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Recycling of Titanium Production Waste with the Extraction of Valuable Components

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ABSTRACT

Chloride wastes of the Ust-Kamenogorsk Titanium-Magnesium Plant of the Republic of Kazakhstan are formed in the production of titanium spongy by reduction of titanium tetrachloride with metallic magnesium. Multi-tonnage waste contains a number of rare and alkaline earth metals, including titanium. A significant part of this waste in the form of chlorides is neutralized with milk of lime and stored in sludge ponds, the reserves of which can be attributed to technogenic. The studies of this work were used to develop a technology for the integrated processing of sludge accumulator sludge with the extraction of titanium dioxide and calcium nitrate. When sludge is leached with nitric acid, calcium transforms into soluble calcium nitrate, and titanium compounds into a precipitate. Purified solutions of calcium nitrate are used to crystallize calcium nitrate. The titanium-containing sediment is subjected to fluoroammonium treatment with ammonium bifluoride. First, the precipitate is sintered with ammonium bifluoride at a temperature of 200 °C for an hour. Ammonium hexafluorosilicate was sublimated from the obtained cake at a temperature of 300 °C for 6 hours, and silicon fluorides were converted into silicon dioxide by alkaline hydrolysis of ammonia water. Then the cinder, in which the titanium compounds remained, is sintered again at a temperature of 200 °C for an hour to convert the remaining titanium into titanium tetrafluoride. Titanium tetrafluoride was sublimated from the cake at a temperature of 800 °C for 4 hours, and titanium fluorides were converted into titanium dioxide by alkaline hydrolysis of ammonia water. By drying and calcining, titanium dioxide was obtained in chemical composition close to that of pigment titanium dioxide.

Keywords
Waste; Leaching; Calcium Nitrate; Ammonium Bifluoride; Titanium Dioxide

Introduction

Obtaining titanium sponge in all countries of the world - manufacturers of titanium sponge consists in magnesium-thermal reduction of titanium tetrachloride at 850 °C [1-2]. To carry out the process, the production of magnesium metal by electrolysis from its molten salts is included in the production chain. The raw material for the production of electrolytic magnesium is dehydrated carnallite, and the spent electrolyte is used in the chlorination of titanium slags. Natural carnallite is preliminarily enriched and dehydrated. At the stages of chlorination of titanium slag and electrolysis of magnesium, a significant amount of chloride waste is formed.

Industrial waste is a hazard to the environment, contaminating soil and natural waters when they are released into the atmosphere when forming industrial wastewater is discharged into water bodies, as well as when solid waste is placed in sludge dumps [3].

At Ust-Kamenogorsk Titanium and Magnesium Plant JSC ("UKTMP") of Republic of Kazakhstan 30-35 thousand tons of solid chloride waste containing 700-1400 tons of titanium oxide is generated annually. Part of the titanium production chloride waste is leached with water and neutralized with calcium hydroxide to pH of 7-8,5. The resulting sludge is pumped into sludge dumps and accumulates in them. The reserves of sediments or sludge of titanium production are about 320 thousand tons, the multicomponent composition of which is present in the form of oxides, oxychlorides, and carbonates [4-5]. Spent titanium chlorinator melt (STCM) and spent vanadium chlorinator melt are stored at the landfill.

Spent titanium chlorinator melt (STCM), titanium chlorinator fumes, distillation residues of titanium tetrachloride rectification also belong to a significant part of the solid waste of titanium tetrachloride production. They are disposed of by hydrometallurgical methods, taking place at an ordinary temperature in aqueous solutions [6-9].

The known method that was distinguished by a more complex use of raw materials and consists of the following stages [10]: draining the spent melt into water (“hydraulic washing-out” of the melt); concentration of the pulp by circulation until the formation of chloride-saturated solutions (pulps); pulp treatment with polyacrylamide solution, pulp thickening; precipitation from clarified metal hydroxide solutions with an alkaline reagent in three stages; precipitation in the first stage at pH 3.5-6.0, mainly 4.0-4.5, with separation from the solution of chromium hydroxides, rare and radioactive metals; precipitation in the second stage is carried out in the presence of an oxidizing agent at pH 2.5-3.5 for 20-50 hours with the separation of the precipitate; at the third stage — at pH 9.5-11.0, mainly at pH 10.0-10.5 for 4-6 hours, followed by separation of the sediment.

When using magnesium oxide and hydroxide, the resulting solutions are suitable for producing artificial carnallite according to a known method. To obtain concentrated solutions, 4-5 times circulation is required. STCM consists of 75-80 % of water-soluble metal chlorides, including polyvalent toxic (chromium, manganese, thorium and its decay products, etc.). The disadvantages of the method include unsatisfactory filtration, the duration of the deposition of iron and manganese, a large number of solutions for evaporation to carnallite that leads to cumbersome hardware design.

In [11], a method of chloride dusts neutralization of titanium chlorinators on industrial equipment directly at the place of their formation by the method of thermohydrolysis is considered. Chloride dust in the form of a pulp (pH = 1-2, ρ = 1.07 g/cm3) is injected into the furnace with a working zone temperature of 1250-1300ºC. The process of hydrolysis of iron, manganese, and aluminum chlorides that are part of chloride dust proceeds with the formation of hydrogen chloride.

Waste from titanium production, spent melt of titanium chlorinators are very convenient and promising raw materials for scandium extraction. This is because most of the scandium (75-80 %) is in an easily broken down form of chloride. Therefore, leaching of waste at solid to liquid ratio $\geq$ 1.8 can be carried out with water or various reversible washing solutions. In order not to lose thorium with acidic solutions and the products of its decay, a combined precipitation-sorption technology was proposed and tested on an experimental-industrial scale, which consists in preliminary precipitation from the initial solution of chromium, scandium, titanium, zirconium, thorium and its decay products [12].

The Institute of Metallurgy and Ore Beneficiation JSC (IMOB), together with STCM JSC, has been researching the processing of chloride waste from titanium-magnesium production for some years.

In works [13-14], the results of studies on the production of synthetic carnallite from the spent titanium chlorinator melt (STCM) and sludge of magnesium production are presented. The sludge was leached with water, the solution was purified, and a solution with a carnallite module KCl/MgCl2 = 0.8-1.0 was obtained by combining saline solutions. The resulting saline solution had the following composition, g/dm3: Ti 0,0001-0,0004; Fe 0,001-0,003; Si 0,026-0,033; Mn 0,04-0,06. By evaporation and crystallization from the solution, carnallite was obtained that meets the requirements of GOST 16109-70. The work [15, 16] presents the results of studies on the extraction of rare earth elements (REE) concentrate from the STCM. Through the extraction of REE from the STCM into the bulk concentrate was 66 %. The developed method for extracting niobium from PS sublimates includes their leaching with a solution of sulfuric acid, chloride sublimation of cakes, and hydrolytic treatment of sublimates to obtain niobium-containing middlings [17-18].

So far, no integrated technology has been developed for processing chloride waste from titanium production with the extraction of valuable metals, huge reserves of which are stored in landfills, and sludge collectors that pollute the environment. The growing demand for rare metals and their compounds, as well as the depletion of raw materials, require the involvement of secondary raw materials in processing [19].

Processing of sludge dumps titanium-magnesium production sediments in Kazakhstan, in the CIS and the world is practically not carried out, and early research suggested using them as building materials. Sludge dumps under the influence of natural precipitation and wind are washed out and diffused, polluting the water and soil basins. The titanium-magnesium plant has to pay huge fines for keeping the accumulated waste. The creation of integrated technology to process this technogenic raw material will make it possible to obtain additional products in the form of titanium dioxide and calcium nitrate.

The purpose of this work is to process titanium production sludge to obtain titanium dioxide and calcium nitrate.

Methodology

Materials and equipment

Vibrating grinding mill IV-1 (Russia), stirring device ES VELP (Velp Scientifica), stirring device IKA RW16 (Germany), vertical tube furnace Kejia (China), horizontal tube furnace (Russia), Shimadzu scales (Japan), pH meter 150 IU (Russia), magnetic stirrer AREC (Switzerland), muffle furnace SNOL 7.2/1,300 (Lithuania), drying oven (Russia), distiller (Russia), laboratory plate granulator, heating ceramic tiles of REC VELP Scientifica brand.

The experiments involved: nitric acid (Chemistry Technology company, Russia), calcium oxide (XIMIK.UZ company, Republic of Uzbekistan), aqueous ammonia (Production company “KhIMPEK” LLC, Russia), ammonium fluoride acid (Sigma company, Germany), titanium production sludge of UKTMP JSC (Republic of Kazakhstan) (Table 1).

Table 1. Composition of titanium production sludge, wt. %

Element	Composition wt. %
Ti	6.80
Fe	2.80
Ca	19.40
Al	2.20
S	0.50
Si	8.20
V	0.13
Nb	0.30
C	7.10

Methodology of the experiment

Leaching of titanium production sludge with nitric acid was carried out as follows. A sample of the sludge was placed in a glass beaker with nitric acid and leached at a temperature of 20±5 °C for 30 min. The pulp was filtered; the cake was dried. Neutralization or precipitation of impurity components from the solution was carried out in a glass beaker while stirring the solution with the addition of lime milk to pH 10, then the pulp was filtered, the cake was dried. The composition of impurity components in solutions was determined by the chemical method, and in the cake — by the X-ray fluorescence method. During the ammonium fluoride processing, the cake from the leaching of the sludge in a fluoroplastic boat was placed in a steel tube of a horizontal furnace, which was included in the installation for the sublimation of silicon and titanium fluorides. Initially, silicon hexafluoride was sublimated at 200-300 °C, silicon fluorides sublimates were captured in a refrigerator-condenser. The sublimates were hydrolyzed with a 10 % solution of ammonia water, heating to 50 °C for 60 min, then they were filtered and dried to obtain amorphous silica.

The remaining cinder from the fluoroplastic boat was mixed with ammonium bifluoride and placed in a fluoroplastic glass, water was added and sintered in a vertical tube furnace at 200 °C. The sintered product in a boat was placed in a steel tube of a horizontal furnace and titanium tetra-fluoride was sublimated at temperatures above 650 °C. Titanium fluorides sublimates were subjected to alkaline hydrolysis with a 10 % solution of ammonia water, heated to 50 °C for 60 min, to a pH 9, then the clarified part of the solution was settled and decanted, and the precipitated hydrated titanium dioxide was repulped with water, subjected to filtration, the precipitate was dried at 200 °C for 120 min, then the sintered product was calcined at 500 °C for 120 min to obtain titanium dioxide.

Methods of analysis

Chemical analysis of the samples was carried out on Optima 8300 DV Perkin Elmer atomic-emission spectrometer (USA) and Jenway PFP7 flame photometer (England). X-ray fluorescence analysis was performed on Venus 200 PANalytical B.V. (PANalytical B.V., Holland).

Table 2. Phase composition of sludge

Compound Name	Formula	S-Q
Calcite	$Ca(CO_3)$	31,33%
Vaterite, syn	$Ca(CO_3)$	13,88%
Quartz, syn	SiO_2	12,37%
Hydrogen Titanium Oxide	$H_2Ti_3O_7$	6,90%
Titanium Oxide	Ti_6O_{11}	6,05%
Hydrocalumite, syn	$Ca_4Al_2O_6Cl_2\ 10H_2O$	5,38%
Portlandite, syn	$Ca(OH)_2$	8,15%
Rutile, syn	TiO_2	4,45%
Titanium Aluminum Niobium Oxide	$Ti_{0.8}Al_{0.1}Nb_{0.1}O_2$	3,98%
Akermanite, aluminian, syn	$Ca_2(Al_{0.46}Mg_{0.54})\ ((Al_{0.23}Si_{0.77})_2O_7)$	7,51%

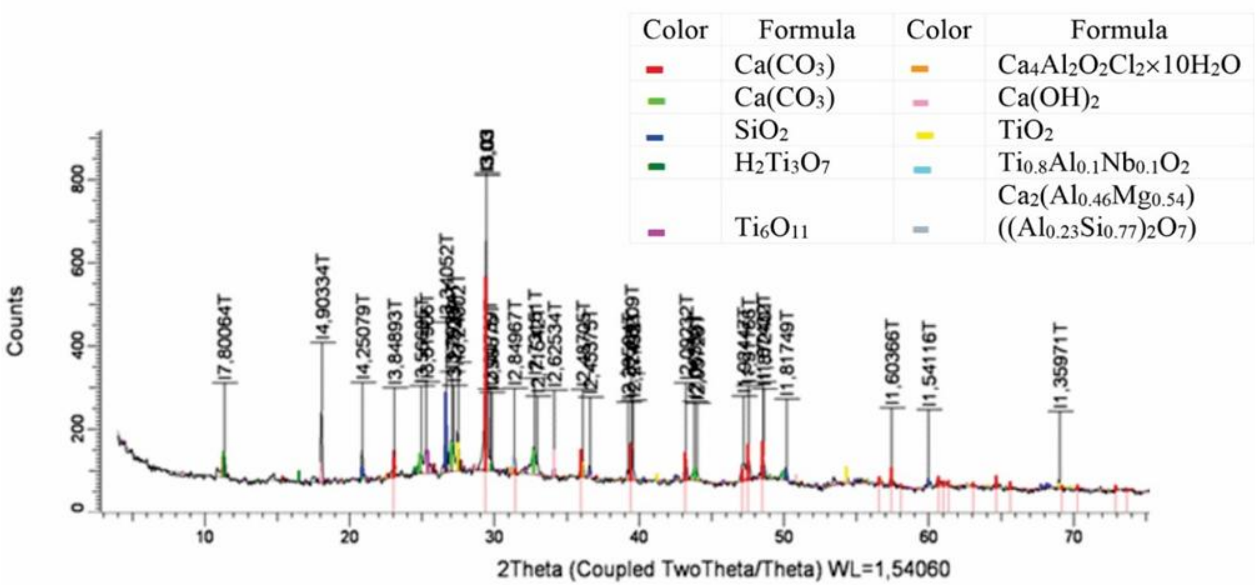

Figure 1. Diffractogram of a sludge sample

According to X-ray phase and mineralogical analyzes, the sample contains the main minerals in the following amount (%): calcite – 31,33, vaterite – 13,88, quartz – 12,37, various titanium phases – 21,38 and others – akermanite from the melilite group, portlandite, hydrocalumite – 21,04.

To transfer calcium into solution, and titanium into the cake, studies were carried out on leaching titanium production sludge with nitric acid. Leaching of a sample of sludge in an amount of 50 g at a given solid to liquid ratio = 1:4, room temperature of 20 °C, within 30 minutes with a change in acid concentration. Distilled water and 45 % nitric acid were added to the glass in the required amount to obtain a certain concentration. A sample of sludge was filled in and the pulp was mixed with a mechanical stirrer at a speed of 300 rpm. At the end of the experiment, the pulp was filtered, the filtration rate was measured, then the precipitate was dried and weighed. The volume of the filtrate was measured. The obtained product cake and solution were submitted for X-ray fluorescence and chemical analysis.

Sludge leaching was carried out at different concentrations of nitric acid, investigating the dynamics of the degree of titanium and calcium extraction into the solution. The studies were carried out at the solid to liquid ratio = 1: 4, temperature 20 °C, time 15 minutes, stirring speed 300 rpm and acid concentrations - 4, 6, 8, 9, 10, 15, 20, 25 %. The results of sludge leaching experiments are shown in Figure 2. Starting concentration of 10 to 25 % HNO_3 showed a gradual increase in the degree of extraction of titanium from 0.2 % to 4.9 %, and the extraction of calcium into solution during this interval of nitric acid concentrations sharply increased [20-21].

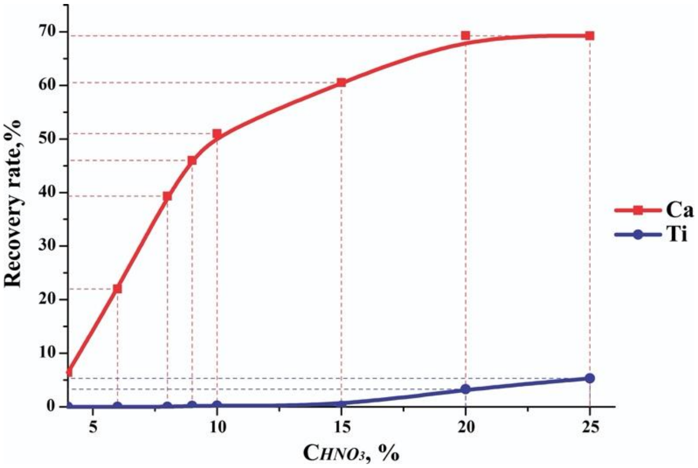

Figure 2. Dependence of the extraction of titanium and calcium into solution on the concentration of nitric acid

Studies on the leaching of titanium production sludge at various solid to liquid ratios were carried out at a concentration of 20 % HNO_3. This is justified by the fact that at such a concentration, the maximum extraction of calcium into the solution is observed, as well as the minimum transition of titanium into the solution. The research results are shown in Figure 3.

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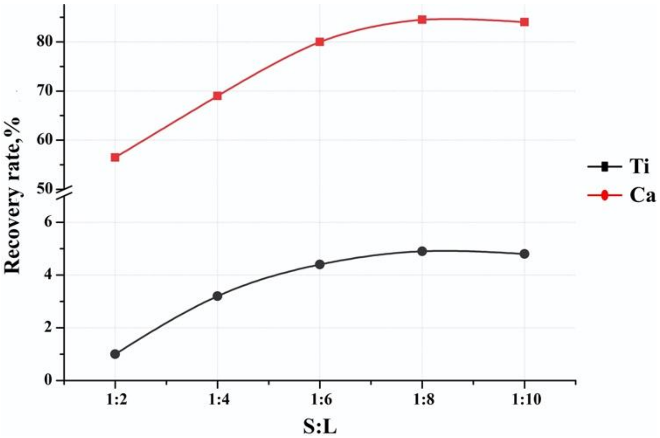

Figure 3. Dependence of the extraction of titanium and calcium into solution on the S: L ratio at

20 % HNO_3

Leaching with nitric acid at the solid to liquid ratio = 1:10 can be considered more efficient in terms of filtration rate and calcium extraction into a solution of 84,3 %. The loss of titanium with the solution is 4,4 %, and at the solid to liquid ratio = 1:8, the loss was 5,04 %, the cake yield is practically the same.

Studies were carried out to increase the temperature under the following leaching conditions: 20 % HNO_3 at the solid to liquid ratio = 1:8, leaching time of 30 min. As the temperature rises, the extraction of calcium, iron, and aluminium decreases due to the formation of gels that impede filtration. The pH values ranged from -0,45 to -0,64. Filtration rate decreased from 0,035 to 0,004 m3/m2•h.

Studies on the duration of leaching with 20% nitric acid were carried out at a temperature of 80 °C with the solid to liquid ratio = 1:8. With an increase in the duration of leaching, the amount of gel increased, the extraction of calcium into the solution decreased from 82 to 45,5 %, and the extraction of titanium into the solution also decreased from 11,2 to 5,9 %. Filtration was very slow.

As a result of the research, the optimal leaching parameters were determined: 20 % concentration of nitric acid, pH<1, solid to liquid ratio = 1:10, time — 30 min, temperature — 20±4 °C, stirring speed — 300 rpm. Under these conditions, the maximum filtration rate was set at 0,044 m3/m2•h., The minimum titanium extraction in the cake was 4,4 %, and the maximum calcium extraction in the solution was 84,3 %.

Calcium hydroxide or lime milk was chosen as a reagent for precipitation of impurities. Calcium oxide was calcined at 900 °C for an hour in a muffle furnace to activate the surface of the oxide in the manufacture of lime milk. 10 litres of the solution were produced during leaching of titanium production sludge with nitric acid under the following leaching conditions: 20 % concentration of HNO_3, the solid to liquid ratio = 1:10, temperature — 20±4 °C, leaching time — 30 min, stirring speed —300 rpm. The 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. The solution is green with a pH value of – 0,86. The initial solution in the experiments on the precipitation of impurity components was taken in a certain amount, the solution of lime milk was gradually added. The experimental conditions and the composition of the solutions with the addition of lime milk are presented in table 3.

Table 3. Phase composition of sludge

Experiment No.	**Quantity of initial solution, ml**	**Solution pH**	**Quantity of lime milk, ml**	**Deposition time, min**	**Composition, g/dm^3**						
					Ti	**Ca**	**Fe**	**Al**	**Si**	**Nb**	**V**
1	200	-0,56	88,5	10	0,44	12,72	0,79	0,67	0,041	0,024	0,035
2	200	0,03	200	10	0,34	19,39	0,52	0,45	0,088	0,011	0,024
3	130	5,0	230	10	0,00012	23,9	0,024	0,16	0,06	-	0,0082
4	100	2,8	85	30	0,00012	31,25	0,0089	0,0086	0,0032	-	0,009

5	100	3,05	95	30	0,00012	30,14	0,0076	0,62	0,088	-	0,0094

It can be seen from the experiments that at pH values of -0,56 and 0,03, the main impurities of iron, aluminium, and titanium remain in the solution. At pH values of 2,8 - 5 in solutions, the composition of impurities of iron, titanium, and aluminium is significantly reduced. An increase in the settling time of impurities also has a positive effect on purifying the solution.

Investigations of the impurity components deposition by the duration of the experiment were carried out. Lime milk was added to 200 ml until pH 5 and the solution was stirred at 300 rpm for 30, 60, 90, 120, 150 min. With an experiment duration of 60 min, impurities of Ti, Fe, Al, Nb are completely precipitated. With increasing time, the extraction of calcium into the solution decreases from 86 to 82,4 %. The extraction of silicon into the solution for 60 min was 0,4 %, but with an increase in time, silicon began to be extracted into the solution; at 150 min, the extraction of silicon into solution was 0,6 %. The optimal precipitation time with calcium oxide was chosen as 60 min.

The technique of the experiments carried out on the precipitation of impurities with lime milk at different temperatures of 20, 40, 80, 100 °C consisted in the fact that the same amount of lime milk was added to the solution of up to pH 5, stirred at a speed of 300 rpm for 30 min. With an increase in temperature, the extraction of calcium into the solution decreases, and the extraction of silicon at 100 °C rose to 0,9 %. With an increase in temperature, the solubility of calcium decreases, the remaining impurities are precipitated into the cake. The optimum deposition temperature is 20 °C.

However, chromium of 0,0018 g/dm3 remained in the solution, and the maximum permissible content for water bodies for household and drinking water and municipal water use in the Republic of Kazakhstan should be 0,05 mg/dm3. The solution was neutralized with lime milk to pH 8, the chromium content decreased to 0,51 mg/dm3, upon neutralization to pH 10, the chromium content in the solution was not detected, the composition of the neutralized solution, g/dm3: 22,02 Ca, ND Ti, 0,006 Si, ND Fe, ND Al, 0,0006 V, ND Mn, ND Zn.

As a result, the optimal parameters of the impurity components precipitation were determined: the addition of lime milk of up to pH 10, at a temperature of 20±5 °C, the precipitation time is 60 min, the stirring speed of the solution is 300 rpm.

When evaporating the purified solution with pH 10, composition, g/dm3: 22,62 Ca, 0,001 Si, <0,001 Fe, <0,001 Mg, <0,001 K, <0,001 Na, <0,001 S at a temperature of 100 °C for 4 hours a viscous amorphous substance was obtained, and it was not possible to obtain crystals of calcium nitrate. However, $Ca(NO_3)_2$ belongs to a series of crystalline hydrates that easily form supersaturated solutions. In the absence of seed crystals, calcium nitrate solutions allow large hypothermia and supersaturation, that is, if the system does not contain ready-made crystals, spontaneous crystallization is impossible. According to some features, $Ca((NO_3)_2$ can be attributed to hard-to-crystallize salts, its hygroscopic point is very low, calcium nitrate is prone to recrystallization and caking during storage [22].

For better crystallization of saturated solutions, 5-7 % ammonium nitrate is used by the weight of calcium nitrate. With the addition of ammonium nitrate, the crystallization rate of $Ca(NO_3)_2$ increases 1,5-2 times with a simultaneous increase in the crystallization temperature by 50 °C. The more ammonium nitrate is contained in the solution, the better the crystallization is [23]. 7 % ammonium nitrate-based on the total amount of calcium nitrate was added to the purified solution. Ammonium nitrate was obtained by adding the calculated amount of nitric acid and ammonia water. The solution was evaporated in a glass beaker at a temperature of 100 °C for 6 hours, the stirring speed of the solution was 300 rpm. It was evaporated to a viscous solution of calcium nitrate salts, then transferred to an evaporating cup and evaporated to obtain dry crystals of composition, wt. %: 89,5 Ca, 0,0008 Fe, 0,05 Mg, 0,05 K, 0,05 Na, 0,02 S. Table 4 shows the results of X-ray phase analysis.

Table 4. X-ray phase analysis of calcium nitrate

Compound Name	Formula	S-Q, %
Calcium Nitrate	$Ca(NO_3)_2$	71
Calcium Nitrate Hydrate	$Ca(NO_3)_2(H_2O)_2$	29

According to MRTU 6-03 195-67, calcium nitrate for fertilization is produced in the form of a flaky light brown product. Containing at least 17,5 % nitrogen, the composition of ammonium nitrate was 4-7 % with a moisture content not exceeding 14 % [24]. The crystallization of calcium nitrate with the addition of ammonium nitrate on cooling rollers is carried out at 90 °C. Most of the salt crystallizes as a dihydrate hydrate. The melt temperature in the roller trough is maintained at about 110 °C.

To obtain flake calcium nitrate, a saturated solution of 70 % concentration of $Ca(NO_3)_2$ was evaporated to form a melt at 100 °C. The melt was evenly distributed over the pelletizer tray, which rotated at 28 rpm. The molten ammonium nitrate salt began to granulate first into medium-sized granules, but due to the presence of physical moisture, fine salt particles began to adhere to the granules and bigger granules with a size of 6-8 mm were formed. The second experiment was also carried out with a saturated solution of 70 % concentration of $Ca(NO_3)_2$, it was evaporated until the formation of a melt at 100 °C. Preliminarily, the granulator plate was heated with a gas cartridge to a temperature of 90 °C while rotating the granulator at a speed of 28 rpm. At elevated temperatures, calcium nitrate can pass into the solid phase in the form of anhydrous salt. The calcium nitrate melt was evenly distributed over the granulator plate, it solidified in a uniform layer, then it was removed in the form of flakes with a stainless steel scraper, and the granulation results are shown in Figure 4.

Figure 4. Obtaining flake calcium nitrate with the help of a granulator

Granulometric analysis of the obtained calcium nitrate was carried out, the results of which are shown in table 5.

Table 5. Granulometric composition of dehydrated calcium nitrate in the granulator

Crystal grain class, mm	**Grain composition, %**
+7	28,2
-7+5	12,7
-5+3	17,5
-3+1	17,5
-1 mm	24,1
Total:	100

The coarse fraction was crushed to a fraction of -3+1, the fine -1 mm was sent to get a melt.

The dehydrated calcium nitrate was obtained by granulation of 92-95 % $Ca(NO_3)_2$ melt in the form of flakes. We grind the coarse fraction to a fraction of -3+1 mm, and a fraction of -1 mm is sent to get melt.

After titanium sludge leaching with nitric acid, cake with a high titanium content remains. For the quantitative elemental composition of the cake sample from the leaching of sludge from titanium production, X-ray fluorescence analysis was carried out. Based on the results of X-ray fluorescence and chemical analyzes, the composition of the cake was determined, wt. %: 18,8 Ti, 3,1 Fe, 1,2 Ca, 3,3 Al, 0,4 S, 18,8 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.

The analysis shows that the main share is oxygen, the cake consists of oxides, the titanium content of metals is the highest, even higher than silicon. Besides titanium, it contains aluminium, calcium, iron, and niobium. Almost all of the calcium from the sludge was converted to calcium nitrate by nitric acid. The results of the X-ray phase analysis of the cake are presented in table 6.

Table 6. The phase composition of the cake

Compound Name	Formula	S-Q, %
Quartz, syn	SiO_2	37,78
Rutile, syn	TiO_2	25,50
Albite, calcian, ordered	$(Na,Ca)Al(Si,Al)_3O_8$	13,16
Titanium Aluminum Niobium Oxide	$Ti_{0.8}Al_{0.1}Nb_{0.1}O_2$	10,06
Sillimanite	$(Al_{1.98}Fe_{0.02})SiO_5$	5,7
Iron Oxide	Fe_2O_3	4,2
Sodium Aluminum Silicate	$Na(AlSi_2O_6)$	3,6

All silicon is in quartz, feldspar in the form of albite, sillimanite, sodium aluminosilicate. In total, these minerals make up the bulk of the cake equal to 60,24 %. Titanium is presented in the form of oxides of rutile and titanium aluminum oxide in the amount of 35,56 %. Iron is part of sillimanite and hematite and makes up about 4,2 %.

To separate titanium dioxide from this multicomponent raw material, the method of fluorine-ammonium treatment of cake was used [25-30]. The installation is assembled, shown in Figure 5. First, the cake in an amount of 20 g was mixed with ammonium bifluoride taken 20% more of the stoichiometric amount, which amounted to 40 g of NH_4HF_2, was placed in a fluoroplastic boat, the boat was placed in a steel tube located in a horizontal furnace. The optimal temperature and duration of the process (300 °C, 6 hours) for the sublimation of ammonium hexafluorosilicate formed by the reaction:

$$SiO_2 + 3NH_4HF_2 = (NH_4)_2SiF_6 + 2H_2O + NH_3 \quad (1)$$

Figure 5. Laboratory installation for the sublimation of silicon and titanium fluorides

When the furnace was heated to 300 °C, the air was first fed into the tube, which helped to divert fumes of ammonium hexafluorosilicate into the condenser refrigerator cooled with water. Under the action of air, a small part of silicon fumes and hydrogen fluoride were recovered in flasks with a 10 % solution of ammonia water. The silicon sublimates were washed out from the refrigerator with a 10 % solution of ammonia water, this mixture was combined with the mixture in flasks by heating up to 50 °C for 60 min, then filtered and dried to obtain amorphous silica of composition, wt. %: 89 SiO2, 0,02 Fe2O3, 0,06 Al2O3, 0,1 CaO, 0,02 MgO, 0,2 Cl, 2,0 F that corresponds to BS-50 GOST 18307-78 brand.

The remaining cinder was added 20 % more of the stoichiometrically required ammonium bifluoride, mixed well, the resulting mixture was placed in a fluoroplastic glass, water was added, and sintered at a temperature of 200 °C for an hour in a vertical tube furnace. Fluorination during sintering proceeds according to the following reaction:

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

As a result of the sublimation process, titanium was transferred to the gas phase in the form of a complex $(NH_4)_2TiF_6$, and also in the form of titanium tetra-fluoride TiF_4 according to the decomposition reaction [31]:

$$(NH_4)_2TiF_6 \rightarrow TiF_4 + 2NH_3 + 2HF \quad (3)$$

The sinter was placed into a fluoroplastic boat of the sublimation unit, then into a steel tube of a horizontal furnace. With the heating of the furnace, argon was fed from a cylinder at a rate of 0,5-1 dm^3/min, and sublimates of titanium tetra-fluoride were distilled off at temperatures above 650 °C into a condenser refrigerator. Part of the sublimates of titanium tetra-fluoride and hydrogen fluoride vapour were captured in two flasks with a 10 % solution of ammonia water. The titanium fluoride sublimation temperature and duration (800 °C, 4 hours) were determined empirically. Alkaline hydrolysis of titanium fluorides was carried out as follows. Titanium fumes were washed out from the refrigerator – condenser with a 10 % solution of ammonia hydrate, this mixture was combined with a mixture from flasks at the solid to liquid ratio = 1:20, heated up to 50 °C at a stirring speed of 50 rpm for 60 min, the pH value was 9, and it was settled for 30 min. The clarified solution was decanted, the precipitate of hydrated titanium dioxide was re-pulped at the solid to liquid ratio = 1:40 in water to remove residual fluorine ions, then filtered. The cake in the form of a precipitate was dried at 200 °C for 2 hours and calcined at 500 °C for 2 hours. Obtained titanium dioxide, close to pigment titanium dioxide, composition, wt. %: 90 TiO_2, 1,1 SiO_2, 0,94 Al_2O_3, 0,01 Nb_2O_5, 0,042 CaO.

Conclusion

According to the data of the physicochemical properties of titanium sludge production, calcium carbonates in the sample make up 45,21 %. Silicon is present in quartz in the proportion of 12,37 %, in akermanite from the mellite group, portlandite, hydrocalumite – 21,04 %, titanium phases – 21,38 %.

Therefore, nitric acid was used to break down the sludge, which made it possible to transfer calcium into solution in the form of ammonium nitrate, and titanium – into the cake. Some of the silicon also went into solution with the formation of colloidal compounds that impede filtration.

The 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. Under these conditions, the maximum filtration rate was set at 0,044 m3/m2 •h. The minimum titanium extraction in the cake was 4.4%, and the maximum calcium extraction in the solution was 84,3 %.

Calcium hydroxide or lime milk was chosen as a reagent for precipitation of impurities from solutions. The optimal parameters of impurity components sedimentation were determined: addition of lime milk of up to pH 10, at a temperature of 20±5 °C, sedimentation time – 60 min, solution stirring speed – 300 rpm.

The optimal conditions for the crystallization process have been established: pH of the initial solution is 10, with the addition of 7 % NH_4NO_3 of the total amount of calcium nitrate, the temperature – 100 °C, the time – 6 hours, the stirring speed of the solution – 300 rpm. Dehydrated calcium nitrate was obtained by granulation of 92-95 % melt in the form of flakes, at a surface temperature of the plate of the granulator equal to 90 °C.

Based on the results of the investigated physicochemical properties of cake from leaching of titanium production sludge with nitric acid, it was found that all silicon in the cake is in quartz, feldspar in the form of albite, sillimanite, sodium aluminosilicate, and in total, these minerals make up the bulk of the cake equal to 71,8 %. Titanium is presented in the form of oxides of anatase, titanium aluminium oxide, and rutile, in the amount of 26,1 %.

For the selective extraction of silicon and titanium, the fluoroammonium method of cake processing was chosen. The optimal parameters of fluorine-ammonium cake processing were established: silicon distillation into sublimates at 300 °C for 6 hours, titanium sublimation in the form of titanium tetra-fluoride at 800 °C for 4 hours.

The optimal parameters of silicon and titanium fluorides alkaline hydrolysis have been determined. Titanium dioxide was obtained in a composition close to the pigment titanium dioxide. A technological scheme was drawn up for the processing of titanium production sludge with the extraction of titanium dioxide. Along the way, calcium nitrate and amorphous silica were obtained.

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