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Technology for Complex Processing of Electric Smelting Dusts of Ilmenite Concentrates to Produce Titanium Dioxide and Amorphous Silica

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Abstract: This paper presents the results of research on the development of a technology intended to process electric smelting dusts of ilmenite concentrate with the extraction of silicon and titanium and the production of products in the form of their dioxides. Dusts were processed for silicon separation using the ammonium fluoride method. The optimum conditions for the fluorination and sublimation process of silicon compounds from the electric smelting dust of the ilmenite concentrate were determined: a temperature of 260 °C, a 6 h duration, and mass ratio of dust to ammonium bifluoride of 1:0.5 ÷ 0.9. The sublimation degree of silicon compounds was ~84–91%. The sublimation of titanium fluorides from the remaining sinter was carried out at a temperature of 600 ± 10 °C for 2 h, the mass ratio titanium-containing residue: ammonium bifluoride of 1:0.5, and the degree of sublimation of titanium fluorides was 99%. Iron, manganese, and chromium impurities in the sublimation of titanium fluorides sublimate to a rather low degree. Pyrohydrolysis of titanium fluoride sublimes at 600 °C and allows for the conversion of fluorides into titanium dioxide by 99.5% in 4–5 h. Titanium dioxide of rutile modification with 99.8% TiO_2 was obtained after hydrochloric acid purification and calcination. A technological scheme for the complex processing of dust from the electric smelting of ilmenite concentrates with the production of silica and titanium dioxide is proposed.

Keywords: dust; sublimate; fluoroammonium processing; silicon dioxide; titanium dioxide

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1. Introduction

Ilmenite concentrate is used in the production of titanium metal as a feedstock. Electric melting of ilmenite concentrates to produce titanium slag and pig iron is accompanied by high dust emissions since the charge is fed in a loose state. Silicon contained in the charge is sublimed in the process of melting and falls into the thin sleeve filters together with gases entrained into the gas duct system, condensing in the form of amorphous silica SiO_2. High silica content in the dust makes it impossible to return it back to the process, so it is stored in designated storage fields for production wastes.

Considerable amounts of titanium are lost together with the dust generated in the electric smelting process of ilmenite concentrate. Its content in the dusts reaches 50%. Additional extraction of titanium from the dusty waste will not only reduce losses but also allow the acquisition of additional commercial products.

Some of the most demanded products in the market of titanium raw materials are titanium dioxide and amorphous silica. Titanium dioxide is used as a white pigment in the paint, optical coatings, pharmaceuticals, ceramics, food, and paper industries. Titanium dioxide has been used in the photoelectrochemical decomposition of water to produce hydrogen [1,2], to purify water from organics [3–9], to clean the environment from toxic

substances [10,11], in high-performance solar cells [12], as a material with antibacterial and antiviral effect for medical applications [13,14], and to create self-cleaning surfaces [15].

Due to the lack of effective technology, most of the waste from titanium production is not currently recycled. Processing is focused on traditional raw materials, the main of which are ilmenite ores and concentrates.

There are two industrial methods of titanium raw material processing for the production of titanium dioxide: sulfate or sulfuric acid and chlorine. In the sulfate method, the titanium-containing raw material (usually ilmenite concentrate) is treated with concentrated sulfuric acid, and the sulfate solution containing sulfuric salt is decomposed to produce titanium dioxide [16–20]. Sulfate technology allows the use of poorer and cheaper raw materials; however, it has several drawbacks, the main of which is the formation of large amounts of waste solutions. According to the chlorine technology [21], rutile or ilmenite is firstly subjected to the action of chlorine gas in the presence of carbon (coke, etc.) at high temperature, and titanium tetrachloride is formed, which is then oxidized by oxygen to its dioxide at 1300–1800 °C. Compared with the sulfate method, the chlorine method is more environmentally friendly. However, it is selective towards raw materials and requires the processing of high-quality rutile.

Fluoroammonium refining is becoming one of the promising methods of rare metal extraction. Ammonium fluoride, ammonium bifluoride, or their mixtures are used as fluorinating agents.

Ammonium hydrofluoride, unlike fluorine, hydrogen fluoride, and hydrofluoric acid, under normal conditions does not represent a significant environmental hazard and becomes a strong fluorinating agent when heated. The physicochemical basis for the process of fluorination with ammonium bifluoride is that oxygen-containing compounds of transition and many non-transition elements in interaction with NH_4HF_2 form very convenient for processing fluoro- or oxofluorometallates of ammonium, whose physicochemical properties ensure product solubility and the possibility to separate mixtures by sublimation [22]. A great advantage of these complex salts is their selective tendency to sublimation or thermal dissociation to non-volatile fluorides which guarantees a deep separation of the components, and the stepwise separation of NH_4F vapors allows forthe collection of the desublimate of the latter and use in a closed cycle.

In [23], during the fluorination of titanium slag with ammonium hydrofluoride, at 380 °C, the degree of sublimation of ammonium hexafluorosilicate was 99%, after sublimation of silicon hexafluoride, titanium dioxide with impurities of other oxides remained in the solid product. The separation of titanium dioxide from other components was carried out using a solution of ammonium hydrofluoride. The precipitation of the titanium compound from the ammonium fluoride solution was carried out by adding a 25% solution of ammonia water. However, titanium compounds $(NH_4)_2TiOF_4$ or $(NH_4)_3TiOF_5$ precipitated from the solution. A further shift of the equilibrium towards the formation of $Ti(OH)_4$ required multiple washing of the precipitate with ammonia water. The content of TiO_2 in the resulting product was more than 90%. A method using another fluorinating agent, ammonium fluoride NH_4F, is known [24]. The method consists in treating the initial flotation quartz-leucoxene concentrate with ammonium fluoride at a mass ratio of 0.6–1.25:1 and 195–205 °C. The compounds of silicon and titanium were separated by heat treatment of the resulting product at 295–305 °C and the sublimation of ammonium fumoride and obtaining the residue of artificial rutile containing 90–95% titanium dioxide. The method for processing titanium-containing ilmenite concentrate raw material [25] includes fluorination of raw materials, thermal treatment of the pro-fluorinated mass, separation of fluorination products through sublimation, and pyrohydrolysis of the residue after sublimation to produce iron oxide. Ammonium fluoride, ammonium bifluoride, or their mixtures was used in the fluorination process as a fluoride reagent in a stream of inert gas. Subliminal products were collected with water to produce a solution of ammonium fluorotitanate, and hydrated titanium dioxide was precipitated by water ammonia solution, followed by heat treatment of the precipitate to obtain anhydrous titanium dioxide. In the method [26], the

fluorination of an ilmenite or quartz-leucoxene concentrate was performed at a temperature of 110–195 °C or without heating, and the subsequent separation of silicon from titanium was carried out by sublimation of ammonium silicofluoride at a temperature of 305–450 °C or by aqueous leaching. The content of silicon dioxide in the titanium-containing residue was 0.3 wt%. The titanium content in silicon sublimes was less than 1 wt%. In another method [27], the ilmenite concentrate was treated with a solution of ammonium fluoride or hydrodifluoride with the separation of titanium from insoluble fluoroammonium salts of iron. Titanium fluoroammonium salts precipitated from the solution were mixed with finely dispersed silicon dioxide, then the mixture was pyrohydrolyzed at a stepwise increase in temperature to 850–900 °C with exposure at each stage for 20–60 min. Titanium dioxide with an anatase structure containing 99.5% TiO_2 and 0.5% SiO_2 was obtained.

As the review of fluoride methods for processing titanium-containing raw materials shows, the separation of silicon from titanium after treatment with a fluorine-containing agent was carried out both by sublimation of silicon fluoride and by leaching with the transfer of silicon into solution in the form of a silicofluoride compound.

The ammonium fluoride processing method makes it possible to regenerate the used fluoride reagents rather well. This has significant advantages over the sulfate method, which produces a large amount of dilute waste sulfuric acid contaminated with various impurities. This makes it difficult to return sulfuric acid back to the process. Also, the method requires a high content of titanium (not less than 46 wt% TiO_2) in the ore material. Moreover, the decomposition of titanium-containing raw materials is carried out with concentrated sulfuric acid, which poses a certain danger, since gas and reaction mass are released in this case. In the chlorine method during the processing of ilmenite, difficulties arise at the stage of separation of titanium, silicon, aluminum, and iron chlorides due to the proximity of their physical and chemical properties, and it is also necessary to strictly observe the technological regulations and safety measures due to the existing danger of phosgene formation during chlorination in the presence of carbon-containing reducing agents. Despite the fact that the use of the ammonium fluoride method requires the use of corrosion-resistant equipment and high sealing of technological stages, this method reduces the number of technological operations. The number of reagents, with the possibility of their regeneration, improves the quality of the products obtained and creates the possibility of using a safer and more environmentally friendly method.

Production waste is a complex multi-component raw material that is formed in technological processes and accumulates in its composition components similar in properties. The processing of such raw materials is already a problem. The ammonium fluoride method makes it possible to separate the target components with high selectivity and obtain end products of the appropriate quality from them.

Information about the use of fluoroammonium treatment in the available patent and scientific literature refers to natural titanium-containing raw materials. There are sporadic studies on the application of the fluoroammonium-processing method to titanium slurries with the production of calcium nitrate and titanium dioxide [28,29]. Silicon with alkali forms a water-soluble sodium silicate; therefore, in our previous studies [30], to separate silicon from titanium, electric smelting dust of ilmenite concentrate was leached with a sodium hydroxide solution. The influence of sodium hydroxide solution concentration, duration, leaching temperature, and S:L ratio on the leaching process was studied. The optimum parameters of sodium hydroxide leaching of electric smelting dust of ilmenite concentrate were determined: NaOH concentration of 110–115 g/dm^3; S:L ratio of 1:5; a temperature of 80–90 °C; and a duration of 90–120 min. The silicon extraction in the alkaline solution was 77.7%. Physicochemical studies of electrical melting dust of ilmenite concentrate showed that the silicon is in the form of a magnesium silicate phase, which, as a result of alkaline leaching, is not completely decomposed, partially remaining in the cake.

Studies were performed using high-temperature fluoroammonium processing to ensure the most complete decomposition of silicon-containing phases and to separate the silicon impurity from titanium. Taking into account the differences in the physicochemical

properties of the dust constituents, it was of interest to determine the optimal conditions for ammonium fluoride processing with the separation of silicon and titanium and the production of products in the form of their oxides with a high content of the main component.

2. Materials and Methods

Materials: all of the reagents used were ammonium bifluoride, aqueous ammonia, and hydrochloric acid were of a grade not lower than "chemically pure".

The fine dust of electric smelting of ilmenite concentrates were provided by the "Ust-Kamenogorsk Titanium-Magnesium Plant" JSC, the content of the main components of the dust is shown in Table 1.

Table 1. Composition of electric smelting dust of ilmenite concentrate (wt%).

Ti	Si	Fe	Cr	Mn	Zn	Al	Mg	O	Others
26.30	12.15	18.14	0.47	3.12	0.52	0.45	0.80	37.03	1.02

X-ray diffraction analysis (XRD) of the dust (Figure 1) showed that the substance of the dust sample is in an X-ray amorphous state and the diffractogram background is high, iron in the dust is mainly in the trivalent state, and the harmful impurity silicon is connected with titanium, magnesium, and iron.

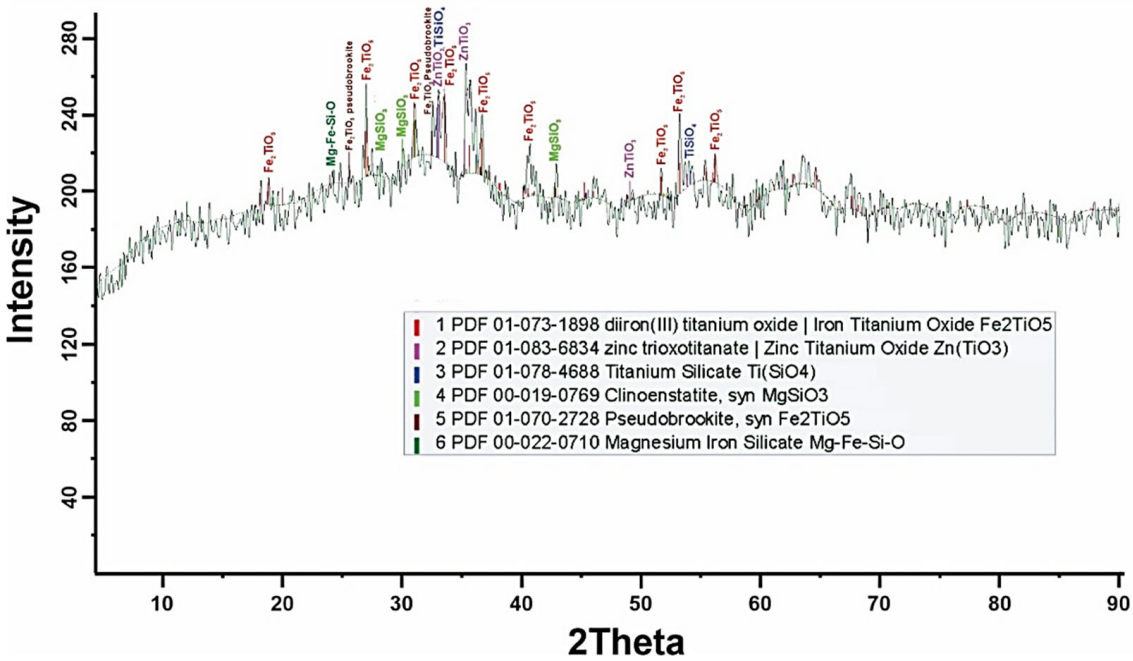

Figure 1. Diffraction pattern of electric smelting dust of ilmenite concentrate.

Analysis methods: X-ray diffraction analysis was performed on a D8 ADVANCE "BRUKER AXS GmbH" diffractometer (Karsruhe, Germany), Cu-Kα emission. The database PDF-2 International Center for Diffraction Data ICDD (Swarthmore, PA, USA) was used.

X-ray fluorescence analysis was performed using an Axios PANalytical spectrometer with wave dispersion (Almelo, The Netherlands).

The chemical analysis of the samples was performed using an Optima 8300 DV inductively coupled plasma optical emission spectrometer (Perkin Elmer Inc., Waltham, MA, USA).

Experimental procedure: to carry out the processes of sublimation of silicon or titanium fluorides, the dust or residue from the sublimation of silicon, respectively, was thoroughly mixed with ammonium bifluoride in the required ratio. The charge sample was placed in

an alundum boat and installed in a LOP LT-50/500–1200 tubular electric furnace. Argon was supplied through a horizontal pipe, and the furnace was heated to a predetermined temperature and maintained at this temperature for a certain period of time. At the end of the experiment, sublimates of ammonium hexafluorosilicate or titanium fluorides were captured at the end of the tube, and the gas-air mixture was captured in a flask with ammonia water. Preliminary experiments on the fluorination of dust from electric smelting of ilmenite concentrate determined the rate of argon supply, which makes it possible to remove fluoride fumes from the reaction zone. The argon feed rate for the used installation was 1.0–1.5 dm^3/h. The degree of fluorination and sublimation of silicon was estimated from the change in the content of the controlled component in the solid residue according to the formula:

$$E_{Si} = \frac{(C_0 - C_i)}{C_0} \cdot 100\ \% \quad (1)$$

where C_0 is the amount of silicon in the initial dust, g; C_i is the amount of silicon in the residue after fluorination and sublimation, g.

The fluorination and sublimation plants are shown in Figure 2.

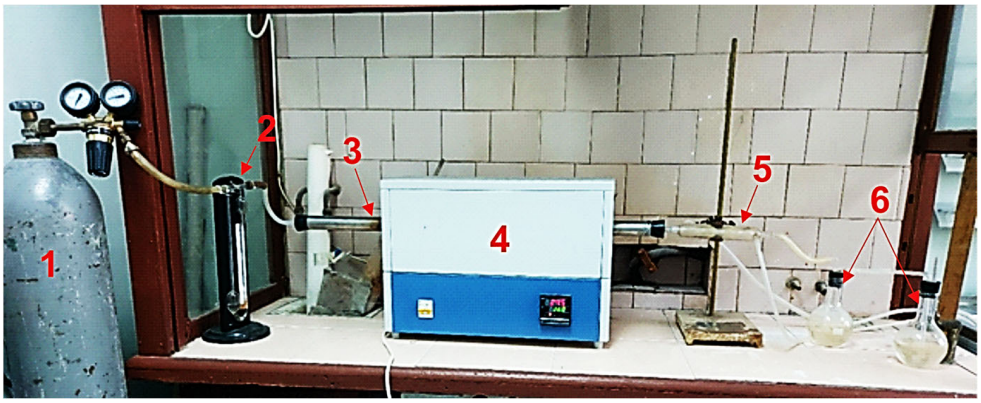

Figure 2. Assembly for laboratory research on fluoroammonium processing of electric melting ilmenite concentrate dust: 1—cylinder with argon, 2—flow meter, 3—pipe with alundum boat and sample, 4—horizontal furnace, 5—water-cooled refrigerator-condenser, and 6—gas trap system (10% NH_4OH solution).

Silicon fluoride sublimates were dissolved in water and treated with water in a ratio of solid to liquid equal to 1:10. After dissolution in water, silicon sublimes were subjected to ammonia hydrolysis. The hydrolysis of a solution of ammonium and oxonium hexafluorosilicates was conducted as follows: in a solution heated to 40 °C containing hexafluorosilicate ion, 10% or 25% ammonia solution was added in portions with active stirring to pH 7.5–8, which upon reaching it was necessary to keep the suspension for 80–90 min by stirring to form and precipitate silica flakes.

During the process of pyrohydrolysis of sublimes of titanium fluorides, a weighed sample of titanium fluorides was placed in an alundum boat and loaded into an electric furnace. After heating to 100 °C, steam was supplied to the furnace, where a boat with a sample of sublimes of titanium fluorides was previously installed. The steam rate was 1.5–2.0 dm^3/h.

Titanium dioxide was purified from impurities by hydrochloric acid solution in thermostatic reactors with a volume of 0.5 dm^3. Purification was made under established conditions and constant stirring of the pulp. Pulp stirring was performed with a glass stirrer. The stirring speed was 450 rpm.

3. Results and Discussion

3.1. Study of Silica Separation from Electric Smelting Dust of Ilmenite Concentrates

Dusts of electric smelting of ilmenite concentrates during their formation, as noted above, can concentrate silicon, the presence of which does not allow their return to the smelting process. Therefore, initially, it is advisable to remove silicon from the dust for its further processing to produce titanium dioxide. It is of interest to separate silicon and obtaining an additional product of amorphous silica.

The authors [23] suggest that the conversion of silica and other silicon compounds into fluorominium salts during the reaction with ammonium hydrofluoride produces $(NH_4)_3SiF_7$ and $(NH_4)_2SiF_6$.

However, in [31], it is argued that the formation of $(NH_4)_2SiF_6$ is thermodynamically advantageous because of the large negative enthalpy of formation and free energy compared with other silicon fluorides.

The interaction of ammonium hydrofluoride with the components of electric smelting dust of ilmenite concentrate at elevated temperatures can proceed by the reactions:

$$TiO_2 + 3NH_4HF_2 = (NH_4)_2TiF_6 + NH_3\uparrow + 2H_2O\uparrow \quad (2)$$

$$SiO_2 + 3NH_4HF_2 = (NH_4)_2SiF_6 + NH_3\uparrow + 2H_2O\uparrow \quad (3)$$

$$4FeO + 12NH_4HF_2 + O_2 = 4(NH_4)_3FeF_6 + 6H_2O\uparrow \quad (4)$$

$$Al_2O_3 + 6NH_4HF_2 = 2(NH_4)_3AlF_6 + 3H_2O\uparrow \quad (5)$$

$$2MnO + 3NH_4HF_2 = 2NH_4MnF_3 + NH_3\uparrow + 2H_2O\uparrow \quad (6)$$

The influence of various factors on the sublimation of silicon from electric melting dusts was studied.

3.1.1. Influence of the Temperature of the Fluorination Process

The investigations were performed in the temperature range of 200–280 °C. The duration of the experiments was 6 h, and the ratio of masses of electrofusion dust of ilmenite concentrate to ammonium hydrodifluoride was 1:0.9.

It is shown in Table 2 that with an increase in the process temperature from 200 to 280 °C, the yield of the residue from fluorination decreases, which is associated with an increase in the consumption of the fluorinating agent for the reaction with dust components and the removal of silicon fluoride from the reaction zone by the argon flow.

Table 2. Influence of fluorination temperature on the controlled elements content in the residue.

Temperature, °C	Residue Yield from Fluorination,%	Content of Components in the Residue, wt%							
		Si	Ti	Fe	Cr	Mn	O	F	Others
200	79.6	8.4	17.3	12.9	0.40	3.2	9.1	30.1	18.60
230	68.4	6.4	17.6	14.6	0.51	2.9	-	31.1	26.89
250	54.4	2.7	25.7	19.6	0.65	4.5	10.1	24.3	12.45
260	47.8	1.7	28.7	20.7	0.76	4.7	13.9	26.6	2.94
280	44.9	1.5	29.6	22.0	0.81	5.0	14.8	25.9	0.39

The analysis of the data presented in Table 2 and Figure 3 shows that the process temperature of 260 °C results in the sublimation degree of silicon fluoride up to 84.2% and its content in the titanium-containing intermediate product decreases by eight times compared with the initial dust. Further temperature increase has an insignificant influence on the sublimation degree of silicon fluoride and its content in the residue from fluorination.

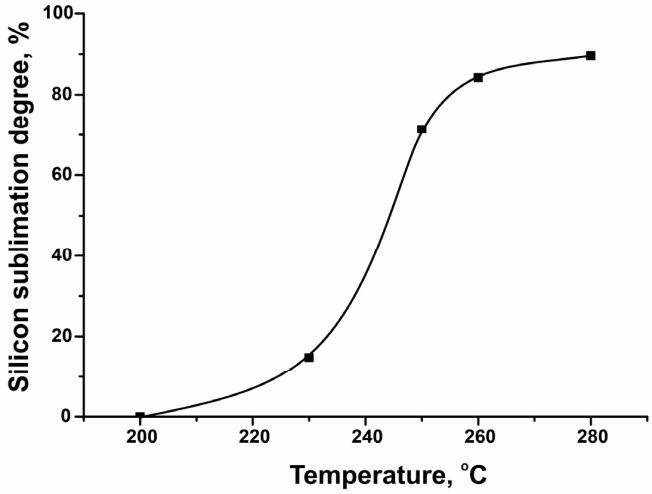

Figure 3. Influence of temperature on silicon fluoride sublimation.

It should be considered that the optimal temperature for fluorination of electric smelting of ilmenite concentrate to separate the silicon should be 260 °C.

3.1.2. Effect of the Fluoridation Duration

The study of the influence of fluorination process duration was performed in a series of experiments with different time intervals of 2–8 h at 260 °C and mass ratio of dust to ammonium bifluoride of 1:0.9. The results of studies are shown in Table 3 and Figure 4.

Table 3. Results of fluorination of electrosmelting dust of ilmenite concentrate. Influence of the process duration.

Duration of Experiment, h	Residue Yield from Fluorination,%	Content in the Residue, wt%							
		Si	Ti	Fe	Cr	Mn	O	F	Others
2	65.3	5.4	21.7	17.2	0.57	3.8	8.1	25.4	17.83
4	58.2	4.8	25.4	17.0	0.72	4.3	10.7	26.9	10.18
6	47.8	1.7	28.7	20.7	0.76	4.7	13.9	26.6	2.94
8	43.7	1.5	30.3	22.2	0.80	5.1	13.0	27.0	0.10

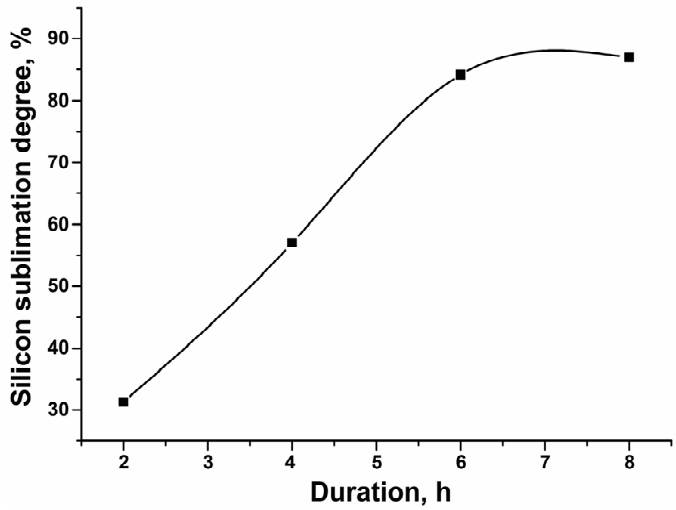

Figure 4. The dependence of the degree of sublimation of silicon from silicon dust of electrofluorination of ilmenite concentrate during fluorination.

The curve in Figure 4 on the segment of 2–6 h describes a rectilinear dependence of silicon fluoride sublimation degree on the process duration. The sublimation rate of silicon decreases and its content in the residue insignificantly changes in 6 h of fluorination (Table 3).

XRD analysis showed that formed ammonium hexafluoride does not sublimate completely in 2–4 h. The reaction of ilmenite fluorination is not completed (Figure 5).

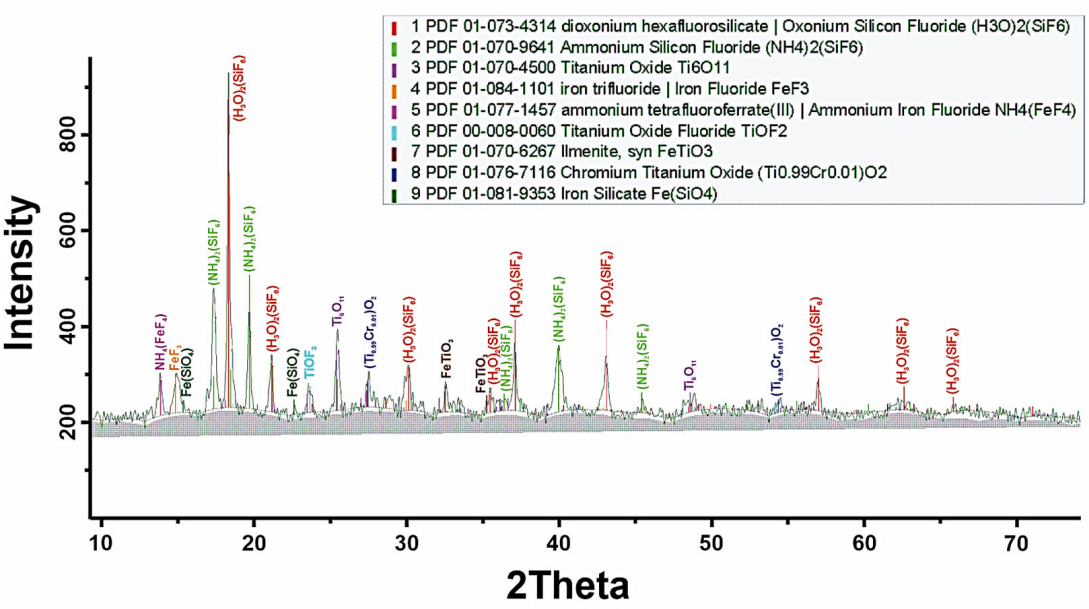

Figure 5. A diffractogram of the residue from fluorination of electrosmelting dust of ilmenite concentrate (2 h, 260 °C, dust:NH_4HF_2 = 1:0.9).

An increase in the fluorination duration up to 6 h allowed almost complete extraction of silicon in the sublimations (Figure 6) [32].

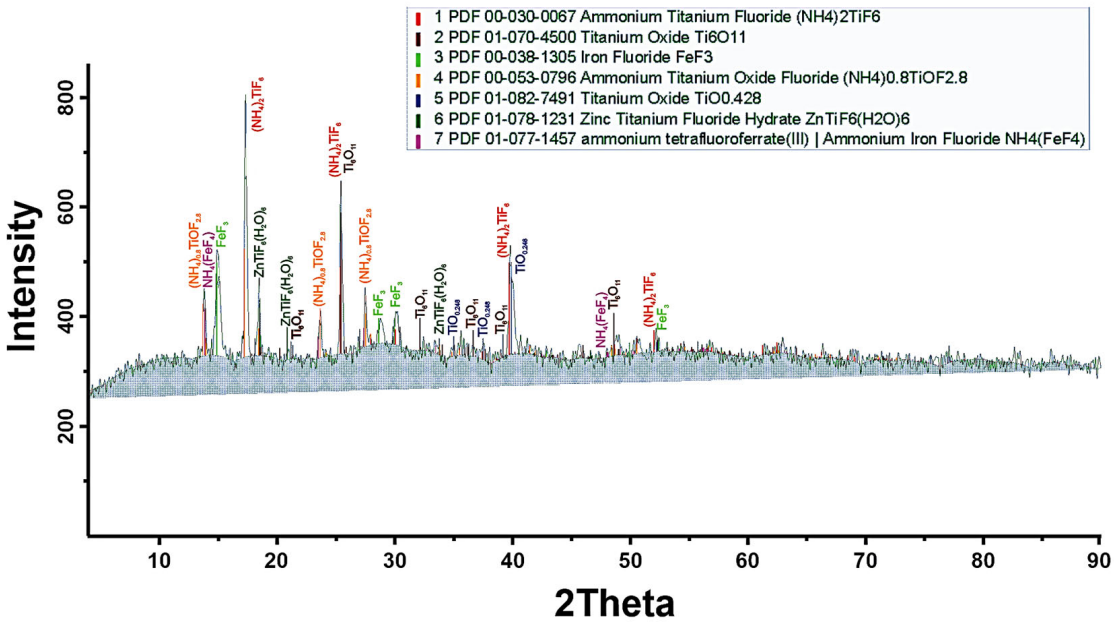

Figure 6. A diffractogram of the residue from fluorination of electrofusion dust of ilmenite concentrate (6 h, 260 °C, dust:NH_4HF_2 = 1:0.9).

3.1.3. Influence of Mass Ratio of Dust from Electric Smelting of Ilmenite Concentrate to Ammonium Bifluoride

The study of the influence of specific ammonium bifluoride consumption on fluorination of electrical melting components of ilmenite concentrate dust with formation and sublimation of silicon fluoride was performed at a temperature of 260 °C with a 6 h duration.

Table 4 represents the data on the change of the content of controlled elements in the residue from fluorination, which shows that the silicon fluoride sublimation degree was 90.6% at a mass ratio of dust to ammonium bifluoride of 1:0.5.

Table 4. Results of fluorination of electric melting dust of ilmenite concentrate. Influence of dust:NH_4HF_2 mass ratio.

Dust:NH_4HF_2 Mass Ratio	Residue Yield from Fluorination,%	Content in the Residue, wt%							
		Si	Ti	Fe	Cr	Mn	O	F	Others
1:0.5	32.1	1.5	29.7	20.6	0.73	4.6	30.2	8.7	3.97
1:0.9	47.8	1.7	28.7	20.7	0.76	4.7	13.9	26.6	2.94
1:1.5	70.8	3.05	19.7	15.4	0.55	3.4	11.0	27.8	19.1

With an increase in the consumption of ammonium hydrodifluoride (mass ratio 1 :0.9), the silicon fluoride sublimation degree remains satisfactory. At the same time, ilmenite, iron oxide, and a part of titanium oxides are completely fluorinated.

Further increase of the specific flow rate of ammonium hydrofluoride decreases the degree of silicon fluoride sublimation (Figure 7). It is connected with the formation of a big mass of the melted dust mixture with ammonium hydrofluoride that made it difficult to free silicon fluoride in the gas phase.

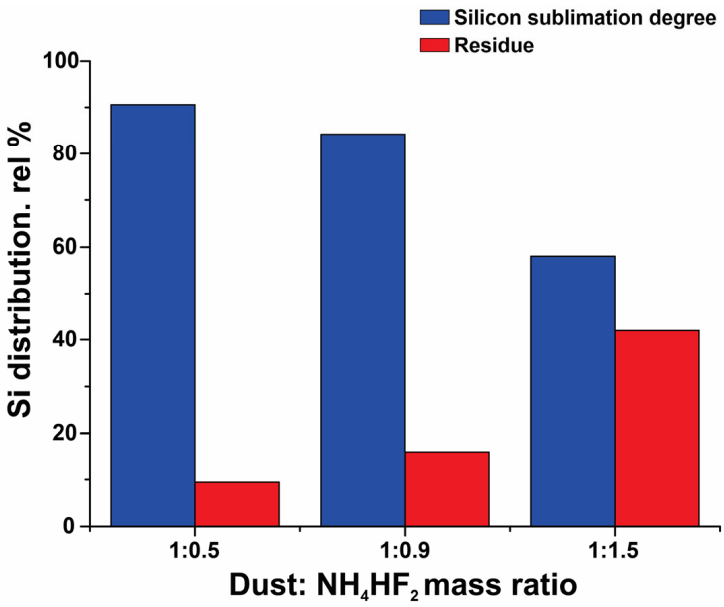

Figure 7. Dependence of silicon sublimation degree from smelting dust of ilmenite concentrate during fluorination on specific flow rate of ammonium bifluoride.

Thus, the optimal conditions for fluorination of electric melting dust of ilmenite concentrate were experimentally established: 260 °C temperature, 6 h duration, and a mass ratio of dust to ammonium bifluoride of 1:0.5–0.9. The degree of sublimation of silicon fluoride was ~84–91% under these conditions.

3.2. Silicon Dioxide Production

The obtained silicon-containing sublime is represented by oxonium hexofluorosilicate $(H_3O)_2SiF_6$ (~98%) and ammonium hexofluorosilicate $(NH_4)_2SiF_6$ (~2%) [32]. Ammonium and oxonium hexafluorosilicates are well soluble in water at room temperature. Precipitation of silicon oxide was performed with ammonia for 30–90 min, and the suspension was held for the formation and precipitation of silicon oxide flakes. The obtained amorphous product had the following composition (wt%): 81.6 SiO_2; 12.9 NH_4F; 0.045 Fe; 0.005 Cu; 0.025 Zn; 0.014 As; 0.003 Sr; and 0.017 Pb. The product contains insignificant amounts of heavy metals and arsenic. The presence of ammonium fluoride is due to its absorption by amorphous particles, and it cannot be removed by washing the sediment with water. Ammonium fluoride is known to decompose when it is heated. The sample was heated and incubated at 530–560 °C for 60–80 min to ensure the most complete decomposition of ammonium fluoride and its removal from the sample composition [33]. The resulting silica had the following composition (wt%): 96.3 SiO_2; n/d F; 0.14 Fe_2O_3; 0.16 Al_2O_3; 0.02 ZnO; 0.03 CaO; and 0.15 TiO_2. According to the content of silicon dioxide and accompanying impurities of iron, calcium, and magnesium, the product meets the requirements of the state standard GOST 18307-78 for the "White soot" brand BS-100 [34].

3.3. Titanium Fluoride Sublimation and Study of the Behavior of Impurity Components during Fluorination

The residue from dust fluorination with sublimation of silicon fluorides mainly consists of titanium compounds (Figure 6). The studies were performed to determine the optimal conditions of the process intended to provide the most complete sublimation of titanium fluorides from the residue. The influence of temperature (450 to 650 °C) and duration (0.5 to 4 h) on titanium fluorides sublimation degree were studied [35]. The optimal conditions of the sublimation process of titanium fluorides were a temperature of 600 ± 10 °C, a duration of 2 h, and a mass ratio of titanium-containing residue (ammonium bifluoride) of 1:0.5. Sublimation degree of titanium fluorides under these conditions reached 99%. Fluoride sublimations were composed of the following phases: $(NH_4)_2TiF_6$, $(NH_4)_3TiF_7$, $(NH_4)FeF_6$, and NH_4HF_2.

Strict requirements for the content of chromophoric impurities are applied to the pigment titanium dioxide which imparts a different color to a white pigment even at a very small content.

The sublimation of iron, manganese, chromium, and residual silicon during the sublimation of titanium fluorides was studied in this connection. Studies on the effect of the process duration on the sublimation degree of iron, manganese, chromium, and silicon were performed at 610 °C in the range of 30–240 min. The results of the experiments on the sublimation of impurities are shown in Figure 8.

The results showed that silicon in the form of ammonium fluorosilicate is almost completely extracted into sublimations in the first 30 min of the process.

The curves of dependence of the sublimation degree on the duration of the experiment for iron, manganese, and chromium are similar and only differ in the value of the sublimation degree (Figure 8). Sublimation of iron within 2 h of the process occurs at 15.1%, of manganese at 9.3%, and of chromium at 13.6%. This behavior is due to the conditions of the experiments. Heating of the furnace to 610 °C occurs at a rate of 20 °C/min which contributes to the sublimation of impurity components.

It should be noted that in spite of a certain sublimation of iron, manganese, and chromium, their content in the residue increases. The content of iron increased by 1.8, manganese by 1.9, and chromium by 2.0 times during 2 h (Table 5).

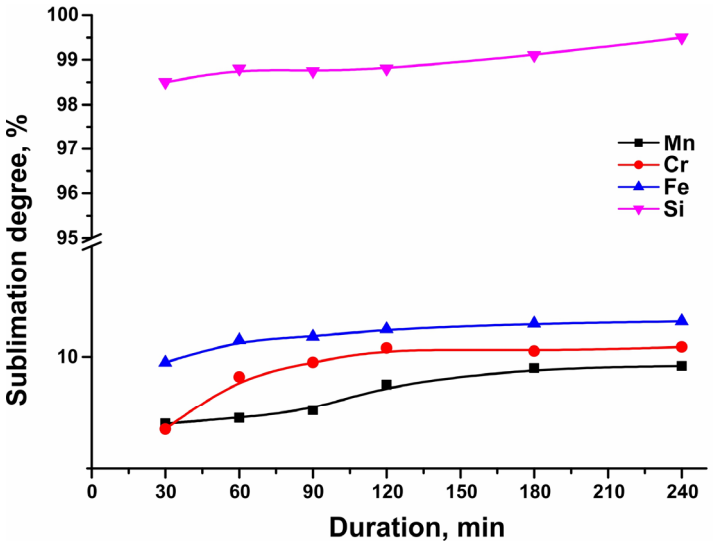

Figure 8. Influence of process duration on sublimation of impurities from fluorinated dust of electric melting of ilmenite concentrate.

Table 5. Effect of the duration of the experiment on the content of impurity components in the cinder.

Duration, min	Content * in the Cinder, wt%			
	FeO	SiO_2	MnO	Cr_2O_3
init.	23.0	1.28	2.35	0.39
30	40.6	0.071	4.32	0.64
60	40.4	0.058	4.36	0.69
90	41.6	0.057	4.39	0.74
120	42.1	0.051	4.44	0.76
180	43.7	0.043	4.50	0.77
240	45.4	0.036	4.58	0.79

* component content is given in terms of the oxide form.

Studies of the process of sublimation of impurity components during the fluorination of titanium from sinter showed that, under experimental conditions, such impurities as iron, manganese, and chromium sublimate with a fairly low degree together with titanium.

3.4. Titanium Dioxide Production and Purification

Pyrohydrolysis of titanium fluorides. Fluoride technology involving pyrohydrolysis of titanium fluorides to produce titanium dioxide is one of the ways to produce high-quality titanium oxide products.

Obtained fluoride sublimations of titanium have the following composition (wt%): 59.0 Ti; 0.6 Fe; 0.005 Si; 0.09 Cr; 0.14 Al; 20.4 F; and 19.8 O. Studies of titanium fluoride pyrohydrolysis with the investigation of the influence of temperature (in the range from 300 to 700 °C) and duration of the process (in the range from 1 to 5 h) have shown that optimal parameters are 600 °C and a duration of 4–5 h [36].

Obtained titanium dioxide was contaminated with impurities and had a grayish hue, therefore *hydrochloric acid treatment* of the product was performed.

Studies of the hydrochloric acid leaching process of pyrohydrolysis products were performed to provide the most complete purification of titanium dioxide. The influence of hydrochloric acid concentration (in the range from 5 to 15% HCl), S:L ratio (from 1:4 to 1:8), and the process duration (in the range from 5 to 60 min) on the conversion degree of manganese, iron, and chromium impurities into the solution was studied. As a result of this

research, the following optimum conditions of the purification process were determined: 12.5–15% HCl; a temperature of 25–30 °C; ratio S:L of 1:6 ÷ 8; and a duration of 20–30 min.

Titanium dioxide after acid processing consisted of two modifications: 94% anatase and 6% rutile. High quality of pigmental titanium dioxide is provided by the rutile phase; therefore, titanium dioxide was calcined at a temperature of 900 °C for 2 h to obtain the rutile modification. The TiO_2 content was 99.8 wt%, and the content of impurities of silicon, chromium, manganese, and iron in recalculation on their oxides was 0.0005, 0.032, 0.005, and 0.039 wt%, respectively, in the obtained rutile product [36]. According to the content of the main component and accompanying impurities, the product complies with the requirements of the state standard GOST 9808-84 for pigment titanium dioxide [37].

3.5. Process Flow of Complex Processing of Electric Smelting Dust of Ilmenite Concentrates

The conducted studies formed the basis for the development of a technology for the integrated processing of fine dusts from the electric smelting of ilmenite concentrates to extract silicon and titanium and the production of oxide products (Figure 9).

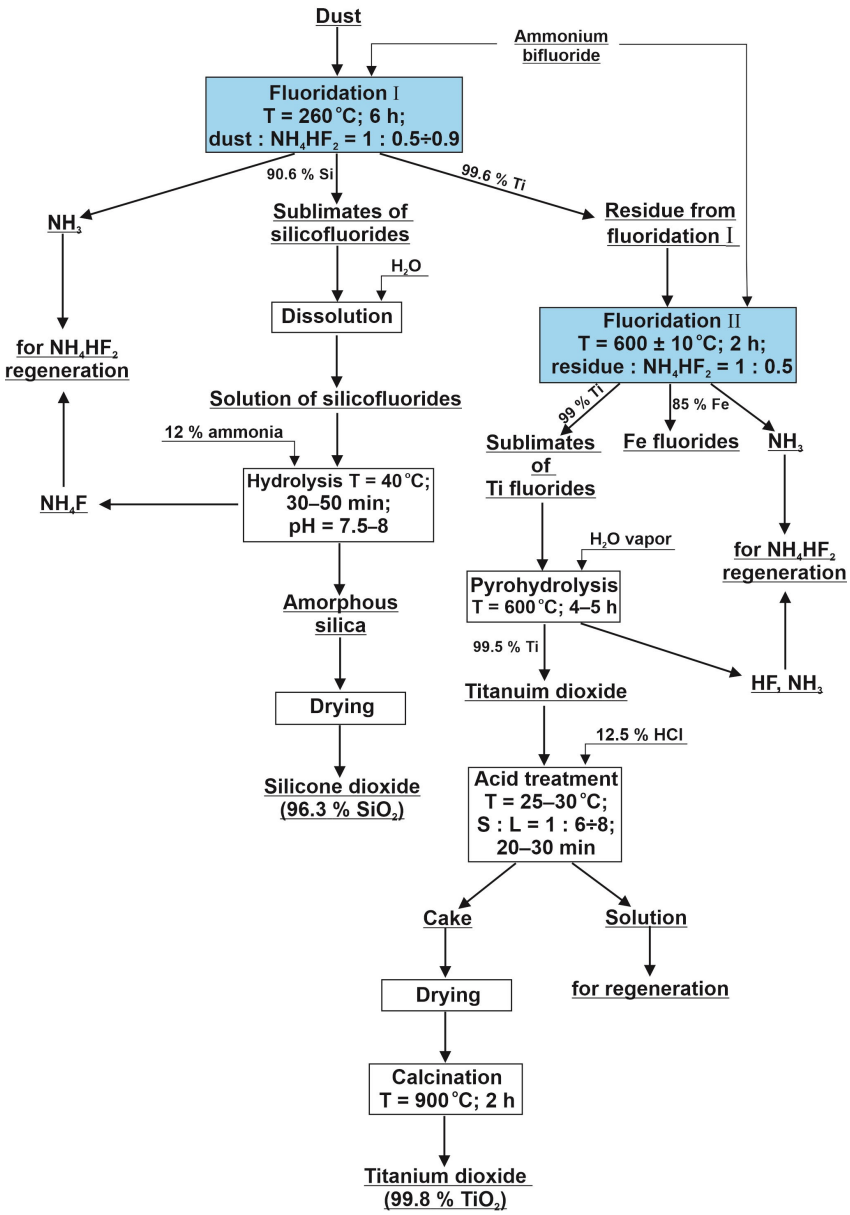

Figure 9. Basic process flow of fine dust processing of electric smelting of ilmenite concentrates.

The dust from the smelting of ilmenite concentrates is hydrofluorinated in a molten ammonium bifluoride at 260 °C, producing silicon fluorides in the form of sublimations and separating them from iron and titanium.

During fluorination of electric smelting dust of ilmenite concentrate, a mixture of gases (water vapor and ammonium fluoride) is formed and sent for condensation (regeneration of ammonium fluoride).

Aspiration containing silicon fluoride is dissolved in water, and amorphous silicon dioxide is precipitated by a 12% ammonia solution. Under these conditions, amorphous silica contains an impurity of fluorine ions. When amorphous silica is dried at 200–300 °C, the fluorine ion is removed along with water vapor, and the remainder is pure amorphous silica.

The residue from fluorination containing iron and titanium is subject to fluorination at 590–610 °C. The titanium component is completely separated from iron and impurities.

Sublimated titanium fluoride goes to the oxidative pyrohydrolysis operation (interaction with superheated water vapor and air oxygen).

Heat-treatment conditions of the final titanium product are maintained depending on the desired structure of the resulting titanium dioxide.

Thus, the complex processing of electric smelting dusts of ilmenite concentrate with the production of silica and titanium dioxide products is possible according to the given regimes.

4. Conclusions

Based on the research results, a technology intended to produce amorphous silica and titanium dioxide from fine-dispersed dust of electrical smelting of ilmenite concentrate was proposed.

A study of the effect of different parameters on the fluorination and sublimation of silicon from the electric smelting dust of ilmenite concentrate showed that the optimum conditions of the process are a temperature 260 °C, duration of 6 h, and a mass ratio of dust to ammonium hydrodifluoride of 1:0.5 ÷ 0.9. As a result, the sublimation degree of silicon fluoride compounds was equal to ~84–91%. After ammonia hydrolysis of silicon fluoride sublimates dissolved in water and further drying of the precipitate, amorphous silica was obtained with a content of 96.3% SiO_2.

The sublimation of titanium fluorides from the remaining sinter was carried out at a temperature of 600 ± 10 °C for 2 h, the mass ratio of titanium-containing residue to ammonium bifluoride was 1:0.5, and degree of sublimation of titanium fluorides was 99%.

A study of impurities behavior during the sublimation of titanium fluorides from the sinter showed that iron, manganese, and chromium were sublimated with a sufficiently low degree. The content of these impurities in the residue after sublimation of titanium fluorides increases by approximately two times.

After pyrohydrolysis of titanium fluoride sublimes, hydrochloric acid purification, and subsequent calcination of titanium dioxide, the product of rutile modification with a content of 99.8% TiO_2 was obtained.

The process flow for complex processing of electric smelting dusts of ilmenite concentrates with the production of titanium dioxide and silicon dioxide was proposed according to the results of the research.

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Symbols and Abbreviations

IMOB JSC	Institute of Metallurgy and Ore Beneficiation Joint Stock Company
UK TMC JSC	"Ust-Kamenogorsk Titanium-Magnesium Combine" Joint Stock Company.
XRD	X-ray diffraction analysis
S:L	ratio of solid phase weight (in grams) to liquid phase volume (in ml)

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