ABSTRACT

of the dissertation work on the topic:

"DEVELOPMENT OF TECHNOLOGY FOR PROCESSING TITANIUM-MAGNESIUM PRODUCTION WASTE TO PRODUCE TITANIUM DIOXIDE AND CALCIUM NITRATE"

submitted for the degree of Doctor of Philosophy (PhD)
in the specialty 6D070900 – "Metallurgy" by

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The purpose of the dissertation work is to develop a technology for the complex processing of solid waste sludge accumulators of "UKTMP" JSC with the extraction of titanium dioxide and calcium nitrate.

Research objectives:

– studies of the material composition of samples of titanium-magnesium sludge and the resulting products according to the processing of the developed technology by methods of chemical, spectral, X-ray phase analysis;

– investigation of kinetic regularities of the process of leaching sludge of titanium-magnesium production with nitric acid;

– determination of optimal conditions for the process of leaching sludge of titanium-magnesium production with nitric acid;

– investigation of the process of fluoroammonium cake processing from sludge leaching;

– conducting alkaline hydrolysis of sublimates and cinders;

– purification from impurities and production of titanium dioxide product;

– purification of solutions after leaching of titanium-magnesium sludge from impurity components;

– carrying out the processes of crystallization and granulation of calcium nitrate from purified solutions from sludge leaching;

– large-scale laboratory tests of the developed technology for obtaining titanium dioxide and calcium nitrate from titanium-magnesium sludge.

Research methods.

The main methods of research and analysis used in the performance of the dissertation work include:

– X-ray experimental data obtained on the BRUKER D8 ADVANCE apparatus on copper radiation at an accelerating voltage of 36 kV, current of 25 mA;

– X–ray fluorescence analysis was performed on a Venus 200 PANalyical B.V. wave dispersion spectrometer (Holland);

– chemical analysis of samples was performed on an optical emission spectrometer with inductively coupled plasma Optima 200 DV (USA, Perkin Elmer);

– mapping of the elemental and phase composition of the samples was carried out on an electron probe microanalyzer JXA - 8230 by JEOL (Japan);

– energy dispersive X-ray fluorescence analysis was performed on the ORBIS MICRO-XRF device of EDAX company (Japan);

– thermal analysis was performed using a synchronous thermal analysis device STA 449 F3 Jupiter. Instruments and measuring instruments have passed state verification;

– calculation of the thermodynamic characteristics of possible reactions of the interaction of the main components of the cake with ammonium bifluoride, performed using the thermodynamic calculation program HSC Chemistry 8.0 of Outokumpu Technology Engineering Research.

The following laboratory and enlarged laboratory equipment were also used: a horizontal tubular furnace LOIP LF-50/500-1200, an electric stove with a temperature controller, a plate granulator, a laboratory top-drive agitator, a glass laboratory refrigerator, a vacuum pump, a thermometer, a cylinder with argon.

All studies were carried out in accredited laboratories using various instruments and measuring instruments that have passed the state metrological verification.

The main provisions (proven scientific hypotheses and other conclusions that are new knowledge) submitted for protection:

– results of physico-chemical methods of analysis of titanium-magnesium sludge and the resulting products according to the processing of the developed technology;

– results of studies of kinetic regularities of the process of leaching sludge of titanium-magnesium production with nitric acid;

– the results of studies to determine the optimal conditions for nitric acid leaching of titanium-magnesium sludge production;

– results of studies of the process of fluoroammonium cake processing from sludge leaching;

– results of alkaline hydrolysis of sublimates and cinders;

– results of purification from impurities and production of titanium dioxide product;

– results of cleaning solutions after leaching of titanium-magnesium sludge from impurity components;

– results of the processes of crystallization and granulation of calcium nitrate from purified solutions from sludge leaching;

– the results of the enlarged laboratory tests on the complex processing of titanium-magnesium sludge.

Description of the main results of the study.

1. The material composition of the titanium-magnesium production sludge and the resulting products according to the processing of the developed technology by chemical, spectral, and X-ray phase analysis methods has been investigated.

2. The kinetics of the process of leaching sludge of titanium-magnesium production with nitric acid has been studied.

3. The influence of the main parameters of the process of leaching sludge of titanium-magnesium production with nitric acid, such as the concentration of nitric acid, the ratio T: W, temperature and duration, on the degree of extraction of calcium, titanium and other related components has been studied.

4. Fluoroammonium processing of cake from nitric acid leaching of sludge was carried out. After alkaline hydrolysis and calcination, titanium and silicon dioxide products with a content of 96.2% TiO_2, 88% SiO_2, respectively, and a niobium-containing intermediate with a content of 11.6% Nb_2O_5 were obtained.

5. Calcium nitrate salts were obtained during the crystallization process with the addition of ammonium nitrate. Optimal conditions of the crystallization process have been established.

6. The process of obtaining commercial calcium nitrate by two methods is investigated: granulation in a fluidized bed and granulation in a container. Dehydrated calcium nitrate in the form of flakes was obtained by granulation in a container with a content of normalized fractions of -7+1 mm to 91.0%.

7. Large-scale laboratory tests were carried out using the developed technology of complex processing of titanium-magnesium sludge to obtain calcium nitrate, titanium dioxide, amorphous silica and a niobium-containing product. A technological scheme for the complex processing of titanium-magnesium sludge has been developed.

Substantiation of the novelty and importance of the results obtained.

The novelty of the topic lies in the development of a technology for complex processing of solid waste sludge accumulators of JSC "UKTMP" with the production of calcium nitrate from a purified solution and titanium dioxide from a cake from nitric acid leaching by fluoroammonium processing.

The main results obtained:

– for the first time, the process of nitric acid leaching of sludge accumulator sediments with the establishment of optimal conditions was applied, which made it possible to remove calcium and obtain a cake enriched in titanium; kinetic patterns of leaching of titanium-magnesium sludge with nitric acid were revealed;

– kinetic regularities of the leaching of titanium-magnesium production sludge with nitric acid were revealed; it was found that the process speed is limited by intradiffusion inhibitions associated with gelation; the apparent activation energy for calcium is 6.04 kJ/mol and the reaction order for nitric acid is 0.83, indicating the process in the intradiffusion mode;

– for the first time, a method of fluoroammonium treatment was applied for cakes from the leaching of sludge accumulators of titanium production with the determination of optimal technological modes of the processes of sequential sublimation of silicon and titanium fluorides, with further hydrolysis and purification of the sublimation product, which made it possible to obtain titanium dioxide of a rutile form;

– a method has been developed for obtaining a stable form of anhydrous calcium nitrate in the $Ca(NO_3)_2 – H_2O$ system, which is achieved by evaporation from purified

solutions with the addition of 5% NH_4NO_3 of the total amount of calcium nitrate, with refinement to melting with 90% $Ca(NO_3)_2$ content and further crystallization and granulation of nitrate salt.

Compliance with the directions of scientific development or state programs.

The dissertation work was carried out at the Department of Metallurgy and Mineral Processing of Satbayev University and in the laboratory of titanium and rare refractory metals of "Institute of Metallurgy and Ore Beneficiation" JSC, within the framework of the state grant of the Committee of Science of the Ministry of Education and Science of the Republic of Kazakhstan on the project on: "Development of technology for complex processing of titanium sludge" (Research Project No. AP05130436 dated 02.03.2018 for 2018-2020), funded by the Ministry of Education and Science of the Republic of Kazakhstan under the subprogram "Grant financing of scientific research" on the priority "Rational use of natural resources, processing of raw materials and products".

Description of the doctoral student's contribution to the preparation of each publication.

Personal participation of a doctoral student consists in direct participation at all stages of the work:

– setting research goals and clear objectives on the research topic;

– preparation of samples for experiments, analyses of starting substances and products obtained;

– conducting experiments on the research topic, processing and analyzing the data obtained;

– calculation of thermodynamic characteristics of possible reactions of interaction of the main components of the cake with ammonium bifluoride;

– writing articles on the topic of the dissertation;

– generalization of research results, formulation of conclusions and scientific novelty.

According to the results of the dissertation work, 12 publications were published, including 2 articles in journals reviewed by the Scopus database, 4 articles from the list of journals recommended by Committee for Quality Assurance in the Sphere of Education and Science of the Ministry of Education and Science of the Republic of Kazakhstan, 1 article in an international scientific publication, 1 patent for an invention was obtained.

The main provisions of the dissertation work were reported at 5 international conferences, including:

1. Есенгазиев А.М., Ультаракова А.А., Кенжалиев Б. К., Бернс П., Улдаханов О.Х. Исследование физико-химических свойств хлоридных отходов титано-магниевого производства // Матер. Межд. научно-практ. конф. «Эффективные технологии производства цветных, редких и благородных металлов». – Алматы, – 2018. – С.153-158.

2. Есенгазиев А.М., Онаев М.И., Ультаракова А.А., Улдаханов О.Х. Переработка отходов титаномагниевого производства // Труды конференции «Сатпаевские чтения 2019». – Алматы, – 2019. – Т.1. – С.728-733.

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

4. Ультаракова А.А., Есенгазиев А.М., Касымжанов К.К., Улдаханов О.Х. Получение кальциевой селитры из растворов от выщелачивания азотной кислотой техногенных отходов титанового производства // Матер. XXV Межд. научно-техн. конф. «Научные основы и практика переработки руд и техногенного сырья». – Екатеринбург, – 2020. – С. 132-136.

5. Есенгазиев А.М., Ультаракова А.А., Касымжанов К.К., Улдаханов О.Х. Фтороаммонийная переработка кека от выщелачивания шламов титаномагниевого производства с извлечением диоксида титана // Международная научно-практическая конференция «Сатпаевские чтения- 2021». – Алматы, – 2021. – Т.1. – С.1302-1306.