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PROCESSING OF TITANIUM PRODUCTION SLUDGE WITH THE EXTRACTION OF TITANIUM DIOXIDE

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An urgent task at the present time is the disposal and processing of large-tonnage waste of titanium production of Ust-Kamenogorsk titanium-magnesium plant of the Republic of Kazakhstan. This work shows research on the development of sludge technology with the extraction of titanium dioxide and calcium nitrate, which will eliminate the formation and discharge of technological waste into the environment. Ammonium fluoride processing of cakes from sludge leaching made it possible to first isolate silicon fluorides in the form of fumes, and then sublimate titanium fluorides. Silicon and titanium fluorides were converted to silicon and titanium dioxides by alkaline hydrolysis.

Keywords: extration, sludge, processing, titanium dioxide, sublimation

INTRODUCTION

Krol process is the main method for producing titanium sponges in all countries of the world – producers of titanium sponges [1], which consists in the magnesium-thermal reduction of titanium tetrachloride at 850 °C. The largest titanium sponge producers are six countries: China, Japan, Russia, Kazakhstan, USA, and Ukraine. In 2014, China provided 34 % of the titanium sponge produced worldwide, with a total production capacity of 150 000 tons per year [2,3].

At Ust-Kamenogorsk Titanium and Magnesium Plant JSC ("UKTMP") of Republic of Kazakhstan annually forms 30-35 thousand tons of solid chloride waste containing 700 – 1 400 tons of titanium oxide. Part of the chloride waste from titanium production is leached by water and neutralized by calcium hydroxide to pH of 7-8,5. The resulting pulp is pumped into sludge dumps and accumulates in them. The reserves of sediments or sludge of titanium production are about 320 thousand tons [4].

The Institute of Metallurgy and Ore Beneficiation JSC (IMOB), together with UKTMP JSC, has been researching the processing of chloride waste from titanium-magnesium production for some years. The works [4] present the results of studies on the production of synthetic carnallite from the spent titanium chlorinator melt (STCM) and sludge of magnesium production. The work [5] presents the results of studies on the extraction of rare earth elements (REE) concentrate from the STCM. 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.

There is practically no processing of sludge dumps from titanium-magnesium production in Kazakhstan. Sludge dumps under the influence of natural precipitation and wind are washed out and diffused, polluting the water and soil basins. 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.

Table 1 **Chemical composition of titanium production sludge / wt. %**

Ti	Fe	Ca	Al	S	Si	V	Nb	C
6,8	2,8	19,4	2,2	0,5	8,2	0,13	0,3	7,1

MATERIALS AND METHODS

The experiments involved: nitric acid, calcium oxide, aqueous ammonia, ammonium fluoride acid, titanium production sludge of UKTMP JSC (Republic of Kazakhstan) (Table 1).

The experiment methodology included nitric acid leaching of titanium sludge. 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. The impurities from the solution were neutralized or precipitated in a glass beaker by mixing the solution with the addition of lime milk to pH 10, then the pulp was filtered and 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.

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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).

RESULTS AND DISCUSSION

The titanium sludge was crushed, averaged and dried before physic-chemical studies, as its moisture composition was 30%.

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 – okermanite 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. 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. 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 [6].

Studies on the leaching of titanium production sludge at various solid to liquid ratios were carried out at a concentration of 20 % HNO_3. With an increase in the solid to liquid ratio, the cake yield decreased from 32,2 to 22 %, and the filtration rate increased from 0,005 to 0,044 m^3 / m^2•h. 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.

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.

Although at 20 ± 5 ºC the silicate colloidal compounds formed less, the filtration rate remained low. One of the methods was applied to improve the filtration of solutions [7]. First, the sludge was leached with a 3 % HNO_3 solution at room temperature for 10 min at the solid to liquid ratio = 1:10, the filtration rate was 0,062 m^3 / m^2•h. The filtered cake was leached with 20 % HNO_3 at room temperature for 30 min at the solid to liquid ratio = 1:10, the filtration rate was 0,094 m^3 / m^2•h.

Calcium hydroxide or lime milk was chosen as a reagent for precipitation of impurities. 2 liters of the solution were produced during leaching of titanium production sludge with nitric acid, 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 experimental conditions and the composition of the solutions with the addition of lime milk are presented in Table2.

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 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 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 %.

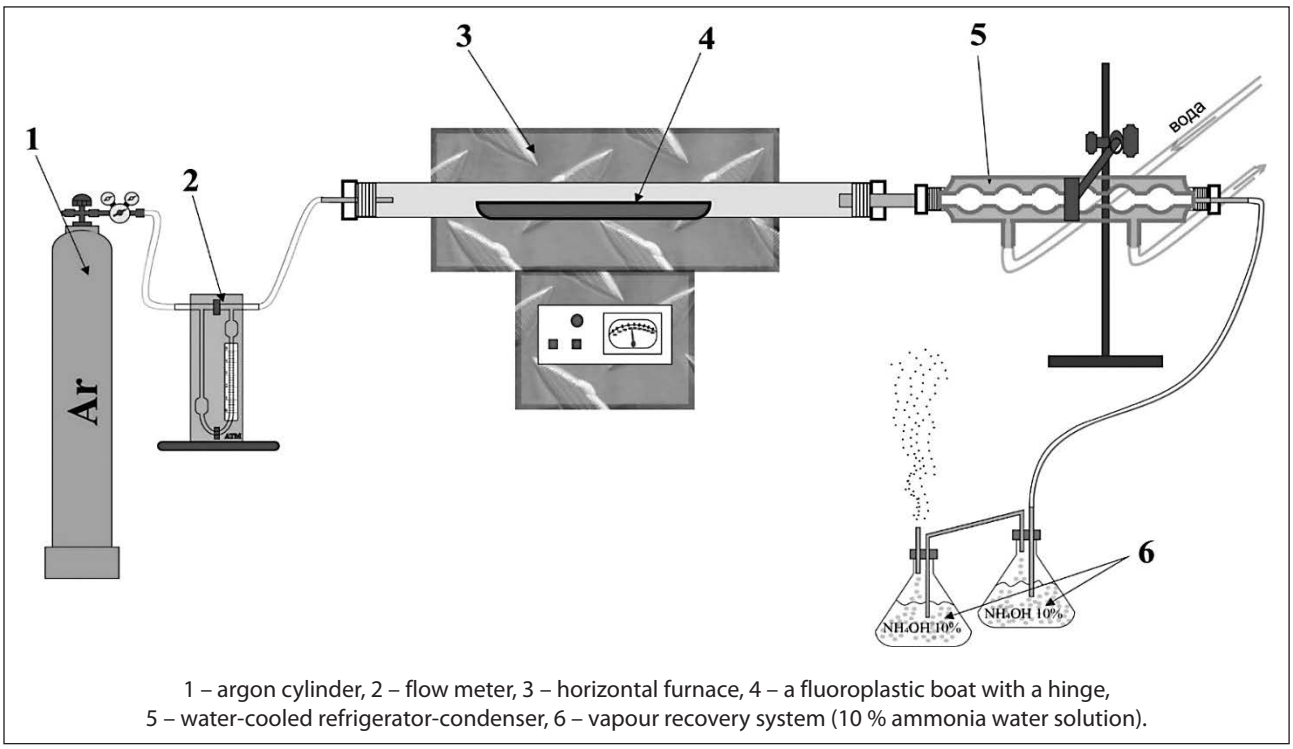
However, chromium of 0,0018 g / dm^3 remained in the solution, and the maximum permissible content for water bodies for household and drinking water and municipal water use in the Republic of Kazakhstan should be 0,05 mg / dm^3. The solution was neutralized with lime milk to pH 10, the chromium content in the solution was not detected, the composition of the neutralized solution / g / dm^3: 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.

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. 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. 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. The dehydrated calcium nitrate was obtained by granulation of 92 - 95 % $Ca(NO_3)_2$ melt in the

Table 2 **Composition of solutions when adding lime milk**

Experiment No	Solution pH	Deposition time / min	Composition / g / dm^3						
			Ti	Ca	Fe	Al	Si	Nb	V
1	-0,56	50	0,44	12,72	0,79	0,67	0,041	0,024	0,035
2	0,03	50	0,34	19,39	0,52	0,45	0,088	0,011	0,024
3	5,0	30	0,00012	23,9	0,024	0,16	0,06	-	0,0082
4	2,8	30	0,00012	31,25	0,0089	0,0086	0,0032	-	0,009
5	3,05	30	0,00012	30,14	0,0076	0,62	0,088	-	0,0094



1 – argon cylinder, 2 – flow meter, 3 – horizontal furnace, 4 – a fluoroplastic boat with a hinge,
5 – water-cooled refrigerator-condenser, 6 – vapour recovery system (10 % ammonia water solution).

Figure 1 Installation for ammonium fluoride treatment of cake

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. Based on the results of X-ray fluorescence and chemical analyzes, the composition of the cake was determined/wt.%: 16,9 Ti, 2,5 Fe, 1,2 Ca, 3,3 Al, 0,4 S, 14,8 Si, 0,1 V, 3,6 Nb, 51,03 O, 0,4 F, 0,7 Zr, 0,2 Cr, 0,06 Mn, 0,4 W. 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 71,8 %. Titanium is presented in the form of oxides of anatase, titanium aluminum oxide, and rutile, in the amount of 26,1 %. Iron is part of sillimanite and hematite and makes up about 3 %.

To separate titanium dioxide from this multicomponent raw material, the method of fluorine-ammonium treatment of cake was used [8, 9]. The installation is assembled, shown in Figure 1. First, the cake in the amount of 20 g was mixed with ammonium bifluoride taken 20 % more from the stoichiometric, which amounted to 40 g of NH_4HF_2 was placed in a fluoroplastic beaker. 15 ml of water was added to the mixture and sintered for an hour at 200 °C in a vertical tube furnace. Next, the cake was processed in a fluorinated mixture sublimation unit, it was transferred to a fluoroplastic boat (4), the boat was placed in a steel tube located in a horizontal furnace (3). The optimal temperature and duration of the process (300 °C, 6 hours) for the sublimation of silicon hexafluoride formed by the reaction:

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

When the furnace was heated to 300 °C, the air was first fed into the tube, which helped to divert fumes of silicon hexafluoride into the condenser refrigerator (5) cooled with water. Under the action of air, a small part of silicon fumes and hydrogen fluoride were recovered in flasks (6) 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. %: 83SiO_2, 0,02 Fe_2O_3, 0,06 Al_2O_3, 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 TiF4 according to the decomposition reaction [10]:

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

The sinter was placed into a fluoroplastic boat (4) of the sublimation unit, then into a steel tube of a horizontal furnace (3). With the heating of the furnace, argon was fed from a cylinder (1) at a rate of 0,5 - 1,2 dm^3 / min, and sublimates of titanium tetra-fluoride were distilled off at temperatures above 650 °C into a condenser refrigerator (5). Part of the sublimates of titanium tetrafluoride and hydrogen fluoride vapour were captured in two flasks (6) with a 10 % solution of ammonia water.

The titanium fluoride sublimation temperature and duration (800 °C, 2 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 = 1:100, 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 = 1:20 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. %: 88,3 TiO_2, 5,3 Al_2O_3, 4,6 SiO_2, 0,8 FeO, 0,6 MgO, 0,4 CaO.

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