

## **ABSTRACT**

to the thesis of **NAZYM AKHMADIYEVA**

on the theme “**EXTRACTION OF RARE METALS AND REE FROM  
BYPRODUCTS OF ALUMINA PRODUCTION**”,

presented for Doctor of Philosophy (PhD) degree by

specialty 6D070900 - Metallurgy

**Evaluation of the current state of the scientific or scientific and technological problem addressed.** Consumption of rare metals and rare earth elements in various fields has been growing rapidly due to the low prices and achievements in the field of basic and applied sciences in the world. World consumption of REE amounted to more than 100,000 tons in 2011 and it is expected that the consumption of REE will increase double from 4% to 9% annually by 2020, and the consumption of neodymium and dysprosium will increase by 700% and 2600% respectively in the next 25 years. Rare metals and REE play a key role in the power engineering (from powerful wind generators and nuclear power plants to a wide range of batteries, electric motors and energy-saving lamps), so they are classified as "critical materials" by the US Department of Energy. Analysis of the rare earth metals world market shows that the volume of industry demand will increase to 225-250 thousand tons by 2020. It will lead to a deficit of neodymium, dysprosium, terbium and praseodymium, and possibly, lanthanum, yttrium and europium.

China owns more than 95% of the world's REE production, from raw material extraction to the production of metals and compounds of varying degrees of purity. The main consumers of REE-containing products have to take actions on reduction the dependence on China in this area. The US Department of energy announced a launch of its critical materials hub and plants to spend \$ 120 million over 5 years. The hub was created support research focused on ensuring a reliable supply of rare earths and other critical materials. Japan invested in the implementation of the REE program of \$ 1.25 billion in 2010 and funding continues, a state reserve of REE metals is being created. State (JOGMEC) and private companies in Japan are implementing projects in Vietnam, Myanmar, India, Kazakhstan and the United States. The European Union forms a resource base abroad. The leader is France, which has allocated hundreds of millions of euros to guarantee supplies of "indispensable metals," including REE. The development of REE production is carried out under the control of AREVA in an alliance with Rhodia South Korea:

1.0-1.5 billion US dollars was allocated to state-owned companies Korea Electric Power Corp and Korea Resources Corp. for the acquisition of promising projects in Africa and Australia in 2011.

Applications of rare metals, rare earth metals and their compounds are varied. The role of rare metals, used in the leading branches of production and ensuring the economic and defense security of any state, has rapidly increased throughout the world with the development of the newest branches of science and technology.

REE are used widely in different areas, they are used in many new electronic devices: such as mobile phones, screens, high-capacity batteries, permanent magnets for wind power stations, ceramics, etc. Scandium is used mainly for the manufacture of lenses and prisms used in film and photographic equipment, as well as for astronomical purposes. Yttrium is used for the manufacture of LEDs, cathode ray tubes, ceramics, computer monitors, temperature sensors; lanthanum for battery, batteries of electric cars, laptop batteries, also for high-tech digital cameras, video cameras, X-ray film, lasers; cerium for the production of catalysts, metal alloys, optical glass, silicon microprocessors; praseodymium - pigments, photographic filters, signal lenses at airports; Neodymium for high-power magnets for laptops, thulium-high-power magnets for laptops, lasers; samarium - high-temperature magnets; lutetium - x-ray phosphorus, dysprosium - high-power magnets, lasers; terbium - phosphors for monitors.

Some of the widely used in various industries of modern production are such rare metals as gallium, vanadium and titanium.

Gallium is one of the most common rare metals, but does not find in high concentrations, except for the gallite mineral. The main sources of gallium are solutions of bauxite and nepheline processing for alumina, waste products of zinc production.

Gallium is the basis of the electronic industry: it is used in the production of optoelectronics and semiconductors. Gallium is the base of compounds such as gallium arsenide and gallium nitride used in the electronics industry.

The global gallium market is projected to increase by 40% to approximately 422 tonnes per year by 2020, while the share of metal use will increase from 18% to 33% of total demand. The use of gallium to control electronic power will remain the largest market, but its part will decrease from 50% to 43% of the total.

China, Japan, the United Kingdom and the United States are the main producers of refined gallium. China is a leading producer of primary gallium, followed by Germany, Kazakhstan, Ukraine, South Korea and Russia.

One of the leaders in the gallium market is the GEO Gallium company. Its main capacities consisted of STADE (Germany) up to 2006, where about 33.0 tons of gallium per year are produced, the Salindres plant processing 20.0 tons per year (France) and Pinjarra (Western Australia) - potential (but not commissioned capacity of up to 50.0 tons per year).

Vanadium is a very important rare metal, which is used in non-ferrous alloys to improve the strength and resistance of the material. About 85% of the produced vanadium is used in the production of steel.

The largest deposits of vanadium are in the US, South Africa, Armenia and Russia. The world leader in the production of vanadium was and remains China. It provides more than half of the vanadium supply and thereby constantly regulates prices.

The main sources of vanadium are metallurgical slags, titanomagnetite ores, carbonaceous shales and oil waste.

Titanium is a unique metal that can be used in the production of a wide range of goods of various types, such as aircraft construction, rocket engineering, automotive, construction, medicine. The advantage of its compound - titanium dioxide, is its non-toxicity and harmlessness. Thus, more than half of the total volume of titanium dioxide is used for the production of paint and varnish products, since titanium dioxide has excellent dyeing properties. The development of semiconductors based on titanium dioxide has been extensively studied due to the effectiveness of this material in the photoelectrochemical splitting of water.

Mineral sources for titanium production are titanium-containing ores - rutile, ilmenite and leucoxene. The richest ones are those containing from 93.0 to 96.0% titanium dioxide; in ilmenite contains from 44.0 to 70.0%  $\text{TiO}_2$ .

The great demand for the production of titanium dioxide and the limited availability of proven rutile reserves in the world lead to the planning and use of titanium-containing slag is actual, and alumina production can be considered as raw material for titanium dioxide.

**Rationale for the research and development work.** In 2015, Kazakhstan started the implementation of the Second Five-Year Plan of the Industrial Development Program, in which the mining and metallurgical complex is one of the priority areas. At the end of 2014, the industry provides 19% of the gross added value in the country economy and 2.9% of the employment of the Republic population.

Nowadays, the mining and metallurgical complex have to produce products of high purities and finished products, as well as the introduction of innovative, science-intensive technologies. The Government is implementing the "Plan for the Rare Metal Industry Development of the Mining and Metallurgical Complex of the Kazakhstan Republic 2015-2019", implying a set of actions in the field of Legislative and Normative Support.

In this regard, the theme of the dissertation work, related to the development of technology for obtaining rare metals and REE, is relevant and corresponds to the direction of the implementation of the Kazakhstan Republic industrialization program.

Kazakhstan has significant reserves of low-quality aluminum raw materials, including ferruginous bauxites. Bauxite is a multicomponent raw material containing rare metals and REE.

In the JSC "Institute of Metallurgy and Enrichment" a complex technology has been developed for processing high-iron bauxites of the Koktal deposit, which is considered as a promising raw material for the creation of a new alumina production in the Republic of Kazakhstan.

In earlier studies, the issue was considered only from the point of view of extracting alumina and alkali. It is also necessary to solve the problem of extracting rare metals and REE for the organization of deeper processing of raw materials with complete utilization of byproducts

The presented work determined the possibility of obtaining rare metals and REE from industrial products of processing of Koktal bauxites and it is one of the sections of complex technology.

### **Relevance of the work.**

One of the possible sources of rare metals is byproduct of alumina production. More than 100 million tones of red mud are produced globally each year, and it causes a significant impact on the environment, at the same time it contains 14-45% Fe, 5-14% Al, 1-9% Si, 1-6% Na, 2-12% Ti, 0.05-0.8%  $V_2O_5$ , 60-80 g / t gallium, and REE in the amount of 500-1700 g / t. About 50-100 thousand tons of REE, 5 million tons of  $TiO_2$ , 200-300 thousand tons of vanadium and 6-8 thousand tons of gallium are usually lost per year. It is very important to develop an efficient technology for complex processing of aluminum raw materials as the additional sources of raw materials for the production of rare metals and REE.

**The goal of this thesis is to** development the technology for extraction rare metals as metallic gallium, vanadium pentoxide, concentrate of titanium dioxide and rare earth elements concentrate from byproducts of alumina production.

**The object and subject of the research** – aluminate solutions and hydrogarnet mud – byproduct of processing of ferruginous bauxites of the Koksalsk deposit by Bayer-hydrogarnate technology.

**Research objectives and their role in conduction of the research work, in general:**

- to develop the technology for obtaining gallium and vanadium from aluminate solutions and concentrates of rare-earth elements and titanium from hydrogarnate mud - byproducts of processing of high-iron bauxite by the Bayer-hydrogarnate technology;

- to study of kinetics and the mechanism of discharge of gallium ions in an alkaline solution;

- to develop an effective method for electrodeposition of gallium;

- to test an electrolyser with a rotating gallium cathode;

- to study the conditions of regeneration of gallium covering the surface.

**Scientific novelty of the results is as follows:**

- for the first time, the technology for processing aluminate solutions was first developed to produce vanadium pentoxide (89.8%  $V_2O_5$ ) and a gallium concentrate (0.5%  $Ga_2O_3$ );

- the kinetics and the mechanism of gallium ions discharge from the alkaline solution were investigated. It was found that when the proton-donor additive to the electrolyte is added, the rate of the gallium reduction reaction sharply increases. A method for electrochemical recovering gallium from alkaline solutions with the addition of ammonium hydroxide, which reduces the power consumption by 2-3 times;

- cathode surface's gallium covering conditions were investigated. The highest resistance of the coating was obtained on a copper electrode. It is determined that only with the use of hydrochloric acid, it is possible to cover the metal electrode with gallium;

- the technology for processing hydrogarnet mud, which includes reduction melting, magnetic separation, hydrometallurgical processing of the non-magnetic fraction to obtain REE and titanium concentrates;

- It was determined that the preliminary activation of the non-magnetic fraction of slag increases the degree of recovery of REE under nitric acid leaching.

### **Scientific hypothesis and results of the dissertation.**

- results of substantiation of production of rare-earth elements and rare metals from byproducts of alumina production;
- results of extraction of gallium and vanadium from byproducts of alumina production;
- results of processing of the hydrogarnet mud to obtain a concentrate of rare earth elements and titanium;
- results of electrochemical extraction of gallium from alkaline solutions on a gallium cathode;
- results of the study of the kinetics of electrochemical gallium extraction from an alkaline solution;
- results of testing of hydrogarnate technology in experimental metallurgical production.

### **Practical significance of the work:**

The results of the studies and tests were included in the developed Technological Regulations, on which the Technical and Economic Assessment of the Construction of an Alumina Plant in the Kostanay Region of the Republic of Kazakhstan was issued.

### **Approbation.**

According to the results of the thesis, 7 articles were published, including:

- 1 article in the journal, included in the Thomson Reuters database (Hydrometallurgy);
- 1 article in the journal, included in the Scopus database (Annals of the Brazilian Academy of Sciences);
- 5 articles in journals recommended by the Committee for Control of Education and Science of Republic of Kazakhstan Department of Education and Science.

The hypothesis and main results of the thesis were presented and discussed at international conferences Proceedings of the Bauxite residue valorisation and best practices conference. Leuven, Belgium (October 5-7, 2015); Proceedings of the 16<sup>th</sup> International Multidisciplinary scientific geoconference SGEM 2016, Albena, Bulgaria (30 June- 6 July, 2016); Proceedings of the International conference Resource-saving and environmental protection for the enrichment and processing of mineral raw materials, Saint-Petersburg (2016); Proceedings of the International conference Combined processes of processing of mineral raw materials: theory and practice, Saint-Petersburg (May 19-20, 2015); Proceedings of the International

conference Resource-saving technologies in the enrichment of ores and metallurgy of non-ferrous metals, Almaty (2015); Proceedings of the International conference Recycling of industrial wastes as a pledge of environmental safety, Pavlodar (2016).

The novelty is confirmed by the Patent of the Republic of Kazakhstan "Method of electrochemical gallium extraction from alumina-alkaline solutions" №32400 dated 29.09.2017 and by the application for patent "Method for processing red mud" № 2017/1023.1.

**Volume and structure of the work.** The dissertational work is stated on 140 pages, contains 43 figures, 31 formulas and a list of references of 122 tiles.