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Sequential recovery of calcium, silicon, and titanium from titanium-magnesium production wastes by nitric acid leaching and ammonium bifluoride treatment

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ABSTRACT
This study examines sequential processing routes for calcium-rich neutralization sludge and silicon-rich electric smelting dust generated during titanium-magnesium production. The sludge was subjected to nitric acid leaching to recover calcium, followed by solution purification, production of a calcium nitrate-based product, and ammonium bifluoride treatment of the solid residue. The smelting dust was processed by staged ammonium bifluoride treatment to separate silicon- and titanium-bearing compounds, followed by hydrolysis, purification, and thermal treatment of the recovered products. Nitric acid leaching extracted 84.7% of calcium from the sludge, while subsequent processing produced a calcium nitrate-based product and amorphous silica. Treatment of the smelting dust enabled silicon separation and the production of amorphous silica containing 96.3% SiO_2. Further processing of the titanium-bearing concentrate yielded rutile containing 99.8% TiO_2. Comparison of the two routes identified residual fluorine in the sludge-derived residue and impurity co-sublimation during dust processing as the main technological limitations. The results demonstrate the potential for differentiated recovery of valuable components from titanium-magnesium production wastes.

Keywords: ilmenite smelting dust; neutralization sludge; ammonium bifluoride; amorphous silica; calcium nitrate; titanium dioxide.

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Introduction

Titanium production generates large amounts of solid and dusty wastes containing titanium, silicon, calcium, iron, aluminum, and other components. Conventional processes for titanium and its compounds involve many stages and yield by-products that must be neutralized or stored [[1], [2]]. The environmental burden comes from the consumption of mineral raw materials and energy, gas emissions, liquid effluents, and solid waste [[3], [4]]. Titanium-magnesium plants face a particular problem with two wastes: sludge from the neutralization of process solutions and fine dust from the electric smelting of ilmenite concentrates. Long-term storage of these materials can pollute water bodies and means a loss of valuable components [5].

The neutralization sludge is rich in calcium because lime reagents are used to treat the process solutions. It also contains titanium, silicon, iron, aluminum, and niobium compounds. Earlier

work showed that nitric acid leaching transfers most of the calcium into solution as calcium nitrate and concentrates titanium in the solid residue [6]. A subsequent study demonstrated that this residue can be processed further into a titanium-bearing product [7]. However, the formation of a silicon- and fluorine-bearing cake, the lack of an effective defluorination step, and an incomplete material balance prevent direct industrial use of these solutions.

Dust from the electric smelting of ilmenite concentrate contains substantial amounts of titanium, iron, and silicon. Its high SiO_2 content prevents direct return to the smelting furnace, because silicon compounds can alter melt properties and lower the quality of titanium products. Studies of ammonium fluoride processing of this dust have shown that silicon can be converted into volatile fluorosilicate compounds and then into amorphous silica [8]. Integrated processing of the dust also concentrates titanium in the solid residue, from which TiO_2 can be obtained after further treatment [9].

Ammonium fluoride methods rely on the reaction of oxide and silicate phases with NH_4F or NH_4HF_2 to form fluoride and ammonium fluoride compounds. These methods have been studied for titanium-bearing raw materials, titanium slags, and silicon-bearing concentrates [[10], [11], [12]]. Components separate because the resulting compounds differ in volatility and solubility. Silicon, for example, can form ammonium or oxonium hexafluorosilicates, whose hydrolysis yields amorphous SiO_2 [13]. Recent investigations have also demonstrated the role of ammonium fluoride in the conversion of silicon-bearing metallurgical residues into silica products [14]. Fluoride metallurgy can also process stable aluminosilicate and quartz phases that resist conventional acid and alkaline reagents [15].

Ammonium fluoride processing of ilmenite can produce fluorotitanate compounds, which give anatase or rutile titanium dioxide after hydrolysis or pyrohydrolysis [16]. Gordienko et al. prepared TiO_2 from the ammonium hexafluorotitanate/silicon dioxide system and examined how silicon compounds affect titanium pyrohydrolysis [17]. Fluorination of ilmenite with ammonium bifluoride forms ammonium oxofluorotitanates [18], and the reaction of NH_4HF_2 with titanium-bearing minerals converts individual components into volatile or soluble fluorides [19]. The main limitations of these processes are fluorinating reagent consumption, co-volatilization of impurities, corrosive media, and the formation of fluoride-bearing solutions that require regeneration or treatment.

Recent studies have highlighted the potential of titanium recovery from secondary resources and the importance of selecting processing technologies according to the composition of the feed material [20]. Fluoride-based methods have also demonstrated potential for silicon removal from complex metallurgical residues and selective titanium separation [[21], [22]].

Despite previous investigations into the recovery of valuable components from titanium-magnesium production wastes, several technological limitations remain insufficiently addressed. Calcium-rich neutralization sludge and silicon-rich electric smelting dust differ substantially in chemical and mineralogical composition, requiring different sequences of treatment. In particular, the accumulation of fluorine in titanium-bearing residues, the co-sublimation of impurities, and the incomplete assessment of intermediate products complicate further utilization of these materials. A comparative evaluation of the two processing routes is therefore necessary to identify their recovery potential, product quality, and technological limitations.

The aim of this study was to evaluate and compare two sequential processing routes for titanium-magnesium production wastes: nitric acid leaching followed by ammonium bifluoride treatment of calcium-rich neutralization sludge, and staged ammonium bifluoride treatment of silicon-rich electric smelting dust. The evaluation focused on calcium and silicon separation, titanium concentration and recovery, the composition of the resulting products, and the technological limitations associated with residual fluorine and impurity co-sublimation.

Experimental part

Raw materials

Two processing routes were investigated according to the composition of the initial wastes. The calcium-rich neutralization sludge was subjected to nitric acid leaching, purification of the calcium-bearing solution, and ammonium bifluoride treatment of the resulting solid cake. The silicon-rich electric smelting dust was processed by staged ammonium bifluoride treatment to separate silicon-bearing compounds and subsequently recover titanium. The experimental procedures and product characterization methods for each route are described below.

Two types of titanium-magnesium production wastes were investigated: calcium-rich sludge generated during the neutralization of industrial process solutions and fine dust collected by the gas-cleaning system during electric smelting of ilmenite concentrate. The formation of these wastes is associated with different technological operations, resulting in substantial differences in their chemical

and mineralogical compositions. The neutralization sludge contains calcium-bearing phases together with titanium and silicon compounds, whereas the smelting dust is characterized by relatively high concentrations of titanium, iron, and silicon. These compositional differences were considered when selecting the subsequent treatment routes.

Before the experiments, the sludge sample was dried to constant mass, ground, and homogenized. The smelting dust was mixed, and a representative sample was taken. The prepared materials were stored in sealed containers to prevent changes in moisture and contamination.

Table 1 - Main components of the studied wastes

Material	Ti, %	Fe, %	Ca, %	Al, %	Si, %
Titanium production sludge	6.8	2.8	19.4	2.2	8.2
Ilmenite concentrate smelting dust	20.6	14.1	*n.d.	n.d.	12.8

Source: compiled by the authors based on data from [[6], [8], [9]].
*Note: n.d., not determined

Table 1 gives the contents as elements. Expressed as oxides, the smelting dust contained 34.29 wt% TiO_2 and 27.53 wt% SiO_2. Elemental and oxide compositions are considered separately below, because comparing them directly without stoichiometric conversion would be incorrect.

The selection of the processing routes was based on the chemical composition and expected behavior of the major mineral phases. For the calcium-rich sludge, nitric acid leaching was selected as the first stage to dissolve calcium-bearing compounds while retaining a substantial proportion of titanium and silicon in the solid residue. The resulting cake was subsequently treated with ammonium bifluoride to separate silicon-bearing compounds. In contrast, the silicon-rich smelting dust was subjected directly to ammonium bifluoride treatment, followed by staged separation of silicon- and titanium-bearing compounds. This approach enabled the two waste streams to be evaluated using different treatment sequences according to their compositions.

Reagents and equipment

The experiments used chemically pure HNO_3 and CaO, analytical-grade NH_4HF_2 and aqueous ammonia, and distilled water. Milk of lime was prepared by mixing the calculated amount of CaO with water. Argon provided an inert atmosphere during ammonium fluoride treatment.

The starting material was ground in an IV-1 vibratory mill (Russia). Leaching, solution purification, and sublimate hydrolysis were carried out in glass reactors with ES VELP (Velp Scientifica) and IKA RW16 (Germany) overhead stirrers and an AREC VELP Scientifica magnetic stirrer. A 150MI pH meter (Russia) was used to monitor pH, and raw materials, reagents, and products were weighed on a Shimadzu analytical balance (Japan).

Heat treatment was performed in a Kejia vertical tube furnace (China), a LOIP LF-50/500-1200 horizontal tube furnace (Russia), and a SNOL 7.2/1300 muffle furnace (Lithuania). Samples were dried in a laboratory drying oven. Calcium nitrate was produced with a laboratory granulator and a REC VELP Scientifica ceramic hot plate.

For ammonium fluoride treatment, the reaction mixture was placed in an alundum boat inside the steel tube of the horizontal tube furnace. Argon was fed through the tube at 1.0–1.5 L/h. Volatile compounds were captured by a water-cooled condenser followed by gas traps in series filled with 10% ammonia solution.

Figure 1 shows the laboratory setup used for ammonium fluoride treatment and capture of volatile compounds.

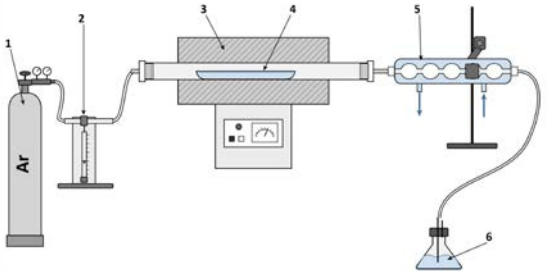


Figure 1 - Laboratory setup for ammonium fluoride treatment: 1, argon cylinder; 2, flow meter; 3, tube furnace; 4, alundum boat with reaction mixture; 5, water-cooled condenser; 6, gas trap with 10% ammonia solution
Source: developed by the authors

Analytical methods

The phase composition of the raw materials and solid products was determined by X-ray diffraction (XRD) on a Bruker D8 Advance diffractometer with Cu radiation at 36 kV and 25 mA. The elemental composition of solids was determined by X-ray fluorescence (XRF) on a Venus 200 wavelength-dispersive spectrometer (PANalytical B.V., the Netherlands). Solution compositions were measured by inductively coupled plasma optical emission

spectrometry (ICP-OES) on an Optima 2000 DV spectrometer (PerkinElmer, USA).

Processing of calcium-rich sludge

A portion of dried, homogenized sludge was placed in a glass reactor, and 20% nitric acid was added at S:L = 1:10. Leaching was carried out at 20 ± 4 °C for 30 min with stirring at 300 min^{-1}. The pH of the medium was below 1.

During leaching, calcium-bearing phases dissolved to form calcium nitrate, while titanium compounds and most silicon-bearing phases remained in the solid. The pulp was then filtered. The filtrate went to purification and production of the calcium nitrate-based product. The cake was washed with distilled water to remove soluble nitrates, dried to constant mass, weighed, and analyzed.

Calcium recovery into solution was calculated as

$$\eta_{Ca} = \frac{C_{Ca} * V}{m_0 * w_{Ca,0}} * 100\%, \qquad (1)$$

where η_{Ca} is the calcium recovery, %; C_{Ca} is the calcium concentration in solution, g/L; V is the solution volume after leaching, L; m_0 is the initial sludge mass, g; and $w_{Ca,0}$ is the mass fraction of calcium in the initial sludge (fraction of unity).

The calculation included calcium in the wash water and used the actual solution volume after filtration.

The solution from nitric acid leaching contained calcium and impurities of titanium, iron, aluminum, silicon, niobium, and vanadium. To remove these impurities, the solution was placed in a glass reactor and stirred at 300 min^{-1}.

Milk of lime was added gradually under continuous pH control. Once pH 10 was reached, the suspension was held at 20 ± 5 °C for 60 min with constant stirring. Under these conditions, titanium, iron, and aluminum compounds formed sparingly soluble species and precipitated, whereas calcium nitrate stayed in solution.

The suspension was then filtered. The precipitate was washed with distilled water, dried to constant mass, and analyzed. The purified calcium-bearing filtrate went to evaporation and production of the calcium nitrate-based product.

Calcium introduced with milk of lime must be accounted for separately in the material balance. For this reason, calcium recovery from the initial sludge was determined using the solution before neutralization.

NH_4NO_3 was added to the purified solution in an amount equal to 7% of the calculated $Ca(NO_3)_2$ mass. Ammonium nitrate accelerated crystallization and gave a more uniform salt product.

The solution was evaporated at 100 °C for 6 h with stirring at 300 min^{-1} to obtain a concentrated melt containing 92–95% $Ca(NO_3)_2$. The melt was spread evenly on the surface of a pan granulator preheated to 90 °C and rotating at 28 min^{-1}. On cooling, the melt solidified into a layer that was removed as separate flakes.

After cooling, the particle size distribution of the product was determined. Particles larger than 7 mm were crushed, and the fraction below 1 mm was returned to melting and regranulation. The 1–7 mm fraction was taken as the target. The product was characterized by its phase composition, main substance and impurity contents, and particle size distribution.

The cake from nitric acid leaching contained silicon mainly as quartz and aluminosilicate phases, and ammonium fluoride treatment was used to remove it.

The dried cake was mixed with NH_4HF_2 taken in 20% excess over the stoichiometric amount needed to bind silicon. After thorough mixing, water was added to a moisture content of 20%.

The mixture was placed in a PTFE vessel and held in the vertical tube furnace at 200 °C for 1 h. Fluorination of the silicon-bearing phases produced fluorosilicate compounds that can pass into the gas phase on further heating.

The sinter was transferred to an alundum boat placed inside the steel tube of the horizontal tube furnace. Argon flowed through the reaction zone at 1.0–1.5 L/h. Silicon compounds were sublimed at 300 °C for 6 h. Gaseous products passed into the water-cooled condenser, and uncondensed vapors and fluorine-bearing gases passed into absorbers in series filled with 10% ammonia solution.

After treatment, the furnace was cooled. The solid titanium-bearing residue was removed, weighed, and analyzed. The silicon-bearing product deposited in the condenser was rinsed out with 10% ammonia solution and combined with the gas trap solutions for hydrolysis.

The combined solutions (condenser rinse and ammonia absorbers) were heated to 50 °C and held with stirring for 60 min. Reaction of the fluorosilicates with ammonia precipitated amorphous silica.

The suspension was filtered. The precipitate was washed with distilled water to remove soluble ammonium fluorides and associated impurities and then dried to constant mass. The product was analyzed for SiO_2, Fe_2O_3, Al_2O_3, CaO, MgO, Cl, and F.

Processing of electric smelting dust

The smelting dust was mixed thoroughly with NH_4HF_2 at a dust: NH_4HF_2 mass ratio of 1:1. The mixture was placed in an alundum boat inside the steel tube of the horizontal tube furnace.

Before heating, the setup was checked for leaks. Argon was fed through the reaction zone at 1.0–1.5 L/h. Ammonium fluoride treatment was carried out at 260 °C for 6 h.

On heating, the silicon-bearing phases reacted with ammonium bifluoride to form volatile fluorosilicates. The argon flow carried them out of the reaction zone, and they condensed in the cooled part of the setup. Uncondensed vapors and fluorine-bearing gases went to absorbers containing ammonia solution. Titanium, iron, manganese, and other low-volatility components stayed mostly in the solid residue.

After treatment, the setup was cooled, and the solid residue was removed, weighed, and analyzed. Under these conditions, the degree of sublimation of silicon fluoride compounds reached 84.2%.

The silicon-bearing sublimate was dissolved in distilled water at S: L = 1:10. The solution was heated to 40 °C, and 25% ammonia solution was added gradually under vigorous stirring until the pH reached 7.5–8.0, which took 20–30 min.

The suspension was then held for 80 min to allow amorphous silica particles to form and grow. The precipitate was filtered off, washed with distilled water, and dried to constant mass.

Washing with water did not remove all the adsorbed NH_4F, so the dried product was heat-treated at 530–560 °C for 60–80 min. After cooling, the SiO_2 and impurity contents were determined.

After silicon removal, the Ti–Fe residue underwent a second ammonium fluoride treatment. Titanium fluoride compounds were sublimed at 600 ± 10 °C for 2 h. The argon flow carried the volatile compounds out of the reaction zone, and they were collected in the cooled part of the setup. Under these conditions, up to 99% of the titanium passed into the sublimate. The sublimate consisted mainly of ammonium fluorotitanates, with impurities of ammonium hexafluorosilicate and ammonium hexafluoroferrate.

The collected titanium sublimate was pyrohydrolyzed in a tubular electric furnace. A weighed sample was placed in an alundum boat, and steam was supplied at 1.5–2.0 L/g. Pyrohydrolysis at 600 °C for 4–5 h converted 99.5% of the titanium fluorides to titanium dioxide.

The product was washed with 12.5–15% hydrochloric acid at 25–30 °C and S: L = 1:6–1:8 for 20–30 min. After filtration, washing, and drying, it was calcined at 900 °C for 2 h to convert anatase to rutile.

Main chemical reactions

Ammonium bifluoride fluorinates silicon dioxide according to the reaction

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

Equation (2) represents the overall stoichiometric transformation of silica in the presence of ammonium bifluoride. The formation of ammonium hexafluorosilicate is consistent with the fluoride treatment of silicon-containing materials described in the literature. However, the reaction equation does not establish the detailed mechanism or sequence of intermediate transformations.

The formation of fluorosilicate compounds during fluoride treatment of silicon-bearing materials has been investigated in previous studies [[14], [21]]. These findings support the proposed overall chemical transformations, although the specific reaction pathways under the present experimental conditions require further verification.

On heating, part of the ammonium bifluoride decomposes to ammonia and hydrogen fluoride:

$$NH_4HF_2 \rightarrow NH_3\uparrow + 2HF\uparrow \quad (3)$$

The hydrogen fluoride reacts with silicon dioxide:

$$SiO_2 + 6HF \rightarrow H_2SiF_6 + 2H_2O \quad (4)$$

Amorphous silica precipitates from ammonium hexafluorosilicate solution by the reaction

$$(NH_4)_2SiF_6 + 4NH_4OH \rightarrow SiO_2\downarrow + 6NH_4F + 2H_2O \quad (5)$$

Oxonium hexafluorosilicate reacts with ammonium hydroxide as follows:

$$(H_3O)_2SiF_6 + 6NH_4OH \rightarrow SiO_2\downarrow + 6NH_4F + 6H_2O \quad (6)$$

The proposed chemical transformations are based on the known reactivity of silicon-containing phases with ammonium bifluoride and on the phase

compositions identified by X-ray diffraction. During thermal treatment, ammonium bifluoride can decompose with the release of ammonia and hydrogen fluoride, while silicon-bearing phases react to form fluorosilicate compounds. The subsequent treatment of fluorosilicate-containing solutions with ammonia promotes the precipitation of amorphous silica. The reaction equations describe the overall stoichiometric transformations and should not be interpreted as a complete description of the reaction mechanisms.

Results and Discussion

Calcium extraction from titanium-magnesium production sludge

XRD showed that calcium in the initial sludge occurred mainly as calcite, vaterite, portlandite, and calcium aluminosilicates. Silicon was present in quartz and silicate phases, and titanium mainly as oxides. Calcium carbonate and hydroxide phases dissolve in nitric acid, whereas titanium oxides and quartz resist it. Calcium could therefore be leached selectively, with most of the titanium kept in the solid residue.

Leaching with 20% HNO_3 at S: L = 1:10, 20 ± 4 °C, and 30 min transferred 84.7% of the calcium into solution. The titanium content of the solid rose from 6.8% in the sludge to 16.9% in the cake, about 2.5-fold.

Titanium content increased because the calcium-bearing phases dissolved and the mass of the solid residue decreased. The higher mass fraction of titanium thus reflects its relative concentration.

These data are insufficient to determine the distribution of titanium between the products, as this would require information on the cake yield and the amount of titanium transferred into solution.

The nitrate leach solution had a pH of −0.86 and contained impurities of iron, aluminum, titanium, silicon, niobium, and vanadium. Therefore, the solution required purification before the production of the calcium nitrate-based product.

Purification of the nitrate solution

As milk of lime was added and the pH increased, iron, aluminum, and titanium compounds hydrolyzed and precipitated. Their concentrations dropped noticeably at pH 2.8–5.0, but the most complete purification occurred at pH 10.

After treatment at 20 ± 5 °C for 60 min, the purified solution contained 22.02 g/L calcium. Residual silicon and vanadium concentrations were 0.006 and 0.0006 g/L, respectively. Titanium, iron, aluminum, manganese, and zinc were not detected in the purified solution by ICP-OES.

Calcium stays in solution at pH 10 because calcium nitrate is highly soluble, whereas the impurity metals form sparingly soluble hydroxides. Milk of lime both neutralized the residual acid and precipitated the impurities. Part of the calcium, however, entered the solution directly from CaO and must be accounted for separately in the material balance. The value of 84.7% refers to calcium extraction from the sludge before milk of lime was added.

The purified solution went to production of the calcium nitrate-based product, and the cake went to silicon removal.

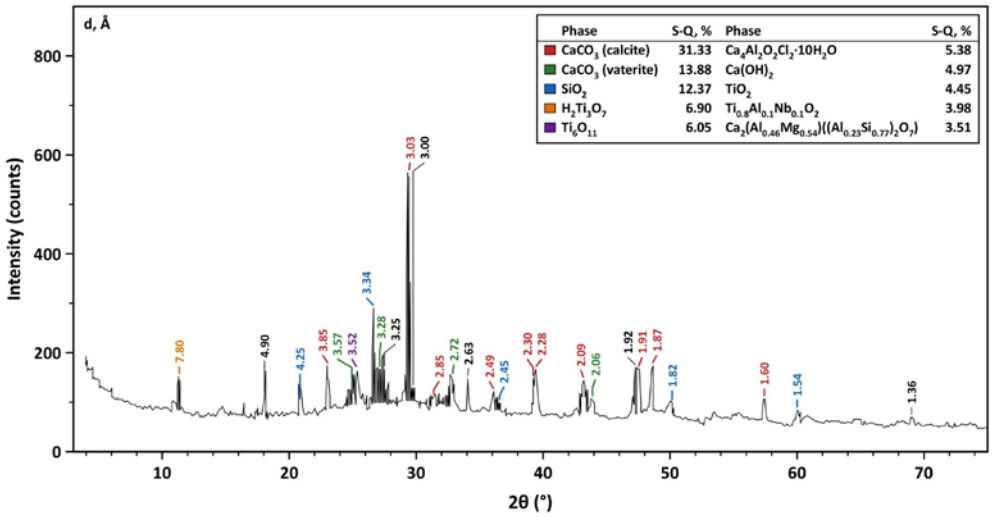


Figure 2 - XRD pattern and semi-quantitative phase composition of the initial titanium-magnesium production sludg

Source: prepared by the authors based on data from [6].

Production and granulation of the calcium nitrate-based product

Evaporation of the purified solution without an additive gave a viscous product that crystallized poorly. To improve crystallization, NH_4NO_3 was added at 7% of the calculated $Ca(NO_3)_2$ mass.

Evaporation at 100 °C for 6 h produced a concentrated melt containing 92–95% $Ca(NO_3)_2$. XRD identified anhydrous $Ca(NO_3)_2$ and its dihydrate $Ca(NO_3)_2 \cdot 2H_2O$ as the main crystalline phases, at relative contents of 71 and 29%, respectively. The dihydrate forms because calcium nitrate is highly hygroscopic and absorbs moisture during cooling and storage.

When the melt was spread on the granulator pan heated to 90 °C, it formed a solid layer that was removed as flakes. The primary product had a wide size distribution: 28.2% of the particles were larger than 7 mm and 24.1% smaller than 1 mm, giving 52.3% off-size material.

Particles larger than 7 mm were crushed, and the fraction below 1 mm was remelted and regranulated. After this step, the 1–7 mm fraction reached 91.0%. The proportion above 7 mm fell to 3.0%, and that below 1 mm to 5.7%.

The material is described as a calcium nitrate-based product because NH_4NO_3 was used in its preparation and its phase composition included both anhydrous and hydrated $Ca(NO_3)_2$. Total nitrogen, moisture, ammonium nitrogen, and impurity contents still need to be determined to confirm its suitability for practical use.

Table 2 - Particle size distribution of the calcium nitrate product

Size class, mm	Primary product, %	Product after recycling of off-size fractions, %
Above 7	28.2	3.0
5–7	12.7	26.9
3–5	17.5	35.1
1–3	17.5	29.0
Below 1	24.1	5.7

Source: compiled by the authors based on data from [7].
Note: The total differs slightly from 100% because of rounding.

Returning the off-size fractions raised the yield of the 1–7 mm fraction from 47.7 to 91.0% (Table 2) and reduced the amount of material that would otherwise go to waste.

Ammonium fluoride processing of the titanium-bearing cake

Chemical analysis of the cake after nitric acid leaching gave the following composition (wt%): 16.9 Ti, 14.8 Si, 3.6 Nb, 3.3 Al, 2.5 Fe, 1.2 Ca, 0.7 Zr, 0.4 F, 0.4 W, 0.2 Cr, 0.1 V, and 0.06 Mn.

Compared with the initial sludge, the cake contained less calcium (1.2 vs. 19.4%) and more titanium (16.9 vs. 6.8%) and silicon (14.8 vs. 8.2%). The remaining 14.8% Si limits direct use of the cake in electric smelting, because silicon compounds can impair the melt properties and the quality of the titanium product.

XRD showed that the main silicon-bearing phases of the cake were quartz, calcian albite, sillimanite, and sodium aluminosilicate. Titanium occurred as anatase, rutile, and a complex titanium-aluminum-niobium oxide.

Table 3 - Phase composition of the cake after nitric acid leaching of the sludge

Mineral phase	Chemical formula	Content, %
Quartz	SiO_2	43.3
Calcian albite	$(Na,Ca)Al(Si,Al)_3O_8$	17.2
Anatase	TiO_2	9.1
Titanium-aluminum-niobium oxide	$Ti_{0.8}Al_{0.1}Nb_{0.1}O_2$	8.6
Rutile	$Ti_{0.912}O_2$	8.4
Sillimanite	$(Al_{1.98}Fe_{0.02})SiO_5$	5.7
Sodium aluminosilicate	$Na(AlSi_2O_6)$	5.6
Iron oxide	Fe_2O_3	2.2

Source: compiled by the authors based on data from [[6], [7]].

Quartz, calcian albite, sillimanite, and sodium aluminosilicate together made up 71.8% of the cake, and the identified titanium-bearing phases 26.1%. Quartz and aluminosilicates did not decompose during nitric acid leaching, so a fluorinating reagent was needed.

To remove silicon selectively, the cake was treated with ammonium bifluoride. Preliminary fluorination at 200 °C allowed NH_4HF_2 to react with quartz and the silicate phases. Raising the temperature to 300 °C then drove the resulting fluorosilicates into the gas phase and separated them from the low-volatility titanium, iron, and aluminum compounds.

After treatment, the silicon content of the solid residue fell to about 0.1% (as element). This is roughly 82 times lower than in the initial sludge and about 148 times lower than in the cake before fluorination. XRD of the titanium-bearing residue confirmed the presence of titanium and iron fluorides and oxyfluorides (Figure 3).

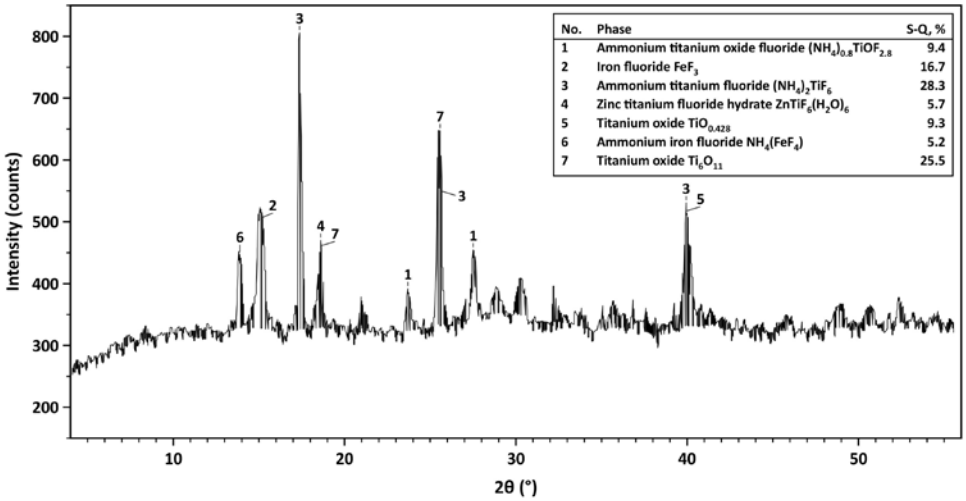


Figure 3 - XRD pattern of the titanium-bearing residue after ammonium fluoride treatment of the cake
Source: prepared by the authors based on data from [7].

Production of amorphous silica

The silicon-bearing sublimates were collected in the cooled condenser and in absorbers with 10% ammonia solution. The combined solutions were heated to 50 °C and held for 60 min, during which amorphous silica precipitated.

After filtration, washing, and drying, the product had the following composition (wt%): 83.0 SiO_2, 0.02 Fe_2O_3, 0.06 Al_2O_3, 0.10 CaO, 0.02 MgO, 0.20 Cl, and 2.0 F. The low iron, aluminum, calcium, and magnesium contents indicate that silicon passed preferentially into the sublimate and that little of the non-volatile impurities was carried over.

Fluorine was the main impurity. It comes from ammonium fluoride that forms and adsorbs on the large surface of the amorphous silica particles. Ordinary water washing does not remove all the adsorbed fluorine compounds, so additional washing followed by heat treatment is advisable to raise product purity.

At 83.0% SiO_2, the product cannot yet be classed as commercial amorphous silica. Such a classification requires data on specific surface area, moisture, bulk density, particle size, and fluorine content, as well as compliance with the relevant standard.

Characterization of the titanium-bearing residue

The solid residue after sublimation of the silicon compounds had the following composition (wt%): 21.3 TiO_2, 12.0 Fe_2O_3, 15.7 Al_2O_3, 1.5 CaO, 0.2 SiO_2, and 17.5 F.

A residual fluorine content of 17.5% is unacceptably high for direct return of the material to electric smelting. Fluorides can form volatile compounds, accelerate equipment corrosion, and change the composition of the gas phase.

Ammonium fluoride processing of electric smelting dust

The ilmenite smelting dust contained 34.29% TiO_2 and 27.53% SiO_2 (as oxides). The high silicon content prevented direct return of the material to the smelting furnace, while the high titanium content makes the dust a potential secondary titanium raw material.

Alkaline treatment of the dust extracted 77.7% of the silicon. Part of the silicon compounds, however, remained in the solid residue because of stable magnesium silicates and anosovite particles coated with a shell of amorphous silica.

Ammonium fluoride treatment was used to remove silicon more completely. The dust was mixed with ammonium bifluoride at a dust:NH_4HF_2 mass ratio of 1:1 and treated at 260 °C for 6 h. Under these conditions, 84.2% of the silicon compounds sublimed.

XRD detected no crystalline silicon-bearing phases in the solid residue after treatment. The quartz and silicate phases had therefore decomposed, and most of the silicon had passed into volatile fluorosilicates.

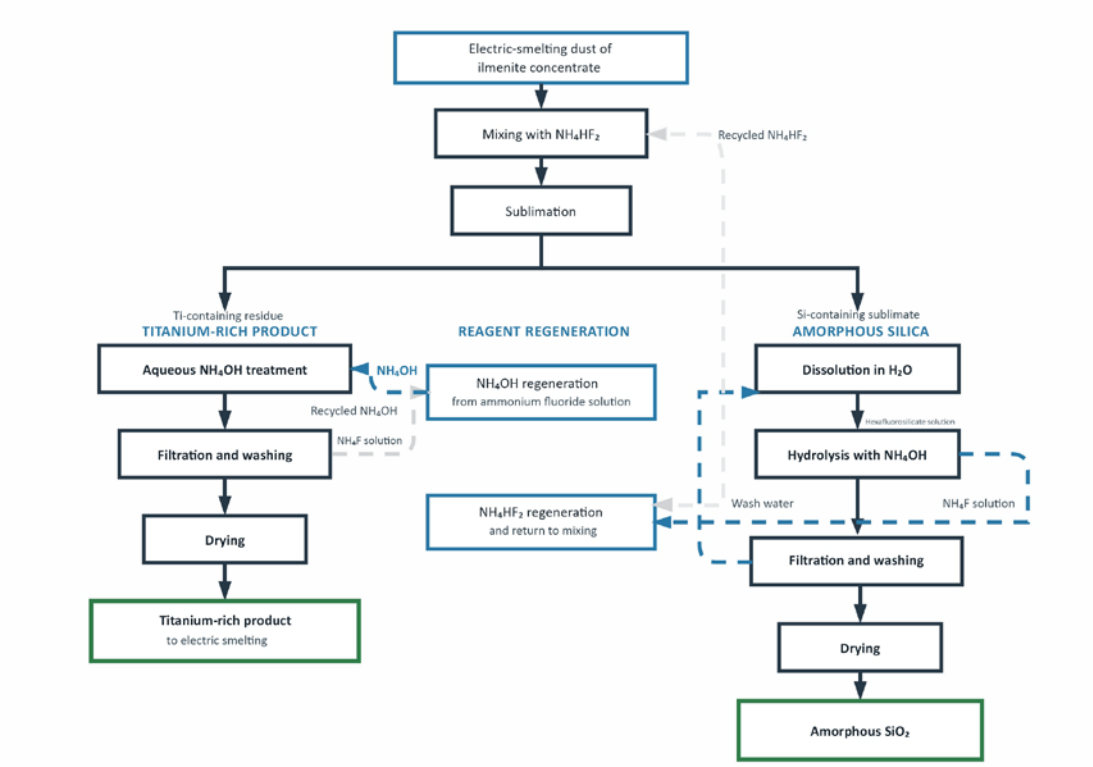


Figure 4 - Proposed flowsheet for ammonium fluoride processing of ilmenite concentrate smelting dust
Source: adapted from [9].

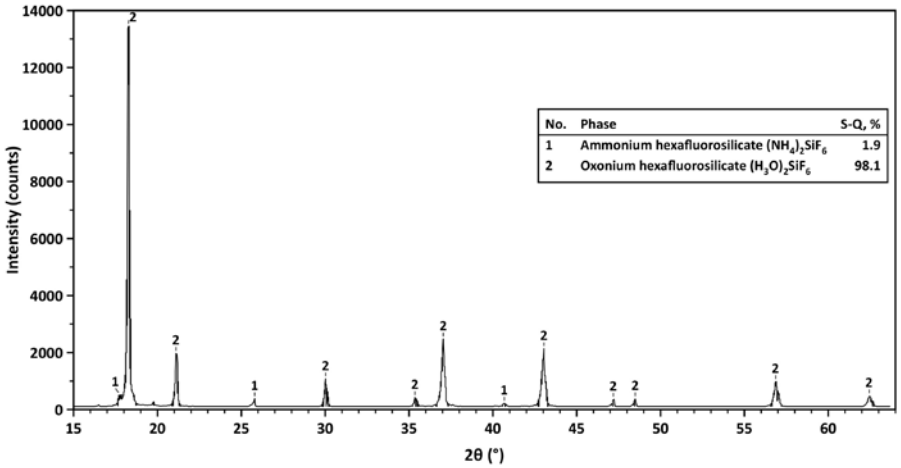


Figure 5 - XRD pattern of the silicon-bearing sublimate obtained by ammonium fluoride treatment of the smelting dust
Source: prepared by the authors based on data from [[8], [9]].

Formation of the silicon-bearing sublimate

The main compound identified in the sublimate was oxonium hexafluorosilicate, $(H_3O)_2SiF_6$. Its formation may be associated with the thermal decomposition of NH_4HF_2 and subsequent reactions involving HF and silicon dioxide, as represented by Equations (3) and (4). The sublimate also contained ammonium hexafluorosilicate, $(NH_4)_2SiF_6$, consistent with the reaction described by Equation (2).

Figure 5 shows the phase composition of the sublimate.

Production and purification of amorphous silica

The sublimate was dissolved in water at S: L = 1:10. The solution was heated to 40 °C, and 25% ammonia solution was added under vigorous stirring until the pH reached 7.5–8.0. The suspension was held for about 80 min to allow amorphous silica particles to form and grow.

After filtration, washing, and drying, the primary amorphous product contained (wt%): 81.6 SiO_2, 12.9 NH_4F, 0.045 Fe, 0.025 Zn, 0.017 Pb, 0.014 As, 0.005 Cu, and 0.003 Sr.

The high NH_4F content results from its adsorption on the large surface of the amorphous silica particles. Water washing did not remove all the ammonium fluoride, so the product was heat-treated at 530–560 °C for 60–80 min.

After heat treatment, the SiO_2 content rose to 96.3%. The final product contained (wt%) 0.14 Fe_2O_3, 0.16 Al_2O_3, 0.02 ZnO, 0.03 CaO, and 0.15 TiO_2. Fluorine was below the detection limit of the analytical method.

The increase in SiO_2 from 81.6 to 96.3% is due mainly to the thermal decomposition and removal of NH_4F. The product has low levels of metal impurities. Its possible applications will depend on specific surface area, particle size, bulk density, moisture, and residual soluble salts, which remain to be measured.

Characterization of the titanium-bearing residue

The solid residue after sublimation of the silicon compounds had the following composition (wt%): 54.0 TiO_2, 32.0 Fe_2O_3, 7.6 MnO_2, 1.4 SiO_2, 1.5 Al_2O_3, 1.2 ZnO, 0.9 PbO, 0.36 K_2O, and 0.14 ZrO_2.

Compared with the initial dust, the TiO_2 content increased from 34.29 to 54.0%, about 1.57-fold, and the SiO_2 content decreased from 27.53 to 1.4%, about 19.7-fold. With 54.0% TiO_2 and 32.0% Fe_2O_3, the residue is a Ti–Fe concentrate.

The 1.2% ZnO and 0.9% PbO must be considered when choosing further processing. On heating, zinc and lead compounds can volatilize, accumulate again in the dust, and increase the load on the gas cleaning equipment. Returning the residue to electric smelting therefore requires control over the volatile impurities.

Additional titanium recovery

To recover more titanium, the Ti–Fe residue was given a further ammonium fluoride treatment. On heating, volatile fluorotitanates formed and were separated from less volatile components by sublimation.

At 600 ± 10 °C and 2 h, up to 99% of the titanium passed into the sublimate. XRD of the sublimate showed ammonium heptafluorotitanate, ammonium hexafluorosilicate, and ammonium hexafluoroferrate. The iron compounds and residual silicon indicate that titanium sublimation is accompanied by partial volatilization of impurities.

Pyrohydrolysis of the titanium sublimate was carried out at 600 °C for 4–5 h with steam supplied at 1.5–2.0 L/g. Under these conditions, 99.5% of the titanium fluorides converted to titanium dioxide. XRD showed that the pyrohydrolysis product was mainly anatase TiO_2. The anatase-to-rutile transition began at 700 °C, but rutile made up only 5.2%.

The titanium dioxide had a grayish tint caused by iron, chromium, and manganese compounds. To remove these impurities, the product was treated with 12.5–15% HCl at 25–30 °C and S:L = 1:6–1:8 for 20–30 min. After acid purification, it contained about 94% anatase and 6% rutile. Calcination at 900 °C for 2 h then converted the anatase to rutile. The final product contained 99.8% TiO_2, with impurities of (wt%) 0.0005 SiO_2, 0.032 Cr_2O_3, 0.005 MnO_2, and 0.039 Fe_2O_3; fluorine was not detected.

Comparison of sludge and dust processing

The titanium-magnesium production sludge contains 19.4% calcium, so its processing begins with nitric acid leaching, which transfers calcium into solution and concentrates titanium in the solid residue.

Table 4 - Comparison of the sludge and dust processing routes

Parameter	Titanium-magnesium production sludge	Electric smelting dust
Main limiting component	Calcium, then silicon and fluorine	Silicon, then volatile impurities
First stage	Leaching with 20% HNO_3	Ammonium fluoride treatment with NH_4HF_2
Temperature of the main stage	20 ± 4 °C	260 °C
Duration	30 min	6 h
Main recovered component	Calcium	Silicon
Degree of extraction or sublimation	84.7% Ca	84.2% (Si fluoride compounds)
Silicon-bearing product	83.0% SiO_2; 2.0% F	96.3% SiO_2 after heat treatment
Titanium-bearing residue	21.3% TiO_2; 17.5% F	54.0% TiO_2; 1.4% SiO_2
Potential for additional Ti recovery	Requires defluorination and further study	Up to 99% Ti sublimation at 600 ± 10 °C
Main process constraint	High fluorine content in the residue	Co-sublimation of Fe, Mn, Cr, and residual Si

Source: compiled by the authors based on data from [[6], [7], [8], [9]].

In the smelting dust, silicon is the component that prevents its return to the metallurgical process. Ammonium fluoride treatment is therefore applied directly to the raw dust, without prior acid leaching.

Sludge processing yields three potentially useful products: calcium nitrate, an amorphous silica product, and a titanium-bearing residue. Dust processing yields amorphous silica, a concentrated Ti–Fe residue, and, after further ammonium fluoride treatment, high-purity titanium dioxide.

The comparison demonstrates that the initial chemical composition of titanium-magnesium production wastes determines the appropriate sequence of component separation. For calcium-rich neutralization sludge, selective nitric acid leaching is an effective preliminary stage because it transfers most of the calcium into solution while increasing the relative titanium concentration in the solid residue. In contrast, the high silicon content of electric smelting dust makes ammonium bifluoride treatment the principal separation stage.

The effectiveness of the two routes also differs in terms of product quality and further utilization. The amorphous silica obtained from the sludge-derived cake contained 83.0% SiO_2 and 2.0% F, whereas the thermally treated dust-derived product contained 96.3% SiO_2. Although the difference is consistent with the removal of residual ammonium fluoride during thermal treatment, the available experimental data do not establish the individual contributions of feed composition and purification conditions.

A further distinction concerns the titanium-bearing residues. The sludge-derived residue retained 17.5% fluorine, preventing its direct return to electric smelting without additional treatment. In contrast, the dust-derived Ti–Fe concentrate contained 54.0% TiO_2 and was subjected to further titanium recovery, yielding rutile with 99.8% TiO_2. These results indicate that the dust-processing route provides a more developed pathway to a high-purity titanium product under the investigated conditions, whereas the sludge-processing route requires additional defluorination studies.

The observed differences highlight the importance of product purification and impurity control in both processing routes. Additional washing and thermal treatment of the sludge-derived silica should be investigated to reduce residual fluoride compounds. For the dust-processing route, further optimization should focus on minimizing the co-sublimation of iron and other impurities during titanium recovery. These measures could improve product quality and facilitate the subsequent utilization of the recovered materials.

Possible integration of the two routes

Both wastes could be processed in one plant with separate feed preparation lines and shared units for ammonium fluoride treatment, gas capture, sublimate hydrolysis, and reagent regeneration.

The two routes could share the NH_4HF_2 feeding and dosing system, tube furnaces, cooled condensers, absorbers, the ammonia hydrolysis unit, and the equipment for regenerating ammonium fluoride solutions.

Environmental and process constraints

Ammonium fluoride processing releases HF, NH_3, and volatile fluorosilicates and fluorotitanates. The equipment must therefore be gas-tight, and the gas phase must pass through a cooled condenser and then through absorbers.

The NH_4F solutions formed after hydrolysis of the silicon and titanium compounds should be regenerated or returned to the process, and the wash water should be recycled. Without closed-loop reagent circulation, the reduction in solid waste may come at the cost of large volumes of fluoride-bearing liquid effluent.

Industrial implementation requires material balances for calcium, silicon, titanium, and fluorine. The specific consumption of HNO_3, NH_4HF_2, NH_4OH, CaO, water, and energy must be determined, along with the capture efficiency for fluorine compounds, the yield of each product, and component losses to intermediate streams.

The integrated flowsheet can be regarded as resource-saving only if the reagents are regenerated, wash water is recycled, gases are cleaned, and the quality of the calcium, silicon, and titanium products is confirmed.

Conclusions

The comparative evaluation of calcium-rich neutralization sludge and silicon-rich electric smelting dust demonstrated that the sequence of component recovery should be selected according to the chemical and mineralogical composition of the initial waste. Nitric acid leaching was effective as the first treatment stage for calcium-rich sludge, whereas direct ammonium bifluoride treatment was more appropriate for silicon-rich smelting dust under the investigated conditions.

Nitric acid leaching of the neutralization sludge with 20% HNO_3 at a solid-to-liquid ratio of 1:10, a temperature of 20 ± 4 °C, and a duration of 30 min

extracted 84.7% of calcium into solution. The titanium content of the solid residue increased from 6.8 to 16.9 wt%, primarily because of the dissolution of calcium-bearing phases. Subsequent purification and granulation produced a calcium nitrate-based product with 91.0% of particles in the target 1–7 mm fraction.

Ammonium bifluoride treatment enabled silicon separation from both waste streams, but the resulting products differed substantially in composition. The sludge-derived amorphous silica contained 83.0% SiO_2 and 2.0% F, whereas the dust-derived product reached 96.3% SiO_2 after thermal treatment. These findings indicate the importance of additional purification for reducing residual fluoride compounds and improving the quality of the silicon-bearing products.

The titanium-bearing residues exhibited different potentials for further processing. The sludge-derived residue contained 17.5% F, which restricts its direct metallurgical utilization. In contrast, desilication of the smelting dust increased the TiO_2 content from 34.29 to 54.0 wt% and reduced the SiO_2 content from 27.53 to 1.4 wt%. Subsequent fluorination transferred up to 99% of titanium into the sublimate, and pyrohydrolysis, acid purification, and calcination yielded rutile containing 99.8% TiO_2.

The results identify two principal directions for further technological development: defluorination of titanium-bearing residues obtained from neutralization sludge and improved control of impurity co-sublimation during smelting dust processing. Industrial application will additionally require complete material balances for calcium, silicon, titanium, and fluorine, evaluation of reagent consumption, and regeneration of fluoride-containing solutions. These measures are necessary to assess the technological feasibility and environmental performance of the proposed processing routes.

Conflicts of interest. On behalf of all authors, the corresponding author states that there is no conflict of interest.

CRediT author statement: **N. Tolegenova**: Conceptualization, Methodology, Investigation, Writing – original draft; **A. Yessengaziyev**: Investigation, Formal analysis, Validation; **A. Ultarakova**: Methodology, Supervision, Writing – review and editing; **B. Mishra**: Supervision, Validation, Writing – review and editing.

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Титан-магний өндірісі қалдықтарынан азот қышқылымен шаймалау және аммоний бифторидімен өңдеу арқылы кальцийді, кремнийді және титанды кезең-кезеңімен бөліп алу

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ТҮЙІНДЕМЕ

Бұл жұмыста титан-магний өндірісі кезінде пайда болатын кальцийге бай бейтараптандыру шламы мен кремнийге бай электрбалқыту шаңын өңдеудің тізбекті технологиялық сұлбалары қарастырылды. Кальцийді бөліп алу үшін шлам азот қышқылымен шаймаланды, содан кейін ерітінді тазартылып, кальций нитраты негізіндегі өнім алынды және қатты қалдықты аммоний бифторидімен өңдеу жүргізілді. Электрбалқыту шаңы кремний мен титан қосылыстарын бөлу үшін аммоний бифторидімен сатылы өңдеу арқылы өңделді, содан кейін алынған өнімдер гидролизденді, тазартылды және термиялық өңдеуден өтті. Азот қышқылымен шаймалау нәтижесінде шлам құрамындағы кальцийдің 84,7%-ы ерітіндіге өтті, ал кейінгі өңдеу барысында кальций нитраты негізіндегі өнім және аморфты кремний диоксиді алынды. Электрбалқыту шаңын өңдеу кремнийді бөліп алуға және құрамында 96,3% SiO_2 бар аморфты кремнезем алуға мүмкіндік берді. Титанқұрамды концентратты одан әрі

	өңдеу нәтижесінде құрамында 99,8% TiO_2 бар рутил алынды. Екі технологиялық сұлбаны салыстыру шламды өңдеуден алынған өнімде фтордың қалдық мөлшері мен шаңды өңдеу кезіндегі қоспалардың бірге айналымға өтуі негізгі технологиялық шектеулер екенін көрсетті. Алынған нәтижелер титан-магний өндірісінің қалдықтарынан құнды компоненттерді сараланған түрде алу мүмкіндігін көрсетеді.
	Түйін сөздер: ильменит электр балқыту шаңы; бейтараптандыру шламы; аммоний бифториді; аморфты кремний диоксиді; кальций нитраты; титан диоксиді.
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Последовательное извлечение кальция, кремния и титана из отходов титаномагниевого производства азотнокислотным выщелачиванием и бифторидно-аммонийной обработкой

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АННОТАЦИЯ

В работе рассмотрены последовательные технологические схемы переработки богатого кальцием шлама нейтрализации и богатой кремнием пыли электроплавки, образующихся при титаномагниевом производстве. Шлам подвергали азотнокислотному выщелачиванию для извлечения кальция с последующей очисткой раствора, получением продукта на основе нитрата кальция и обработкой твёрдого остатка бифторидом аммония. Пыль электроплавки перерабатывали путём поэтапной обработки бифторидом аммония для разделения соединений кремния и титана с последующим гидролизом, очисткой и термической обработкой полученных продуктов. При азотнокислотном выщелачивании из шлама в раствор извлечено 84,7% кальция, а последующая переработка позволила получить продукт на основе нитрата кальция и аморфный кремнезём. Обработка пыли электроплавки обеспечила отделение кремния и получение аморфного кремнезёма с содержанием SiO_2 96,3%. Дальнейшая переработка титансодержащего концентрата позволила получить рутил с содержанием TiO_2 99,8%. Сравнение двух технологических схем показало, что основными ограничениями являются остаточный фтор в продукте переработки шлама и совместная возгонка примесей при переработке пыли. Полученные результаты демонстрируют возможность дифференцированного извлечения ценных компонентов из отходов титаномагниевого производства.

Ключевые слова: пыль электроплавки ильменита; шлам нейтрализации; бифторид аммония; аморфный диоксид кремния; нитрат кальция; диоксид титана.

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