ABSTRACT

from the thesis paper on the subject of:

«DEVELOPMENT OF THE TECHNOLOGY OF PRODUCTION OF THE COMMERCIAL TITANIUM DIOXIDE FROM THE OFF-GRADE TITANIUM DROSS »

made by the doctoral candidate of the PhD degree

on the specialty 6D070900 - «METALLURGY»

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Evaluation of the contemporary state of the feasible scientific or technological problem.

Titanium dioxide is the most highly-demanded of the titanium compounds. It was first produced commercially at the beginning of the XX century and is being widely used in paints, as the filler for paper and plastic, in solar batteries, in cosmetics, and as the food additive, in production of the non-toxic tanning materials, as the ingredient in formulations of the coverings, adhesives and joint compounds.

Currently, titanium dioxide is produced in 53 plants in 26 countries of the world. Capacity utilization at manufacturing enterprises averages 92%, incl. in the USA and Europe - 96%, in the countries of the Asia-Pacific region - 85–91%.

Traditional manufacturing flow charts of the titanium production are oriented on use of the ilmenite concentrates. Since ilmenite deposits are depleted, a need arises of the conversion on use of the complex ores of complex composition – titano-magnetite in nearest future.

In the coming years consumption of the titanium dioxide will grow with highest rate in production of the laminated paper – by 4-6% in one year, and also in plastics industry – by 4% in one year. Growth of the titanium dioxide consumption in paint and coatings industry won't be that fast – not less than 1,8–2% in a year.

Around 12–13% of the titanium dioxide is being used as the coloring agent in production of the paper articles in form of rutile (fine paper) or anatase (skip, carton). Averagely 1,4 kg of TiO_2 is being used in manufacture of 1 ton of paper.

The most widespread method for producing the titanium dross – reduction melting in electrically-heated furnace, during which the ferrous oxides recover to metal. Primary melting product – titanium dross contains 75-85% TiO_2. Secondary product – crude iron, is used as the raw material in production of steel.

Titanium dross could be used to obtain rutile with titanium dioxide contents - 92-96%. Industrial production of the synthetic rutile consists of two stages: reduction melting and acid elution, during the which a large amount of the liquid disposals appear – 2 KT of TiO_2.

There are two basic industrial techniques of preparation of titanium dioxide – sulfuric and chloric. In sulfuric process, titanium-containing product is being processed with concentrated spirit of sulfur with preparation of sulfate compound, which is being hydrolyzed and landing of the titanium dioxide, and iron transits in

compound in form of sulfates. According to the chloric technology, rutile is first being exposed to the chlorine gas, titanium transfers to the chloride form, further it transfers to the pigment with dechlorination at high temperature in compound of the air and oxygen. Both of the technologies have a high level of waste or toxic products release and require strong environmental measures.

In present time global capacity of the production of titanium dioxide with chloric approach exceeds the capacity of the sulfate approach and still growing.

Advantages of the chloric approach to produce the pigment against the sulfate approach involves significantly lower level of waste, that have to be neutralized, somehow higher quality of the product, and also lower level of relative capital investment, involving 60-75% of the investments in sulfate approach.

Assay of the patent literature has shown that during the development of the approach of producing titanium dioxide from the off-grade titanium dross with high content of trace constituents individual approach for each certain slag is demanded.

Relevance of the study.

Republic of Kazakhstan possesses significant reserves of the titanomagnetites, which could be a raw material for titanium and it's pigmentary dioxide production. In this context the main task is to chemically enrich them.

There is a production of titanium metal at « Ust-Kamenogorsk Titanium Magnesium Plant» JSC, however there is no production of the pigmentary titanium dioxide, which forces the manufacturers of the paints and lacquers to import the pigmentary titanium dioxide.

TENIR-LOGISTIC LLP conducts work at the Tymlay deposit in the Kordai district. The field is located in the Zhambyl region north-west of the railway station Khantau. The need to carry out research work on the development of technology for obtaining commercial titanium dioxide from non-conforming raw materials is due to the fact that the processing of high-titanium-magnetite concentrate obtained from Tymylaya ore, along with iron, which is the main component in its two-stage processing, the titanium content in the resulting slag is low about 60%, instead of the required 80%). The production technology of titanium dioxide from such substandard slag is absent.

At the same time, pigmentary titanium dioxide is not produced in the Republic of Kazakhstan, and manufacturers of paints and varnishes import it from abroad, spending free hard currency to import.

Developed treatment process of the off-grade titanium dross from electrosmelting of the Tymlay deposit, allows to release the pigmentary titanium dioxide, which will be demanded in market.

Work objective.

The objective of the doctorate thesis is development of the technology of titanium dioxide production from the off-grade titanium dross.

Subject of research.

The off-grade titanium dross, produced from titanium magnetite concentrate of the Tymlay deposit.

Research tasks.

- informational-patent search related to the problem of producing pigmental titanium dioxide. Obtaining of the titanium dross from the titanium magnetite concentrate;
- study of process of agglomerating of the low-titanium dross with natron. Physical-chemical study of phase conversions of the titanium dross components upon different agglomerating condition;
- determination of the optimal mode of water leaching of the sintered mass. Study of phase conversions of the sintered mass components during the water leaching;
- dressing-off of the mother solutions of water leaching of sintered materials from chrome and vanadium;
- determination of the effect of acid type on the titanium dioxide's structure;
- study of the effect of acid concentration and solid to liquid ratio on the degree of purity of hydrated titanium dioxide;
- determination of the optimal duration of acid leaching and grain size on the degree of impurities transition to compound;
- treatment of the hydrated titanium dioxide from silicon;
- obtaining pigmentary titanium dioxide.

Metrology provision data.

While conducting this work metrological support was determined by presence of modern physical-chemical methods of analysis, performed with use of approved procedures, calibrated tools and gauges, and also high-temperature furnaces.

National scientific laboratory with focus area of "Technologies for hydrocarbon and mining and smelting sectors and related service industries» of the «Institute of Metallurgy and Ore Benefication» JSC accredited for technical expertise in National Center of Accreditation of Committee of Regulation and Metrology – Accreditation certificate №KZ-И.02.1138 dated February 23, 2016 (valid until February 23, 2021 , for compliance to the requirements of GOST ISO/IEC 17025-2009 « General Requirements for the Competence of Testing and Calibration Laboratories ».

«Institute of Metallurgy and Ore Benefication» JSC has: State license for operation with precursors № 16011676 dated 21.07.2016, State license for operation with toxins №16011643 dated 20.07.2016 .

Scientific novelty of the studies.

Phase transformations occurring in the sintering process of substandard Tymlaevsky titanium slags with soda:

- it was found that in the temperature range of 400-800 ° C in oxidizing conditions, the anasovite lattice of these slags is destroyed with the release of impurities in the form of sodium vanadates, chromates and aluminum silicates;
- It was revealed that in the temperature range 858-1131 ° C, the formation of practically insoluble in acids lower and higher sodium titanates occurs.

2. The kinetic laws of impurity dissolution in the process of obtaining hydrated titanium dioxide were determined. It is shown that the internal diffusion is the limiting stage for the dissolution of impurities in hydrochloric acid. A

mechanism for the dissolution and purification of chromophore impurities from hydrated titanium dioxide has been proposed.

3. It has been established that to obtain monophasic titanium dioxide of rutile modification it is necessary to calcine hydrated titanium dioxide in an oxidizing atmosphere.

Key points to be presented:

– justification of the subject of research, reagents, methods of analysis and examination of the obtaining products;

– results of physical-chemical studies of phase conversions of titanium dross under different agglomeration conditions;

– results of the studies of the effect of acid type on the degree of titanium dioxide's treatment from impurities;

– results of the studies of the phase conversions during the dehydration of the hydrated titanium dioxide;

– results of the balance experiment in production of the pigmentary titanium dioxide.

Scientific merit of the results obtained in thesis paper.

For the first time ever physical-chemical studies of the phase conversions of the titanium dross components, obtained from the titanium magnetite concentrate of the Tymlay deposit at different conditions of agglomeration with natron. It has been set that at higher temperatures than 900 °C, different phase conversions of titanium dioxide may form. In addition forms vitreous phase that troubles the melting of the product.

As the result of the conducted studies type of acid that provide the obtaining of titanium dioxide with rutile structure was chosen.

Optimal concentration of acid and solid to liquid rate were determined, which are 20,4 % wt and solid to liquid ratio is 1:8.

Optimal duration of leaching and grain size are determined.

Optimal parameters of treatment of ortho-titanic acid from silicon. Pulp heating rate, which allows the treatment of the titanium dioxide from silicon and iron to the content that meets the regulations for pigmentary titanium dioxide.

Practical relevance of the results of thesis.

Based on the analysis of the results of the experimental studies technology of obtaining pigmentary titanium dioxide that may supply foreign and domestic markets of manufacturing the following products was developed:

– Paintings, for bleaching and for improved opacity, for protection of the surfaces from harmful ultraviolet rays, for prevention of film aging and yellowing of the painted products;

– Papers, for bleaching and for improved opacity of paper stock, also in production of means of covering the paper;

– In food industry, for adding the high-bleaching and covering effects to products, for protection of color and package (plastic) of product from ultraviolet eradiation;

– Catalysts, is used as catalyst, as photocatalyst and as the nonreactive basic ceramic material for active components.

Mission need statement.

Republic of Kazakhstan accommodates significant reserves of titanium magnetites, technology of its processing with forming of titanium dross with low content of titanium 35-50% by TiO_2, which may become the raw material for production of titanium and its pigmentary dioxide, which imports in present time has been developed.

Publications and evaluation of thesis.

Based on the results of the thesis paper 11 works, including the following ones were published:

– 1 article in the journal that is listed in Scopus (Journal of Chemical Technology and Metallurgy) data base

– 4 articles in journals, that are recommended by The Control Committee in Education and Science under the Ministry of Education and Science of the Republic of Kazakhstan

Key points and results of the paper are evaluated at 7 international conferences in the form of oral reports:

– International Scientific GeoConferences SGEM 2016. (Albena, Bulgaria);

– World Multidisciplinary Earth Sciences Symposium «IOP Conf. Series: Earth and Environmental Science 44, 2016. (Prague, Czech Republic);

– International research-to-practice conference «Integration of science, education and manufacture – basis of implying the Nation's masterplan». (Almaty);

– International research-to-practice conference «Innovations in complex processing of mineral raw materials». (Almaty);

– International scientific-practical conference "Effective technologies of production of colorful, precious and precious metal" (Almaty), 2018;

Novelty of the technical solutions is validated by the issue of RK Patent «Approach to process of low-titanic titanium magnetites», № 97861 dated 13.11.2015.

Connection between the paper and state programs and researches.

Thesis paper is made within the framework of public grant from the Scientific repository of Ministry of Education and Science of the Republic of Kazakhstan within the project regarding: «Development of the technology of production of the commercial titanium dioxide from the off-grade titanium dross» (R&D № 0586/ GF4 dated 12.02.2015. as of 2015-2017 years), sponsored by the Ministry of Education and Science of the Republic of Kazakhstan within the framework of "Grant financing of scientific researches" subprogram by "Rational use of natural resources, processing of raw materials and production".

Structure and volume of thesis paper.

Thesis paper consists from introduction, five chapters, conclusions, list of references and appendixes. The work is embodied in 127 pages of typewritten text, contains 50 tables and 46 figures. List of references includes 100 articles.