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# Calcium nitrate generating out of nitrogen-acid solutions after breaking up slurries of titanium production

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**Abstract:** This article provides the results of studies of qualitative, quantitative and material composition of titanium production slurry, which is man-made waste. The leaching of slurry parameters by nitric acid are studied: concentration, solid to liquid ratio, temperature and time. The effective leaching parameters were determined: 1.7 mol/l of nitric acid concentration, solid to liquid ratio = 1:8, pH<1, temperature 20±5 °C, leaching time is 30 minutes. The rate of filtration was 0.035-0.044 m<sup>3</sup>/ m<sup>2</sup>·h. A gradual leaching method was used to improve the solutions filtration. At the beginning, the slurry was leached with a 0.5 mol/l HNO<sub>3</sub> solution at room temperature for 10 min at solid to liquid ratio = 1:10, the filtration rate was 0.062 m<sup>3</sup>/ m<sup>2</sup>·h. Then the cake was again leached with 3.5 mol / l HNO<sub>3</sub> at room temperature for 30 min at solid to liquid ratio = 1:10, the filtration rate was 0.094 m<sup>3</sup>/ m<sup>2</sup>·h. Calcium hydroxide or lime milk was selected as the reagent to precipitate impurities out of solutions. The content of impurities of iron, titanium and aluminum is significantly reduced when 2.8-5 pH values. The best purification of calcium nitrate solutions by lime milk was at pH 8. Calcium nitrate crystals were obtained by evaporation of a purified solution of 8 pH value out of a slurry leaching when 5% ammonium nitrate was added to it by weight of Ca(NO<sub>3</sub>)<sub>2</sub>. The dehydrated calcium nitrate was obtained by granulating 92-95% of the melt in the form of flakes at 90 °C of a surface temperature of the granulator plate.

**Keywords:** leaching, chloride waste, nitric acid, filtration, precipitation, calcium nitrate, crystallization, granulation.

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### Introduction

The titanium sponge production by magnesium thermal reduction of titanium tetrachloride at 850 °C involves the production of magnesium metal by electrolysis from its molten salts [1]. The raw material for the production of magnesium electrolysis is dehydrated carnallite, and the spent electrolyte is used in the chlorination of

titanium slurries. At the stages of titanium slurry chlorination and magnesium electrolysis, a significant amount of chloride wastes is generated.

These industrial wastes pose a danger to the environment, polluting soils and natural waters when they are released into the atmosphere, when industrial wastewater is discharged into the waters, and when solid wastes are stored in the slurry storages [2]. The Institute of Metallurgy and Ore Benefication JSC (IMOB), along with the Ust-Kamenogorsk Titanium-Magnesium Plant JSC (UKTMP), has been conducting researches to process chloride titanium-magnesium wastes for several years.

In [3,4] the results of synthetic carnallite generating studies out of worked out molten titanium chlorinator (MTC) and magnesium slurries are presented. Slurries were leached with water, the solution was purified, and a solution with a carnallite module  $KCl/MgCl_2 = 0,8-1,0$  was obtained by combining the saline solutions. The resulting saline solution was g/dm<sup>3</sup>: Ti 0.0001-0.0004; Fe 0.001-0.003; Si 0.026-0.033; Mn 0.04-0.06. A carnallite that meets the State Standard 16109-70 requirements was obtained by evaporation and crystallization out of solution. In [5], the results of studies of REE concentrate extraction out of MTC are provided. The through recovery of the rare earth elements out of MTC into collective concentrate was 66%. The developed method [6] for extracting niobium from PC sublimates involves their leaching with a solution of sulfuric acid, chloride distillation of cakes, and hydrolytic treatment of sublimates to obtain niobiumcontaining intermediate product [7].

Each year UKTMP JSC produces 30-35 thousand tons of solid chloride wastes containing 700-1400 tons of titanium oxide. Some titanium chloride wastes are leached with water and neutralized with calcium hydroxide to 7-8.5 pH. The resulting pulp is pumped to the slurry collectors and accumulated in them. Reserves of sediments or slurries are about 320 thousand tons, the multicomponent composition of which is present in the form of oxides, oxychlorides and carbonates [8]. Titanium slurry is a man-made raw material that is stored in the slurry collectors. Retrieving valuable products out of it is an urgent task. Currently, IMOB JSC is developing a technology for processing titanium slurry. An objective is to study the process of slurry leaching with nitric acid, purification of the obtained slurries from impurities, evaporation of solutions and calcium nitrate crystallization.

# Testing and discussing results

The titanium slurry was crushed, aggregated and dried before the physicochemical studies, since its humidity was 30%. The chemical composition of the slurry, wt. %: 6.82 Ti, 2.78 Fe, 19.4 Ca, 2.19 Al, 0.48 S, 8.19 Si, 0.13 V, 0.32 Nb, 7.09 C.

*Methods of analysis.* X-ray phase analysis of the slurry was carried out using D8 Advance diffractometer (BRUKER), Cu  $-K\alpha$  radiation, the

results are provided in Table 1. The samples were decrypted and the phases were searched with the help of the Search / match program using the ASTM Card Database.

**Table 1** – A slurry phase composition

		S-Q,
Compound Name	Formula	%
Calcite	Ca(CO <sub>3</sub> )	31,33
Vaterite, syn	Ca(CO <sub>3</sub> )	13,88
Quartz, syn	$SiO_2$	12,37
Sulfur, syn	$\mathbf{S}_{8}$	7,18
Hydrogen Titanium		
Oxide	$H_2Ti_3O_7$	6,90
Titanium Oxide	$Ti_6O_{11}$	6,05
Hydrocalumite, syn	Ca <sub>4</sub> Al <sub>2</sub> O <sub>6</sub> Cl <sub>2</sub> 10H <sub>2</sub> O	5,38
Portlandite, syn	Ca(OH) <sub>2</sub>	4,97
Rutile, syn	TiO <sub>2</sub>	4,45
Titanium		
Aluminum Niobium		
Oxide	Ti0.8Al0.1Nb0.1O2	3,98
Akermanite,	Ca2(Al0.46Mg0.54)	
aluminian, syn	((Al0.23Si0.77)2O7)	3,51

*Effect of nitric acid concentration.* Slurry leaching was carried out at different concentrations of nitric acid, studying the dynamics of the degree of titanium and calcium extraction into the solution.

The testing methods. The experiments were carried out under the following condition: a slurry weight is 50 g; solid to liquid ratio = 1:4, temperature is 20 °C, within 30 minutes with a change in acid concentration. Distilled water and 9.1 mol / 1 nitric acid were added to the glass in the required amount to obtain the necessary concentration with a measurement of the density of the solution. The pulp was mixed with a mechanical stirrer at a speed of 300 rpm. After the experiment, the pulp was filtered, the filtration rate was measured, and then the precipitate was dried and weighed. The volume of the filtrate was measured. The resulting cake and solution products were tested for X-ray fluorescence and chemical analyzes.

The degree of titanium extraction into the solution is closer to zero, with leaching with a concentration of 0.7-1.7 mol / 1 HNO<sub>3</sub>. At the same time, the extraction of calcium into the solution increased from 6.4% at a concentration of 0.7 mol / 1 HNO<sub>3</sub>, and at a concentration of 1.7 mol / 1 HNO<sub>3</sub> to 52%. A subsequent increase in the concentration of nitric acid led to a gradual transition of titanium into a solution of leachable slurry. With an increase in concentration from 1.7 to 4.5 mol / 1 HNO<sub>3</sub>, titanium recovery gradually increased from 0.2% to 4.9%, and calcium sharply. At 0.5-0.7 mol / 1 HNO<sub>3</sub>, the calcium

recovery in the solution was 60-64%. The yield of cakes changed with increasing concentration of nitric acid from 46.3 to 29.5%, and the filtration rate decreased from 0.45 to 0.044 m<sup>3</sup> / m<sup>2</sup>·h.

The influence of solid to liquid ratio. Leaching slurry studies out of titanium production at various solid to liquid ratio were carried out at a concentration of  $3.5 \text{ mol} / 1 \text{ HNO}_3$ . This is justified by the fact that at such a concentration there is a maximum extraction of calcium into the solution, as well as a minimum transition of titanium into the solution. The research results are shown in Figure 1. The diagram demonstrates an increase in solid to liquid ratio leads to the increase calcium into the solution extraction, but titanium does not significantly. But with a solid to liquid ratio = 1:10, the extraction of titanium into the solution was 6.2%.

With an increase in solid to liquid ratio, the extraction of calcium in the solution increases sharply, the extraction of titanium in the solution practically does not change. With a solid to liquid ratio = 1:2, calcium extraction into the solution is 56.7%, in cake - 10.6%. The filtration rate was 0.005 m<sup>3</sup>/m<sup>2</sup>·h.

Leaching with nitric acid at solid to liquid ratio = 1:4 provided the extraction into a solution of wt. %: titanium 3.28; calcium 69.3. With a solid to liquid ratio = 1:6, the extraction into a solution of wt. %: titanium 4.57; calcium 79.9; silicon impurities 0.6; iron 28.7; aluminum 36.3. The filtration rate was  $0.026 \text{ m}^3 / \text{m}^2$ ·h.

Leaching at a solid to liquid ratio = 1:8, extraction into a solution of wt. %: titanium 5.04; calcium 84.7. With a solid to liquid ratio = 1:10, the extraction into a solution of wt. %: titanium 4.4; calcium 84.3; silicon impurities 0.73; iron 27; aluminum 39.1. The filtration rate was 0.035-0.044 m<sup>3</sup> / m<sup>2</sup>·h.



1-titanium; 2-calcium.



With an increase in 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<sup>3</sup> / m<sup>2</sup>·h.

Leaching with nitric acid at a solid to liquid ratio = 1:10 can be considered more effective in terms of filtration rate and the extraction of calcium in a solution of 84.3%. The loss of titanium with a solution is 4.4%, and with a solid to liquid ratio = 1:8, the loss was 5.04%, the yield of cake is almost the same.

*The temperature effect.* Experiments about the temperature effect were carried out under the following leaching conditions:  $3.5 \text{ mol} / 1 \text{ HNO}_3$  at a solid to liquid ratio = 1:8, leaching time 30 minutes. The results of the experiments are provided in Figure 2.



extraction into the solution on the temperature of 3.5 mol/ 1 HNO<sub>3</sub>

As the Figure 2 provides, the extraction of calcium, iron, and aluminum decreases as the temperature increases due to the formation of gels that impede filtration. PH values ranged from -0.45 to -0.64. The filtration rate decreased from 0.035 to 0.004 m<sup>3</sup> / m<sup>2</sup>·h.

Duration effect: Studies about leaching duration of 3.5 mol/l with the nitric acid were carried out at a temperature of  $80 \text{ }^{\circ}\text{C}$  with a solid to liquid ratio = 1:8. The results of the experiments are provided in Figure 3.



Figure 3 - Dependence of the main components extraction into the solution on the leaching duration at 3.5 mol/l HNO<sub>3</sub>

With an increase in the leaching duration, 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.

When the slurry was leached with 3.5 mol / 1 nitric acid, the solid to liquid ratio = 1:8, the effective temperature of  $20 \pm 5$  °C and the efficient leaching time of 30 minutes were chosen. With these effective parameters, the extraction in titanium solution was 2.2%, and the extraction in calcium solution was 84.7%, the filtration rate was 0.035-0.044 m<sup>3</sup> / m<sup>2</sup>·h.

However, at concentrations of 2.6-3.5 mol / 1 nitric acid and temperatures above 60 °C, silicate colloidal compounds are formed into solutions in large quantities, which impede filtration. At a temperature of  $20 \pm 5$  °C, colloidal compounds formed less, but the filtration rate remained low. To improve the filtration of solutions, one of the methods was used [9]. First, the slurry was leached with a 0.5 mol / 1 HNO<sub>3</sub> solution at room temperature for 10 min at a solid to liquid ratio = 1:10, the filtration rate was 0.062 m<sup>3</sup> / m<sup>2</sup>·h. The filtered cake was again leached with 3.5 mol / 1 HNO<sub>3</sub> at room temperature for 30 min at a solid to liquid ratio = 1:10, the filtration rate was 0.094 m<sup>3</sup> / m<sup>2</sup>·h.

The next step is the deposition process. Calcium hydroxide or lime milk was selected the reagent for the precipitation of impurities from solutions of calcium nitrate. A 2 liters' solution was obtained by leaching titanium production slurry with nitric acid under the following leaching conditions:  $3.5 \text{ mol/} 1 \text{ HNO}_3$  concentration, solid to liquid ratio = 1:10, temperature  $20 \pm 5$  °C, leaching time 30 min, stirring speed 300 rpm / min. 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 green solution with pH value is -0.86. The initial solution in the experiments on the deposition of

impurity components was taken in a certain amount; a solution of lime milk was gradually poured. The conditions of experiments and the composition of the solutions with the addition of lime milk are provided in Table 2.

The experiments resulted in at pH values of -0.56 and 0.03, the main impurities of iron, aluminum, and titanium remain in the solution. At pH values of 2.8-5, the content of impurities of iron, titanium and aluminum is significantly reduced. An increase in the deposition time of impurities also positively affects the cleaning of the solution.

After 5 pH solution was evaporated at a temperature of 100 °C for 4 hours, a viscous amorphous substance was obtained; it was not possible to obtain crystals of calcium nitrate. According to a number of signs,  $Ca(NO_3)_2$  can be attributed to hard-crystallizing salts, its hygroscopic point is very low, calcium nitrate is prone to recrystallization and caking during storage of [10]. For these purposes, 5-7% ammonium nitrate is used by weight of calcium nitrate for better crystallization. With the addition of ammonium nitrate, the crystallization rate of Ca(NO<sub>3</sub>)<sub>2</sub> increases 1.5-2 times with a simultaneous increase in the crystallization temperature by 50 °C. The more ammonium nitrate is contained in the solution; the better is crystallization [11]. Therefore, 5% by weight of Ca(NO<sub>3</sub>)<sub>2</sub> ammonia and nitric acid was added to the solution to produce ammonium nitrate. But when ammonia was added from the solution, flakes of iron oxide remained in the form of nitrate, the pH of the solution was 8. The composition of the solution, wt.%: N/D Ti, 28.1 Ca, 0.004 Si, 0.001 Fe, N/D Nb, 0.001 Al, N/D V. Crystals of calcium nitrate were managed to evaporate from this solution, their x-ray phase analysis has been provided in Table 3.

Table 2 - The content of solutions when adding lime milk

Test No.	Initial	pH of	Lime milk,	Deposition	Composition, g / dm <sup>3</sup>						
	solution,	solution	ml	time, min	Ti	Ca	Fe	Al	Si	Nb	V
	ml										
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

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

 Table 3 - Phase composition of calcium nitrate

The composition of the calcium nitrate salt was studied using a JEOL JXA 8230 Electron Probe Microanalyses.

An electron probe study of slurry was carried out in the following modes: 1. COMPO - salt image in the back-scattered electrons; 2. WDS - waveguide dispersive spectroscopy with a sharper and more sensitive image. Figure 4 provides the calcium nitrate zones in the backscattered and secondary SEI electrons.





Figure 4 - Calcium nitrate crystals in the COMPO (1) and SEI (2) modes. 1000 zoom

The obtained crystals from the purified solution to pH 8 with the addition of ammonium nitrate in an amount of 5% of the total weight of the obtained calcium nitrate were subjected to grade analysis. Figure 5 provides the results of a sieve

analysis. The +7 mm fraction was 36.2%, the -7 + 5 mm fraction was 14%, the -5 + 3 mm fraction was 15%, the -3 + 1 mm fraction was 18%, and the -1 mm fraction was 16.8%. The main fraction of -3 + 1 mm was 18% of the total weight, the loss was 1.5%.

Grade analysis showed that the more acceptable fractions of -5 + 3 mm and -3 + 1 mm in total amounted to 33%. Large fractions of +7 mm, -7 + 5 mm made up the bulk of the grade analysis of 50.2%.

According to Inter-Republic specifications 6-03 195-67, calcium nitrate for fertilizer is produced in the form of a scaly product. Light brown color. Containing at least 17.5% nitrogen, the content of ammonium nitrate is 4-7%, and the moisture content is not more than 14% [11]. Crystallization of calcium nitrate with the addition of ammonium nitrate on a cooling roll is carried out at 90 °C. Most of the salt crystallizes as a two-water hydrate. The melt temperature in the trough of the rollers is maintained at about 110 °C. Before loading into the container, calcium nitrate should be cooled to at least 30 °C, since hot salt is prone to sticking and impairs its dispersibility. Calcium nitrate is cooled in a drum through which cooled air is blown. At elevated temperatures, calcium nitrate can go into the solid phase as an anhydrous salt.



Figure 5 - Fractions of grade analysis when adding 5% ammonium nitrate to the solution

In the first experiment, a saturated solution of 70% concentration of  $Ca(NO_3)_2$  was prepared and

evaporated to form a melt at 100 °C. The melt was evenly distributed over the granulator plate, which rotated at a speed of 28 rpm. The molten salt of ammonium nitrate began to granulate first into medium-sized granules, but due to the presence of physical moisture, small salt particles began to stick to the granules and granules of 6-8 mm in size formed. The second experiment was also carried out with a saturated solution of 70% concentration of  $Ca(NO_3)_2$ , and it was evaporated to form a melt at 100 °C. Preliminarily, the granulator plate was heated with a gas can to a temperature of 90 °C during rotation of the granulator at a speed of 28 rpm. At elevated temperatures, calcium nitrate can go into the solid phase as an anhydrous salt. The calcium nitrate melt was evenly distributed over the granulator plate, it solidified with an even layer, then it was removed in the form of flakes with a stainless steel scraper, and the granulation results are shown in Figure 6.



Figure 6 - Obtaining flake calcium nitrate using a granulator

Table 4 provides the results of grade analysis of the obtained calcium nitrate. The results of X-ray analysis of calcium nitrate are provided in Table 5.

**Table 4** - Grade composition of dehydrated calcium nitrate using a granulator

Grain type of crystals, mm	Grade composition, %
+7	28,2
-7+5	12,7
-5+3	17,5
-3+1	17,5
-1 мм	24,1
Total:	100

Table 5 - X-ray phase analysis of dehydrated calciumnitrate.

Compound Name	Formula	S-Q, %
Calcium Nitrate	$Ca(NO_3)_2$	100

A large fraction was crushed to a fraction of -3 + 1, a small -1 mm was sent to receive melt. Thus, dehydrated calcium nitrate was obtained by granulation of 92-95% melt in the form of flakes. We grind a large fraction to a fraction of -3 + 1 mm, and a -1 mm fraction is sent to receive melt.

# Conclusion

According to the results of X-ray phase analysis, the main phases of the slurry are calcite 31.33%, vaterite 13.88%, quartz 12.37%; titanium is present in the phases of rutile 4.45%, lower titanium oxide 6.05%, titanium hydrogen oxide 6.9%; calcium is also present in the phases of hydrocalumite 5.38%, portlandite 4.97%, aluminum ackermanite 3.51%, also sulfur 7.18%.

The titanium and calcium distribution was studied at effective parameters of the leaching process: acid concentration, solid to liquid ratio, pH. The effective leaching parameters were determined: 3.5 mol / 1 nitric acid concentration, solid to liquid ratio = 1:8, pH<1, the temperature  $20 \pm 5$  °C, leaching time 30 minutes. The filtration rate was 0.035-0.044 m<sup>3</sup> / m<sup>2</sup>·h.

To improve the solutions filtration, the following method was applied. First, the slurry was leached with a 0.5 mol / 1 HNO<sub>3</sub> solution at room temperature for 10 min at a ratio of solid to liquid ratio = 1:10, the filtration rate was 0.062 m<sup>3</sup> / m<sup>2</sup>·h. The filtered cake was again leached with 3.5 mol / 1 HNO<sub>3</sub> at room temperature for 30 min at a ratio of solid to liquid ratio = 1:10, the filtration rate was 0.094 m<sup>3</sup> / m<sup>2</sup>·h.

Crystals of calcium nitrate were obtained from the purified solution to pH 8 with the addition of ammonium nitrate in an amount of 5% of the total weight of the obtained calcium nitrate. Grade composition of dehydrated calcium nitrate on a granulator, %: type + 7 mm - 28.2; type -7 + 5 mm -12.7; type -5 + 3 mm - 17.5; type -3 + 1 mm - 17.5, type -1 mm - 24.1. A large fraction was crushed to a fraction of -3 + 1, a small -1 mm was sent to receive melt.

The dehydrated calcium nitrate was obtained by granulating 92-95% of the melt in the form of flakes at a surface temperature of the granulator plate of 90 °C. We grind a large fraction to a fraction of -3+ 1 mm, and a -1 mm fraction is sent to receive melt. Cite this article as: Yessengaziyev A. M., Ultarakova A.A., Uldakhanov O. H. Calcium nitrate generating out of nitrogen-acid solutions after breaking up slurries of titanium production // Комплексное использование минерального сырья (Complex Use of Mineral Resources). – 2019. – №4 (311). – C. 74-81. https://doi.org/10.31643/2019/6445.40

# Титан өндірісіндегі қоқырларды ашу барысында түзілген азотқышқылды ерітінділерден кальций селитрасын алу

#### Есенгазиев А.М., Ультаракова А.А., Улдаханов О.Х.

**Түйіндеме:** Техногенді қалдық болып табылатын титан өңдірісіндегі қоқырларды шаймалау бойынша эрттеулер жүргізілген. Шаймалауды азот қышқылымен әр түрлі концентрцияда, Қ:С қатынасында, температурада және уақытта жүргіздік. Шаймалаудың оптималды параметрлері анықталған: 3,5 моль/л азот қышқылы концентрациясы, Қ:С=1:8, pH<1, температура  $20\pm5^{\circ}$ С, шаймалау уақыты 30 минут. Фильтрация жылдамдығы 0,035-0,044 м<sup>3</sup>/м<sup>2</sup> сағ құрады. Ерітіндінің фильтрациясын жақсарту мақсатында шаймалаудың кезеңдік әдісі қолданылған. Бастапқыда коқырды 0,5 моль/л HNO<sub>3</sub> ерітіндісімен Қ:С=1:10 қатынасында, бөлме температурасында 10 мин мерзімде шаймаладық, фильтрация жылдамдығы 0,062 м<sup>3</sup>/м<sup>2</sup> сағ құрады. Сосын кекті 3,5 моль/л HNO<sub>3</sub>, бөлме температурасында, Т:Ж=1:10 қатынасында, 30 мин мерзімде, тағы да шаймаладық. Фильтрация жылдамдығы 0,094 м<sup>3</sup>/м<sup>2</sup> сағ құрады. Ерітіндіде рН 2,8-5 мәнінде темір, титан және алюминий қоспаларды тұндыруда реагент ретінде таңдалды. Ерітіндіде рН 2,8-5 мәнінде темір, титан және алюминий қоспаларды нитраты елудады. Кальций нитраты ерітіндісін сұйық әктаспен ең үздік тазалау рН 8 жүзеге асты. Аммоний нитраты алуда Са(NO<sub>3</sub>)<sub>2</sub> салмағынан 5% мөлшерде аммиак және азот қышқылын қоса отырып, pH 8 де тазаланған ерітіндін буландыру арқылы кальций нитраты кальций нитраты 92-95 % балқыманы грануляциялау арқылы алынған. Гранулятор тарелкесі температурасы 90 °С құрады.

**Түйін сөздер:** шаймалау, хлоридті қалдықтар, азот қышқылы, фильтрация, тұндыру, кальций нитраты, кристаллизация, грануляция.

# Получение кальциевой селитры из азотнокислых растворов от вскрытия шламов титанового производства

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**Резюме:** В статье представлены результаты исследований по изучению качественного, количественного и вещественного состава шлама титанового производства, являющийся техногенным отходом. Изучены параметры выщелачивания шлама азотной кислотой: концентрация, соотношение T:Ж, температура и время. Были определены оптимальные параметры выщелачивания: 1,7 моль/л концентрация азотной кислоты, T: $\mathbb{X}$ =1:8, pH<1, температура 20±5 °C, время выщелачивания 30 минут. Скорость фильтрации составила 0,035-0,044 м<sup>3</sup>/м<sup>2</sup>·ч. Для улучшения фильтрации растворов был применен поэтапный способ выщелачивания. Сначала шлам выщелачивали 0,5 моль/л растворов был применен поэтапный способ выщелачивания. Сначала шлам выщелачивали 0,5 моль/л раствором HNO<sub>3</sub> при комнатной температуре в течение 10 мин при T: $\mathbb{X}$ =1:10, скорость фильтрации составила 0,062 м<sup>3</sup>/м<sup>2</sup>·ч. Затем кек вновь выщелачивали 3,5 моль/л HNO<sub>3</sub> при комнатной температуре в течение 30 мин при T: $\mathbb{X}$ =1:10, скорость фильтрации составила 0,062 м<sup>3</sup>/м<sup>2</sup>·ч. Затем кек вновь выщелачивали 3,5 моль/л HNO<sub>3</sub> при комнатной температуре в течение 30 мин при T: $\mathbb{X}$ =1:10, скорость фильтрации составила 0,094 м<sup>3</sup>/м<sup>2</sup>·ч. Реагентом для осаждения примесей из растворов был выбран гидроксид кальция или известковое молоко. При значениях pH 2,8-5 в растворах значительно уменьшается содержание примесей железа, титана и алюминия. Наиболее лучшая очистка растворов нитрата кальция известковым молоком была при значении pH 8. Получены кристаллы нитрата кальция выпариванием очищенного раствора со значением pH 8 от выщелачивания шлама при добавлении в него 5 % нитрата аммония от веса Ca(NO<sub>3</sub>)<sub>2</sub>. Получен обезвоженный нитрат кальция путем грануляции 92-95 % плава в виде чешуек, при температуре поверхности тарели гранулятора 90 °C.

**Ключевые слова:** выщелачивание, хлоридные отходы, азотная кислота, фильтрация, осаждение, нитрат кальция, кристаллизация.

#### ЛИТЕРАТУРА

[1] Тарасов А.В. Металлургия титана. М.: ИКЦ «Академкнига» 2003. – 328 с.

[2] Теплоухов А.С. Предотвращение загрязнения водных объектов отходами титано-магниевого производства. Автореферат дисс. канд. техн. наук. 2005. 143 с.

[3] Ультаракова А.А., Найманбаев М.А., Онаев М.И., Уласюк С.М., Алжанбаева Н.Ш. Исследования по очистке растворов, пригодных для синтеза карналлита. Комплексное использование минерального сырья, Алматы. 2013. №2. – С. 43-53. www.kims-imio.kz

[4] Ультаракова А.А., Найманбаев М.А., Онаев М.И., Халелов А.М., Уласюк С.М. Пути получения синтетического карналлита из отходов титано-магниевого производства. Комплексное использование минерального сырья, Алматы. 2012. №3. – С. 52-58. www.kims-imio.kz

[5] Ультаракова А.А., Лохова Н.Г., Найманбаев М.А., Балтабекова Ж.А., Алжанбаева Н.Ш. Разработка комплексной технологии переработки отходов титаномагниевого производства. Материалы шестой межд. науч.-практич. конф. ««ГЕОТЕХНОЛОГИЯ-2013: Проблемы и пути инновационного развития горнодобывающей промышленности. Институт горного дела им. Д.А. Кунаева. Алматы. 2013. – С. 351-355.

[6] Инновационный патент РК № 27912. Способ переработки возгонов титановых хлораторов. Ультаракова А.А., Найманбаев М.А., Онаев М.И., Уласюк С.М., Халелов А.М., Алжанбаева Н.Ш. Опубл.25.12.2013, бюл. №12. – С. 22.

[7] Инновационный патент РК № 22784 Способ извлечения ниобия из отходов титанового производства. Найманбаев М.А., Павлов А.В., Онаев М.И., Женисов Б.Ж., Халелов А.М. Опубл. 16.08.2010, бюл. №8.

[8] Ultarakova A.A., Naymanbaev M.A., Onayev M.I., Alzhanbayeva N.Sh. Processing of chloride waste of titanium-magnesium production. XV Balkan Mineral Processing Conress. – Sozopol, Bulgaria, June 12-16, – 2013. – P.1002-1004.

[9] Пат. 2244035 РФ. Способ кислотного разложения силиката кальция и извлечения циркония / Синегрибов В.А., Юдина Т.Б.; опубл. 10.01.2005. Бюл. №1.

[10] Хамский Е.В. кристаллизация в химической промышленности. -М.: Химия. 1969. - 344 с.

[11] Клевке В.А., Поляков Н.Н., Арсеньева Л.З. Технология азотных удобрений. М.: 1956. – 289 с.

#### REFERENCES

[1] Tarasov A.V. Metallurgiya titana. M.: IKTs «Akademkniga» 2003.-328 s. (in Russ).

[2] Teploukhov A.S. Predotvrashcheniye zagryazneniya vodnykh obyektov otkhodami titano-magniyevogo proizvodstva. Avtoreferat diss. kand. tekhn. nauk. **2005**. 143 s. (in Russ).

[3] Ultarakova A.A., Naymanbayev M.A., Onayev M.I., Ulasyuk S.M., Alzhanbayeva N.Sh. *Issledovaniya po ochistke rastvorov. prigodnykh dlya sinteza karnallita. Kompleksnoe Ispol'zovanie Mineral'nogo Syr'a.* Almaty. **2013**. №2. S. 43-53. (in Russ). www.kims-imio.kz

[4] Ultarakova A.A., Naymanbayev M.A., Onayev M.I., Khalelov A.M., Ulasyuk S.M. Puti polucheniya sinteticheskogo karnallita iz otkhodov titano-magniyevogo proizvodstva. Kompleksnoe Ispol'zovanie Mineral'nogo Syr'a. Almaty. **2012**. №3. S. 52-58. (in Russ). www.kims-imio.kz

[5] Ultarakova A.A., Lokhova N.G., Naymanbayev M.A., Baltabekova Zh.A., Alzhanbayeva N.Sh. *Razrabotka kompleksnoy tekhnologii pererabotki otkhodov titanomagniyevogo proizvodstva*. Materialy shestoy mezhd. nauch.-praktich. konf. ««GEOTEKhNOLOGIYa-2013: Problemy i puti innovatsionnogo razvitiya gornodobyvayushchey promyshlennosti. Institut gornogo dela im. D.A. Kunayeva. Almaty. **2013**. S. 351-355. (in Russ).

[6] Innovatsionnyy patent RK № 27912. *Sposob pererabotki vozgonov titanovykh khloratorov*. Ultarakova A.A.. Naymanbayev M.A., Onayev M.I., Ulasyuk S.M., Khalelov A.M., Alzhanbayeva N.Sh. Opubl.25.12.**2013**. byul. №12. S. 22. (in Russ).

[7] Innovatsionnyy patent RK № 22784 Sposob izvlecheniya niobiya iz otkhodov titanovogo proizvodstva. Naymanbayev M.A., Pavlov A.V., Onayev M.I., Zhenisov B.Zh., Khalelov A.M. Opubl. 16.08.2010. byul. №8.

[8] Ultarakova A.A., Naymanbaev M.A., Onayev M.I., Alzhanbayeva N.Sh. *Processing of chloride waste of titanium-magnesium production*. XV Balkan Mineral Processing Conress. – Sozopol. Bulgaria. June 12-16. – **2013**. –P.1002-1004. (in Eng).

[9] Pat. 2244035 RF. Sposob kislotnogo razlozheniya silikata kaltsiya i izvlecheniya tsirkoniya / Sinegribov V.A., Yudina T.B.; opubl. 10.01.2005. Byul. №1. (in Russ).

[10] Khamskiy E.V. kristallizatsiya v khimicheskoy promyshlennosti. -M.: Khimiya. 1969. -344s. (in Russ).

[11] Klevke V.A., Polyakov N.N., Arsenyeva L.Z. Tekhnologiya azotnykh udobreniy. M.: 1956. -289 s. (in Russ).