Fluoroammonium method for processing of cake from leaching of titanium-magnesium production sludge

1Yessengaziyev A.M., 1Ultarakova A.A., 2Burns P.C.

1 Satbayev University, "Institute of Metallurgy and Ore Beneficiation"
JSC, Almaty, Kazakhstan
2 University of Notre Dame, "Center for Sustainable Energy"
USA, South Bend, USA

* Corresponding author email: a.esengaziev@satbayev.university

ABSTRACT
We present the results of the physical and chemical properties of cake from nitric-acid leaching of titanium production sludge. It was found that all silicon in the cake is in the form of quartz, albite, sillimanite, sodium aluminosilicate. In total, these minerals make up the majority of the cake 60.24%. Titanium is presented in the form of rutile, titanium aluminum oxide, which in total is 35.56%. Iron is part of sillimanite and hematite, the total content of which is about 4.2%. The optimal parameters of fluoroammonium processing of cake were determined: silicon distillation into sublimates at 300°C for 6 hours, sublimation of titanium in the form of titanium tetrafluoride at 800°C for 2 hours. The process of alkaline hydrolysis of sublimates of fluoride compounds and cinder was carried out. Purification of impurities and calcination of hydrated titanium dioxide were carried out. The resulting titanium and silicon dioxide products contain: 96.2% TiO₂, 88% SiO₂, respectively; a niobium-containing intermediate product with a content of 11.6% Nb₂O₅ was also obtained.

Keywords: cake, sublimates, cinder, fluoroammonium processing, alkaline hydrolysis, titanium dioxide.

Yessengaziyev Azamat Muratovich
Information about authors:
Ph.D. candidate, Institute of Metallurgy and Ore Beneficiation JSC, Almaty, Kazakhstan. ORCID ID: 0000-0002-4989-4119. E-mail: a.esengaziev@satbayev.university

Ultarakova Almagul Amirovna
Candidate of Technical Sciences, Institute of Metallurgy and Ore Beneficiation JSC, Almaty, Kazakhstan. ORCID ID: 0000-0002-9428-8508. E-mail: a.ультаракова@satbayev.university

Peter C Burns
Professor of Civil & Environmental Engineering & Earth Sciences, Director, Center for Sustainable Energy at Notre Dame, South Bend, USA. ORCID ID: 0000-0002-2319-9628. E-mail: pburns@nd.edu

Introduction
The Kroll process is the main method for producing titanium sponges in all countries manufacturing titanium sponges [1], which consists of magnesium-thermal reduction of titanium tetrachloride at 850°C. The production chain of this process includes the production of magnesium metal from its molten salts by electrolysis. Dehydrated carnallite is the raw material for the production of electrolytic magnesium, and the spent electrolyte is used in the chlorination of titanium slags. Natural carnallite is preliminarily enriched and dehydrated. At the stages of titanium slag chlorination and magnesium electrolysis, a significant amount of chloride waste is formed.

Industrial waste is a hazard to the environment, as it contaminates soil and groundwater during neutralization and storage of solid waste in sludge dumps and the resulting industrial wastewater [2].

Part of the titanium production chloride waste is leached with water and neutralized with calcium hydroxide to pH 7-8.5. The resulting slurry is pumped into sludge collectors and accumulates therein. The reserves of sediments or sludge of titanium production are about 320 thousand tons. The multicomponent composition thereof is present in the form of oxides, oxychlorides, and carbonates [3].

In Russia, the Bereznikovsky Titanium-Magnesium Plant (AVISMA JSC) obtains iron oxide pigments from waste [4]. However, the available research on hydrometallurgical processing of titanium-magnesium production waste was economically ineffective and lengthy due to the low filtration rate of slurries after leaching of chloride waste from titanium-magnesium production. Therefore, according to the existing technology, the Bereznikovsky Titanium-Magnesium Plant, washes out this waste with water and neutralizes acidic effluents with alkaline effluents of soda production, and sends to a sludge dump.

Thus, titanium-magnesium plants usually do not process solid chloride waste and often discharge
wastewater that contains chlorides and harmful substances into water bodies, polluting the soil and water of the surrounding area [5]. The plant has to pay huge fines for waste management. The creation of integrated technology for the processing of this technogenic raw material will make it possible to obtain additional products in the form of titanium dioxide and calcium nitrate. Titanium dioxide can be returned to production for chlorination of titanium slags and calcium nitrate will be used as a fertilizer and a component in the cement industry, so these products will be in demand both in Kazakhstan and on the world market.

In recent years, fluoroammonium processing of multicomponent raw materials has been of great interest [6]. Ammonium bifluoride is a white crystalline substance with good solubility in water of 434 g/L, a melting point of 126.2°C, and a boiling point of 238°C, accompanied by decomposition into NH₃ and HF.

The interaction of oxygen-containing compounds of titanium and other metals with ammonium bifluoride is of great importance in terms of the technological attractiveness of the method for extracting components from raw materials through the formation of ammonium fluorometallates [7] that, due to their physical and chemical properties, ensure the solubility of products and the possibility of separating mixtures by sublimation. Fluorination by-products (water vapor, ammonia, hydrogen fluoride) in gas-collecting systems are regenerated into ammonium fluoride and, upon drying, are formed into ammonium bifluoride, which ensures environmental safety of production and allows such by-products to be used in the circulation of a fluorinating agent.

[8] and [9] show the possibility of separating aluminosilicates with ammonium bifluoride into alumina and silicon oxide by sintering. In the complex processing of kaolin concentrates, ammonium bifluoride (NH₄HF₂) was used as a fluorinating reagent. Under normal conditions, ammonium bifluoride does not pose a significant environmental hazard and is a strong fluorinating reagent when heated. Its melting and decomposition points are 126.2°C and 238°C, respectively. This is because each reaction needs to be activated, and the activation of hydrogen fluoride and halogen fluorides requires less energy than gaseous fluorine, so such reactions can be carried out at a lower temperature. The kaolin concentrate with NH₄HF₂ is sintered at 190-200°C with the formation of a powdery product. This product is desiliconized under oxidizing conditions at a temperature above 320°C. Gaseous ammonia and water vapor are trapped and enter the absorption apparatus; ammonium fluoride enters the same place. Evaporation of the resulting solution obtains regenerated NH₄HF₂ which goes to the head of the process. The method for processing [10] titanium-containing raw material of ilmenite concentrate includes the fluorination of the raw material by sintering with a fluoride reagent, heat treatment of the fluorinated mass to separate fluorination products by sublimation, pyrohydrolysis of post-sublimation residues to obtain iron oxide. Fluorination uses ammonium fluoride, ammonium bifluoride, or their mixture in a stream of inert gas as a fluoride reagent. The sublimation products are trapped in water when obtaining an ammonium fluorotitanate solution, and hydrated titanium dioxide is precipitated with an aqueous solution of ammonia, then the precipitate is heat-treated to obtain titanium dioxide.

In the available patent and scientific literature, almost all presented information about the fluoroammonium treatment is related to the processing of ores or concentrates, but not to the processing of titanium production waste by this method. Taking into account the differences in the physical and chemical properties of ammonium fluorometallates, we can select the conditions for the complete separation of the mineral product fluorinated with ammonium bifluoride into individual components. All this is a prerequisite for the development and creation of a more progressive and promising fluoride technology for processing titanium-containing raw materials.

The main purpose of this work was to study the physical and chemical properties of the previously obtained cake [11] from nitric-acid leaching of sludge from Ust-Kamenogorsk Titanium Magnesium Plant JSC and the processing of cake from leaching of sludge by the fluoroammonium method to obtain marketable products.

**Experimental part and discussion of results**

This research proposes to use a cake from nitric-acid leaching of sludge from Ust-Kamenogorsk Titanium Magnesium Plant JSC as a raw material source; its phase composition is shown in Table 1. Based on the results of X-ray fluorescence and chemical analyzes, the elemental composition of the cake was determined as follows, wt. %: 19.7 Ti, 3.1
Fe, 1.2 Ca, 3.3 Al, 0.4 S, 20.5 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 polished surface of a polished section prepared from the cake from nitric-acid leaching of sludge was examined using an EDAX ORBIS MICRO-XRF X-ray fluorescence spectrometer. The research results are shown in Figure 1.

**Table 1 – Phase composition of the cake**

| Phase                  | Formula                  | Si-O, % |
|------------------------|--------------------------|---------|
| Quartz                 | SiO₂                     | 37.8    |
| Rutile                 | TiO₂                     | 25.5    |
| Albite                 | (Na,Ca)Al(Si,Al)O₈        | 13.2    |
| Niobium-aluminum-titanium oxide | Ti₉₈Al₀₁Nb₀₁O₂ | 10.0    |
| Sillimanite            | (Al₁.₉₈Fe₀.₀₂)SiO₅        | 5.7     |
| Iron oxide             | Fe₂O₃                    | 4.2     |
| Sodium aluminum silicate | Na(AlSi₂O₆)              | 3.6     |

The results of physical and chemical studies draw the following conclusions: all silicon is in the form of quartz, feldspar as albite, sillimanite, sodium aluminosilicate. In total, these minerals make up the majority of the cake (60.24%). Titanium is presented in the form of rutile, titanium aluminum oxide, which in total is 35.56%. Iron is part of sillimanite and hematite with a total content of about 4.2%.

Experiments on fluoroammonium processing of cake from sludge leaching were carried out. For the interaction of ammonium bifluoride with cake, preliminary sintering was carried out. Preliminary sintering of the cake with ammonium bifluoride and a small amount of water (25% of the initial mixture) was carried out in a vertical furnace at 200°C for 60 min in a fluoroplastic crucible. The cake sintering at 200°C with ammonium bifluoride is necessary for the interaction of the silicate components of the cake with ammonium bifluoride [12]. The following reactions occur during fluoridation:

\[
\begin{align*}
2\text{SiO}_2 + 7\text{NH}_4\text{HF}_2 & = 2(\text{NH}_4)_3\text{SiF}_7 + 4\text{H}_2\text{O} + \text{NH}_3 \\
\text{SiO}_2 + 3\text{NH}_4\text{HF}_2 & = (\text{NH}_4)_2\text{SiF}_6 + 2\text{H}_2\text{O} + \text{NH}_3
\end{align*}
\]

At the same time, the sinter yield for each experiment was stably in the range of 85-87%; the rest was losses with the gas phase in the form of ammonia, water vapor, and hydrogen fluoride. Silicon and titanium were sublimated in a stainless steel tube with an argon supply at a rate of 1 to 1.5 dm³/min. Silicon was sublimated at 200°C and 300°C with a change in the duration of the process from 60 to 360 min. The results of studies on the sublimation of silicon are shown in Table 2. Based on the results of silicon sublimation, a histogram of silicon extraction into sublimates and a cinder was built (Figure 2).

According to Table 2 and the diagram in Figure 2, the increase in the time of the sublimation process from 60 to 360 min at both temperatures increased the extraction of silicon into sublimates from ~55 to ~91-94%, respectively. At the same time, the extraction of titanium into sublimates increased in a small amount, in the range from ~1.6 to ~3.2%, respectively. The best results were shown by experiment 8, which was carried out at a sublimation temperature of 300°C for 360 min, at an argon flow rate of 1.2 dm³/min, where the extraction of silicon into sublimates was 94.2%. The content of silicon and titanium in sublimates was 25.9% and 1.9%, respectively. The sublimate yield was 29.5%, the cinder yield in the boat was 29.0%, the rest was the gaseous phase trapped in the flask with 10% ammonia water for the regeneration of ammonium bifluoride.

![Figure 1 – Energy Dispersive X-ray (EDX) Analysis](image-url)
Titanium sublimation was the next stage. For sublimation of titanium, cinders from experiments 5-9 were combined. The resulting material was crushed, averaged, and divided into 5 experiments. For each sample, an additional amount of ammonium bifluoride was added to maintain the ratio with the amount of cinder equal to 1:1. The sinter yield for each experiment was in the range of 90-94%. The second sintering of the cinder at 200°C with ammonium bifluoride was carried out for the complete fluorination of titanium oxides and impurity components according to the following reactions:

\[
\text{TiO}_2 + 2\text{NH}_4\text{HF}_2 = \text{(NH}_4\text{)}_2\text{TiF}_6 + 2\text{H}_2\text{O} + \text{NH}_3 \quad (3)
\]

\[
\text{Fe}_2\text{O}_3 + 6\text{NH}_4\text{HF}_2 = 2\text{(NH}_4\text{)}_3\text{FeF}_6 + 3\text{H}_2\text{O} + \text{NH}_3 \quad (4)
\]

\[
\text{Al}_2\text{O}_3 + 6\text{NH}_4\text{HF}_2 = 2\text{(NH}_4\text{)}_3\text{AlF}_6 + 3\text{H}_2\text{O} \quad (5)
\]

Impurity compounds such as Mg, Mn, Nb, Al, Fe, emerging during fluorination, form simple and complex fluorides, which remain in the cinder.

The ammonium hexafluorotitanate formed during fluorination with an excess of ammonium bifluoride decomposes to titanium tetrafluoride stepwise with the elimination of the ammonium fluoride molecule from the complexes according to the following reactions:

\[
\text{(NH}_4\text{)}_2\text{TiF}_6 = \text{NH}_4\text{TiF}_5 + \text{NH}_3\uparrow + \text{HF}\uparrow \quad (6)
\]

\[
\text{NH}_4\text{TiF}_5 = \text{TiF}_4\uparrow + \text{NH}_3\uparrow + \text{HF}\uparrow \quad (7)
\]

If there is not enough ammonium bifluoride, part of the titanium dioxide is not completely fluorinated to the formation of ammonium oxyfluorotitanates, which form titanium oxyfluoride (TiOxFy) upon thermal decomposition [13].

Titanium tetrafluoride was sublimated at 700-800°C during 60-120 min. The argon supply rate in all experiments was maintained at 1.2 dm³/min. The results of studies on titanium sublimation are presented in Table 3. Figure 3 shows the extraction of titanium into sublimates and cinder.

The research results presented in Table 3 and on the diagram (Figure 3) show that the increase in the process temperature from 700 to 800°C and duration from 60 to 120 min increases titanium extraction into sublimates from ~68 to ~92%. The extraction of silicon into sublimates was in the range of ~6.25 to ~6.75%. The best performance was achieved at the temperature of 800°C, duration of 120 min, argon flow rate of 1.2 dm³/min, while titanium extraction into sublimates was 91.82%. The content of titanium and silicon in the sublimates was 35.75% and 2.56%, respectively. The sublimate yield was 33.41%; the cinder yield in the boat was 17.5%.
Table 3 – Study of the titanium sublimation process

| Exp. No. | Sinter yield, % | T, °C | τ, min | Argon, dm³/min | Sublimate yield, % | Cinder yield, % |
|----------|-----------------|-------|--------|----------------|-------------------|-----------------|
| 1        | 93.5            | 700   | 60     | 1.2            | 21.67             | 24.24           |
| 2        | 90.95           | 750   | 60     | 1.2            | 27.61             | 20.36           |
| 3        | 92.9            | 750   | 90     | 1.2            | 27.54             | 17.45           |
| 4        | 92.98           | 800   | 90     | 1.2            | 32.5              | 18.85           |
| 5        | 93.98           | 800   | 120    | 1.2            | 33.41             | 17.50           |

Table 4 shows the chemical composition of the products of fluoroammonium processing.

According to Table 4, the titanium content in the initial cinder was 24.45%; after fluoroammonium processing with its transfer to sublimates, the residual titanium content in the final cinder was 3.1%. At the same time, the content of such impurities as iron, calcium, aluminum, niobium, and sodium in the final cinder increased in comparison with their value in the initial cinder supplied to the ammonium fluoride processing. Only an insignificant part of iron, a little calcium with aluminum, and a residual amount of silicon passed into titanium sublimates.

To transfer the obtained fluoride products into oxides, experiments on alkaline hydrolysis were carried out. To carry out studies of the alkaline hydrolysis process, batches of fluoride sublimates of silicon and titanium, as well as cinder, were preliminarily produced under the established optimal conditions of previous experiments. Alkaline hydrolysis of ammonium hexafluorosilicate and titanium tetrafluoride was carried out according to the following reactions ([13], [14]):

\[(\text{NH}_4)_2\text{SiF}_6 + 4\text{NH}_3 + (n+2)\text{H}_2\text{O} = 6\text{NH}_4\text{F} + \text{SiO}_2 \times n\text{H}_2\text{O} \quad (8)\]
\[\text{TiF}_4 + 4\text{NH}_3 + 2\text{H}_2\text{O} = \text{TiO}_2 + 4\text{NH}_4\text{F} \quad (9)\]

Experiments on alkaline hydrolysis of titanium fluorides were carried out to remove fluorine and obtain titanium dioxide. For this, 20 g of titanium fluoride sublimates were taken, placed in a glass with 400 ml of 10% ammonia water at a S:L ratio of 1:20, and heated to 50°C with stirring at 50 rpm. Upon reaching the desired temperature, the mixture was kept for 60 min, then cooled and defended for 30 min. The clarified part was decanted, water was added to the precipitate at a S:L ratio of 1:20, stirred for 10 min, and filtered. Then, the precipitate was dried at 105-110°C to constant weight. Hydrated titanium dioxide with the following composition was obtained, wt. %: 45.54 Ti, 1.6 Fe, 0.8 Si, 0.59 Al, 0.1 Nb, 0.03 Ca (75.9 TiO₂, 1.7 SiO₂).

The resulting hydrated titanium dioxide contains impurities of iron, aluminum, etc., which may affect the quality of the final product. For purification from impurities, the obtained hydrated titanium dioxide was subjected to nitric-acid processing.

Nitric acid purification was carried out under the following conditions: 10% HNO₃, at 60°C, at a S:L ratio of 1:10, for 60 min. After washing, the titanium dioxide precipitate was dried at 105-110°C to constant weight, then calcined in a chamber furnace at 500°C for 120 min. As a result, we obtained a product corresponding to a rutile concentrate in terms of chemical composition, %: 57.7 Ti, 1.1 Fe, 0.64Si, 0.28Al, 0.03Ca, 39.50, etc. (96.2 TiO₂, 1.57 Fe₂O₃, 0.52 Al₂O₃, 1.37 SiO₂, 0.014 CaO, etc.).

Table 4 – Chemical composition of fluoroammonium processing products

| Name   | Sinter | Silicon sublimates | Cinder | Titanium sublimes | Final cinder |
|--------|--------|--------------------|--------|-------------------|-------------|
| Element | Content, % | Content, % | Content, % | Content, % | Content, % |
| Ti     | 7.65   | 1.85               | 24.45  | 35.75             | 3.1         |
| Fe     | 0.98   | 0.24               | 3.13   | 1.0               | 11.6        |
| Ca     | 0.15   | 0.14               | 0.37   | 0.06              | 1.56        |
| Al     | 1.15   | 0.4                | 3.50   | 0.40              | 15.06       |
| Si     | 8.10   | 25.85              | 1.61   | 1.56              | 0.10        |
| Nb     | 0.79   | 0.01               | 2.62   | -                 | 5.5         |
| Cr     | 0.07   | -                  | -      | -                 | -           |
| P      | 0.23   | 0.03               | -      | -                 | -           |
| Na     | 0.70   | -                  | 0.85   | -                 | 3.9         |
| F      | 61.96  | 65.38              | 35.86  | 53.02             | 39.54       |
| O      | 12.74  | 2.90               | 23.39  | 4.50              | 17.84       |
| Other  | 5.48   | 3.2                | 4.22   | 3.71              | 1.8         |
According to the results of the XRD analysis of the titanium dioxide obtained, which is presented in Table 5 and Figure 4, the product mainly consists of rutile (TiO$_2$) and has small amounts of iron impurities in the form of hematite, as well as aluminum oxides.

### Table 5 – Phase composition of the titanium dioxide product

| Phase            | Formula | Content, % |
|------------------|---------|------------|
| Rutile           | TiO$_2$ | 95.2       |
| Iron oxide       | Fe$_2$O$_3$ | 4.0       |
| Aluminum oxide   | Al$_2$O$_3$ | 0.8       |

Figure 4 – Diffractogram of the titanium dioxide product

Alkaline hydrolysis of silicon sublimates and final cinder was carried out according to a similar scheme. Amorphous silica, wt. %: 41.8 Si, 4.2 Ti, 0.075 Ca, 0.054 Al, 0.027 P, 0.08 Fe, 0.16 F (88.07 SiO$_2$, 7 TiO$_2$) and a niobium-containing product of the following composition, wt. %: 6.7 Ti, 0.35 Si, 20.5 Fe, 19.3 Al, 8.1 Nb, 4.2 Na, 0.7 Ca, 0.1 F. (11.17 TiO$_2$, 0.75 SiO$_2$, 29.32 Fe$_2$O$_3$, 36.45 Al$_2$O$_3$, 11.6 Nb$_2$O$_5$, 5.7 Na$_2$O) were additionally obtained.

Thus, according to the results of the studies, titanium dioxide of rutile modification, containing 96.2 TiO$_2$, was obtained. In terms of titanium dioxide as the main component and the content of impurities, the obtained one corresponds to the rutile concentrate according to GOST 22938-78.

### Conclusions

The results of the investigated physical and chemical properties of cake from nitric-acid leaching of titanium production sludge show that all silicon in the cake is in quartz, feldspar in the form of albite, sillimanite, sodium aluminosilicate; in total, these minerals make up most of the cake (60.24%). Titanium is presented in the form of rutile, titanium aluminum oxide, which in total is 35.56%.

For the selective extraction of silicon and titanium, the fluoroammonium method of cake processing was chosen. The optimal parameters of fluoroammonium processing of cake were determined: silicon distillation into sublimates at 300°C for 6 hours, sublimation of titanium in the form of titanium tetrafluoride at 800°C for 2 hours.

The alkaline hydrolysis process for titanium tetrafluoride sublimates was carried out. Hydrated titanium dioxide was obtained and subjected to nitric-acid treatment, drying, and calcination at 500°C for 120 min. As a result, rutile titanium dioxide containing 96.2% TiO$_2$ was obtained. Alkaline hydrolysis of fluoride silicon compounds and the final cinder additionally gave amorphous silica with a content of 88% SiO$_2$ and a niobium-containing intermediate product with a content of 11.6% Nb$_2$O$_5$.

### Conflict of interests

On behalf of all authors, the author declares that there is no conflict of interest.

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Фтораммонийный метод переработки кека от вышелачивания шлама титаномагниевого производства

Есенгазиев А.М., Ультаракова А.А., Бернс П. С.

1 Саутбейв Университет, АО «Институт металлургии и обогащения», Алматы, Казахстан,
2 Университет Нотр-Дам, «Центр устойчивой энергетики» США, Саут-Бенд, США.

Аннотация
Приведены результаты физико-химических свойств кека от вышелачивания азотной кислотой шлама титанового производства. Установлено, что весь кремний в кеке находится в форме кварца, альбита, силилиманит, алюмосиликата. В сумме эти минералы составляют большую часть кека 60,24%.

Научные слова: кек, возгон, огарок, фтораммонийная переработка, щелочной гидролиз, диоксид титана.

Информация об авторах:
Есенгазиев А.М.: Докторант PhD, АО «Институт металлургии и обогащения», г. Алматы, Казахстан. ORCID ID: 0000-0002-4989-4119. E-mail: a.esengaziev@satbayev.university
Ультаракова А.А.: Кандидат технических наук, АО «Институт металлургии и обогащения», г. Алматы, Казахстан. ORCID ID: 0000-0001-9428-8508. E-mail: a.ultarakova@satbayev.university
Бернс П. С.: Профессор гражданской и экологической инженерии и наук о Земле, директор Центра устойчивой энергетики в Нотр-Даме, Саут-Бенд, США. ORCID ID: 0000-0002-2319-9628. E-mail: pburns@nd.edu

Reference
[1] Chervonyy IF, Listopad DA, Ivashchenko VI, Sorokina LV. O fiziko-khimicheskikh zakonomernostyakh obrazovaniya titanovoy gubi [On the physicochemical laws of the formation of a titanium sponge]. Scientific works "Donetsk National Technical University". Donetsk, Metallurgiya. 2008;141(10):37-46. (In Russ.).
[2] Teploukhov AS. Predotvraschiuije zagryazneniya vodnykh ob’ektov otkhodami titanov-magniyeyvoogo proizvodstva
Prevention of pollution of water bodies with wastes of titanium-magnesium production.

Abstract dissertation. Cand. tech. sciences. 2005, 143. (in Russ.).

Kudryavskiy Yu.P. Utilizatsiya zheleza, khroma i margantsa pri kompleksnoy pererabotke otkhodov titanovogo proizvodstva [Utilization of iron, chromium and manganese in the complex processing of titanium production waste]. Tsvetnyye metally = Non-ferrous metals. 1998;4:58-62. (in Russ.).

Pat. 2058404 RU. Sposob pererabotki otrabotannogo rasplava titanovykh khloratorov [Method for processing waste melt of titanium chlorinators]. Kudryavsky Yu.P., Freidлина R.G., Firstov G.A., Rzyankin S.A., Bondarev E.I., Ushakova N.L. Opubl. 20.04.1996, 4. (in Russ.).

Ultarakova A, Kenzhaliyev B, Onayev M, Yessengaziyev A, Kasyymzhano K. Investigations of waste sludge of titanium production and its leaching by nitric acid. 19th International Multidisciplinary Scientific Geoconference & Expo SGEM 2019, Albena, 2019. 861–868.

Medkov MA, Krysenko GF, Epov DG. Gidrodiftorid ammoniya - perspektivnyy reagent dlya kompleksnoy pererabotki syr'ya [Ammonium hydrodifluoride is a promising reagent for complex processing of raw materials]. Vestnik Dal'nevostochnogo otdeleniya Rossiiyskoy akademii nauk = Vestnik of Far Eastern Branch of Russian Academy of Sciences. 2011;5:60-65. (in Russ.).

Medkov MA, Krysenko GF, Epov DG. Gidrodiftorid ammoniya [Ammonium fluorides]. Moscow: VINITI, (Results of science and technology; ser. Inorganic chemistry; V.15). 1988, 154. (in Russ.).

Rakov EG. Ftoridy ammoniya [Ammonium fluorides]. Moscow: VINITI, (Results of science and technology; ser. Inorganic chemistry; V.15). 1988, 154. (in Russ.).

Rimkevich VS, Pushkin AA, Malovitskiy YuN, Yeranskaya TYu, Girenko IV. Kompleksnaya pererabotka kaolinovykh koncentratov sposobami ftoridnoy metallurgii [Complex processing of kaolin concentrates by methods of fluoride metallurgy]. Izvestiya Vuzov. Tsvetnaya Metallurgiya = Izvestiya. Non-Ferrous Metallurgy. 2010;2:29-36. (in Russ.).

[10] Pat. 2365647 RU. Sposob pererabotki titanoderzhashchego syr'ya [Method for processing titanium-containing raw materials]. Andreyev A.A., D'yachenko A.N. Opubl. 27.08.2009, 24. (in Russ.).

[11] Yessengaziyev A, Ularakova A, Kenzhaliyev B, Peter C Burns. Research of the leaching process of industrial waste of titanium production with nitric acid. Journal of chemical technology and metallurgy, Bulgaria. 2019;5:1061-1071.

[12] Dem'yanyova LP, Buynovskiy AS, Rimkevich VS, Malovitskiy YuN. Ratsional'naya pererabotka kvartssoderzhashchego syr'ya ftoridnym sposobom [Rational processing of quartz-containing raw materials by the fluoride method]. Izvestiya Tomskogo politekhnicheskogo universiteta = Bulletin of the Tomsk Polytechnic University. 2010;3:77-81. (in Russ.).

[13] Andreyev AA, D'yachenko AN, Kraydenko RI. Termodinamicheskiye issledovaniya vzaimodeystviya ftorida i klorida ammoniya s komponentami teknogennogo syr'ya [Thermodynamic studies of the interaction of fluoride and ammonium chloride with components of technogenic raw materials]. II-oy mezhdunar. sibirskiy seminar «Sovremennyye neorganicheskiye ftoridy». [II-nd int. Siberian seminar "Modern inorganic fluorides"]. Tomsk, 2006. 11–14. (in Russ.).

[14] Andreyev AA. Razrabotka ftoridnoy tekhnologii polucheniyu pigmentnogo dioksida titanu iz il'menita [Development of a fluoride technology for producing pigment titanium dioxide from ilmenite]. Tomsk, Diss., 2008, 140. (in Russ.).