Obtained platinum group metals alloy was used as a fuse with smelting of the bulk of platinum group metals concentrate in electroalumina crucible. The first treatment stage is implemented in the concentrator TsVK-100-2M (6). The second treatment

Table 3
Results of upgrading of metal content in the concentrates, obtained during the gravity concentration of the samples of fire-clay grit wastes with the weight of 3,415 kg (for the data – refer to the Fig. 2)

Treatment stage	Content of platinum group metals in the concentrate of centrifugal vibration concentrator, %	Content of platinum group metals, %		Extraction into the mold, containing 98% of platinum group metals, %
		Upgrading of metal content in the concentrate of centrifugal vibration concentrator on the pan	Upgrading of metal content in bromoform	
1	40.71	72.2/0.20	89.7/0.44	98/0.09
2	6.17	43.10/ 0.014	90.0/ 0.005	98.00/0.102
3	0.75	6.448/0.004	90.00/0.0019	98/0.1

Note. The numerator shows the concentrate data, and the denominator shows the tailings data.

Table 4
Distribution of platinum group metals in the treatment products of the wastes sample of fire-clay lining of glass-melting apparatuses

Product	Weight, g	Content of platinum group metals	
		%	g
Initial sample	3,415,000.00	0.4200	14,343.00
Tailings of treatment on the concentrator TsVK-100-2M	3,348,750.00	0.0400	1,339.50
Tailings of upgrading of metal content on the pan of the first treatment stage concentrate	12,696.50	0.2000	25.39
Tailings of upgrading of metal content on the pan of the second treatment stage concentrate	14,339.60	0.0140	1.98
Tailings of upgrading of metal content on the pan of the third treatment stage concentrate	18,117.91	0.0040	0.72
The bromoforming tailings of the first treatment stage concentrate	3,202.30	0.4400	14.09
The bromoforming tailings of the second treatment stage concentrate	1,245.73	0.0050	0.062
The bromoforming tailings of the third treatment stage concentrate	2,202.19	0.0019	0.04
Melt slags of the first treatment stage concentrate	1,113.20	0.0939	1.05
Melt slags of the second treatment stage concentrate	93.54	0.1022	0.10
Melt slags of the third treatment stage concentrate	16.99	0.1000	0.02
Mold of the first treatment stage concentrate	12,018	98.0000	11,777.64
Mold of the second treatment stage concentrate	1,051.13	98.0000	1,030.11
Mold of the third treatment stage concentrate	152.91	98.0000	149.85
Total	3,415,000.00		14,340.55*
Degree of extraction of platinum group metals into the mold	90.34%		
* The discrepancy of 2.45 g of platinum group metals (0.017%) is caused by the measurement uncertainty.			

stage is confined in re-delivery of the first treatment stage tailings to the concentrator TsVK-100-2M (6). Concentrates of the first and second stages undergo the metal content upgrading separately (9–13). The third treatment stage is confined in the delivery of the tailings of the second treatment stage for platinum group metals concentration to the Knelson separator (7). Use of the unit of concentrate etching in hydrochloric and hydrofluoric acid solutions and upgrading of metal content in the concentrate on the pan (9) facilitates the obtainment of the platinum group metals alloy, which is subsequently used as a seed in melting of the bulk of annealed and pressed concentrate.

Conclusions

1. High indices of extraction of platinum group metals into the gravity concentrate were obtained during the treatment of the waste of fire-clay lining of glass-melting apparatus. Subsequent upgrading of metal content in gravity concentrate guarantees the alloy mold with 98% of platinum group metals content with extraction of 91%.

2. Concentrator TsVK-100-2M enables the possibility of platinum group metals concentration from the batches of fire-clay lining waste with a reproducible result of treatment. Content of platinum group metals in obtained concentrates can reach 70%.

3. Gravity treatment of waste of fire-clay lining of glass-melting apparatus can be implemented at the enterprises, which exploit the glass-melting apparatuses, in the regional centers of recycling of precious metals containing scrap and wastes. The tailings with 340–400 g/t of platinum group metals, formed during the treatment, can be profitably recycled at metallurgical enterprises.

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