Studies on the opportunities of producing superpure graphite from the high-carbone rocks of the Jiamusi-Hankaiskaya province

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Abstract. The results of the research of the conditions of the purification of the natural graphite with the usage of the processes of the hydrodifluoride technology are given. The interaction of the major impurity elements of the concentrate with NH₄HF₂ resulting in the formation of the complex fluorine ammonium salts and simple fluorides is established to occur during processing of the graphite concentrate with ammonium hydrodifluoride. Conducting the fluoridization with usage of 20% of surplus of NH₄HF₂ has been found to allow reaching the complete fluoridization of the impurity components which are present in the graphite. The complex fluorine ammonium salts and the fluorides of alkaline metals have appeared to be removed from fluoridated concentrate by means of the water leaching.

1. Introduction
The majority of high technologies which are indicators of the level of development of the industrial production in the advanced countries are inconceivable without graphite use. Unique properties of this mineral together with the latest discoveries in the field of nuclear power, electronics and nanotechnologies have completely changed our vision of opportunities of its usage [1]. Low-ash crystal graphite is widely applied in the various fields of industries. Graphite serves as an additive for increasing the fireproof properties of materials in metallurgy. Thanks to its high conductivity, plasticity and mechanical strength graphite is widely used for producing galvanic cells, electrodes, alkaline accumulators, etc in electrical engineering. High-quality graphite is used as a moderator of nuclear reactions in atomic reactors, it’s also applied in jet propulsion (rocketry) for producing bladed turbines and rockets, the colloidal graphite, oxidized and thermal expanded graphite [2]. Graphite is included in the list of critical minerals in the countries of the European Union and China. The main deposits of high-quality crystal graphite are located in China, India, Brazil, the Czech Republic, Canada and Mexico. At the same time, the main producer and exporter of graphite raw materials is China. Few Russian enterprises specializing in extraction of graphite provide rather insignificant supply of graphite for our country. Most of the crystal graphite is imported from abroad.

Enormous resources of crystal graphite are concentrated in ore deposits of the Jiamusi-Hankaiskaya province with submeridional strike towards the adjacent territories of the South of the Far East of Russia and the northeast of China. There are features of Dalnerechensk group (with Filinskoye being...
the largest of them), deposits of of Lesozavodsk group (Tamginskoye, Turgenevskoye) and graphite-ore giant of Liumao Mashan group of the Heilongjian province in the Northern, central and Southern sides of this province respectively [3]. These deposits are built up by biotite-feldsparic-graphite and biotite-muscovite-feldsparic schists interstratified with graphite-containing granite-diopsite scarns and the concordant injections of granite-gneisses. Carbon content in these rocks reaches 39% of the mass. The mineral graphite is the major carbon concentrator. Ore minerals are generally represented by native metals (Au, Pt, rare earth elements, Fe, Cu, Al, etc) [4].

Application conditions make different requirements to the purity and crystal structure of graphite. All known methods of the purification of graphite can be divided into three types: chemical-, thermal- and gas-thermal refinements. Thermal purification of graphite is the most widespread method although processes of refinement are very power-intensive since they are conducted at the temperature 2500-3000°C [5]. Chemical refinement means sintering the graphite powder with water solution of the alkaline agent, the subsequent washing with water and the diluted [6,7]. Gas-thermal purification is based on the method producing low-ash crystal graphite by means of chemical treatment of high-carbon mineral raw materials with ammonium hydrodifluoride [8]. The physico-chemical peculiarity of the process of fluorodization with ammonium hydrodifluoride is based on the ability of oxygen-containing compounds of transitional and many intransitional elements to form very convenient for processing fluoro metallates of ammonium due to the interaction of the first ones with NH4HF2.

The purpose of our work is studying the conditions of refining the graphites of the Jiamusi-Hankaiskaya province from the impurities.

2. Methodology of experiment

The series of the graphite concentrate produced due to the enrichment of the graphite-bearing rocks of the Ruzhinskaya Square by means of floatation method were chosen. The pine oil being used as a foaming agent, the long-chained amine served as a collector. In the conditions of floatation graphite’s ground mass (~90%) and some quantity of impurity are concentrated in the foam product. The structure of the dried-foam product is given in table 1. Ash-content of the studied graphite concentrate was 5.83%. The ammonium hydrodifluoride was used as the reagent for purifying the concentrate.

| Table 1. The content of the dried foam product |
|---------------------------------------------|
| Element | Content, wt.% |
| Si      | 1.438         |
| Al      | 0.601         |
| Fe      | 0.409         |
| Ca      | 0.185         |
| Mg      | 0.088         |
| Na      | 0.602         |
| K       | 0.249         |

The chemical treatment of the graphite concentrate with ammonium hydrodifluoride was carried out at a mass ratio between the concentrate and the fluorinating agent equal to 5:1 in a glass-carbon container which was placed in the reactor with an electrical heating and 2 tandem condensers — the first one made of nickel and the second one was fluoroplastic. The temperature of the electric furnace was set by means of the high-accuracy temperature regulator HTR-2. The quantities of the concentrate weighed 20-40 g. To maintain the equal distribution and tight contact with the reagent the graphite concentrate was mixed with ammonium hydrodifluoride solution made due to dissolving the estimated quantity of NH4HF2 in 20-30 ml of H2O. The obtained heavy homogeneous mass was heated slowly (~1.5 hails/min.) to the temperature of 170-180°C and the temperature was kept at this point for 2 h.
Process of leaching the fluoridated graphite concentrate was conducted at the room temperature by means quadruplicated dissolution of 10 g of the product in 100 ml of water (S(olid):L(iquid) : = 1:10) in glasses for 15 min and subsequent filtering. The changes happening to substance in the process of heating and leaching were controlled proportionally to the decrease of the mass of the initial mixture, according to the atomic absorbing the analysis of leaching solutions and X-ray phase analysis of the samples obtained due to hydrodifluoride processing of a graphite concentrate.

X-rayograms of the samples were made on the automatic D-8 ADVANCE diffractometer with rotation of a sample in Cu Kα-radiation. The X-ray phase analysis was carried out with the usage of the search program EVA containing the file of powder data called PDF-2.

The content of the elements in the filtrates extracted due to the leaching of the fluorated graphite concentrate with water was determined by the method of the atomic and absorbing spectrometry (the spectrometer Solaar 6 M) according to analytical lines (traces) of silicon, iron, aluminum, magnesium, calcium, potassium and sodium. The content of the elements in graphite the insoluble constituents was determined by a mass spectrometry method with inductively-coupled plasma on Agilent 7500 spectrometer. Before that the studied samples had been alloyed with the metaborate of lithium.

Kinetic studies on processing of the graphite concentrate with ammonium hydrodifluoride were conducted with the 10 g quantities of the concentrate in isothermal conditions in the drying furnace BINDER (Germany) equipped with the electronic controller with the digital display. The reaction mixture had been prepared just before experiment. The sample was placed into the furnace heated to the set temperature. Time reckoning began since the moment of placing of the sample into the furnace. The calculation of kinetic parameters of the fluoration process was performed according to contents of generated salts of silicon, aluminum and iron.

Thermogravimetric researches are conducted on Q-1000 derivatograph in platinum crucibles in air at the heating speed of 2.5 deg./min and with the usage of quantities weighing of 100-200 mg.

3. Results of experiment and their discussion
The research showed that the reflexes \((\text{NH}_4)_2\text{SiF}_6\), \((\text{NH}_4)_3\text{FeF}_6\), and ones of \((\text{NH}_4)_3\text{AlF}_6\) appear on the X-rayogram of the furnace charge on already the next day and in through 7 days correspondingly if the mixing of the graphite concentrate with the ammonium hydrodifluoride is conducted with keeping the room temperature. The mass of the soluble salts produced due to the fluoration of the impurity components of the graphite concentrate allowed to establish that 20 days of interaction at the room temperature increase the extent of the process course up to 68%. The conditions of the interaction of the impurity components contained in the graphite concentrate with ammonium hydrodifluoride were investigated for finding out the modes of the purification of graphite.

The thermogravimetric research was conducted for the determination of the characteristic temperatures of interaction of impurity components of the studied concentrate with ammonium hydrodifluoride, the first one showed that reaction of the fluoration of the impurities of the graphite’s concentrate with the ammonium hydrodifluoride starts at the temperature of \(\sim 70^\circ\text{C}\) Registration of higher starting temperature of interaction on the thermogram is connected with the fact that the first portions of the ammonia released at fluoration are absorbed by ammonium hydrodifluoride with formation of \(\text{NH}_4\text{F}\) which is proved by the endothermic effect at the temperature of 111°C connected with melting of small amounts \(T_{\text{melting eutectics}} = 109^\circ\text{C}\) [9] of the generated eutectic of \(\text{NH}_4\text{HF}_2\)-\(\text{NH}_4\text{F}\) and thus process proceeds without weight decrease. The endothermic effect of melting of the fluorinating reagent accompanies the previously mentioned process if the temperature is above 126°C, and further reaction proceeds in the melt, with the maximum speed reached at 172°C and finishes at the temperature of 195°C (figure 1). The product released at a temperature of 195°C represents a graphite with impurities of mainly complex fluorine-ammonium salts of iron, aluminum, silicon together with simple fluorides of calcium and sodium.
Figure 1. The thermogram of interaction of a graphite concentrate with NH₄HF₂.

Thus, when the chemical treatment of the graphite concentrate with the ammonium hydrodifluoride is conducted the interaction of impurity elements of the concentrate with NH₄HF₂ takes course which results in the formation of complex or simple fluorides, and, judging by the chemical composition of the concentrate, purified by the ammonium hydrodifluoride, the following main reactions can take place:

\[
\begin{align*}
\text{SiO}_2 + 3 \text{NH}_4\text{HF}_2 &= (\text{NH}_4)_2\text{SiF}_6 + \text{NH}_3 \uparrow + 2 \text{H}_2\text{O}, \\
\text{Al}_2\text{O}_3 + 6 \text{NH}_4\text{HF}_2 &= 2 (\text{NH}_4)_3\text{AlF}_6 + 3 \text{H}_2\text{O}, \\
\text{Fe}_2\text{O}_3 + 6 \text{NH}_4\text{HF}_2 &= 2 (\text{NH}_4)_3\text{FeF}_6 + 3 \text{H}_2\text{O}, \\
\text{CaO} + \text{NH}_4\text{HF}_2 &= \text{CaF}_2 + \text{NH}_3 \uparrow + \text{H}_2\text{O}, \\
\text{Na}_2\text{O} + \text{NH}_4\text{HF}_2 &= 2\text{NaF} + \text{NH}_3 \uparrow + \text{H}_2\text{O}.
\end{align*}
\]

According to the given equations either the quantity of released ammonium or the content of generated salts allows to make assertions about the degree of the interaction of the impurities of the graphite concentrate with ammonium hydrodifluoride. It should be noted that the complex fluorne-ammonium salts and the simple fluorides of alkaline metals which are formed during fluoration of the graphite concentrate are highly soluble in water, and they can be easily separated by the water leaching of the fluoridated concentrate, while the calcium fluoride is insoluble in water compound. Besides, summing up of the given equations (1)-(5) allows to calculate the stoichiometric quantity of the fluornating reagent which is sufficient for fluoration of the principal impurity components of the studied concentrate.

The research showed that at temperatures below 100°C considerable part of the ammonia released in the course of reaction is dissolved in the water which is present at reactionary mixture (700 volumes of NH₃ are dissolved in 1 volume of H₂O at the room temperature) that does not allow to make a highly reliable judgment about the degree of the passing of the reaction. That was why the kinetic researches of the fluoration process of the graphite concentrate of the ammonium hydrodifluoride were conducted taking into account the content of the soluble salts formed due to the interaction. For this purpose 6 samples were installed into the furnace simultaneously and were taken out in 15, 30, 45, 60, 90 and 120 min, the derived product was leached by means of quadruple dissoluting in 100 ml of water for 15 min and purified via filter. The produced filtrates were combined determining their content of the elementary component such as Si, Al and Fe by means of the atomic and absorbing method. The degree of passing of the reaction of fluoration was measured by comparing the content of the specified elements in the filtrates with the estimated data obtained from the equations of the reactions (1)-(3) with taking into account the contents of the given associated impurity components in the graphite.

The calculations showed that the general speed of the hydrodifluoride processing of the graphite concentrate is determined by the speed of transformation of Al₂O₃ therefore the kinetic parameters were calculated on the basis of the dependence of the degree of formation of fluorne-ammonium salt of aluminum on time. The results of the kinetic research are represented in the figure 2.
Figure 2. The dependence of the degree of the fluoration of Al₂O₃ impurity on time at various temperatures.

The mathematical processing of the experimental data was carried in accordance with the widely-used topochemical models: Avrami-Erofeyeva, the reduced sphere, Ginstlinga-Brounstein, Taman, power and exponential laws. The calculations showed that during the first 20 min the interaction proceeds according to the model of the reduced sphere which indicates the instantaneous nucleation and is later described by the diffusive model of Ginstlinga-Brounstein.

The calculations of the activation energy activation and constants of speeds of reaction of hydrodifluoride processing of the graphite concentrate were performed on the basis of the obtained experimental data. The key kinetic parameters were defined using the Arrhenius's equation. For this purpose the functional dependences of $f(1/T) = \ln(k)$ were built where $T(\text{K})$ — temperature of process, $k$ — coefficient of topochemical reaction the last one being determined by the slope coefficient of the corresponding straight line. The definition of the activation energy showed that the Taman's models and geometrical one do not describe process of fluoration of impurities of the graphite concentrate by the ammonium hydrodifluoride because the points of the $f(1/T)$ function $\ln(k)$ do not lay down on the straight line. The process of hydrodifluoride processing of a graphite concentrate proceeding in diffusive area is well described by the Erofeyev's model. The results of the data processing in accordance with the generalized topochemical equation of Erofeyev are represented in figure 3.

It is evident that the obtained points lie on the straight line which allows to calculate value of the activation energy of the process as the product of multiplication of the universal gas constant by the tangent of the slope angle of the curve $(1/T) = \ln(k)$. The calculated values of the constants of the reaction speeds of the interaction at various temperatures and the energy of the activation process of the hydrodifluoride processing of the graphite concentrate are given in the Table 2.

The data provided in the table proves that the speed of the fluoration of the impurity elements of the concentrate depends on the temperature at which the process is carried out, at the same time the interaction speed sharply increases in the melt of the fluorinating reagent ($t_m{\text{NH}_2}\text{HF}_2 = 126.2^\circ\text{C}$) [9]. The low value of the activation energy indicates to the possibility of conducting the chemical cleaning of a graphite concentrate by means of processing of the last one by the ammonium hydrodifluoride at low temperatures.
Figure 3. The definition of the energy of activation according to the Erofeyev's model.

Table 2. The basic kinetic parameters of the fluoridation process of the impurity components of the graphite concentrate

| Temperature, °C | The speed constant $k$, min⁻¹ | The activation energy $E_{act}$, kJ/mol |
|----------------|--------------------------------|--------------------------------------|
| 80             | 0.001                          | 37.350                               |
| 110            | 0.003                          |                                      |
| 140            | 0.008                          |                                      |
| 170            | 0.152                          |                                      |

The dependence of the degree of the fluoridation of the concentrate on time (figure 2) makes it evident that at the stoichiometric ratio of the concentrate to the fluorinating reagent it is not possible to reach full interaction of the impurity elements with NH₄HF₂. The slight incrustation of the fluorinating reagent on the cover of the reactionary crucible (the fusion furnace) indicated to the partial sublimation (~10-15%) to NH₄HF₂ in these conditions and the removal of the last one from the reactionary zone. The conditions of using 20% surplus of NH₄HF₂ during the fluoration process proved to allow to achieve the full fluoridation of the impurity components of the graphite. So in these conditions the temperature of 170°C permits to reach 97.5% and 99.98% of the degree of fluorination for an hour (60 min) and hour and half (90 min) correspondingly.

Both the fluorine-ammonium salts of silicon, aluminum and iron generated due to the processing of the graphite concentrate with the ammonium hydrodifluoride and the fluorides of alkaline metals are highly soluble in water and can be removed from the fluoridated product during the water leaching. Besides, the atomic and absorbing analysis has shown that the partial passing into the solution of magnesium and calcium is observed during the water leaching of the fluoridated concentrate which is caused by the insignificant solubility of the fluorides of the last ones. The results of the atomic-absorbing determination of the content of the impurity elements which passed into solution due to the water leaching of 10 g of the processed NH₄HF₂ of the graphite concentrate are given in Table 3. The filtrates produced due to the quadruple dissolution of 10 g of the product in 100 ml of water were combined and the content of the elements was determined in the in the integrated solution. The calculation of the initial content of the impurity elements in the fluoridated concentrate has been performed taking into account that 45 g of the fluoridated product is released during the fluorination of 40 g of the graphite concentrate.

The data from the above given table indicated that during the water leaching of the fluoridated graphite concentrate the impurities of silicon and iron pass into the water solution completely. The same happens with 90% of aluminium and 50% of magnesium ones. Only insignificant part of calcium impurities pass into the solution. The purity of the graphite refined with the usage of the method is equal to 99.54-99.60%.
Table 3. The content of the impurity elements in the graphite at the various stages of cleaning

| Element | Si | Al | Fe | Ca | Mg | Na | K |
|---------|----|----|----|----|----|----|---|
| The content in 10 g |  |  |  |  |  |  |  |
| the fluoridated graphite, mg | 127.81 | 53.44 | 36.33 | 16.46 | 7.79 | 53.44 | 22.14 |
| The content in the scouring waters, mg | 127.0 | 47.3 | 35.8 | 1.8 | 3.9 | 46.8 | 22.0 |

4. Conclusion
The conditions of the purification of the natural graphite with the usage of the hydrodifluoride processing of the floatation concentrates have been studied. The interaction of the impurity elements of the concentrate with NH₄HF₂ leading to the formation of the mixture of the complex fluorne-ammonium salts and simple fluorides was established to occur during the processing of the concentrate with ammonium hydrodifluoride. The process of the hydrodifluoride processing of the graphite concentrate was found to proceed in the diffusive area and appeared to be adequately described by the Erofeyev model. The analysis of change of speed constants has shown that the speed of the fluorination of the impurity elements of the concentrate depends on temperature at which the process is conducted during the purification of the graphite concentrate with the ammonium hydrodifluoride.

The water leaching of the product of processing of the graphite concentrate with NH₄HF₂ was established to allow to pass the impurities of silicon and iron into the solution completely; the same was found to happen with 90% of aluminium and 50% of magnesium impurities; only insignificant part of calcium impurities appeared to pass into the solution.

The conducting of the process of fluoration at the temperature of 170-180°C with the usage of 20% surplus of NH₄HF₂ and the subsequent water leaching of the fluoridated product has proved to result in purification of the natural graphite with generating the mineral-dressing products with the percentage of carbon content equal to not less that 99.5%.

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