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The Technology of Getting Cryptocrystalline Graphite Having Low Ash Content Mined in the Deposits of Krasnoyarsk Territory

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There is studied the possibility of increasing the quality of cryptocrystalline graphite which is connected with searching for more complete opening, the aggregates of graphite and ash admixtures. To achieve this purpose, there was used mechanoactivation and microbiological processing. The developed technology including mechanoactivation, sintering, chemical and microbiological processing, allows to reduce the ash content of cryptocrystalline graphite from 20–25 down to 1–10 % depending on the initial quality and the area of using graphite

Keywords: cryptocrystalline graphite, mechanoactivation, sintering, chemical processing, microbiological processing, complex activation methods.

Introduction

Krasnoyarsk Territory is one of the regions which are especially rich in natural resources [1, 2 and others].

A great number of works are devoted to studying them. Practically all the reserves of cryptocrystalline graphite in Russia are concentrated in Siberian Federal Okrug (Krasnoyarsk territory, Evenk autonomous okrug). The combined reserves of these graphites in the three, registered deposits of Tungus basin (Noginskoye, Kureiskoye, Fatyanikhovskoye) and in some graphite manifestations have been estimated to be hundreds of millions tons. This is undoubtedly a huge possession of Krasnoyarsk territory, which has been used not in full extent up to now. From the technical and economical viewpoint, another important fact is that although the volumes of the processed ores are the same, the extraction of low ash content concentrates of cryptocrystalline graphite is much less than in case of extracting crystalline concentrates.

The Noginskoye deposit was mined till 2004. At first there was mined the graphite marked as GLS-1 and GLS-2. During the last ten years it was presented as type GLS-3. However, it didn't find wide application both in casting and other branches of industry. It was explained by the fact that it contained high ash content impurities (to 25–30 %) and by the difficult dressability of graphitic ores.

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At present there is mined graphite at Kureickoye deposit. This graphite has the ash content of 8–15 % on the average. The mined graphite is delivered to the industry. As compared to the graphite of Noginskoye deposit, the Kureika graphite is more perspective because its deposit has the reserves of qualitative amorphous graphite. But to mine it efficiently, it is necessary to create and develop the following industries in the region: transport, mining, processing. It is also necessary to have the corresponding social infrastructure.

The graphite of the deposits of Krasnoyarsk territory is processed (which includes crushing, drying, grinding and packing) at the factory «Krasnoyarskgraphit». As a result of this processing, there are produced casting types. But they are far from meeting the requirements of the industry. Now the situation in producing and using graphites in Krasnoyarsk territory is the following. Although there are great reserves of cryptocrystalline graphites delivered in limited amounts to other regions, the enterprises are in great need of a wide range of high-quality materials and products made from these graphites.

The quality of Krasnoyarsk cryptocrystalline graphites is heterogeneous. According to the research we conducted earlier, the graphites of Noginsk type GLS (N) and those of Kureika type GLS-2 (K) belong to high-ash and hard-concentrated ones. The mineral composition of the ore, except for the main component – graphite, was presented by quartz, calcite, feldspar, pyrite, copper pyrite, montmorillonite and others [3].

The aim of our work is developing the technology of increasing the quality of the natural cryptocrystalline graphite mined in the deposits of Krasnoyarsk territory.

The traditional scheme of concentrating the graphitic ore provides for crushing, grinding, preliminary flotation, the final many-staged grinding of the preliminary concentrate with subsequent flotation [4]. The best quality of the Noginsk graphite having the initial ash content of 20–25 %, is reached according to the flotation scheme during the two-stage grinding, of the ore to 90 % of the type of 0.07 mm with the intercycle flotation. By using this method, there was obtained the concentrate containing 15–18 % of the ash residue. So the traditional method of concentrating the graphitic ore does not provide obtaining low ash concentrates.

At the Open Joint Stock Company «Zalalyevck graphite plant» (Ukraine) which is the main supplier of the crystalline graphite of industrial importance, there was developed a method of concentrating the crystalline graphite. This includes sintering graphite with soda ash at 800–900 ºC, followed by water leaching and chemical processing with acid solutions [5]. The application of the given technology for the cryptocrystalline graphite turned out to be practically impossible because of the close intergrowth of graphitic particles and nonmetallic minerals. The latter spread in the ore irregularly (from 5 to 40 %). The spreading is presented by the dispersed dissemination (the particle size is from 0,05 to 0,001 mm) as well as separate grains or aggregate formations, cutting the ore in all directions. The sizes of the large extraction reach 0,2 mm.

The principal possibility of the further increase of the graphitic concentrates quality is connected with searching for conditions of possibly more complete opening of aggregations of graphitic particles and ash admixtures. To reach this, it was decided to use mechanoactivation as the first stage of graphite concentration. During the mechanoactivation, there takes place not only the grinding of the graphitic particles and the opening of the aggregations but also the increase of the graphite reactivity [6].

The development of the mechanoactivation technology of concentrating graphites

The graphite activation was carried out in a planetary centrifugal mill AGO-2. With increasing the activation time the ash content of the graphite of the type GLS-3 (N) increased by 5–7 %. During the further activation, it did not change (Fig. 1). The observed phenomenon increasing the ash content may be explained by a lighter grinding and releasing ash admixtures from the graphitic particles.

Under these conditions, the ash content of the graphite of the type GLS-2 (K) does not change essentially.

Since the technology of concentrating the crystalline graphite, which was developed at the Open Joint Stock «Zavalyesk graphite plant» and intended for the studied cryptocrystalline graphites did not produce any positive results. It was decided to process the graphite of the type GLS-3 (N) during its mechanoactivation with soda ash with subsequent chemical leaching. It was supposed that during the process of activation, the admixed particles must actively react with the soda ash while the high temperatures during the mechanoactivation, must replace the sintering process (Fig. 2).

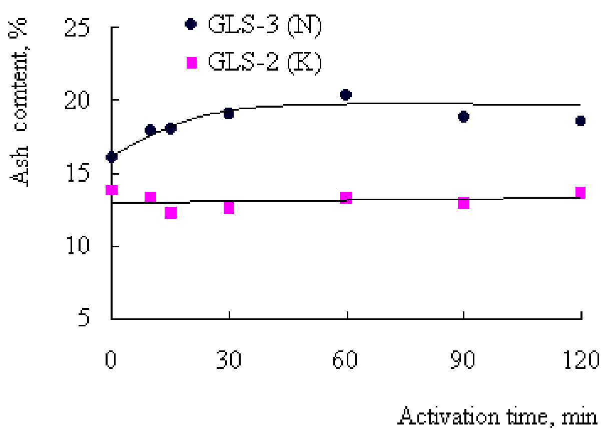


Fig. 1. Dependence of graphite ash content for GLS-3 (N) and GLS-2 (K) on graphite activation time

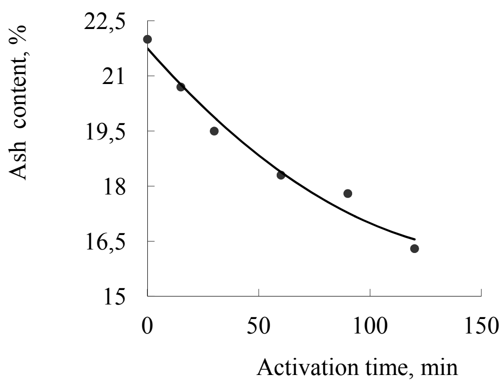


Fig. 2. Dependence of graphite ash content for GLS-3 (N) on the time of graphite activation together with soda ash

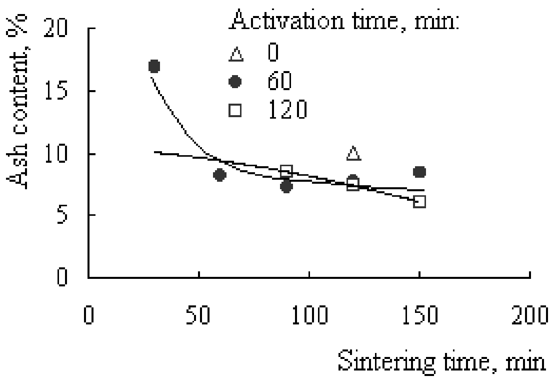


Fig. 3. Dependence of the ash content of graphite GLS-3 (N) on the activation time and sintering time (sintering temperature is 860 ºC)

The obtained results show that the mechanoactivation of the mixture of graphite and soda ash with the subsequent water leaching and chemical concentration, promote the stable decrease of ash admixtures down to 16,5 %. Increasing the duration of this process (more than 120 min) is inexpedient because it does not lead to the noticeable improving of the final product quality. The essential decrease of the ash admixtures of the samples of GLS-3 (N), when they are processed in the planetary and centrifugal mill, in the presence of the soda ash, is connected with the possibility of spot development of high temperatures in the processed material. At the same time, there happens the solid phase of sintering ash admixtures and soda ash without being influenced by external temperatures.

The possibility of the high-speed deformation of the material under the influence of great loads, as well as the spot sintering of the mixture components lead to forming the silicates (Na_2SiO_3), aluminates ($NaAlO_2$), and ferrites ($NaFeO_2$) – from the soda ash components – SiO_2, Fe_2O_3, Al_2O_3 and soda ash.

The further water leaching of the obtained mixture for 60 min allows to remove their soluble component – sodium silicate.

Ferrite and sodium aluminate are partially hydrolyzed in a light alkaline medium. As a result, there are formed high-dispersed precipitates (($Al(OH)_3$ and $Fe(OH)_3$) which impedes the pulp filtration.

To reach the maximum extraction of insoluble ash admixtures, the samples containing aluminium hydroxide and iron hydroxide, calcium carbonate, magnesium carbonate – were treated with a 5 % sulphuric acid solution. After that they were washed till getting the neutral medium. The interaction between calcium carbonate and magnesium carbonate and the acid leads to forming sulphates being soluble under these conditions. The graphite ash content during the considered chemical concentration decreased from 22 down to 16 %.

As a method of concentrating the material, the mechanoactivation cannot completely replace the sintering process. The variation of the conditions of the heat treatment of the mixture «graphite–soda ash» shows that the optimum parameters of this process are the temperature of 700–900 ºC which is kept during 60–120 min during the time of the mixture activation – 60–120 min (Fig. 3).

Decreasing the sintering temperature from 860 down to 740 ºC allowed to reduce a little the graphite ash content of GLS-3 (N)– from 6 % (at 860 ºC) down to 5,5 % (at 740 ºC). The increase of the temperature had to remove the silicon component of the ash residue. However the process is

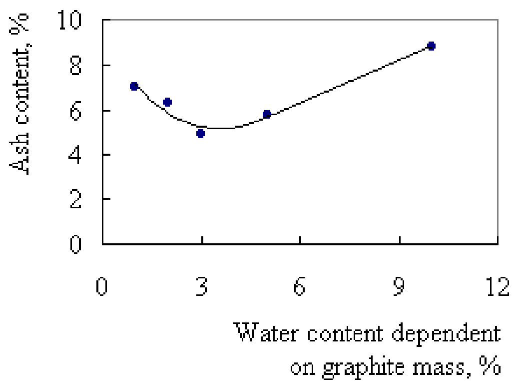


Fig. 4. Dependence of the ash content of graphite GLS-3 (N) on water content in the mixture «graphite–soda ash – water»

accompanied by burning the charge when coming into contact with oxygen. This is promoted by the highly developed surface of the activated graphite as well as its increased chemical activity. Some increase of the ash content is probably connected with more complete burn – out of the graphitic mass.

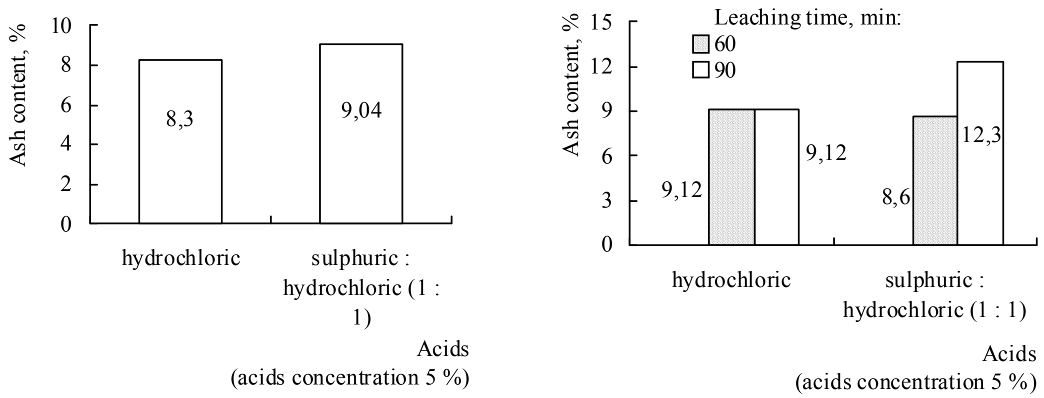
The application of this technology for concentrating the graphite of the type GLS-2 (K) decreases its ash content from 13,8 down to 2,2 %.

So, the preliminary combined activation of graphite and alkaline metal salt decreases the temperature of heat treatment from 850–900 down to 700–750 ºC. Besides, it reduces the consumption of the alkaline metal salt by 40–45 % per ton of the cryptocrystalline graphite (as compared to the technology of concentrating the crystalline graphite).

In addition to the above – described method, there was used a method of the wet mixing of the charge components (graphite + soda ash) when preparing it for sintering. The graphite is mixed in the saturated soda solution and dried at a temperature of 350–450 ºC. In this case, there is reached a more complete contact of the soda particles with the particles of ash admixtures. But there is required a great energy consumption for drying the charge. The obtained data testify to the fact that the wet mixing of graphite with the soda ash and the combined activation of these components allow the charge components to come into reaction before the sintering process.

To study the further intensification of the interaction processes, there was investigated the influence of the water content as a component, on the graphite ash content. It was carried out in the mixture «graphite–soda ash–water» (Fig. 4). The research of the optimum ratio, during the combined activation of the components of the mixture «graphite–soda ash–water» did not lead to decreasing the ash content lower than 5 %.

The next stage was studying the influence of the mill type on the content of the admixtures in the graphite during the activation. The grinding was carried out in the vibration mill RVM-45 and in the planetary and centrifugal mill AGO-2. During the activation in the mill AGO-2, the graphite ash content decreases down to 5,5 %, as regards the mill RVM-45 – down to 5 %. A slight difference in the indexes testifies to the possibility of using the principally different devices on the condition of optimizing the activation modes.



a b

Fig. 5. Dependence of the ash content of the graphite GLS-3 (N) on the chemical concentration parameters: *a* – the mixture «graphite–soda ash» (the time of leaching with hot water is 60 min); *b* – activated mixture «graphite–soda ash» (the time of leaching with not water is 60 and 90 min)

A great role in the practice of mechanothermochemical concentration is played by the washing of the charge and separating it from the soluble admixtures. A high milling fineness reached by grinding the charge in the mill-activator AGO-2 and the formation of the gel of silicic acid impedes the process of washing and filtrating the sinter with cold water, hot water and the acids solutions.

To optimize the chemical concentration, there were studied the following dependences: the influence of the sulphuric acid concentration on the graphite ash content; the possibility of using hydrochloric acid for the concentration (Fig. 5); the possibility of the combined application of 5 % solutions of the hydrochloric acid and the sulphuric acid.

It turned out that the indicated parameters of the chemical concentration (except for the sulphuric acid concentration) do not essentially influence the graphite ash content. The content of the admixtures in the graphite samples turns out to be a minimum one when the sulphuric acid concentration is 5–10 %.

Using the hydrochloric acid and the mixture of hydrochloric acid and sulphuric acid did not produce any positive results. The graphite ash content made up 8–9 %.

A high content of quartz (SiO_2) in the graphite samples allowed to suppose that introducing fluorine – containing compounds into the system, would decrease the silicon component. By adding the soluble salt of ammonium fluoride into the reaction mixture, we could decrease the admixtures content in the graphite by 5 % (from 21,4 down to 16,1 %). And the processing of the samples with 8 % fluorohydrogen acid by heating it to 50 °C during 120 min decreased the ash content down to 5 % (Fig. 6). The further increase of the acid concentration did not produce any positive results.

It should be noted that fluorohydrogen acid is a specific chemical reagent and it requires using not simple equipment.

So, as a result of the conducted research there was developed the mechanothermochemical way of concentrating cryptocrystalline graphite of the deposits of Krasnoyarsk territory. This includes activating graphite with soda ash, sintering the activated mixture with the subsequent water leaching and chemical processing.

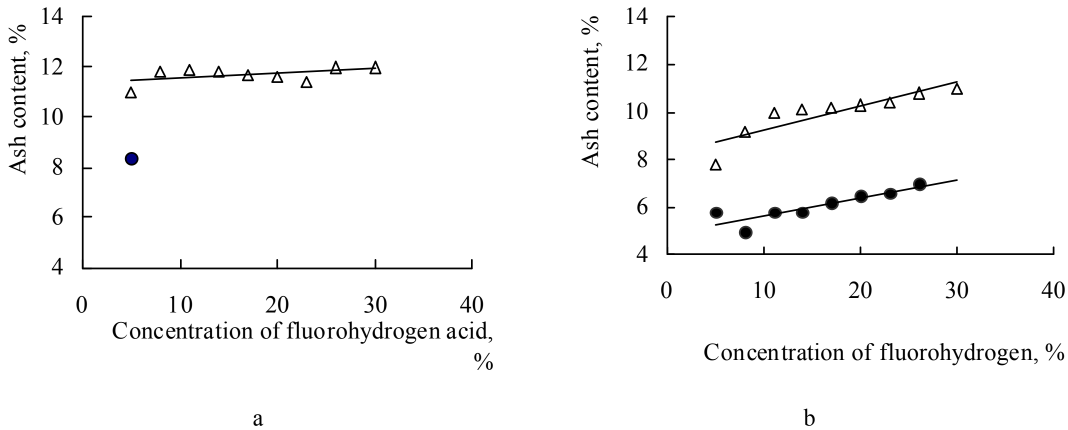


Fig. 6. Dependence of the ash content of non-activated graphite and activated graphite GLS-3 (N) on the concentration and temperature of the fluorodydrogen acid: *a* – initial graphite; *b* – activated graphite; Δ – without heating; ● – with heating

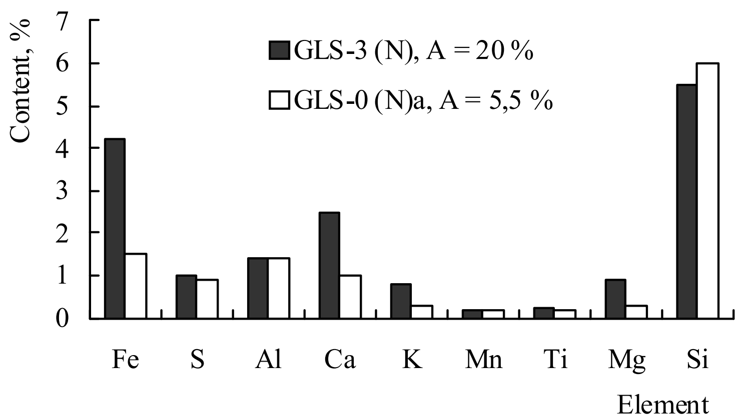


Fig. 7. Element composition of graphite GLS-3 (N) (A – ash content)

Using this method allowed to reduce the ash content of Noginsk graphite from 20–25 % (graphite of the type GLS-3 (N)) down to 4–6 % (graphite of the type GLS-0 $(N)_a$), for Kureika graphite – from 10–15 % (graphite of the type GLS-2 (K)) down to 2–4 % (graphite of the type GLS-0 $(K)_a$).

The data on the element composition (Fig. 7–8) show the decrease of the components of iron in Kureika graphite – from 5,6 down to 0,25 %, the components of aluminium – from 1,1 down to 0,2 %, the components of calcium – from 2,2 down to 0,5 %. As regards Noginsk graphite, there was a decrease of iron – from 4,2 down to 1,5 %, calcium – from 2,5 down to 1 %, potassium – from 0,8 down to 0,3 % and magnesium – from 0,9 down to 0,5 %.

The phase composition of the samples of the concentrated graphite GLS-3 (N) and GLS-2 (K) showed a slight (to 1 %) content of admixture phases (calcite, montmorllonite, kaolinite and others) (Fig. 9–12). Quartz as being the least reactive component, is removed from graphite not completely. It is ground not so easily and it is chemically inert.

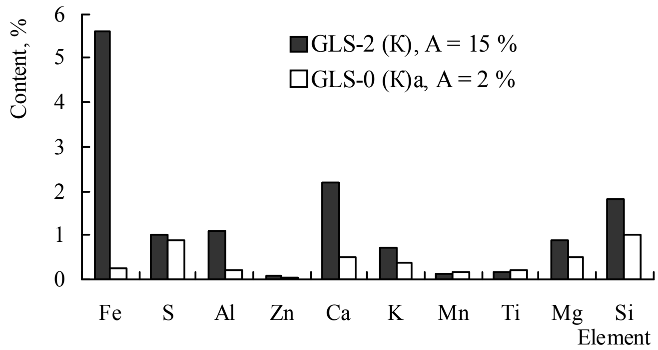


Fig. 8. Element composition of graphite GLS-2 (K) (A – ash content)

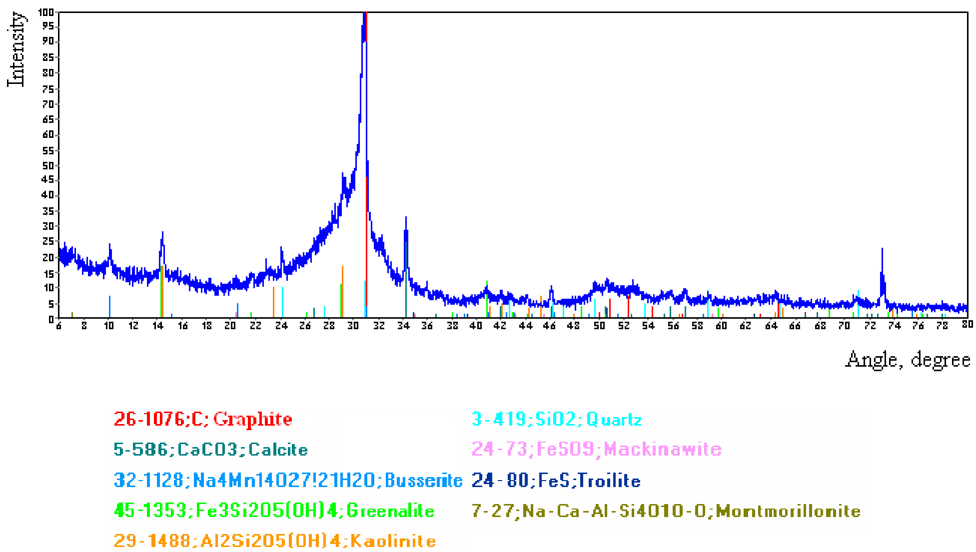


Fig. 9. Phase composition of graphite GLS-3 (N)

The development of microbiological and complex technologies for getting low ash content cryptocrystalline graphite

At present there are well-known microbiological methods of removingsilicon oxide, aluminium oxide, iron oxide from the mineral raw material with the cultures A.niger, Hyphomicrobium sp. [7].

Especially effectively the concentration takes place when separating the processes of creating the reagent – the cultural liquid containing organic acids and the products of metabolism of microorganisms. Another thing that accompanies this is removing admixture minerals from the initial substance [7].

In the series of the model experiments on reducing the ash content of Noginsk graphite of the types GLS-3 (N), GLS-3 $(N)_a$ and GLS-0 $(N)_a$, there was used the solution imitating the cultural medium of the microorganism A.niger. the time of processing the graphite was 48 and 96 hr and the temperature – 20 and 80 ºC.

The scheme of processing the graphite included preparing a leaching solution (cultural liquid) and introducing admixture components into it.

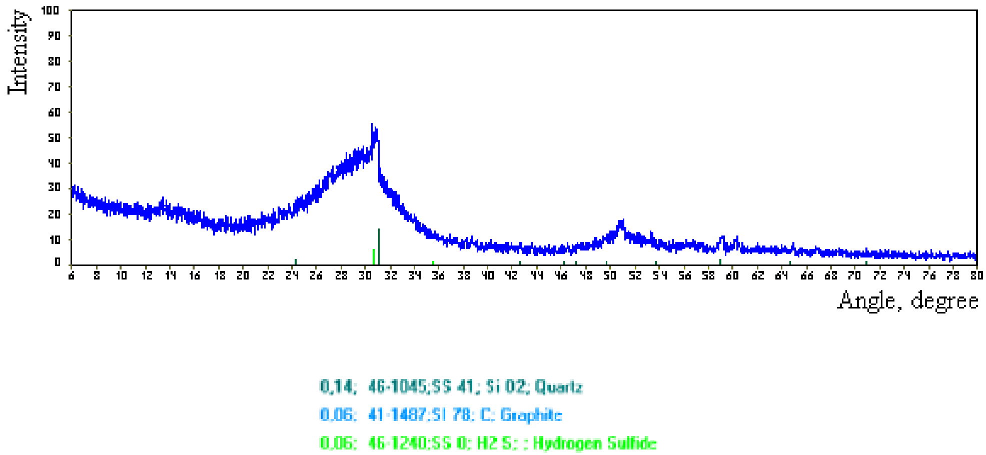


Fig. 10. Phase composition of the processed Noginsk graphite GLS-0 $(N)_a$

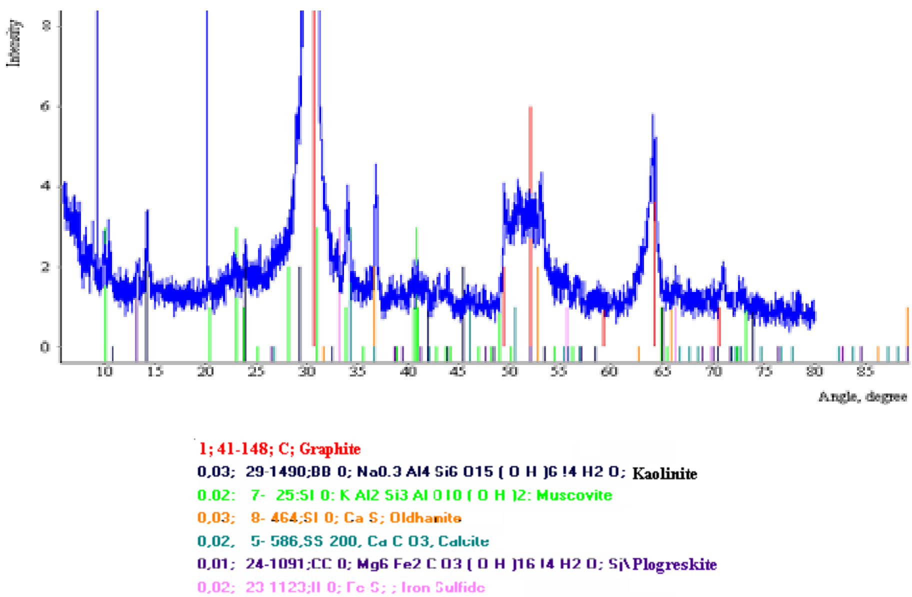


Fig. 11. Phase composition of graphite GLS-2 (K)

The solution imitating the cultural medium was prepared by getting the solution of oxalic acid with the concentration of 100 g/l using a mixture of sulphuric acid and hydrochloric acid (2 : 1) to pH 0,5. On finishing the incubation the cultural liquid was separated from mycelium by filtration. Then it was diluted by water and acidified again to the hydrochloric acid pH 0,5.

As it was turned out, increasing the time for microbiological processing of graphite from 48 hr to 72 hr (Fig. 13) didn't provide the decrease of ash content. The growth of temperature to 80 ºC leads to increasing the activity of microorganisms of this type oxidizing carbon alongside with admixtures.

By using the X-ray spectrometry (Fig. 14), there was proved the removing of iron and potassium from graphite which was the result of microbiological processing. The content of the elements of

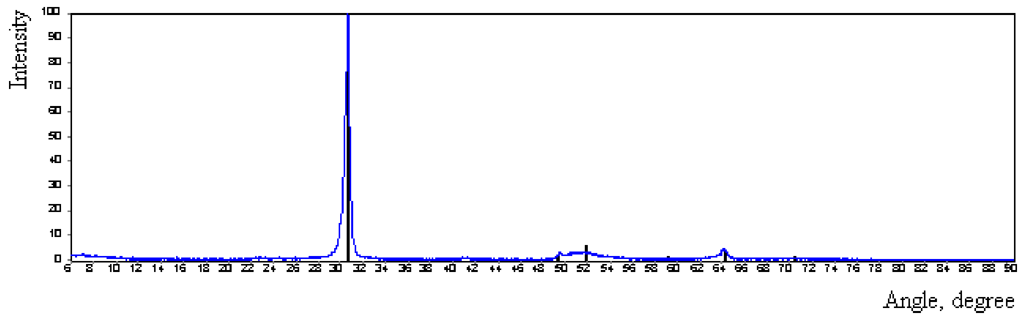


Fig. 12. Phase composition of the processed Kureika graphite GLS-0 (K)

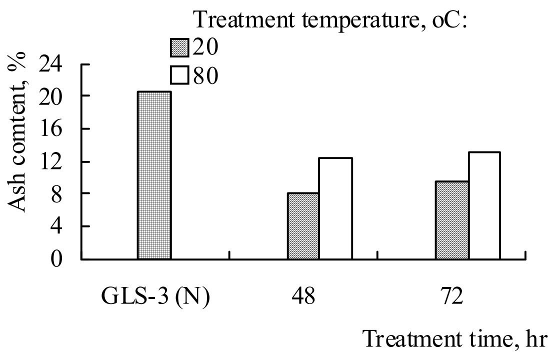


Fig. 13. Influence of microbiological treatment temperature on the ash content of graphite GLS-3 (N)

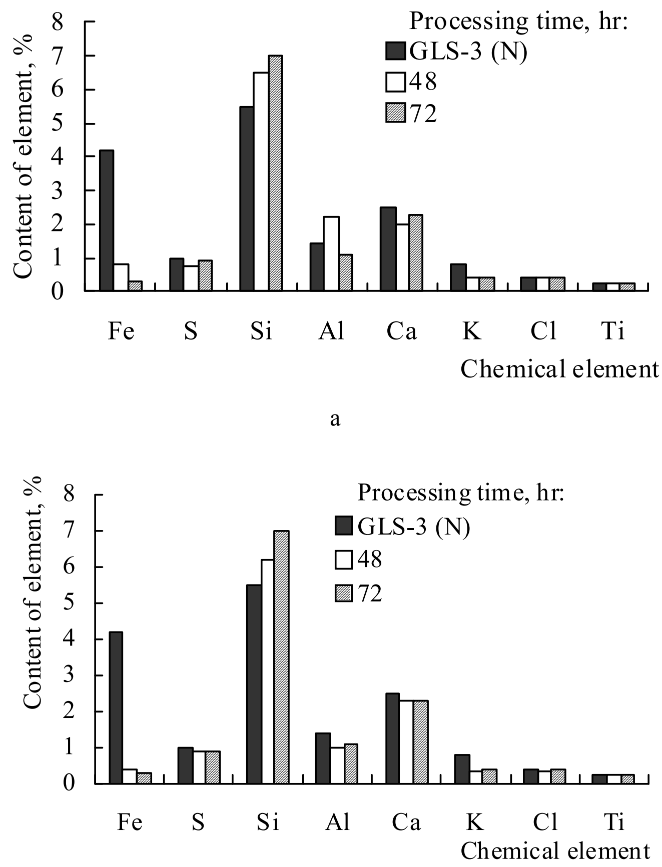
titanium, calcium and sulphur practically does not change. Quartz which is finely disseminated into the scales of graphite is oxidized by microorganisms.

The graphite processed by the cultural liquid during 48 hr at 80 ºC as it was shown by the phase analysis, contained a new phase vevelite (CaC_2O_4). Its appearance is connected with forming gaseous products CO and CO_2 during oxidizing the graphite in the air. It is known [8] that the edge places of graphite particles may contain carbon atoms, forming radicals CO^- and CO_2^- with oxygen atoms.

The formation of the oxalate ion, which is present in the phase of vevelite is possible through the radical CO_2^- whose carbon is not saturated from the viewpoint of valency and it may react with another similar radical: $\begin{matrix} O=C-O^- \\ O=C-O^- \end{matrix} \rightarrow [C_2O_4]^{2-}$.

The microorganisms A.niger used during the concentration, leach aluminium and iron, moving them info the solution. As for calcium, interacting with the oxalate ion, it forms the phase of vevelite.

The composition of the samples of graphite GLS-3 (N) treated by the cultural liquid at various temperatures, shows that the increasing of the time for processing graphite to 72 hr, does not influence greatly on the content of admixture phases (that is of quartz, vevelite and clayey minerals).



a

b

Fig. 14. Dependence of the element composition of the ash admixtures of Noginsk graphite GLS-3 (N), on the time and temperature of processing (*a* – 20 °C; *b* – 80 °C)

So the optimum conditions for microbiological processing cryptocrystalline graphite with microorganisms A.niger are the following: time – 48 hr and the temperature – 20 ºC. Using this method of concentration allows to obtain graphite with the ash content less than 10 %.

The efficiency of the suggested method concentration to a great extent depends of the sizes and activity of the particles of the initial mineral raw materials. The polydispersity of the graphite of the type GLS-3 (N) and the close intergrowth of graphitic and ash particles lead to the fact, that the microorganisms do not leach sufficiently completely the admixture components.

Then there were studied the preliminarily mechanoactivated samples of graphite GLS-3 $(N)_a$. The processing of graphite GLS-3 $(N)_a$ with microorganisms A.niger was carried out under the same conditions as for the natural graphite (see the table).

The optimum temperature of leaching admixture compounds makes up 20 ºC. The ash content of graphite decreases from 22 down to 14 % (when it is activated in the planetary and centrifugal mill) and down to 7 % (when activated in the vibratory mill). The obtained results are explained by the fact that in the mill of both types, under the action of great loads, there appears the possibility of high-speed deforming the graphite. As a result, there are opened the aggregations of the graphite and

Table. Element composition of graphite GLS-3 $(N)_a$ after the microbiological processing

Mechanoactivation		Temperature of microbiological processing, °C	Ash content, %	Chemical element, %							
mill	time, min			Fe	S	Si	Al	Ca	K	Cl	Ti
–	–	–	20,50	4,20	1,00	5,5	1,4	2,5	0,8	0,40	0,25
AGO-2	15	20	14,47	0,85	1,00	6,5	1,9	1,9	0,5	0,35	0,30
		80	16,85	0,80	0,75	8,5	1,3	4,0	0,6	0,50	0,40
RVM-45	120	20	6,77	0,75	0,80	7,5	1,2	2,4	0,4	0,40	0,35
		80	13,6	0,65	0,75	7,3	1,1	2,3	0,5	0,55	0,35

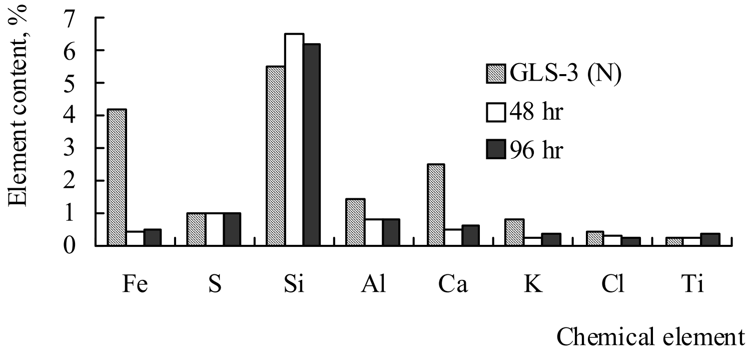


Fig. 15. Dependence of the element composition of graphite GLS-0 (N)a on the processing time

ash admixtures. During the activation in the vibratory mill, the release of the ash admixtures from the graphite particles takes place more intensively, which leads to the more essential reduction of the ash content.

For the purpose of the further increase of efficiency of concentrating graphite GLS-3 $(N)_a$, there was added the microbiological leaching as a stage of mechanothermochemical way of clearing the graphite. For this, graphite, processed according to the mechanothermochemical technology, was subjected to the additional microbiological processing for 48 and 96 hr at a temperature of 20 ºC (Fig. 15).

As a result of the research the ash content of graphite GLS-0 $(N)_a$ made up 3 %. By using X-ray spectrometry, it was found out that the iron content decreases down to 0,4 % and the calcium content – down to 0,5 %.

As a result of the conducted research, there were developed some separate and complex technologies of concentrating cryptocrystalline graphites of the deposits in Krasnoyarsk territory (Fig. 16).

The developed technologies allow to reduce the ash content of cryptocrystalline graphites from 20–25 down to 1–10 % depending on the area of its application.

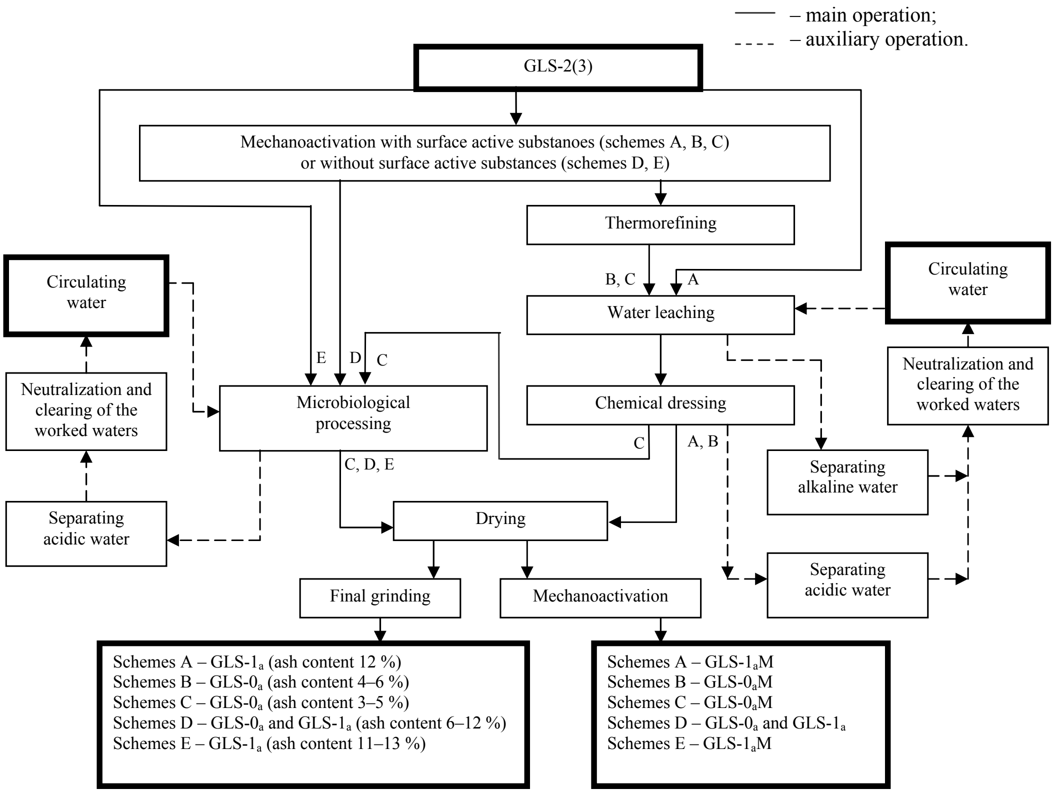


Fig. 16. Schemes of dressing cryptocrystalline graphites

Conclusions

1. There is grounded the possibility of increasing the quality of cryptocrystalline graphites at the expense of reducing the ash content by means of using such methods of processing as mechanical activation, sintering, chemical and microbiological dressing.

2. It is determined, that the mechanical activation considerably intensifies all the subsequent processes of concentrating the cryptocrystalline graphite more completely releasing ash admixtures from its particles. This allows to recommend this way as a method of preliminary processing the graphites.

3. Using the preliminary mechanoactivation during applying the mechanoactivation method of concentrating graphites with soda ash, allows to decrease the consumption of the salt of the alkaline metal by 40–50 % and the sintering temperature – by 100–150 ºC.

4. There is shown the effectiveness of using complex activation methods (such as mechanochemical, mechanothermochemical, mechanomicrobiolothermochemical).

These allow to reduce the graphite ash content down to 1–10 % depending on the initial quality and the field of the further application of graphite. This also allows to obtain the activated graphites of the type GLS-2, GLS-1 of a higher quality.

Reperences

[1] *Nikitin A.* // Jornal of Siberian university. Series: Machines and technologies. 2009. – V. 2. N 4. P. 368–375.

[2] *Kuznetsov P.* Magazine of Siberian federal university. Series: Machines and technologies. 2008. V. 1. N 2. P. 168–180.

[3] *Zatkhei R.A.* Account. Krasnoyarsk. 1970.

[4] *Bragina V.I.* Processing non-metallic minerals : textbook [Text] / V. I. Bragina, V. I. Bragin. Krasnoyarsk: State Academy of Non-Ferrous metals and gold, 1990 – 100 p.

[5] *Shokin V.N. and othes* // Graphites and their application in industry : proceedings of scientific pfpers.

[6] *Khasiyev D.R., Korolyova Y.A.* [and othes] // Perspective materials, technologies, constructions. Krasnoyarsk: State Academy of Non-Ferrous metals and gold, 1999. P. 24

[7] *Korobuchkina, E. D.* Microbiology [Text]. – 45. – 3. – 1976. – P. 535.

[9] *Baranov, V. N.* Activation of graphite of various crystalline chemical for refractory products and paints is casting [Text] / V. N. Baranov // Author's abstract for getting the scientific degree of the Candidate of technical sciences if speciality 08/16/04 – Casting – Krasnoyarsk, 2005. – 26 p.

Технологии получения низкозольного скрытокристаллического графита месторождений Красноярского края

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С целью повышения качества скрытокристаллического графита месторождений Красноярского края исследована возможность поиска условий более полного раскрытия сростков графита и зольных примесей. Для достижения этой цели и применяли комплексные технологии, основанные на использовании механоактивации, спекания, химической и микробиологической. Комплексная технология, включающая механоактивацию, спекание, химическое и микробиологическое обогащение, позволяет снижать зольность скрытокристаллического графита с 20-25 до 1-10 % в зависимости от исходного качества и области применения графита.

Ключевые слова: скрытокристаллический графит, механоактивация, спекание, химическое обогащение, микробиологическое обогащение, комплексные методы активации.