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TO THE QUESTION OF PURIFICATION OF ALUMINUM-CONTAINING WASTE OF ALUMINUM ELECTROLYSERS*

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Abstract

At the enterprises for the production of aluminum, equipped with electrolyzers with self-baking anodes, during technological operations for the maintenance of baths and adjusting the chemical composition of the electrolyte, alumina and fluoride salts spill out through the ventilation grilles to the "zero" marks of the potrooms. As a result, an alumina-containing estimate of a complex variable composition is formed, containing a significant amount of valuable components - Na3AlF6, Al2O3, AlF3. In the process of sweepings collecting the estimate particles of valuable alumina turn out to be mixed with various materials (pieces of asphalt and concrete, sand), which leads to contamination of raw materials with iron and silicon-containing compounds (SiO2, Fe2O3) and makes it impossible to return it to the electrolysis process. This article is devoted to the issue of creating a technological scheme for processing alumina-containing estimates to reduce the content of SiO2, Fe2O3 impurities. According to the results of studying the phase composition of the samples, it was found that the estimate mainly consists of cryolite, chiolite, corundum, quartz, feldspar, carbonaceous matter and the technogenic phase of the composition (NaF)·1,5CaF2·AlF3. Highest concentrations of Si (1,91 %) and Fe (0,62 %) were found in size class of -0,63+0,315 mm. On the basis of microscopic studies, the contrasting properties of the raw materials were established. The developed hardware and technological scheme of processing allows for the processing of alumina-containing estimate, which will provide a product yield in the amount of 90% with Fe2O3 content - up to 1% and SiO2 - 1.5%, which will improve the technical and economic performance of production.

Keywords: aluminum, electrolysis, ferrum, impurities, mineralogical study, sweepings, silicon

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1. Introduction

The production cycle of industrial enterprises is an unbalanced system, characterized by the formation of a large amount of waste of different aggregate states. The aluminum industry makes a significant contribution to environmental pollution, the waste of which is about 20% of all waste generated in the production of non-ferrous metals in the country (Burdonov and Zelinskaya, 2019; Petlin and Malyutin, 2014).

The main reason for the formation of a large amount of waste at Russian aluminum plants is the use of Soderberg technology (Belykh and Maksimova, 2018; Sanderson et al., 2005). Abroad, the transition to a progressive method of producing aluminum in electrolyzers with pre-baked anodes was practically completed. Along with higher technical and economic indicators, this technology is characterized by a greater environmental safety of production. This is due to the absence of a number of wastes typical for the technology of self-baking anodes, in particular, dust from electrostatic precipitators, gas cleaning sludge, flotation tailings. The amount of this type of waste is significantly reduced, such as a mechanical mixture of alumina and recycled electrolyte, called "dampings" or "sweepings", which wake up at the "zero" marks of the potrooms and are collected by industrial vacuum cleaner (IVC) (Mohamed et al., 2019; Tang et al., 2018).

As a rule, the collected alumina-containing estimate, the formation of which reaches 36,000 tons per year, only at the Bratsk aluminum plant, is sent to a sludge storage facility, or to temporary storage sites. In turn, the accumulations formed are a source of strong dusting, due to the presence in the estimate of a significant amount of finely dispersed fraction. Carrying out a fine fraction (-0.16 mm) has a negative impact on both human health and the state of environmental objects.

In addition, most of the listed waste contains valuable components, for example, Na_3AlF_6, Al_2O_3, AlF_3, which increases the relevance of their recycling (Vasyunina et al., 2019; Wang et al., 2017).

The development of the aluminum industry is directly related to innovative technologies aimed at processing secondary resources and man-made waste. Effective involvement of illiquid waste and industrial products in processing will increase the competitiveness and environmental safety of aluminum production.

The main goal of this study was to improve the environmental safety and efficiency of aluminum production through the reuse of the estimate.

To achieve this goal, the following tasks were solved:

- study of the composition of alumina-containing raw materials
- obtaining data on the distribution of components by size classes
- analysis and ensuring the possibility of using secondary alumina-containing raw materials in the electrolysis process by reducing the content of impurities, in particular iron and silicon oxides, to the recommended values.
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2. Materials and methods

As a material for the study, we used samples taken in the course of work from the territory of the electrolysis shops of PJSC RUSAL Bratsk from a mark of ± 0. Samples are a mixture of fine powder and lumpy material (Figs. 1-2).

In the process of studying the sample of alumina-containing estimate, the following research methods were used: granulometric analysis, optical emission spectroscopy, mineralogical studies, including powder X-ray diffraction, a complex of optical studies.

Fig.1. Finely dispersed sweepings from the territory of the electrolysis shop.

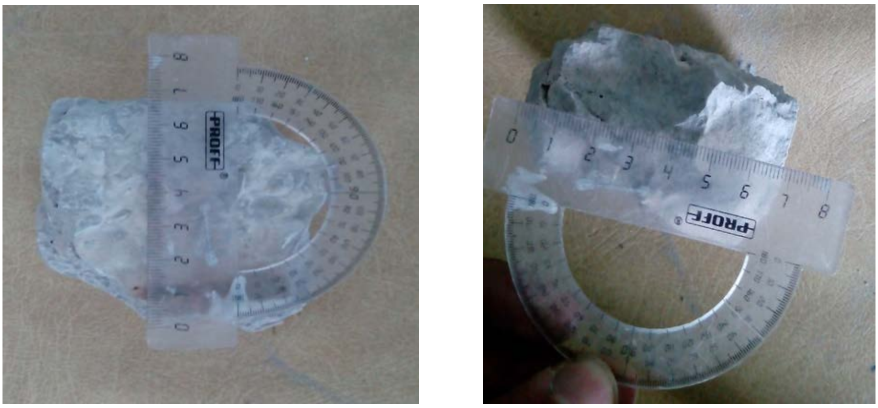


Fig. 2. Rough material of the test sample.

3. Results and discussion

Selected mainly in size - 2.5 mm (average 62.78% by weight) with the presence of large pieces of material ranging from 5.0 to 60 mm (average 20.26% by weight). Samples contain pieces of hardened aluminum ranging in size from 5.0 to 20 mm (average 16.96% by weight). Large pieces of material are found in a single quantity, represent a solidified melt of electrolyte, pieces of concrete, iron reinforcement and can reach sizes of several tens of centimeters.

Based on the granulometric analysis data, the largest yield for the size class -0.315 + 0.16 mm is 29.85% and the largest class of +2.5 mm is 37.22%.

For a more detailed understanding of the ratio of fine particles in the material, a sample of the -0.315 mm class was studied on a laser particle size analyzer Analysette 22 Nano Tecplus (Fritsch, Germany). The largest amount of material is presented by the size classes -0.045 + 0.025 mm and -0.1 + 0.045 mm.

The study of the chemical composition of the estimate was carried out in the laboratory of institute "TOMS", Irkutsk, on an optical emission spectrometer "VARIAN" 730-ES. The analysis was carried out in accordance with the methods NSAM 155-X, STO AC 3.001-2011, NSAM 478-XC, NSAM 130-C. The results of the analysis of the averaged samples are shown in Fig.3.

It was found that the largest amount of Al is concentrated in fractions -0.315 + 0.16 mm and 0.16 + 0 mm, which is 45.7% and 48.8%, respectively. The Al contents in other fractions are practically the same and vary from 15.9% (+5 mm) to 18.3% (-1.25 + 0.63

mm). The highest concentration of Si (1.91%) is contained in the fraction -0.63 + 0.315 mm. High concentrations were recorded in the size classes -2.5 + 1.25 mm (1.49%) and -1.25 + 0.63 mm (1.31%). The smallest content in the size class is -0.16 + 0 (0.252%). The highest Fe content in the size class is -1.25 + 0.63 mm (0.601%) and -0.63 + 0.315 mm (0.62%). The minimum Fe content is found in the +2.5 mm fraction (0.103%).

The results of studying the distribution of impurities (silicon in terms of SiO_2 and iron in terms of Fe_2O_3) by sample size classes are presented in Figs. 4-6. As noted above, the maximum silicon content (in terms of SiO_2 –4.146%) was recorded in the size class –0.63 + 0.315 mm, however, due to the small yield of this size class SiO_2 (3.18% by weight), its amount is only 8 , 9% of the total amount of SiO_2 in the material.

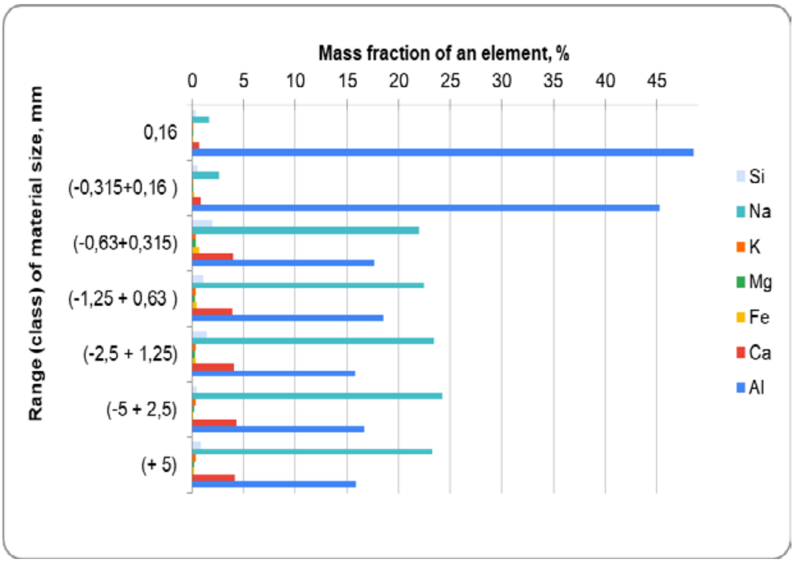


Fig. 3. Results of analytical studies of the sample estimate
* Elements Zn, Pb, Cu, Cr, Cd, Ti, Mn, P were recorded in insignificant amounts.

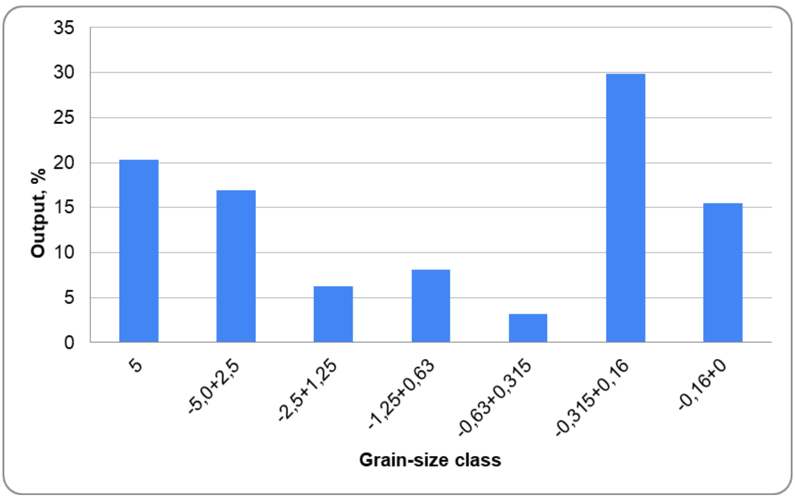


Fig. 4. Particle distribution by size class

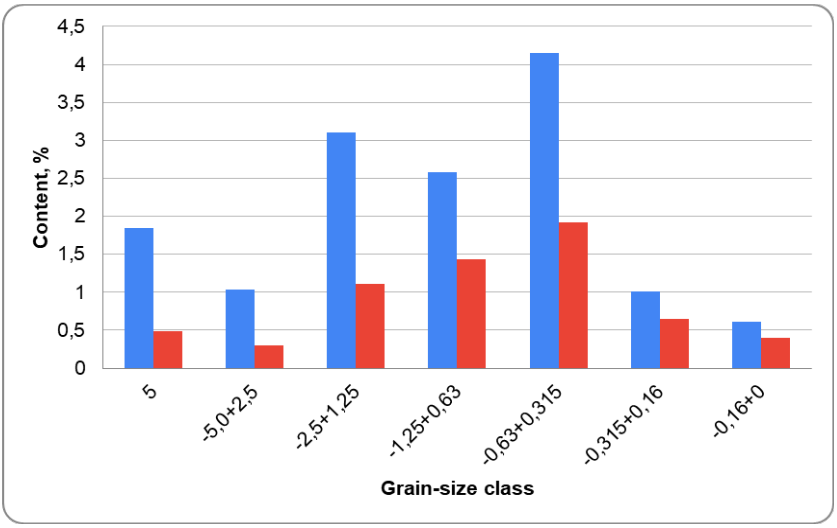


Fig. 5. Content of impurities in size classes of sweepings

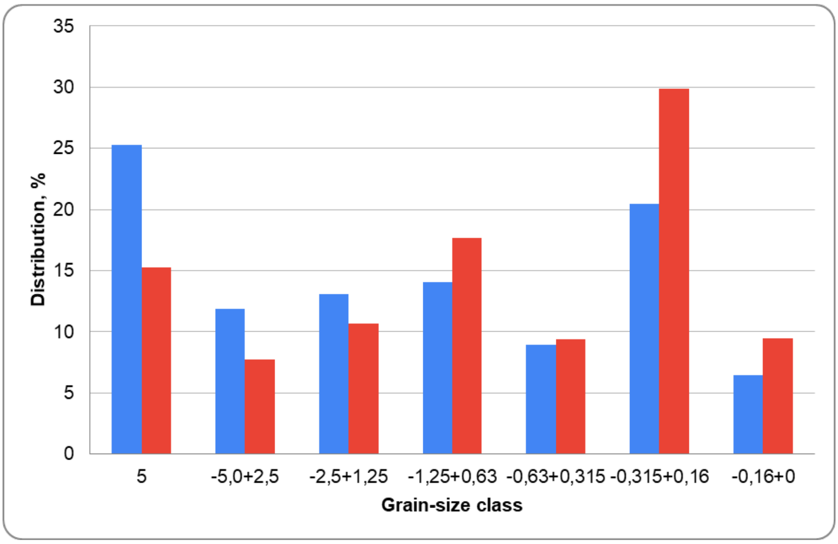


Fig. 6. Distribution of impurities by size class of sweepings

The minimum silicon content, as noted earlier, (in terms of SiO_2 - 0.617%) is in the -0.16 + 0 mm class and its amount is 6.4% of the total amount of SiO_2 in the material. The predominant fraction in the material is -0.315 + 0.16 mm (29.85% by weight). in which more than 20% SiO_2 is concentrated.

It has been established that the highest iron content (in terms of Fe_2O_3 –1.9%) is found in material with a particle size of –0.63 + 0.315 mm. But according to the distribution of Fe_2O_3, the predominant class is -0.315 + 0.16 mm (29.85% of the total). The minimum amount of iron is in the size class -5 +2.5 mm (7.7% by weight) with a content in terms of Fe_2O_3 - 0.297%.

Thus, for the possible return of the resulting technogenic raw materials into the technological process, it is not enough to separate the product (even with a preliminary reduction in the iron content) by size classes.

To achieve this goal and establish possible methods for separating raw materials, a search for contrasting properties of the studied alumina-containing estimate was carried out. In this connection, a complex of additional studies was carried out.

It was found that the sample of alumina-containing estimate consists of cryolite (Na_3AlF_6), chiolite ($Al_3F_{14}Na_5$), corundum (Al_2O_3). quartz (SiO_2), feldspar (Ca, Na) (Al, Si) $AlSi_2O_8$)), carbonaceous matter and the technogenic phase of the composition (NaF) · $1{,}5CaF_2 \cdot AlF_3$. Material in different size classes differs only in the phase ratio. Fig. 7 shows a diffractogram of one of the samples of alumina-containing sweepings.

It is not possible to reliably determine the quantitative ratio of minerals in each sample due to the heterogeneity of the material and the presence of an X-ray amorphous phase in all fractions in different amounts.

In this regard, each fraction was studied using a binocular microscope. There are two phases in the products: dark, black-gray and light, grayish-white. The light phase is represented mainly by spheres that differ only in size. Two mono-fractions were isolated from the products. For each of their fractions, the chemical composition is determined (table 3). The quantitative ratio in all products is dominated by the light gray phase (the ratio of fractions in the samples is 90: 10–95: 5).

It was established that precipitates of metallic aluminum are associated with light particles, which is also found in the form of free individuals. A detailed study of the structure of the particles revealed that they are aggregates of various types (Fig. 8):

- massive, homogeneous in texture and structural parameters;
- lumpy porous formations, represented by aggregates of smaller particles;
- technogenic conglomerates - mixed aggregates of the above types.

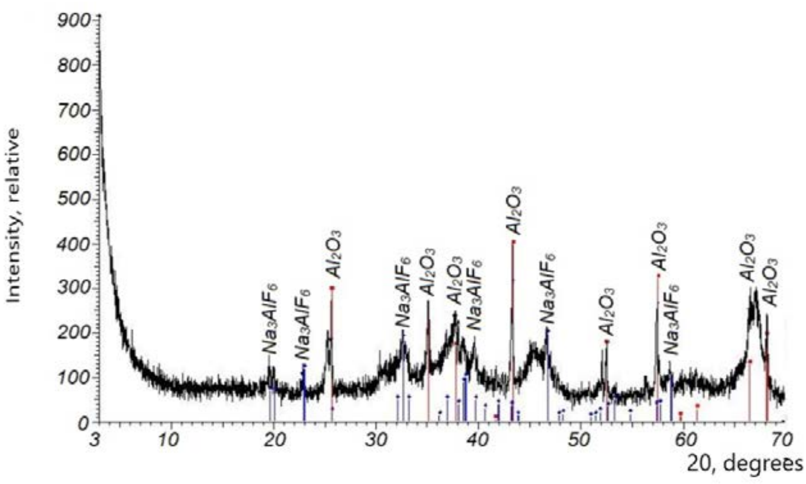


Fig. 7. Diffraction pattern of a sample of alumina-containing sweepings

Table 3. Chemical composition of the main mono-fractions

Element	*Mass fraction of an element, %*	
	Grayish-white mass	*Grayish-black mass*
Al_2O_3	27.8	15.7
CaO	5.85	4.07
$Fe_2O_{3\Sigma}$	0.179	3.62
SiO_2	1.06	31.0

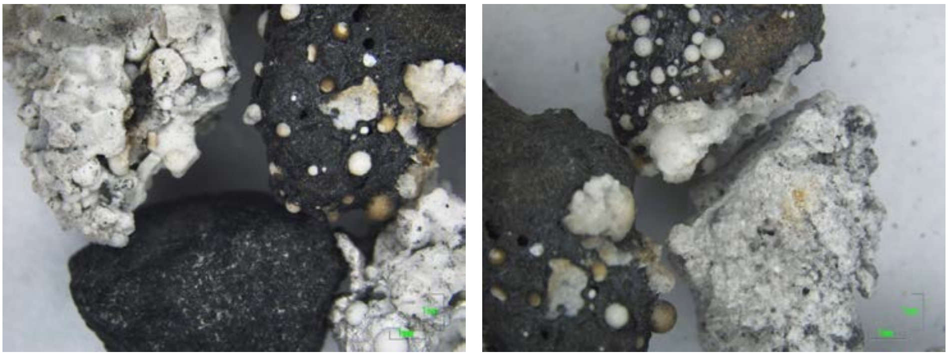


Fig. 8. Lumpy aggregates of mineral phases of various composition in coarse fraction sweepings of alumina

Optical studies of the average fraction of the estimate found that the composition of the bulk material contains the following morphological types of particles, which correlate with the phase composition of the aggregates:

- rounded light particles;
- angular fragments and irregularly shaped aggregates, most often darkysh-gray and black.

The data obtained allow us to conclude that the elimination of the dark (grayish-black mass) will significantly solve the set research problem. In contrast to work (Vasyunina et al., 2019), where the result is achieved using flotation separation methods, cleaning the estimate can be carried out by "dry" methods, which excludes expensive product drying processes from the technological process and significantly reduces the economic costs of processing.

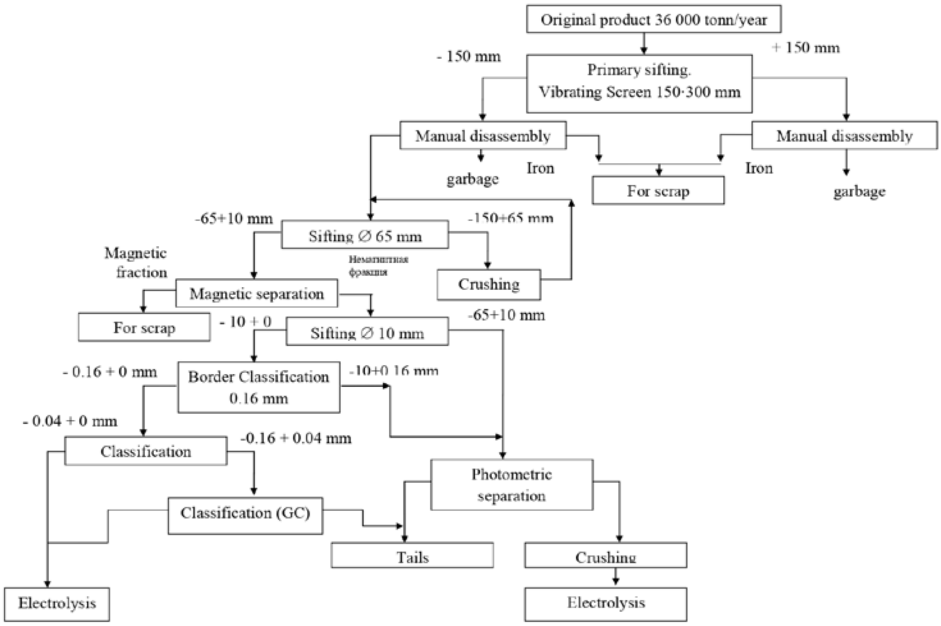
With the aim of disintegration of technogenic raw materials and the release of pollutants, studies of the working indices of destruction and abrasiveness were carried out. It was found that the material under study is characterized as non-abrasive (working index Ai - 0.0184) and very soft in relation to impact crushing (working index CWi - 3.64). The combination of these two factors makes it possible to recommend impact crushers (centrifugal, hammer, etc.) for ore preparation. The wear of the crushing bodies and lining will be minimal, provided that no metallic inclusions of aluminum enter the crusher. These inclusions must be removed before feeding the material for crushing. Bond Ball Working Index (BWi - 6.47) characterizes the material's very low resistance to ball grinding. Detailed studies on this issue are presented in (Burdonov et al., 2018).

The introduction of the crushing operation of the alumina-containing estimate allows the use of dry cascade-gravity and centrifugal classification to separate impurities in the form of SiO_2 and Fe_2O_3 when using alumina-containing material in primary aluminum technology.

4. Case Study: Sweep sieving line of JSC RUSAL Bratsk

On the basis of the Irkutsk National Research University, together with PJSC RUSAL Bratsk, an estimate sieving line has been developed, the purpose of which is to obtain secondary alumina-containing raw materials with a low SiO_2 content to return the estimate to the production process.

The scheme for processing alumina-containing estimates implemented on this technological line is shown in Fig. 9.



Fie. 9. Technological scheme for processing the sweepings of PJSC RUSAL Bratsk.

As mentioned earlier, the secondary use of substandard raw materials in the electrolysis process leads to a significant decrease in technical and economic indicators due to the increased content of Fe_2O_3 and SiO_2 impurities.

The use of the developed technological scheme will make it possible to process the alumina-containing estimate, which will provide a product yield in the amount of 90% with Fe_2O_3 content - up to 1% and SiO_2 - 1.5%.

The introduction of the instrumental and technological scheme will make it possible to reduce the consumption of fresh alumina due to the return to circulation of 10,000-12,000 tons of secondary raw materials per year.

This will significantly improve the environmental situation at the plant by utilizing more than 15,000 tons of waste, both for reuse and for the improvement of the plant's territory, namely, filling the roads of the inter-building courtyards of the electrolysis buildings.

In addition, this will have a positive effect on the technical and economic indicators of electrolysis production: the estimated cost savings for alumina due to the receipt of secondary raw materials will amount to 193,000 million rubles per year. The payback period will be less than six months.

5. Conclusion

In the course of the research, it was found that in the man-made waste - the estimate of aluminum production, the largest output is for the size classes -0.315 + 0.16 mm (29.85% by weight) and +2.5 mm (37.22% by weight). Aluminum is concentrated in fractions -0.315 + 0.16 mm (Al content - 45.3%) and 0.16 + 0 mm (48.6%), silicon in fraction -0.63 + 0.315 mm (Si content - 1, 96%), iron in the fraction -1.25 + 0.63 mm (Fe content - 0.474%) and -0.63 + 0.315 mm (0.72%).

During the analysis of the mineralogical composition of the raw materials, it was found that the material has a mineral composition: cryolite (Na3AlF6), chiolite

($Al_3F_{14}Na_5$), quartz, feldspars, carbonaceous matter and the technogenic phase of the composition $(NaF)\cdot 1{,}5CaF_2\cdot AlF_3$.

For the possible return of raw materials to the technological process, it is not enough to separate the product (even with a preliminary reduction in the iron content) by size classes. Only a fine fraction of a number of products can be returned without additional processing, since the content of impurities in it meets the requirements.

The data obtained in the study of the chemical composition of mono-fractions allow us to conclude that the exclusion of a dark (grayish-black mass), in which the content of impurities is maximum, will allow to a large extent to solve the posed research problem..

An apparatus and technological scheme for processing has been developed, which allows processing of an alumina-containing estimate, which will provide a product yield in the amount of 90% with Fe_2O_3 content - up to 1% and SiO_2 - 1.5%, which will improve the technical and economic indicators of production.

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