

## Processing of Titanium-Magnesium Production Waste

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### ABSTRACT

The article presents the results of research on the processing of such wastes of titanium-magnesium production as sludge from sludge dumps and fine dump dusts from the electric smelting of ilmenite concentrates. The results of nitric acid leaching of sludge with the transfer of calcium into solution and the production of calcium nitrate are given. Titanium-containing cake after nitric acid leaching of sludge and electric smelting dust cannot be returned to the technological process due to its high silica content, so the silicon impurity was removed from their composition. Silicon removal was performed by fluoroammonium processing with sublimation of hexafluorosilicate compounds. An amorphous silicon dioxide product was obtained, after ammonia hydrolysis of silicon-containing sublimations and appropriate treatment of the sediment. The residue from the sublimation of silicon fluorides consists mainly of titanium-containing phases and can be suitable for return for electrofusion after ammonia treatment.

**Keywords:** waste, sludge, dust, leaching, sublimation, ammonium bifluoride, calcium nitrate, amorphous silicon dioxide.

### INTRODUCTION

The Kroll process is the main method of titanium sponge production in all titanium sponge producing countries of the world (Chervony et al., 2008), which consists in magnesium thermal reduction of titanium tetrachloride at 850 °C. The largest producers of titanium sponge are China, Japan, Russia, Kazakhstan, the USA and Ukraine (World titanium market: trends and prospects, 2018; Liu et al., 2015; Gao et al., 2018). The Kazakhstani enterprise “Ust-Kamenogorsk Titanium and Magnesium Plant” JSC (“UKTMP” JSC) supplies about 18% of the world production of titanium sponge. Ilmenite concentrate is used, as a raw material for the production of titanium, during the reduction electric smelting of which titanium slag and substandard cast iron are obtained. Electric smelting of ilmenite concentrates is accompanied by a large dust emission. Dust cannot be returned to the electric smelting process or fed into chlorinators due to the high content of silica. The captured dust cannot be recycled back

into the process, so it is stored together with other solid waste in designated areas, landfills. Up to 76 thousand tons of chloride waste is generated annually at “UKTMK” JSC, including about 600 tons of fine sleeve filter dust. Part of chloride waste from titanium production is leached with water and neutralized with calcium hydroxide to pH 7–8.5. The resulting slurry is pumped to the sludge collectors by pumps and accumulates in them. Reserves of sediments or sludge from titanium production are about 320 thousand tons, the polycomponent composition of which is present in the form of oxides, oxychlorides and carbonates (Baybekov et al., 1987; Belonozhko et al., 1988). Industrial waste poses a danger to the environment, polluting soils and natural waters when they are released into the atmosphere, when industrial wastewater is discharged into water bodies, and also when solid waste is placed in sludge storage facilities (Teploukhov, 2005; Ospanov et al., 2022). Therefore, it is of great interest to find ways to reduce the formation of titanium production waste, as well as to extract valuable

components from them. Waste from sludge collectors and dust from ore-thermal smelting can become a source of calcium nitrate and amorphous silicon dioxide, which are currently in high demand all over the world.

There is no effective integrated processing of titanium production waste in the world. Existing industrial technologies are aimed at processing natural mineral raw materials. The main methods of titanium raw material opening are sulfuric acid and chlorine methods, which were introduced in the middle of the twentieth century in a number of countries. The sulfuric acid process treats titanium-containing raw material with concentrated sulfuric acid and produces a sulfate solution, which hydrolytic decomposition precipitates titanium dioxide (Weintraub, 1912; Weizmann and Blumenfeld, 1925; Mecklenburg, 1930). Sulfuric acid technology is accompanied by the formation of a large amount of hydrolytic acid and contaminated wastewater. Rutile is first exposed to the action of chlorine gas, according to the chlorine technology, while titanium tetrachloride is formed, which is then transferred to a pigment at a high temperature in a mixture of air and oxygen (Barksdale, 1966). Only high-quality rutile should be used for chlorine technology, which requires additional preliminary preparation of titanium raw material.

Traditionally, non-ferrous metal ore raw materials are enriched using classical methods before metallurgical processing (Mukhanova et al., 2022). Waste from titanium production, especially such as waste sludge, has a very complex polycomponent composition. Hydrometallurgical methods can be reasonable for preliminary processing of such raw materials. One of the main components in sludge is calcium (~27–30 % CaO), the presence of which is explained by neutralization of discharged waste. When extracting calcium from the sludge, the residual titanium product can be concentrated. Nitric acid leaching is one method of extracting calcium in solution as a soluble calcium nitrate compound. The nitrate salt solution may be suitable for obtaining fertilizers. There are works, which use nitric acid decomposition of calcium-containing raw materials to produce calcium nitrate solution. The phosphorites from the AbuTartur deposit (Egypt), containing more than 40 % of calcium in terms of its oxide, were leached with nitric acid (Monir et al., 1999). The solution, after extraction of rare-earth metals from it, was

cooled for crystallization  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ . Nitric acid was also used in studies (Jorjani et al., 2011) to decompose apatite concentrate of Chadormalu plant (Iran). There is a known method for extracting rare-earth metals during the processing of Khibiny apatite concentrate (Goldin et al., 1982), which consists in decomposing the concentrate with nitric acid, separating calcium nitrate from the resulting nitric phosphate solution, and further processing the solution. In studies on the processing of phosphorus production slag (Abisheva et al., 2017; Akcil et al., 2018), which contains about 40% CaO, the slag is leached with nitric acid, and after the extraction of rare earth metals, the resulting nitrate solution is proposed to be used for fertilizer production.

The presence of a significant amount of other impurities, in particular silicon, in titanium production wastes will not allow titanium-containing wastes or products of their processing to be returned to the technological process. Therefore, it is of interest to remove silicon from waste to obtain such a sought-after product as amorphous silica.

Fluoroammonium recycling has recently become one of the most promising methods of extracting valuable components. There are studies on the processing of silicon-containing and titanium-containing raw materials with the use of fluoroammonium compounds. The possibility of separating aluminosilicates by ammonium bifluoride into alumina and silicon oxide by sintering was shown in works (Rimkevich et al., 2010; Nasekan et al., 2011). Ammonium bifluoride ( $\text{NH}_4\text{HF}_2$ ) was used as a fluorinating reagent for complex processing of kaolin concentrates. Ammonium bifluoride under normal conditions is not a significant environmental hazard and is a strong fluorinating reagent when heated, its melting point is 126.2 °C and decomposition is 238 °C. Sintering of kaolin concentrate with  $\text{NH}_4\text{HF}_2$  takes place at 190–200 °C to form a powdery product; desiliconization of this product under oxidizing conditions takes place at temperatures above 320 °C. Capture ammonia gas and water vapor enters the absorption apparatus, and ammonium fluoride enters there as well. Evaporation of the resulting solution produces regenerated  $\text{NH}_4\text{HF}_2$ , which goes to the head of the process. Hydrochemical fluorination of kaolin can achieve complete extraction of silica. Processing of titanium-containing raw materials of ilmenite concentrate includes fluorination of raw materials by sintering with fluoride reagent, heat treatment of profluorinated mass for separation

of fluorination products by sublimation, pyrohydrolysis of residue after sublimation to obtain iron oxide (Andreev and Dyachenko, 2009). Ammonium fluoride is used in the process of fluorination as a fluoride reagent, ammonium bifluoride or a mixture of them in a stream of inert gas, the sublimation products are captured with water to obtain a solution of ammonium fluorotitanate and sedimentation of hydrated titanium dioxide with aqueous ammonia, followed by heat treatment of the precipitate to obtain anhydrous titanium dioxide. In the work (Dmitriev et al., 2021), during the fluorination of titanium slag with ammonium hydrodifluoride, sublimation of hexafluoride occurs almost completely at a higher temperature of 380 °C; after sublimation of hexafluoride, titanium dioxide with impurities of other oxides remains in the solid product. There is a method of using another fluorinating agent ammonium fluoride  $\text{NH}_4\text{F}$  (Fedun et al., 2005). The method consists in the fact that the initial flotation quartz-leukoxene concentrate is treated with ammonium fluoride at a mass ratio to the concentrate (0.6–1.25): 1 and at a temperature of 195–205 °C. The separation of silicon and titanium compounds is carried out by heat treatment of the resulting product at a temperature of 295–305 °C with sublimation of ammonium silicofluoride and obtaining artificial rutile in the residue containing 90–95% titanium dioxide.

An analysis of scientific, technical and patent literature has shown that, the use of nitric acid leaching and fluorination methods makes it possible to effectively separate calcium and silicon from other valuable components in the processing of silicon-containing and titanium-containing raw materials. Research on the processing of titanium-magnesium production waste will make it possible to create technologies for their utilization to obtain a titanium-containing product suitable for return into the process of electric melting, calcium nitrate and amorphous silicon dioxide, which would supplement our market with additional products in demand.

## MATERIALS AND METHODS

Materials and equipment: nitric acid, purity grade “chemically pure (C.P.)”; calcium oxide, purity grade “chemically pure (C.P.)”; acidic fluoride ammonium, purity “Reagent grade”; water ammonia, purity “Reagent grade”; slime of titanium production and dust of bag filters for electrical melting of ilmenite concentrates, provided by

“UKTMK” JSC (Republic of Kazakhstan). The content of the main components of titanium production sludge, wt. %: 6.8 Ti; 2.8 Fe; 19.4 Ca; 2.2 Al; 8.2 Si; 0.13 V; 0.3 Nb; 7.1 C. The content of the main components of the dust of the electric smelting of ilmenite concentrate, wt. %: 20.6 Ti; 12.8 Si; 14.1 Fe; 3.2 Mn; 0.5 Cr. Vibrating grinding mill IV-1 (Russia), stirrer ES VELP (Velp Scientifica), stirrer IKA RW16 (Germany), Kejia vertical tubular furnace (China), horizontal tubular furnace (Russia), Shimadzu balance (Japan), pH meter 150 MI (Russia), AREC magnetic stirrer (Switzerland), SNOL 7,2/1300 muffle furnace (Lithuania), drying cabinet (Russia), distiller (Russia), laboratory granulator, REC VELP Scientifica heating ceramic tile.

Methodology of experiments. Nitric acid leaching of titanium sludge was performed as follows. A slime sample was placed in a glass beaker with nitric acid, leached at a given temperature for a given time. The pulp was filtered; the cake was dried. Neutralization or precipitation of impurity components from the solution was performed in a glass beaker while stirring the solution with the addition of lime milk to a given pH value, then the pulp was filtered, the cake was dried. A weighed portion of dust or cake was thoroughly mixed with ammonium bifluoride in a certain ratio and placed in an alundum boat, after sludge leaching, which was installed in a steel pipe located in a LOIP LF-50/500-1200 horizontal tube furnace. Argon was supplied through a steel pipe and the furnace was heated to a predetermined temperature for a certain period of time. Ammonium hexafluorosilicate sublimates were captured at the end of the steel pipe, and the gas-air mixture was captured in a flask with ammonia water, at the end of the experiment. The degree of fluorination was estimated from the change in the content of controlled components in the solid residue. The argon feed rate was 1.0-1.5  $\text{dm}^3/\text{h}$ .

Silicon-containing sublimate and the residue after hydrolysis were treated with water at a solid-liquid ratio of 1:10÷20, then heated to 40–50 °C solution containing hexafluorosilicate ion was injected in portions with active agitation to pH 7.5–8, then the precipitate after hydrolysis was filtered, washed and dried, we obtained amorphous silica.

Methods of analysis: X-ray experimental data were obtained on a BRUKER D8 ADVANCE apparatus using copper radiation at an accelerating voltage of 36 kV, current 25 mA. X-ray fluorescence analysis was performed on a Venus 200 PANalytical B.V. wave dispersion spectrometer.

(PANalytical B.V., Holland). Chemical analysis of the samples was performed on an optical emission spectrometer with inductively coupled plasma Optima 2000 DV (USA, Perkin Elmer).

## RESULTS AND DISCUSSION

### Processing of waste sludge from titanium production

Sludge from titanium production was crushed, averaged and dried before physicochemical studies. The main minerals present in the sample are calcite, vaterite, quartz, various titanium phases and others – ockermanite from the mellilite group, portlandite, hydrocalumite, according to XRD and mineralogical analyses. XRD analysis of the slurry is shown in the Figure 1.

#### Sludge leaching with nitric acid

The leaching of titanium slurry with nitric acid was investigated in order to convert calcium to solution and titanium to cake. The influence of nitric acid concentration, S:L ratio, temperature and duration on the leaching process was studied (Ultrarkova et al., 2019). The following optimal leaching parameters were determined: 20% concentration of nitric acid, pH<1, ratio S:L=1:10, time 30 min, temperature 20±4 °C, stirring speed 300 rpm. The extraction of calcium into solution under these conditions was 84.7%.

#### Purification of nitrate solution from impurities

The nitrate solution obtained after sludge leaching contained impurities. Composition of the

solution, wt.%: 0.72 Ti, 18.1 Ca, 0.047 Si, 1.15 Fe, 0.032 Nb, 1.09 Al, 0.025 V solution pH -0.86. The reagent for precipitation of impurities was chosen milk of lime. Experiments on precipitation of impurities from the solution were performed beforehand. The solutions were analyzed for the content of the main component and impurities after filtration. Conditions of experiments and composition of filtered solutions are presented in Table 1. The Table 1 shows that the main impurities of iron, aluminum and titanium remain in the solution at pH values -0.56 and 0.03. The content of iron, titanium and aluminum impurities significantly decreases in solutions at pH values of 2.8–5. Increasing the time of precipitation of impurities also positively affects the purification of the solution.

The following parameters were studied to clarify the conditions and determine the optimum conditions of the precipitation process: stirring time after adding the precipitant (30, 60, 90, 120, 150 min), temperature (20, 40, 80, 100 °C); acidity of the medium after adding the precipitant (pH equals 5, 8 and 10). Optimal parameters of precipitation of impurity components were determined: the addition of lime milk to pH 10, at a temperature of 20±5 °C, precipitation time 60 min, stirring speed of the solution 300 rpm. The composition of the solution obtained under optimum conditions, g/dm<sup>3</sup>: 22.02 Ca, 0.006 Si, 0.0006 V, and Ti, Fe, Al, Mn, Zn were not detected.

#### Obtaining calcium nitrate salt

A viscous amorphous substance was obtained by evaporation at a temperature of 100 °C for 4 hours of a purified solution with pH 10,

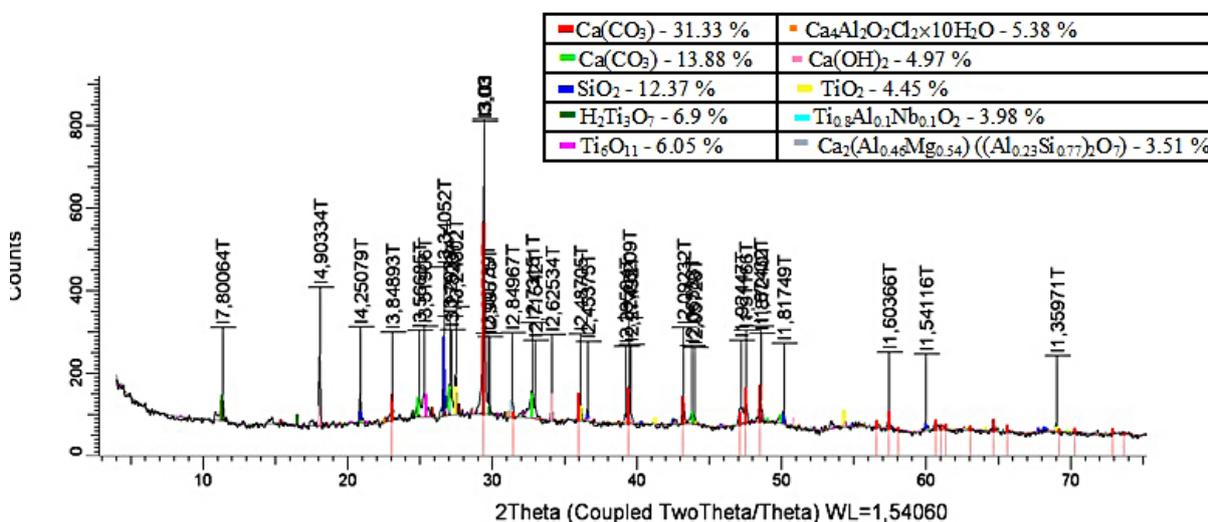


Figure 1. Diffractogram of a sludge sample

**Table 1.** Content of solutions when adding milk of lime

Experience No.	Solution pH	Precipitation time, min	Composition, g/dm <sup>3</sup>						
			Ti	Ca	Fe	Al	Si	Nb	V
1	-0,56	10	0.44	12.72	0.79	0.67	0.041	0.024	0.035
2	0.03	10	0.34	19.39	0.52	0.45	0.088	0.011	0.024
3	5.0	10	0.00012	23.9	0.024	0.16	0.06	-	0.0082
4	2.8	30	0.00012	31.25	0.0089	0.0086	0.0032	-	0.009
5	3.05	30	0.00012	30.14	0.0076	0.62	0.088	-	0.0094

composition, g/dm<sup>3</sup>: 22.62 Ca, 0.001 Si, <0.001 Fe, <0.001 Mg, <0.001 K, <0.001 Na, obtain calcium nitrate crystals failed.

Ammonium nitrate 5–7% of the weight of calcium nitrate is used for better crystallization of saturated solutions. The rate of crystallization of Ca(NO<sub>3</sub>)<sub>2</sub> increases 1.5–2 times with a simultaneous increase in the crystallization temperature by 50 °C when ammonium nitrate is added. The more ammonium nitrate is in the solution, the better is the crystallization (Melnichenko, 2002). 7% of ammonium nitrate of total calcium nitrate was added to the purified solution in order to obtain nitrate salt. Ammonium nitrate was obtained by adding calculated amounts of nitric acid and ammonia water. Evaporation to a viscous solution of calcium nitrate salts was performed in a glass beaker at 100 °C for 6 hours, stirring speed 300 rpm. The evaporation was then continued in an evaporation cup until dry crystals of composition, wt. %: 89.5 Ca, 0.0008 Fe, 0.05 Mg, 0.05 K, 0.05 Na. Table 2 shows the results of XRD analysis of the obtained nitrate salt.

Calcium nitrate for fertilizer is produced in the form of a flaky product, according to inter-republican specifications 6-03 195-67. Ammonium nitrate content is 4–7%, moisture content is not more than 14%, having at least 17.5% nitrogen (Klevke et al., 1956). Crystallization of calcium nitrate with the

addition of ammonium nitrate on cooling rollers is performed at 90 °C. Most of the salt crystallizes as two-water hydrate. The melt temperature in the trough of the rollers is maintained at about 110 °C.

The saturated solution with 70% concentration of Ca(NO<sub>3</sub>)<sub>2</sub> was evaporated to melt at 100 °C in order to obtain flake calcium nitrate. The pelletizer plate was preheated with a gas cylinder to a temperature of 90 °C while rotating the pelletizer at a speed of 28 rpm. The calcium nitrate melt was evenly distributed on the pelletizer plate, it froze as a uniform layer, then it was removed with a stainless steel scraper in the form of flakes, the results of granulation are shown in Figure 2. The results of granulometric analysis of the obtained calcium nitrate are shown in Table 3.

**Figure 2.** Production of flake calcium nitrate on a granulator**Table 2.** XRD analysis of calcium nitrate

Compound Name	Formula	S-Q, %
Calcium nitrate	Ca(NO <sub>3</sub> ) <sub>2</sub>	71
Calcium nitrate hydrate	Ca(NO <sub>3</sub> ) <sub>2</sub> ·(H <sub>2</sub> O) <sub>2</sub>	29

**Table 3.** Granulometric composition of dehydrated calcium nitrate on the granulator

Crystal grain class, mm	Granulometric composition of the primary product, wt. %	Granulometric composition after finishing the primary product, wt. %
+7	28.2	3.0
-7+5	12.7	26.9
-5+3	17.5	35.1
-3+1	17.5	29.0
-1 mm	24.1	5.7
Total	100	100

The primary product obtained has significant amounts of fractions +7 and -1 mm, which do not belong to the normalized fractions, as shown in Table 3. Therefore, the coarse fraction was crushed to a fraction of -7+1, the fine -1 mm was sent to obtain the melt with its subsequent regranulation. The results of granulometric composition of the product after finishing are shown in Table 3. Dehydrated calcium nitrate was obtained by granulation of 92–95 %  $\text{Ca}(\text{NO}_3)_2$  melt in the form of flakes.

#### *Fluoroammonium processing of cake from nitric acid leaching of sludge and production of amorphous silica*

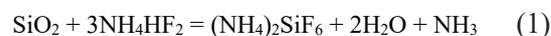
The cake with high titanium content was obtained after leaching of titanium production sludge with nitric acid. The cake composition was determined by X-ray fluorescence (XRF) and chemical analyses, wt. %: 16.9 Ti, 2.5 Fe, 1.2 Ca, 3.3 Al, 14.8 Si, 0.1 V, 3.6 Nb, 51.03 O, 0.4 F, 0.7 Zr, 0.2 Cr, 0.06 Mn, 0.4 W.

It can be seen from the analysis that titanium has the highest content among metals, and a significant amount of silicon is also present in the cake. Half of the cake is oxygen, which may indicate that it consists mostly of oxides. The cake also contains aluminum, calcium, iron, and niobium. Almost all calcium from the sludge was transferred to solution by nitric acid leaching. The results of the XRD analysis of the cake are presented in Table 4. All silicon is in quartz, feldspar in the form of albite, sillimanite, sodium aluminosilicate. In total, these minerals account for the major part of the cake 71.8%. Titanium is represented in the form of anatase oxides, titanium-aluminum niobium oxide, and rutile, totaling 26.1%. Iron is a part of sillimanite and hematite and makes about 3%.

**Table 4.** Cake phase composition

Compound Name	Formula	S-Q, %
Quartz, syn	$\text{SiO}_2$	43.3
Albite, calcian, ordered	$(\text{Na,Ca})\text{Al}(\text{Si,Al})_3\text{O}_8$	17.2
Anatase	$\text{TiO}_2$	9.1
Titanium aluminum niobium oxide	$\text{Ti}_{0.8}\text{Al}_{0.1}\text{Nb}_{0.1}\text{O}_2$	8.6
Rutile, syn	$\text{Ti}_{0.912}\text{O}_2$	8.4
Sillimanite	$(\text{Al}_{1.98}\text{Fe}_{0.02})\text{SiO}_5$	5.7
Sodium aluminum silicate	$\text{Na}(\text{AlSi}_2\text{O}_6)$	5.6
Iron Oxide	$\text{Fe}_2\text{O}_3$	2.2

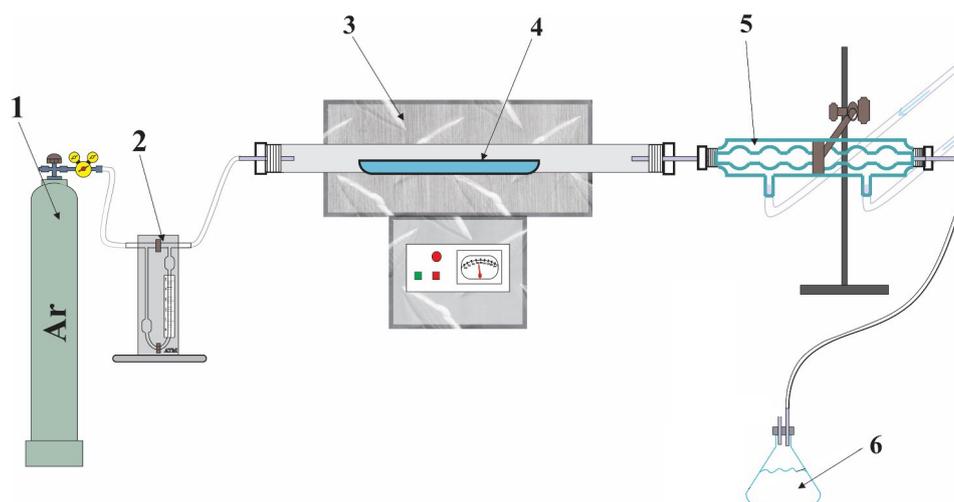
The fluoroammonium treatment method was used to separate silicon dioxide from the titanium-containing cakes (Diachenko, 2006; Kantayev et al., 2011). The setup shown in Figure 3 was assembled. The cake was first mixed with ammonium bifluoride taken 20% more than stoichiometric, placed in a fluoroplastic beaker. Water was added to obtain 20% humidity of the mixture and sintered for one hour at 200 °C in a vertical tube furnace. The sinter was further processed in a sublimation unit, in which a fluoroplastic boat (4) with a profluorinated mixture was placed, the boat was installed in a steel tube located in a horizontal furnace (3). The optimum temperature and duration of the process (300 °C, 6 hours) for the sublimation of silicon hexafluoride formed by the reaction were found experimentally:



The furnace was heated up to 300 °C and air was first fed into the tube, which helped to remove sublimations of silicon hexafluoride into the condenser cooler (5), which was cooled with water. A small part of silicon sublimates and hydrogen fluoride were captured in flasks (6) with 10% ammonia water solution. Silicon sublimates were washed out of the refrigerator with 10% ammonia water solution, this mixture was mixed with the mixture in flasks, heated to 50 °C for 60 min, after filtration, washing and drying, amorphous silica of the composition was obtained, wt. %: 83  $\text{SiO}_2$ , 0.02  $\text{Fe}_2\text{O}_3$ , 0.06  $\text{Al}_2\text{O}_3$ , 0.1  $\text{CaO}$ , 0.02  $\text{MgO}$ , 0.2  $\text{Cl}$ , 2.0  $\text{F}$ , what matches the brand BC-50 GOST 18307-78. A titanium-containing residue of the following composition was obtained, wt. %: 21.3  $\text{TiO}_2$ , 12.0  $\text{Fe}_2\text{O}_3$ , 15.7  $\text{Al}_2\text{O}_3$ , 1.5  $\text{CaO}$ , 0.2  $\text{SiO}_2$ , 17.5  $\text{F}$  after sublimation of silicon fluorides. The results of analysis of the composition of titanium-containing residue show that the silicon content after sublimation decreased by a factor of 82 relative to the original slurry and amounts to 0.1% in terms of elemental composition. The titanium-containing product can be returned for electrofusion together with ilmenite concentrate, after ammonia treatment of the residue and removal of fluorides.

#### **Processing of dusts from ilmenite concentrate electric smelting**

Silicon may concentrate in the dusts of ilmenite concentrates electric smelting in the process of their formation, as noted above, whose presence does not allow them to be returned to the smelting



**Figure 3.** Cake ammonium fluoride treatment unit; 1 – cylinder with argon, 2 – flow meter, 3 – horizontal furnace, 4 – fluoroplastic boat with a load, 5 – water-cooled refrigerator-condenser, 6 – gas trap system (10 % ammonia water solution)

process. Therefore, it was initially expedient to remove silicon from the dust composition. The studies intended to remove silicon from the composition of dusts were previously performed on their leaching with sodium hydroxide solution (Yessengaziyev et al., 2021). The research results showed the maximum silicon extraction in an alkaline solution by 77.7%. Physical and chemical studies of the dust from the electric smelting of the ilmenite concentrate showed that part of the titanium is bound into a hard-to-open anosovite that can be enclosed in a shell of amorphous silicon oxide. Along with it, silicon is in the form of a magnesium silicate phase that is not completely decomposed, remaining partially in the cake as a result of alkaline leaching. In order to ensure the most complete decomposition of silicon-containing phases and the separation of silicon impurities from titanium, studies were carried out using high-temperature ammonium fluoride processing.

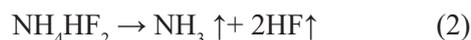
#### *Silicon sublimation from dust*

High-temperature ammonium fluoride processing of ilmenite concentrate electric smelting dusts was performed while maintaining the following fluorination conditions: temperature 260 °C, duration 6 h, mass ratio dust: ammonium bifluoride = 1 : 1, in order to completely decompose silicon-containing phases and separate silicon impurities from titanium. The degree of silicon fluoride sublimation at these conditions is 84.2 %. XRD analysis shows that silicon-containing phases are not detected in the residue after dust

fluorination and may indicate almost complete extraction of silicon in sublimate (Fig. 4).

#### *Hydrolysis of silicon fluorides*

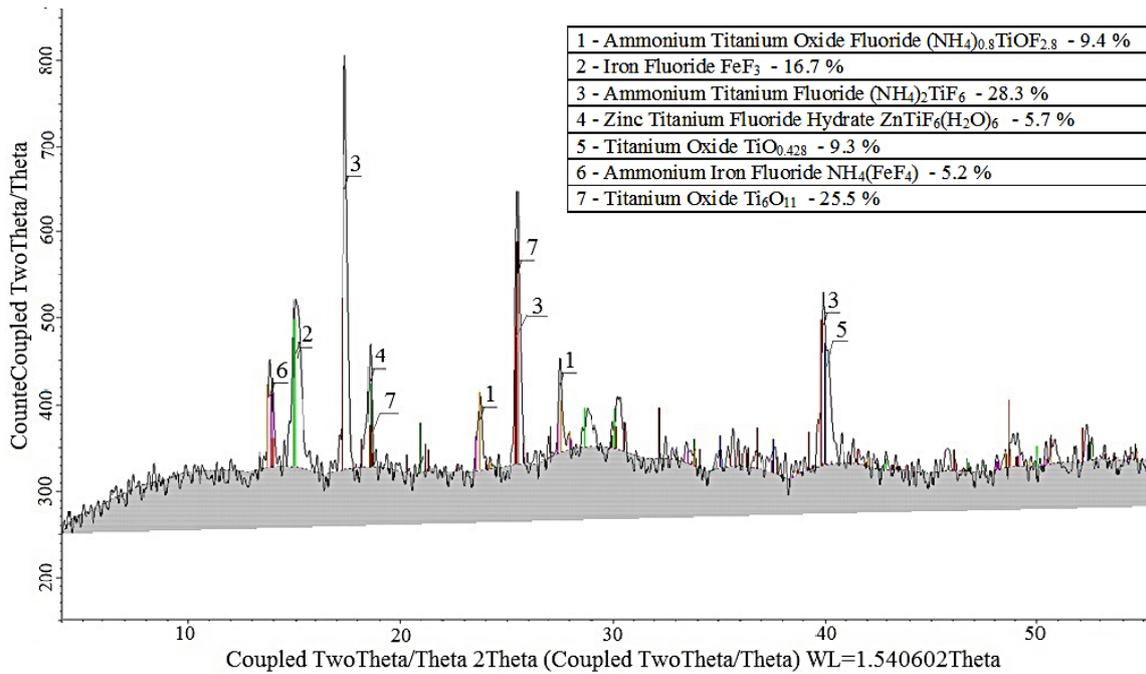
XRD analysis of the silicon-containing sublimate obtained after dust fluorination is shown in Figure 5. The sublimate mainly consists of oxonium hexafluorosilicate  $(\text{H}_3\text{O})_2\text{SiF}_6$  phase, as it can be noted from the obtained XRD data. It is known (Lidin et al., 2000) that at temperature 238 °C and higher the decomposition of ammonium bifluoride occurs in the reaction:



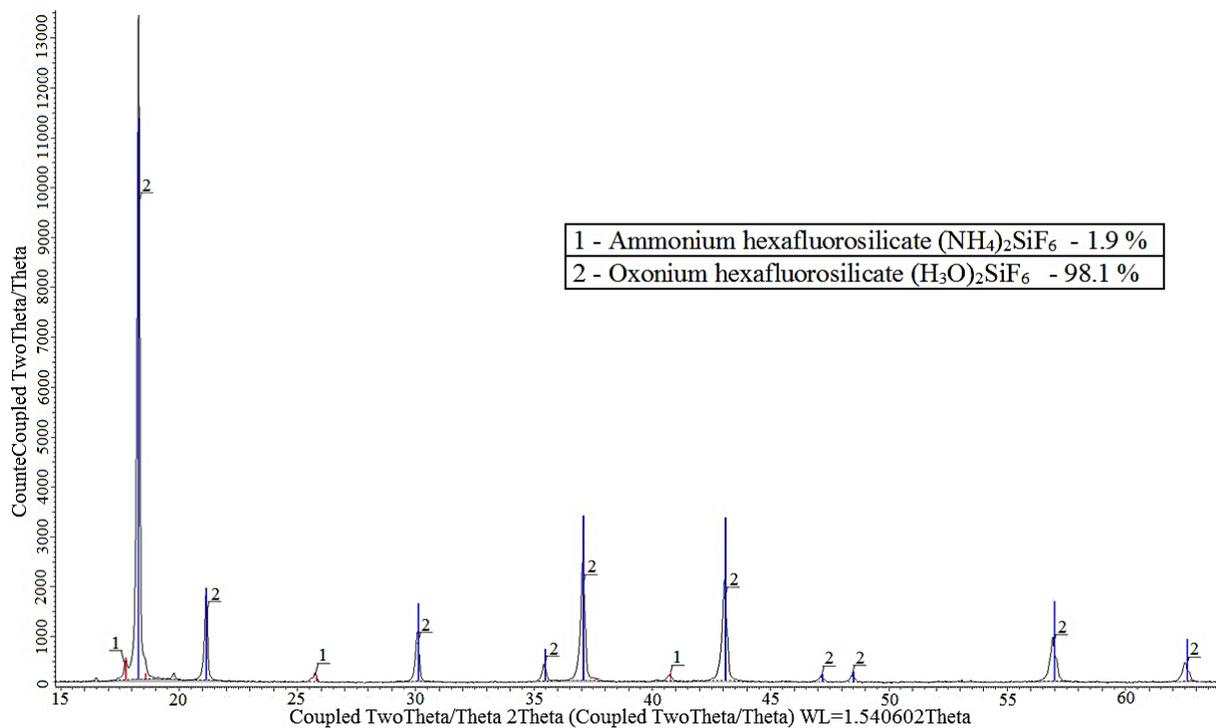
It is assumed that during the sublimation process at a temperature of 260 °C, ammonium bifluoride, not having time to react with the dust components of the electric smelting of the ilmenite concentrate, in particular with silica-containing compounds, according to reaction (2), decomposes into components  $\text{NH}_3$  and  $2\text{HF}$ . Oxonium hexafluorosilicate  $(\text{H}_3\text{O})_2\text{SiF}_6$  is nothing more than the dihydrate of hexafluorosilicic acid  $\text{H}_2\text{SiF}_6 \times 2\text{H}_2\text{O}$  (Helmboldt et al., 2004), which, apparently, is formed as a result of the interaction of silica, present in the dust of an electric smelter, with HF decomposition product of ammonium bifluoride according to the reaction:



Ammonium and oxonium hexafluorosilicates are well soluble in water at room temperature. It is necessary to act with alkali to precipitate silicon oxide, e.g. ammonia by the reactions:



**Figure 4.** Diffractogram of the residue from fluorination of ilmenite concentrate electric smelting dust (6 h, 260 °C, dust :  $\text{NH}_4\text{HF}_2$  = 1 : 1)



**Figure 5.** Diffractogram of silicon-containing sublimate (260 °C, 6 h, dust :  $\text{NH}_4\text{HF}_2$  = 1 : 1)



The deposition of amorphous silicon dioxide, according to thermodynamic calculations, must be performed in the temperature range of 25–100 °C (Dmitriev et al., 2021). Silicon-containing

sublimate was dissolved in water beforehand while maintaining the ratio of solid to liquid 1:10. Hydrolytic decomposition of the obtained hexafluorosilicate solution was performed at 40 °C by ammonia solution to pH 7.5–8, which was achieved in 20–30 min. However, the formation and precipitation of silicon oxide flakes requires holding the

**Table 5.** The content of the main components and impurities in the precipitated amorphous product

Content (wt. %)							
SiO <sub>2</sub>	NH <sub>4</sub> F	Fe	Cu	Zn	As	Sr	Pb
81.6	12.9	0.045	0.005	0.025	0.014	0.003	0.017

**Table 6.** The content of the main components and impurities in amorphous silica

Content (wt. %)						
SiO <sub>2</sub>	F	Fe <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>	ZnO	CaO	TiO <sub>2</sub>
96.3	no detected	0.14	0.16	0.02	0.03	0.15

suspension, which is about 80 minutes when using a 25% ammonia solution. The composition of the precipitated amorphous product is shown in Table 5. The data in Table 5 indicate a low content of heavy metals and arsenic in the product. The presence of ammonium fluoride is due to its absorption by amorphous particles, and it cannot be removed by washing the precipitate with water. Ammonium fluoride is known to decompose when heated. Heating at temperatures of 530–560 °C for 60–80 minutes provides the purification of silicon dioxide from fluorine by 95–99%. The composition of the obtained amorphous silica is shown in Table 6.

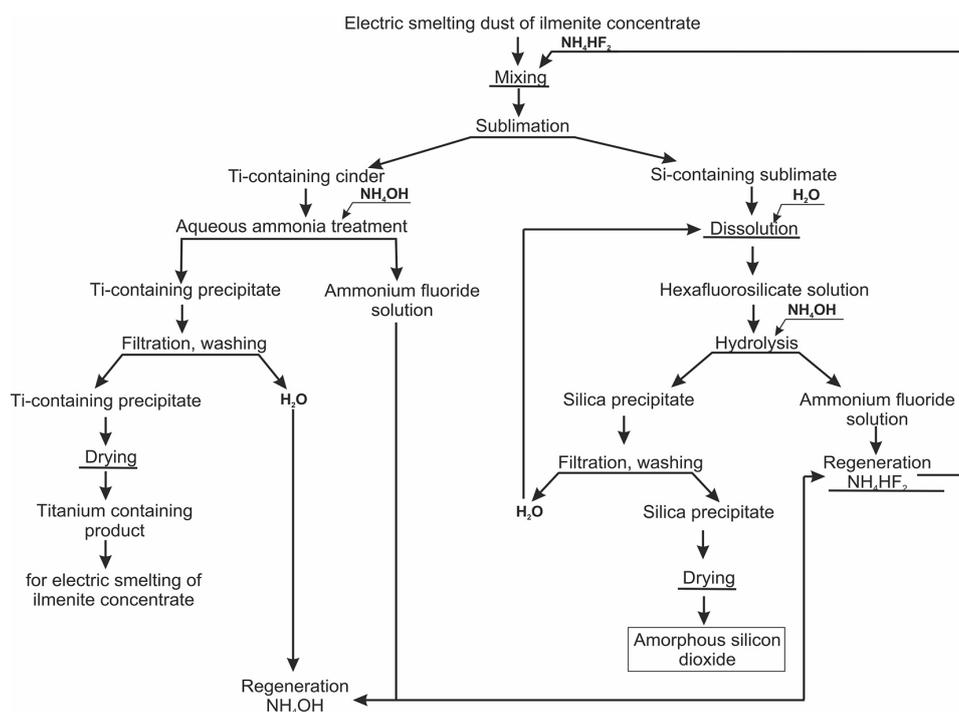
A titanium-containing residue of the following composition was obtained, after sublimation of silicon fluorides wt. %: 54.0 TiO<sub>2</sub>, 32.0 Fe<sub>2</sub>O<sub>3</sub>, 7.6 MnO<sub>2</sub>, 1.4 SiO<sub>2</sub>, 1.5 Al<sub>2</sub>O<sub>3</sub>, 0.36 K<sub>2</sub>O, 1.2 ZnO, 0.14 ZrO<sub>2</sub>, 0.9 PbO. The results of analysis of the titanium-containing residue composition show that

the silicon content was reduced by ~20 times with respect to the initial dust. The titanium containing product can be returned to electric smelting together with ilmenite concentrate after ammonia treatment of the residue with removal of fluorides.

The results of the studies suggest a technological scheme of a complex wasteless technology of electric smelting dust recycling of ilmenite concentrate (Fig. 6). Studies have shown that it is possible to return to the smelting process the titanium lost with the waste dust and to obtain amorphous silica from the waste.

## CONCLUSIONS

Sludge waste from titanium production contains ~20% or more of calcium. Nitric acid was used for sludge stripping, which allowed to

**Figure 6.** Scheme of the complex wasteless technology of ilmenite concentrate electric smelting dust processing

transfer calcium into solution in the form of calcium nitrate and titanium into cakes. Optimal conditions for sludge leaching with nitric acid were determined: 20% concentration of nitric acid,  $\text{pH} < 1$ , S:L=1:10 ratio, time 30 min, temperature  $20 \pm 4$  °C, stirring speed 300 rpm. Extraction of calcium in the solution under these conditions was 84.7%. The optimum parameters for purification of the calcium nitrate solution obtained by lime milk have been determined: addition of lime milk to  $\text{pH} 10$ , at temperature  $20 \pm 5$  °C, precipitation time 60 min, stirring speed 300 rpm. Almost all impurities are removed from the solution under these conditions. The crystallization process was performed under the following conditions: initial solution  $\text{pH} 10$ , adding 7%  $\text{NH}_4\text{NO}_3$  of total calcium nitrate, temperature 100 °C, time 6 hours, solution stirring speed 300 rpm. Dehydrated calcium nitrate was obtained by granulation of 92–95% melt in the form of flakes, at a granulator surface temperature of 90 °C. The fluoroammonium method of cake processing was chosen for selective extraction of silicon. The optimum parameters of fluoroammonium cake processing were established: distillation of silicon into substrates at 300 °C for 6 hours. There were obtained amorphous silica after hydrolysis of silicon-containing sublimations, filtration, washing and drying of the sediment with the following composition 83%  $\text{SiO}_2$ . A titanium-containing residue was obtained with the following composition, wt. %: 21.3  $\text{TiO}_2$ , 12.0  $\text{Fe}_2\text{O}_3$ , 15.7  $\text{Al}_2\text{O}_3$ , 1.5 CaO, 0.2  $\text{SiO}_2$ , 17.5 F. The results of analysis of the composition of titanium-containing residue show that the silicon content after sublimation decreased by a factor of 82 relative to the original slurry and amounts to 0.1% in terms of elemental composition. The titanium-containing residue with 21.3%  $\text{TiO}_2$  and 12.0%  $\text{Fe}_2\text{O}_3$  can be returned for electrofusion together with ilmenite concentrate after alkaline hydrolysis and removal of fluorides.

Analysis of fine dusts of electric smelting of ilmenite concentrate showed that it contains (in terms of oxides) 34.29%  $\text{TiO}_2$  and 27.53%  $\text{SiO}_2$ . High-temperature ammonium fluoride processing of dusts from electric smelting of ilmenite concentrate was performed while maintaining the following fluorination conditions: temperature 260 °C, duration 6 hours, mass ratio dust: ammonium bifluoride = 1 : 1. Performing fluoroammonium processing under these conditions made it possible to almost completely convert silicon into fumes in the form of ammonium hexafluorosilicate and

oxonium hexafluorosilicate. The residue consisting of titanium-containing phases after alkaline hydrolysis is recommended to be returned to the process of ilmenite concentrates electric smelting. The possibility of obtaining amorphous silicon dioxide by hydrolytic decomposition of the obtained silicon-containing sublimate with an ammonia solution is shown. The content of silicon dioxide in the obtained product after heat treatment was 96.3%. A scheme of complex non-waste technology for recycling dusts of ilmenite concentrate electric smelting with obtaining precipitated silicon dioxide and titanium-containing product suitable for return to the technological process of ilmenite concentrate electric smelting was proposed based on the results of conducted research.

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