RESEARCH OF THE LEACHING PROCESS OF INDUSTRIAL WASTE OF TITANIUM PRODUCTION WITH NITRIC ACID

Azamat Yessengaziyev\textsuperscript{1,2}, Almagul U尔tarakova\textsuperscript{1}, Bagdaulet Kenzhaliyev\textsuperscript{1,2}, Peter C. Burns\textsuperscript{3}

\textsuperscript{1}Institute of Metallurgy and Beneficiation JSC, 29/133 Shevchenko str. 050010, Almaty, Kazakhstan
\textsuperscript{2}Satbayev University, 22 Satpayev str., 050000, Almaty, Kazakhstan
\textsuperscript{3}University of Notre Dame du Lac, Notre Dame, IN 46556, South Bend, USA
E-mail: esengazyev@yandex.ru

Received 28 January 2019
Accepted 07 June 2019

ABSTRACT

The paper presents the results of a physico-chemical analysis of titanium sludge produced in studies on the extraction of titanium dioxide and calcium nitrate. The material composition and the main phases of the investigated sludge are determined. According to the results of mineralogical and electron probe analysis, it is established that in the initial slurry the non-metallic part makes up the bulk, more than 60\%, the ore minerals according to optical data are approximately 15 - 17\%. Micrographs obtained with the help of an optical and scanning electron microscope are analyzed. Optimal leaching parameters were determined by adding diluted 0.2\% flocculant Alclar 600 in the amount of 1.3 - 2 ml per liter of pulp: 15\% nitric acid, temperature 20°C, S:L = 1:10, leaching time 30 minutes. With these parameters, extraction in a solution of titanium was 5.0\%, and extraction in solution of calcium was 96.0\%. The filtration rate was 0.062 m\textsuperscript{3}/m\textsuperscript{3} h.

Keywords: sludge, leaching, extraction, solution, titanium, calcium, nitric acid, flocculant, filtration

INTRODUCTION

Six countries China, Japan, Russia, Kazakhstan, USA and Ukraine are the largest producers of titanium sponge [1]. In 2014, China provided 34\% of the titanium sponge produced worldwide, with total production capacity reaching 150,000 tons per year [2, 3].

The Kroll process is the main method for producing titanium sponge in all countries of the world - manufacturers of titanium sponge [4], which consists in the magnesium thermal reduction of titanium tetrachloride at 850°C. For carrying out the process, the production of magnesium metal by electrolysis from its molten salts is included in the production chain. The raw material for the production of electrolysis magnesium is dehydrated carnallite, and the spent electrolyte is used in the chlorination of titanium slags. Natural carnallite is pre-enriched and dehydrated. At the stages of the chlorination of titanium slag and the electrolysis of magnesium a significant amount of chloride wastes are formed.

These industrial wastes pose a danger to the environment, polluting soils and natural waters when they are emitted into the atmosphere, when industrial wastewater is discharged into water bodies, and solid waste is disposed in sludge storage facilities [5].

In connection with the above, and also taking into account that the production of titanium and magnesium in the near future will not be reduced due to the strategic importance of these materials, the development of environmentally safe, economically viable and field-tested methods of disposal and disposal of these industrial wastes in order to minimize the negative impact of these industries on the environment is an urgent task.

Currently, there is a method of neutralizing spent melts and sublimates of titanium chlorinators [6], including:

- hydraulic washout of spent melt;
- pulp circulation to obtain solutions saturated with chloride;
- neutralization with lime milk to pH = 8.0 - 8.5 and flocculation of the precipitate;
- filtering and washing the precipitate.
Unwashed sediment contains, by weight, %: 8.0 Fe; 2.1 Cr; 2.3 Mn; 0.9 Al; ≤ 0.03 Th; 9.4 water soluble sodium, potassium, magnesium and calcium chlorides. This sediment is a stored water-insoluble low-toxic form of waste and can be removed to the dump or used at the enterprises of the construction industry.

It is known [7] that titanium production wastes are effective additives in drilling fluids that improve the various structural and mechanical properties of the latter. It was shown that the introduction of chlorides in the amount of 0.5 - 1.5 % into drilling mud leads to a decrease in the viscosity of drilling fluids due to coagulation of the dispersed clay phase with ions of polyvalent metals.

According to the standard scandium extraction technology [8], spent melt of titanium chlorinators is waste from the production of titanium tetrachloride containing 0.01 - 0.03 % scandium oxide, leached in a weak solution (20 - 40 g/dm³) of hydrochloric acid. Scandium, which is mainly in the form of chloride, goes into solution, which is filtered, adjusted for the content of ferric chloride (the optimal concentration of ferric chloride in the solution is 5 - 10 g/dm³) and then sent for extraction. Extraction of scandium is carried out with a 70 % solution of tributyl phosphate (TBP) in kerosene. The organic phase, enriched with scandium, is treated to wash off impurities with strong (220 - 240 g/dm³) hydrochloric acid, then the scandium is transferred to the aqueous phase (reextract) with 7 % hydrochloric acid solution. From the reextract oxalate of scandium and other metals is precipitated with oxalic acid, the resulting pulp is filtered, the precipitate of oxalate is dried and calcined at 700°C and technical scandium oxide is obtained containing 40 - 60 % scandium oxide.

The results of the improvement of the standard technology are given in [9]. Hydrochloric acid, water, and sulfuric acid were tested as a solvent for the spent melt of titanium chlorinators. It was established that the maximum degree of extraction of scandium into the solution when using sulfuric acid and 1.5 times exceeds the recovery in hydrochloric acid.

At «Ust-Kamenogorsk titanium and magnesium plant» JSC («UKTMP» JSC, Republic of Kazakhstan), with maximum capacity utilization, up to 76 thousand tons of chloride waste is generated annually, the total volume of waste in the three tailings is more than 1.5 million tons. Chloride wastes of the enterprise include: spent melt of titanium chlorinators (SMTC) 30,000 tons - 39.5 %; spent melt of vanadium chlorinators (SMVC) 3000 tons - 3.9 %; spent melt of potassium chloride electrolyte (SPCE) 30,000 tons - 39.5 %; spent molten chlor-magnesium electrolyte (SCME) 6000 tons - 7.9 %; sludge carnallite chlorinators (SCC) - 2000 tons - 2.6 %; sublimates of electrolyzers (SE) 500 tons - 0.7 %; sublimates carnallite chlorinators (CC) 500 tons - 0.7 %; sublimates of the dust chambers of the condensation system of titanium chlorinators (DC) 4000 tons - 5.2 % [10, 11].

Potassium, magnesium, niobium, tantalum, scandium, manganese, chromium and other valuable metals are lost with chloride waste at «UKTMP» JSC. The waste of titanium-magnesium production also contains rubidium and cesium, the distribution of which by industrial products and waste is not well understood.

In the “Institute of Metallurgy and Ore Beneficia- tion” JSC (“IMOB” JSC), together with «UKTMP» JSC for a number of years, research has been conducted on the processing of chloride waste from titanium-magnesium production.

In [12], the results of the study of the possibility of carnallite regeneration from SMTC and sludge from magnesium production: sludge magnesium electrolyzer chlorine magnesium circuit (SMECMC), sludge magnesium electrolyzer carnallite circuit (SMECC) are given. The main goal of the developed technology was to obtain a salt solution with the carnallite module KCl/MgCl₂ = 0.8 - 1.0. In water leaching of SMECC slimes, solutions with a high content of manganese impurities were obtained, which made them unsuitable for further research. It was established that when leaching chloride wastes with water, the solution had a carnallite module of 2.0 - 2.9.

To saturate the leaching solutions with magnesium and simultaneous purification from impurities, slimes of magnesium electrolyzers were used. At the first stage, a water leaching solution with a pH of 1.2 - 1.8 was obtained, which was strengthened with hydrochloric acid to pH 0.5. Then SMECMC was in portions administered up to pH 6.8 - 7.6. This technique allows to precipitate impurity metals and almost completely to dissolve magnesium oxide SMECMC, which provides the required carnallite module 0.8 - 1.0. The resulting salt solution had the composition, g/dm³: Ti 0.0001 - 0.0004; Fe 0.001 - 0.003; Si 0.026 - 0.033; Mn 0.04 - 0.06. By evaporation and crystallization from a solution, carnal-
lite was obtained, corresponding to the requirements of GOST 16109-70.

The study of the distribution of rare earth elements in chloride waste of «UKTMP» JSC showed that spent melts of titanium chlorinators are one of the potential raw material sources of rare earth elements. The composition of the rare-earth elements of SMTC is commercially attractive, since the share of dysprosium is 57%, neodymium is 8%, and the low-demand cerium is only 13% [13].

According to chemical analysis, the content of REE oxalates is 96.0%. The main impurities are oxalates of barium and iron, the total content of which is 3.1%. The through extraction of rare-earth elements from ORTH to the collective concentrate was 66%.

According to «UKTMP» JSC, the distribution of niobium in solid waste from the process of chlorination of titanium slags was analyzed, which showed that the highest content of niobium is in the fumes of dust chambers (DC) of titanium chlorinator from 0.26 to 0.6%. The developed method [14, 15] for the extraction of niobium from sublimates of the DC, the composition of the mass %: 0.7 Nb; 2.8 Ti; 8.2 Fe; 6.3 K; 0.4 Mg; 2.5 Na; 0.27 Cr; 8.4 Al; 0.9 SiO2; 0.44 Mn, includes leaching with a 5% solution of sulfuric acid at a ratio of S:L = 1:10, a temperature of 100°C, a leaching time of 2 hours. The composition of the cake, wt. %: 1.87 Nb; 16.2 Ti; 7.9 Fe; 0.3 Si; 0.1 Cr; 0.2 Mn; 0.7 Al. Extraction of niobium into the cake was 99.5%, titanium 73.3%, iron 6.7%.

In addition to titanium and niobium, other impurity components that need to be separated from the base metals are transferred to the cake. An effective method for this is the process of chloride sublimation, which allows to transfer niobium, titanium in the form of chlorides, into sublimates, and thus separating them from most impurities. The mixture consisted of a cake of 89.1% and anthracite of 10.7%, sugar syrup in the amount of 0.2% by weight of the mixture was used as a binder during granulation.

The optimal process parameters were established: chlorine consumption 0.2 dm³/min, temperature 750°C, time 120 minutes. Extraction of niobium in sublimates was 95.2%. The resulting chlorine extracts were subjected to hydrolytic treatment to obtain a precipitate of composition, wt. %: 20.16 Nb; 25.8 Ti; 0.7 Fe; 0.42 Si; 0.86 Al; 0.046 Mn. The extraction of niobium into the sediment was 98.8% [16]. The resulting precipitate can be recycled to produce pure niobium pentoxide by known methods.

The resulting solution from leaching sublimates DC composition, g/dm³: 12.4 Fe; 4.1 Al; 2.5 Mn; 42 SO₄²⁻; 7.5 K; <0.1 Mg; 3.2 Na was purified by calcined calcium oxide. From the purified solution of the composition, g/dm³: 0.01 Fe; 0.03 Al; 0.04 Mn; 0.01 SO₄²⁻; 24.4 KCl; 156.0 MgCl₂; 4.3 NaCl, was isolated carnallite [17]. «UKTMP» JSC annually produces 30-35 thousand tons of solid chloride wastes containing 700-1400 tons of titanium oxide. Part of titanium chloride wastes are leached with water and neutralized with calcium hydroxide to pH 7-8.5. The resulting pulp pumps are pumped into the sludge collectors and accumulates in them. Stocks of sediments or sludge are about 320 thousand tons, the multicomponent composition of which is present in the form of oxides, oxychlorides and carbonates [18, 19]. Sludge from titanium production is a man-made raw material that is stored in sludge collectors. The growing need for rare metals, their compounds and the depletion of raw materials require the recycling.

**EXPERIMENTAL**

Sludge titanium production had been crushed, aged and dried before physico-chemical studies, since its humidity was 30%. In order to obtain a quantitative elemental composition of a sample of titanium sludge production, an X-ray fluorescence analysis (XRF) was performed on a Venus wave dispersion X-ray fluorescence spectrometer. X-ray fluorescence analysis of the sludge confirmed the results of chemical analysis. In the initial sample, the main share is accounted for by oxygen, which is 46.54%, the share of chlorine is 3.63%, sulfur is 0.88%, and phosphorus is 0.16%. The sludge contains mainly metal oxides. The calcium content is 19.86%, titanium 5.11%, iron 2.10%, silicon 5.76%, aluminum 1.92%, niobium 0.93%, zirconium 0.46%, barium 1.4%, tungsten 0.14%. The content of vanadium was 0.14%, chromium 0.17%, manganese 0.10%. The chemical composition of the sludge, 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.

X-ray phase analysis of sludge was carried out on a D8 Advance diffractometer (BRUKER), CuKα radiation, the results of which are presented in Table 1 and Fig. 1. The processing of the obtained diffractogram data and the calculation of interplanar distances were
performed using EVA software. Sample decoding and phase search were performed using the Search/match program using the ASTM Card Database.

The thermal analysis of the sample provided was carried out using the STA 449 F3 Jupiter synchronous thermal analysis device. Before heating, the furnace space was pumped out (the level of attainable vacuum - 92 %) and then purged with an inert gas for 5 minutes. Heating was carried out at a rate of 15ºС/min. in the atmosphere of high-purity argon. Cooling was carried out at a rate of 17ºС/min to 500ºС. The total volume of the incoming gas was maintained within 100 - 110 ml/ min. The processing of the results obtained with the STA 449 F3 Jupiter was carried out using the software NETZSCH Proteus.

Sludge sample of 0.103 g from the titanium-magnesium production was taken. The derivatogram is shown in Fig. 2.

Table 1. The phase composition of the sludge.

<table>
<thead>
<tr>
<th>Compound Name</th>
<th>Formula</th>
<th>S-Q</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcite</td>
<td>Ca(CO₃)</td>
<td>31.33 %</td>
</tr>
<tr>
<td>Vaterite, syn</td>
<td>Ca(CO₃)</td>
<td>13.88 %</td>
</tr>
<tr>
<td>Quartz, syn</td>
<td>SiO₂</td>
<td>12.37 %</td>
</tr>
<tr>
<td>Sulfur, syn</td>
<td>S₈</td>
<td>7.18 %</td>
</tr>
<tr>
<td>Hydrogen Titanium Oxide</td>
<td>H₂Ti₃O₇</td>
<td>6.90 %</td>
</tr>
<tr>
<td>Titanium Oxide</td>
<td>Ti₆O₁₁</td>
<td>6.05 %</td>
</tr>
<tr>
<td>Hydrocalumite, syn</td>
<td>Ca₄Al₂O₆Cl₂ 10H₂O</td>
<td>5.38 %</td>
</tr>
<tr>
<td>Portlandite, syn</td>
<td>Ca(OH)₂</td>
<td>4.97 %</td>
</tr>
<tr>
<td>Rutile, syn</td>
<td>TiO₂</td>
<td>4.45 %</td>
</tr>
<tr>
<td>Titanium Aluminum Niobium Oxide</td>
<td>Ti₅.₈Al₀.₁Nb₀.₁O₂</td>
<td>3.98 %</td>
</tr>
<tr>
<td>Akermanite, aluminian, syn</td>
<td>Ca₂(Al₀.₄₆Mg₀.₅₄)((Al₀.₂₃Si₀.₇₇)₂O₇)</td>
<td>3.51 %</td>
</tr>
</tbody>
</table>

Fig. 1. Diffraction pattern of a sludge sample.
The DTA curve showed endothermic effects with maximum development at 140.5°C and at 821.2°C. More complete information follows from the analysis of the dDTA curve. Here, endothermic effects of varying intensity appeared with extremes at 114°C, 369.5°C, 457°C, 520.1°C, 561°C, 656.6°C, 717.6°C, 771.9°C 805.9°C, 874.3°C. The peaks of exothermic effects occurred at 200°C, 461.3°C, 787.6°C, 826.6°C, 888.9°C, 1051.8°C. All effects developed against the background of a permanently decreasing weight of the sample.

The endothermic effect with maximum development at 821.2°C on the DTA curve reflects the dissociation of calcite. If we take into account the weak endothermic effect with an extremum at 457°C on the dDTA curve, then we can assume that this is aragonite. At 457°C aragonite monotropically turns into calcite. Apparently, this is the main phase. Further study of the sample is based on the analysis of the curves dDTA and DTG.

The combination of minima on the DTG curve in the temperature range of 700 - 820°C (on the dDTA curve, they correspond to endothermic effects with extremes at 717.6°C, 771.9°C 805.9°C) can be considered as a manifestation of another carbonate - ankerite Ca (Mg, Fe) [CO₃].

Considering together the endothermic effect with an extremum at 114°C and an exothermic effect with a peak at 200°C, we can assume the presence of silicic acid in the sample. The combination of the endothermic effect with an extremum at 114°C, a minimum at 258.8°C on the DTG curve and a weak exothermic effect with a peak at 461.3°C can be associated with the manifestation of a gel-like complex - Na₂O×TiO₂×2.5H₂O. In the overlay, the exothermic effect with a peak at 461.3°C can reflect the crystallization of the metamict pyrochlore impurity - (Na,Ca)₂(Nb,Ta,Ti)O₆(OH,F,O). The exothermic effect with a peak at 787.6°C may be a manifestation of metamict admixture of cirkelite CaZrTiO₇. Considering together the endothermic effect with an extremum at 114°C, an exothermic effect with a peak at 826.6°C, as well as minima on the DTG curve at 258.8°C and 367.7°C, calcium hydrosulfoaluminate - 3CaO×Al₂O₃×CaSO₄×12H₂O can be assumed to be a gel, the formation of which requires the presence of oxides of calcium, silicon and ferric iron [20, 21]. A weak endothermic effect with an extremum at 520.1°C may reflect the dehydration of Ca(OH)₂. A weak endothermic effect with an extremum at 561°C - enantiotropic polymorphic transformation of quartz. The combination of minima at 599.6°C and 661.3°C on the DTG curve with an exothermic effect with a peak at 1051.8°C may be a manifestation of a clay mineral impurity nakrite - Al₂O₃×2SiO₂×2H₂O. The minimum on the DTG curve at 1040.4°C is a possible manifestation of the dehydration...
tion of an impurity of actinolite, monoclinic amphibole - 4CaO10(Mg,Fe)O16SiO22H2O (FeO = 5.4 %). The combination of the endothermic effect with an extremum at 114ºC, as well as two exothermic effects with peaks at 826.6ºC, 888.9ºC can be interpreted as a manifestation of hydrated vitreous ocermanite - 2CaO×MgO×2SiO2.

Peaks of exothermic effects arose from the recrystallization of calcium and magnesium silicates of complex composition.

The mineralogical study was conducted using a JEOL JXA 8230 Electron Probe Microanalyzer scanning electron microscope. In COMPO mode, images of different sections are obtained. Rutile particles were detected, which are found in an intergrowth with columbite (Fig. 3). Also in Fig. 4, small inclusions of barite mixed with lead were found. Obviously, the structure of the mineral formation of sludge from titanium-magnesium production is distinguished by a great variety, combination and imposition of each other.

According to X-ray and mineralogical analyzes, the sample contains basic minerals in %: calcite - 31.33, barite - 13.88, quartz - 12.37, sulfur - 7.18, various phases of titanium - 21.38 and the others, okermanite from the group of mellilit, portlandite, hydrocaluminate - 13.86.

The procedure for conducting experiments on leaching with nitric acid included leaching of a slurry sample in an amount of 50 g at a given ratio of S:L = 1:4, room temperature 20ºC, for 30 minutes with a change in acid concentration. Distilled water and 45 % nitric acid in the required amount were added to the beaker to obtain the required concentration with a solution density measurement. The slurry was weighed and the pulp was mixed with a mechanical stirrer at a speed of 300 rpm. After the expiration of the time of the experiment, the pulp was filtered, the filtration rate was measured, then the precipitate was dried and weighed. The volume of filtrate was measured. The resulting products, the cake and the solution, passed X-ray fluorescence and chemical analyzes.

The results of slurry leaching experiments are presented in Fig. 5.

Sludge leaching was carried out at seven different concentrations of nitric acid. At the same time, the dynamics of the degree of extraction of titanium and calcium into the solution were investigated. At concentrations 4 - 10 % HNO3, the degree of extraction of titanium in the solution was closer to zero. At the same
time, calcium extraction into the solution increased from 6.4% with 4% HNO₃ to 52% with 10% HNO₃. A subsequent increase in the concentration of nitric acid led to a gradual transition of titanium into the leach slurry solution. Starting from a concentration of 10 to 20% HNO₃ in Fig. 5, one can see a gradual increase in the degree of extraction of titanium from 0.2% to 4.9%. The extraction of calcium into the solution over this range of concentration of nitric acid increased sharply; at 20% HNO₃, the extraction of calcium into the solution was 61%. The yield of cakes varied from 46.3 to 29.5%, the filtration rate decreased from 0.45 to 0.044 m³/m²h.

Studies on the leaching of titanium sludge production at various S:L ratios were carried out at a concentration of 20% HNO₃. This is justified by the fact that at such a concentration, the maximum extraction of calcium into the solution is observed, at the minimum transition of titanium into the solution. The research results are shown in Fig. 6. The graph shows that with an increase in the S:L ratio, the extraction of calcium in the solution increases. Extraction of titanium into the solution is insignificant, but at a S:L = 1:10 ratio, the extraction of titanium into the solution was 6.2%.

In the process of leaching slurry with nitric acid at a ratio of S:L = 1:2, the cake yield was 32.2% of the original, extraction of titanium into the solution was 0.89%, in the cake - 62.27%, extraction of calcium into the solution was 56.7%, in the cake - 10.6%. Extraction to a solution of silicon was 0.3%, iron - 13.6%, aluminum 26.4%. The filtration rate was 0.005 m³/m²h.

Leaching with nitric acid at S:L = 1:2 showed extraction of titanium to a solution of 3.28%, extraction of calcium to a solution of 69.3%, cake yield was 22.38% of the initial. Extraction of silicon impurities into the solution was 1.03%, iron 26.4%, aluminum 36.4%. At a ratio S:L = 1:6, the cake yield was 23.14%; extraction of titanium into the solution was 4.57%; extraction of calcium into the solution was 79.9%. Extraction of silicon impurities into the solution was 0.6%, iron 28.7%, aluminum 36.3%. The filtration rate was 0.026 m³/m²h.

Leaching at a ratio of S:L = 1:8, the cake yield was 22.2% of the extraction of titanium in a solution of 5.04%, the extraction of calcium in a solution of 84.7%. Extraction of silicon impurities into the solution was 0.74%, iron - 25.8%, aluminum - 37.1%. When the ratio S:L = 1:10, the cake yield was 22% extraction of titanium in a solution of 4.4%, extraction of calcium in a solution of 84.3%. Extraction of silicon impurities into the solution amounted to 0.73%, iron - 27%, aluminum - 39.1%. The filtration rate was 0.035-0.044 m³/m²h.

With an increase in the S:L ratio, the cake yield decreased from 32.2% to 22%, and the filtration rate increased from 0.005 to 0.044 m³/m²h.

Leaching with nitric acid at a ratio of S:L = 1:10 can be considered more effective in terms of filtration rate and calcium extraction in a solution of 84.3%. The loss of titanium with the solution is 4.4%, and with the S:L = 1:8 ratio, the loss was 5.04%, the cake yield is almost the same. However, taking into account the water consumption during leaching, the best option is the S:L = 1:8 ratio, pH < 1, at 20% concentration of nitric acid. Under these optimal conditions, the extraction of titanium into the solution is 5.04%, and calcium, 84.7%.

Studies on the leaching of sludge with increasing temperature were performed with 15% nitric acid, with a ratio of S:L = 1:10 and a duration of 30 minutes. The research results are presented in Fig. 7. With an increase in leaching temperature, extraction into calcium solution decreased from 83.1 to 72.7%, and extraction of titanium ranged from 4.2 to 5.3%. As in other experiments with a rise in temperature, a large amount of gel is formed, which adsorbs calcium and other impurity components on itself. Gel formation markedly reduced the filtration rate; at temperatures of 80 - 100°C, filtration took place during the day.

Studies on the duration of leaching with 15% nitric acid were carried out at a temperature of 20°C in the ratio S:L = 1:10. The results of the research are presented.
in Fig. 8. The increase in leaching time under these conditions shows that the extraction of calcium into the solution gradually decreases from 83.1 to 67.3 %, and the extraction of titanium varies from 10.7 to 9.4 %.

Flocculants were used to coagulate the gel formed during leaching of sludge from titanium production. Coagulation of the gel with the use of flocculants allows the formation of loose flocculent aggregates - floccules of small particles of the dispersed phase.

Flocculation in the aquatic environment, caused by high-molecular flocculants, polyelectrolytes or non-ionic polymers, is of practical importance. The kinetics and completeness of flocculation, as well as the structure and properties of floccules are influenced, on the one hand, by the molecular mass, the degree of ionization of the flocculant, and on the other, by the sign and density of surface charges, the size and shape of colloidal particles, and the chemical composition of their surface. Excess flocculant can not only worsen flocculation, but also cause a reverse process - deflocculation [22].

Flocculants Kemira 100 and Alclar 600 were used for this research. The pulp was obtained under the established optimal conditions for the leaching of sludge: 15 % nitric acid, the ratio S:L = 1:8, temperature 20°C, leaching time 30 minutes. The experiments were carried out in the following order, when leaching the sludge 10

![Fig. 7. Dependence of extraction of the main components in the solution on the temperature of 15 % HNO₃.](image)

<table>
<thead>
<tr>
<th>Continuation of the process, min</th>
<th>Deposition rate, mm/min</th>
<th>Flocculant consumption, g</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0</td>
<td>0.001</td>
</tr>
<tr>
<td>15</td>
<td>11.7</td>
<td>12.1</td>
</tr>
<tr>
<td>30</td>
<td>5.8</td>
<td>6.03</td>
</tr>
<tr>
<td>60</td>
<td>2.86</td>
<td>2.01</td>
</tr>
<tr>
<td>90</td>
<td>1.86</td>
<td>2.0</td>
</tr>
<tr>
<td>120</td>
<td>1.36</td>
<td>1.46</td>
</tr>
<tr>
<td>180</td>
<td>0.88</td>
<td>0.97</td>
</tr>
<tr>
<td>240</td>
<td>0.65</td>
<td>0.72</td>
</tr>
<tr>
<td>300</td>
<td>0.51</td>
<td>0.58</td>
</tr>
</tbody>
</table>
Fig. 8. Dependence of the extraction of the main components in the solution on the duration of leaching at 15% HNO₃.

minutes before the end of the leaching, a solution of 0.2% flocculant was added with different amounts of its supply. Table 2 presents the results for the sedimentation rate of suspended particles of the pulp from the flow of Kemir 100. Comparing the deposition rates, it is possible to determine how much faster the layer is lightened or the coagulation of the microparticles. Table 3 presents a similar result with the addition of flocculant Alclar 600.

Flocculant 0.2% Alclar 600 in the amount of 1.3 - 2 ml per liter of pulp was added during leaching of sludge with 15% nitric acid, S:L = 1:10, temperature 20°C, leaching time 30 minutes. The filtration rate was 0.058 - 0.062 m³/m² h. When leaching 15% nitric acid, the extraction of calcium in the solution was 93 - 96%.

Consequently, the optimal leaching parameters when adding a flocculant of 0.2% Alclar 600 were: 15% nitric acid, temperature 20°C, S:L = 1:10, leaching time 30 minutes. At these conditions the extraction in a solution of titanium was 5.0%, and extraction in solution of calcium was 96.0%.

Table 3. Results for the deposition rate of suspended particles of the pulp from the flow Alclar 600.

<table>
<thead>
<tr>
<th>Continuation of the process, min</th>
<th>Deposition rate, mm/min</th>
<th>Flocculant consumption, g</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0</td>
<td>0,001</td>
</tr>
<tr>
<td>15</td>
<td>11,7</td>
<td>12,3</td>
</tr>
<tr>
<td>30</td>
<td>5,8</td>
<td>6,2</td>
</tr>
<tr>
<td>60</td>
<td>2,9</td>
<td>3,1</td>
</tr>
<tr>
<td>90</td>
<td>1,86</td>
<td>2,04</td>
</tr>
<tr>
<td>120</td>
<td>1,36</td>
<td>1,52</td>
</tr>
<tr>
<td>180</td>
<td>0,88</td>
<td>1,0</td>
</tr>
<tr>
<td>240</td>
<td>0,65</td>
<td>0,75</td>
</tr>
<tr>
<td>300</td>
<td>0,51</td>
<td>0,59</td>
</tr>
</tbody>
</table>
CONCLUSIONS

According to the results of X-ray fluorescence (spectral) and chemical analyses, the composition of the sludge was determined, wt. %: 6.82 Ti, 2.78 Fe, 19.4 Ca, 2.19 Al, 0.48 S, 8.19 Si, 0.133 V, 0.32 Nb, 7.09 C, 46.54 O, 3.63 Cl, 0.157 P, 0.461 Zr, 1.4 Ba, 0.17 Cr, 0.136 W. According to the results of X-ray phase analysis, the main phases of the sludge are calcite 31.33 %, vaterit 13.88 %, quartz 12.37 %; titanium is present in the phases of rutile 4.45 %, lower titanium oxide 6.05 %, hydrated titanium oxide 6.9 %, alumino-titanium niobium oxide 3.98 %; calcium is also present in the phases of hydrocalumite 5.38 %, Portlandite 4.97 %, aluminum akermanite 3.51 %, elemental sulfur 7.18 %.

According to the results of thermal analysis, the following compounds were identified: calcite, aragonite, ankerite, silicic acid, gel-like complex Na₂O·TiO₂·2.5H₂O, metamictic pyrochlor (Na,Ca)₂(Nb,Ta,Ti)₂O₇(OH,F,О), metacell acidic caeselite CaZrTiO₆, calcium hydrosulfate aluminat-3CaO·Al₂O₃·CaSO₄·12H₂O, calcium hydroxide, nakrit Al₂O₃·2SiO₂·2H₂O, monoclinic amphibole 4CaO10(Mg,Fe)O16SiO₂·2H₂O, glassy ocermanite, elemental sulfur, calcium hydrosulfonic aluminate, gypsum.

According to X-ray and mineralogical analyzes, the sample contains basic minerals in an amount (%): calcite - 31.33, barite - 13.88, quartz - 12.37, sulfur - 7.18, various phases of titanium - 21.38, okermanite from the group of mellilit, portlandite, hydrocaluminate - 13.86.

Optimal leaching parameters when adding diluted 0.2 % flocculant Alclar 600 in the amount of 1.3 - 2 ml per liter of pulp: 15 % nitric acid, temperature 20°C, S:L = 1:10, leaching time 30 minutes. With these parameters, extraction in a solution of titanium was 5.0 %, and extraction in solution of calcium was 96.0 %. The filtration rate was 0.062 m³/m² h.

REFERENCES


