**ABSTRACT**

to thesis research on **«DEVELOPMENT OF HYDROMETALLURGICAL TECHNOLOGY FOR PROCESSING VANADIUM-CONTAINING ORES OF BIG KARATAU»**, Submitted for the Degree of Doctor of Philosophy PhD Majoring in Metallurgy - 6D070900

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**Assessment of the current state of the solved scientific or technological problem.** In recent years, the level of vanadium consumption in the world is constantly growing due to the global increase in the production of structural, stainless and special steels. In addition to the metallurgical and chemical industries, vanadium and its compounds are widely used in atomic-hydrogen energy and in the production of vanadium batteries [1, 2].

In nature, vanadium is often found in iron, titanomagnetite, and phosphorite ores.

It is important to note that the Republic of Kazakhstan currently ranks first in the world in terms of reserves of tungsten and vanadium ores, second in terms of chromium (23%), and third in terms of manganese [3].

The raw materials for the production of vanadium products are titanomagnetite ores. Vanadium deposits are known in Africa, Australia (broken hill), Mexico (Lamentos), and Kazakhstan (Karatau) [4].

During the blast furnace melting of titanium-magnetite ores, vanadium (0.1-0.2% $V_2O_5$) is completely converted to cast iron, and during the processing of cast iron into steel, it is converted to Converter slag. From this slag, commercial vanadium pentoxide and ferrovanadium are obtained hydrometallurgically.

Production of vanadium products is carried out in 20 countries, while developed and developing countries account for more than 75% (of world production), of which in the United States - more than 10%, in China - 15%, in South Africa - about 45% , etc.

Western European countries produce vanadium products mainly from imported raw materials (vanadium-containing slag from South Africa).

The production of vanadium products in the CIS, including the entire complex of enterprises (mining, metallurgical, ferroalloys), is concentrated in Russia (23%).

Kazakhstan titanomagnetite ores are not currently processed. Titanium slag is obtained from ilmenite ores of the Satpayev deposit with the associated extraction of vanadium pentoxide at the Ust-Kamenogorsk titanium-magnesium plant, and the resulting high-quality vanadium pentoxide (98-99% $V_2O_5$) is then sent to the production of steel for aircraft construction.

To date, only titanomagnetite ores are mainly involved in the production of vanadium, their processing was initially considered economically disadvantageous [5], nevertheless, vanadium is extracted from these ores by the pyrometallurgical method to produce pig iron and titanium slag. Vanadium-containing slag is extracted from pig-iron, and slag is converted into commercial vanadium pentoxide, which accounts for about 70% of the total world production of

vanadium [6]. The average content of vanadium pentoxide in titanomagnetite ores is 0.1-0.2%.

One of the largest deposits of vanadium in Kazakhstan (with reserves of more than 2 million tons) is the vanadium-bearing basin of Big Karatau, with an average content of vanadium pentoxide of 0.8-1.3%. The Big Karatau basin includes the Balasauskandyk, Jabagly and Kurumsak deposits, discovered in the 40s of the last century. To date, the ores of these deposits have not been processed. Although, according to many Soviet scientists [7, 8], these ores were considered the most «technologically advanced», since the content of vanadium in them is 8-10 times higher than in titanomagnetite ores.

Significant research on the technological properties of vanadium ore was carried out at the Kazakh Polytechnic Institute under the supervision of Academician V.D. Ponomareva [9].

In the first technological tests conducted by the Chusovsky Metallurgical Plant, ferrovanadium was obtained with a high content of phosphorus in it, as a result of which the ore reserves of North-Western Karatau were classified as off-balance [10].

For the first time in the 60-70s, the Institute of Metallurgy and Ore Beneficiation (IMOB) of the Academy of Sciences of the Kazakh SSR and the Chimkent Plant of Phosphorus Salts under industrial conditions proved the possibility of complex processing of vanadium-containing ores by pyro-, hydrometallurgical methods with the associated extraction of vanadium. The plant used vanadium ores as a flux in the production of yellow phosphorus. In this case, ferrophosphorus with a vanadium content of 4-6% was obtained [11].

It should be noted that from 1983 to 1987, on the instructions of the USSR State Planning Commission, a series of industrial tests was conducted at NDFP JSC (Novodzhambul phosphorus plant) using about 14 thousand tons of vanadium-carbon-containing quartzite from the Balasauskandyk deposits as a flux in the production of yellow phosphorus. From the iron-phosphorous alloy containing vanadium formed in the process of electrothermal smelting (at JSC NDFP), the vanadium-containing commercial product vanadium pentoxide at JSC Tulachermet was obtained in the traditional way. Based on the test results, a feasibility study was prepared with a recommendation for the introduction of yellow phosphorus into production [12, 13].

In 1993-1994, domestic plants (CPA « Phosphorus », the city of Chimkent, «Ferrochrome», the city of Aktyubinsk) used vanadium ore as a flux for the phosphoric and ferroalloy industry.

«Ferrochrome» JSC used vanadium-containing ores of the Balasauskandyk field for testing, while the tested technology was recommended for further implementation at these plants, but with the collapse of the USSR and, as a result, loss of production connections, as well as the absence of a mining enterprise at the Balasauskandyk field was suspended [14-16].

Within the framework of the sectoral budget program (for 2010-2014) for the development of the mining and metallurgical industry of the Republic of Kazakhstan, the employees of the RSE «NC CPMRM RK» carried out applied

scientific research of a technological nature. The studies involved pilot tests and development of a technology for processing mineral raw materials from the Kurumsak and Balasauskandyk deposits to organize the production of rare and rare-earth metals [17, 18].

In 2012, as a result of research, the ore preparation technology for the Kurumsak deposits was developed and technological regulations were issued for pilot testing of the ore preparation unit and the creation of a pilot industrial site for the production of rare and rare earth metals from black shale ores of the Balasauskandyk deposits with an annual output of 15,000 tons of ore [19, 20 ]. In the course of the work, the researchers found that, due to the uncertainty of the condition of vanadium ores, the reserves in both deposits according to the content of vanadium pentoxide can be attributed to the off-balance group, with an average $V_2O_5$ content in the range of 0.9-1.5%. Studies of the technological process in laboratory conditions have shown the possibility of processing ores of the Balasauskandyk deposits with the integrated extraction of vanadium and uranium from them.

At the end of 2012 and at the beginning of 2013, the «Balausa» LLP, with the involvement of researchers from the RSE «NC CPMRM RK», planned to launch a pilot production of commercial ammonium metavanadate by autoclaved sulfuric acid leaching of vanadium-containing ores from the Balasauskandyk deposit, initially in the presence of oxygen, then in the presence of elemental sulfur It was also proposed to introduce schemes with low-temperature roasting and ore processing by heap leaching with the extraction of vanadium using ion-exchange resins. From the complex of the proposed options, low vanadium extraction is planned at the leaching stage - at the level of 75% [21].

Numerous studies conducted in recent years on the development and implementation of ore processing technology at the Balasauskandyk and Kurumsak deposits have not yielded effective results due to the low vanadium extraction and the complexity of the processes. Therefore, it is necessary to continue scientific research in this direction. A thorough study of the mineralogical composition of vanadium-containing ores and determination of their valency, search and study of an effective method for the oxidation of vanadium to a pentavalent state are required. Based on such studies, it is possible to develop a hydrometallurgical technology for processing vanadium-containing ores to produce marketable products, which provides for oxidation and leaching in the anode zone, with additional activation of the leaching solution.

**The basis and initial data for the development of the topic.** Today, the mining and metallurgical complex is faced with the task of manufacturing products of high processing and finished products, as well as the introduction of high technology. The Government is implementing the «Development Plan for the rare-metal industry of the mining and metallurgical complex of the Republic of Kazakhstan for 2015-2019», which implies the implementation of a package of measures in the field of Legislative and regulatory support [22, 23].

In this regard, the topic of the dissertation related to the development of hydrometallurgical technology for processing vanadium-containing ores of Big

Karatau is relevant and corresponds to the directions of the implementation of the industrialization program of the Republic of Kazakhstan.

In previous studies, the issue was examined from the point of view of extraction of vanadium pentoxide by pyrometallurgical or hydrometallurgical methods. However, to date there is no effective way to process vanadium-containing ores. At the same time, for a more complete extraction of vanadium from complex, difficult to process and difficult to open raw materials, it is possible to use new methods of leaching under the influence of an electric current in the anode space.

In the dissertation, the possibility of obtaining vanadium from vanadium-containing ores of Big Karatau in the anode space with the combination of three operations - oxidation, leaching of vanadium and activation of the leaching solution is considered.

**Rationale for the need for research work.** Until now, vanadium-containing ores from the Balasauskandyk, Jabagly and Kurumsak deposits have not been processed. For the ore of the Balasauskandyk Deposit, tests were carried out and a feasibility study was drawn up on the feasibility of creating a vanadium production on the basis of phosphorus plants using a pyrometallurgical method. The results of the tests showed the prospects of new production, but due to the collapse of the USSR, this work was suspended, and research on the development of vanadium ores of Karatau with the extraction of valuable components from them has not been continued.

Within the framework of the industry budget program for 2010-2014 for the development of the mining and metallurgical industry of the Republic of Kazakhstan, a pilot production of commercial ammonium metavanadate was created on the basis of the Balasauskandyk field with the participation of scientists of the RSE «NC CPMRM RK» and employees of the company «Balausa» LLP. However, due to insufficient study of the nature, composition and properties of vanadium ores of this Deposit, this pilot production has not yet produced effective results for extracting vanadium into a commercial product [21].

In connection with the above, it is necessary to conduct scientific research aimed at further studying the mineralogical composition and properties of ores, as well as creating effective methods of hydrometallurgical processing that allows more fully extracting vanadium into commercial products.

**Information about the planned scientific and technical level of development, patent research and conclusions from them.** When performing work, an analysis of scientific, technical and patent information was carried out. As a result of the analysis of literature data and patent studies, it was found that in the vanadium-containing ores of Big Karatau, vanadium can be in pentavalent form only in the weathering crust of shales, and in the ore bodies of the lower seam can be in both cationic and anionic forms. Also, over time, the mineralogical and chemical composition of the ore may gradually change. It should be noted that in the literature there are no data on the use of electrometallurgical methods for the extraction of vanadium from vanadium-containing ores.

**Information about the metrological support of the dissertation.** When conducting research work, metrological support was determined by the presence of modern physicochemical methods of analysis performed using certified methods, measuring instruments, equipment and instruments verified by the State Standard of the Republic of Kazakhstan.

**Relevance of the topic.** In recent years, due to an increase in the production of various grades of steel, demand for vanadium is constantly growing (especially in China). Vanadium is mainly produced from titanomagnetite ores, which are considered economically disadvantageous. Carbon-siliceous shales and quartz – Roscoelite vanadium-containing ores of Big Karatau (Kurumsak, Balasauskandyk, Jabagly deposits) containing vanadium are the most technologically advanced than iron and titanomagnetite ores, but are not processed on an industrial scale. From the analysis of literature data it was revealed that the ores of Big Karatau are complex in chemical composition and difficult to open, which can affect the technological parameters of the processes. The tested methods (heap, autoclave leaching, etc.) based on Balasauskandyk have not yet yielded the required results. At a time when the largest foreign manufacturers of vanadium (Australia, South Africa) are forced to reduce production capacity due to lack of raw materials, the creation of its own production of vanadium in Kazakhstan is appropriate and relevant.

**The novelty of the topic** is the development of hydrometallurgical technology for processing vanadium-containing ores of the Big Karatau by electrochemical oxidation with the extraction of vanadium in solution (up to 92%).

Scientific novelty of the results obtained.

New data have been obtained on the characteristics of oxidized vanadium-containing ore from the Balasauskandyk and Kurumsak deposits. It is shown that vanadium in these ores is distributed dispersively, unevenly in quantity and is present in sparingly soluble two, three and tetravalent forms.

For the first time, the mechanism of the sulfuric acid leaching of calcined ore in the presence of hydrogen peroxide was studied. Determined that:

- under conditions of oxidative roasting of ore together with carbonate and sodium chloride in the range of roasting temperatures of 700-850°C, duration $\tau$=2 hours, complete combustion of coal is achieved and a cinder with a high concentration of readily soluble pentavalent form of vanadium in the form of meta- ($NaVO_4$), ortho- ($Na_3VO_4$) and sodium pyrovanadate ($Na_4V_2O_7$);

- a positive effect of hydrogen peroxide on the sequence of reactions of the interaction of sodium vanadates with sulfuric acid and the completeness of their course has been established, while the values of the Gibbs energy loss of the reactions increase by 2.5 times compared with the data obtained by leaching without an oxidizing agent. The maximum extraction of vanadium into the solution (~ 80%) under cinder leaching is achieved with the following optimal parameters: consumption of $H_2O_2$=10% of the mass of cinder, $C_{H2SO4}$=10%, temperature – 65ºC, phase ratio S:L=1:4, $\tau$=1 hour.

For the first time, kinetic regularities and the mechanism of the processes of electrochemical leaching of various vanadium-containing materials were

established depending on the influence of sulfuric acid concentration, duration, S:L ratio, temperature and current density, characterizing the course of processes in the diffusion region and their limitation by the growth of films of insoluble reaction products (oxides, sulfates metals) on the surface of grains. The optimal parameters of the electrochemical oxidation process were established: the concentration of the initial solution, $C_{H2SO4}$=10%, temperature – 65°C, duration - 1 hour, phase ratio S:L=1:4, anode current density - 200 A/m$^2$, providing high vanadium recovery into the solution (up to 92%) from prebaked vanadium-containing ores.

**Connection of this work with other research works.** The dissertation was carried out as part of the project «Development of an innovative technology for processing vanadium ores of Kazakhstan» at the department «Metallurgy and mineral processing» KazNRTU named after K.I. Satbayev, at the Institute of Geological Sciences named after K.I. Satbayev.

**The purpose of the work** of the research is to develop a hydrometallurgical technology for processing vanadium-containing ores of Big Karatau, which provides for the conversion of a hard-to-open part of vanadium-containing minerals into a soluble form with joint electrooxidation and leaching.

**The objects of research** are the fields Balasauskandyk and Kurumsak (Big Karatau).

**The subject of research** is vanadium-containing ores.

**The objectives of the study, their place in the implementation of research work as a whole:**

- study of mineralogy and the study of the forms of vanadium in the main minerals of the Balasauskandyk and Kurumsak deposits;
- study of the enrichment of vanadium-containing ores in the grinding and flotation cycle;
- study of leaching of unfired and calcined vanadium ore in the absence and presence of an oxidizing agent;
- study of the process of anodic oxidation and leaching of vanadium;
- development of a technological scheme for the anode leaching of vanadium from vanadium-containing ores.

**Methodological base of scientific research:**

- a complex of modern methods of analysis, including semi-quantitative X-ray phase, chemical, thermal analyzes of starting materials and products;
- methodology for the processing of vanadium-containing ores;
- methodology for the chemical and electrochemical oxidation of vanadium;
- the method of precipitation and extraction of vanadium from the productive solution in the form of a vanadium-containing product.

When conducting research, the following standard and non-standardized laboratory, enlarged laboratory equipment were used:

- planetary ball mill (Retsch PM-100);
- muffle furnace (SNOL-1,4.2,5.1,2/12,5-I1);
- liquid circulation thermostat (TZh-TS-01M-150);
- mechanical stirrers with an adjustable speed;
- vacuum pump;

- drying cabinet;
- electrolyzer for electrochemical oxidation.

**The main provisions to be defended:**

- the results of the enrichment of vanadium ore in the grinding and flotation cycle;
- results of a study of oxidative roasting of vanadium;
- the results of a study of the oxidation of vanadium by chemical and electrochemical methods;
- the results of the extraction of vanadium pentoxide from the solution;
- technological scheme of the anode leaching of vanadium from vanadium-containing ores.

**The practical significance of the work.**

A new combined technology has been developed for the electrochemical leaching of pre-baked vanadium-containing ores, which differs from the known operations with the exception of crushing and grinding, deslamation and flotation of tailings using the process of oxidative sulfuric acid leaching in the presence of oxidizing agents - a solution of hydrogen peroxide and manganese dioxide.

For the first time, the design of an electrolytic-electrodialysis cell using a cation exchange membrane was developed to study the process of joint oxidation and leaching of calcined vanadium-containing ores by the electrochemical method. The choice of cheaper materials compared to the noble metals used for the manufacture of electrodes, for which lead and titanium are recommended, is justified.

Various options for processing sparingly soluble oxidized vanadium-containing ores are proposed:

- preliminary calcination of the starting material, leaching of the cinder and electrochemical oxidation of vanadium compounds, followed by precipitation of the vanadium-containing product in the form of $V_2O_5$;
- leaching of ore in the presence of an oxidizing agent - hydrogen peroxide, followed by electrochemical oxidation and precipitation of vanadium from solution into a marketable product in the form of vanadium pentoxide;
- electrochemical leaching of calcined vanadium-containing ore, followed by precipitation of vanadium from solution in the form of a commercial product - $V_2O_5$.

**Publications** Based on the results of the thesis, 4 articles were published, including:

- 1 article in a journal included in the Scopus database (Metallurg magazine);
- 3 articles in magazines recommended by the Committee for Control in the Field of Education and Science of the Ministry of Education and Science of the Republic of Kazakhstan.

**Approbation of the work.** The main provisions and results of the work were tested at 5 international conferences in the form of oral presentations:

- International scientific-practical conference «Scientific and personnel support of the innovative development of the mining and metallurgical complex» (Kazakhstan, Almaty);

- 76th International Scientific and Technical Conference «Actual problems of modern science, technology and education» (Russia, Magnitogorsk);

- International scientific-practical conference «Intensification of hydrometallurgical processes of processing of natural and technogenic raw materials. Technologies and equipment» (Russia, St. Petersburg);

- International Conference «Scientific research of the SCO countries: synergy and integration» (China, Beijing);

- International scientific-practical conference «Effective technologies for the production of non-ferrous, rare and precious metals» (Kazakhstan, Almaty).

**The structure and scope of the dissertation.** The dissertation consists of introduction, 7 chapters, conclusion and 5 appendices. The work is presented on 122 pages of typescript, contains 28 tables, 47 figures. The list of sources used includes 100 items.