

ABSTRACT

for the thesis «Development of technologies for enrichment of substandard raw materials and waste of phosphoric industry of the Republic of Kazakhstan» by **Raiymbekov Yerkebulan Batyrbekuly**, submitted for the degree of Doctor of Philosophy (PhD) in educational program 8D07160 – «Chemical Technology of Inorganic Substances»

The relevance of the problem. The Karatau phosphorite-bearing basin is the main source of raw materials for the production of phosphorus compounds in the country. At the global level, it belongs to a large deposit of phosphorites. The reserves of phosphorous rocks of the Karatau basin for P_2O_5 amount to about 700 million tons.

It is known that there are underground and open methods of extraction of phosphorites. In the Republic of Kazakhstan, during the extraction of phosphorites by an open method without sorting, a large amount of residual rocks is produced in the form of a phosphate-siliceous layer around the deposits. They make up the off-balance stock of Karatau phosphorites with an average P_2O_5 content of 14-15%. Currently, 25 million tons of these technogenic mineral formations have been accumulated. In the foreseeable future, another 18-19 million tons of these residual rocks are expected to accumulate. A significant part of it was subjected to enrichment at the accumulation site and used in the production of phosphorous products. At this time, depending on their chemical composition, new secondary enrichment wastes are formed in the form of carbonate and silicon compounds. These wastes only on the territory of one Zhanatas suspension-processing plant amount to 350 thousand tons with a P_2O_5 content of about 15%. On the territory of the Karatau flotation processing plant, this volume of waste is 13 million tons. The average content of P_2O_5 in it is about 14-17%. The problem of enrichment and utilization of the above-mentioned secondary phosphate waste in the production of phosphorus industry has not found a rational solution today. The results of studies conducted using a number of methods of calcination, flotation and special depressants, surfactants, are limited only to the levels of laboratory studies and are still not used in production conditions, since efficiency and rationality are not consistently justified.

At the same time, one of the most urgent issues for the phosphorus industry in the country is to determine the possibility of involving low-grade reserves of phosphate raw materials in industrial exploitation. To do this, it is necessary to implement technological solutions for their enrichment. The reserves of low-grade phosphorites, which currently remain out of operation, amount to about 20 million tons. The depletion of currently existing phosphorite deposits, the presence of phosphorus (V) oxide in their composition at a low level leads to a decrease in demand on the world market of domestic mining raw materials and products made from them, which requires scientific research on enrichment and integrated use, which correspond to the objectives of the "Concept of development of the geological industry of the Republic of Kazakhstan to 2030", approved by the

Resolution of the Government of the Republic of Kazakhstan dated August 13, 2012 No. 1042.

In this regard, the search for new, technologically optimal, cost-effective opportunities for the enrichment of low-grade phosphorous raw materials and waste and the implementation of the results obtained is an urgent issue that meets the target content of the development strategy "Kazakhstan-2050".

Relation to the research work plan. The dissertation work was carried out in accordance with the scientific direction of the Department "Chemical Technology of Inorganic Substances" of the M. Auezov South Kazakhstan University within the framework of the state budget topic B-16-02-03 "Research on the creation of alternative and innovative technologies for the enrichment of raw materials and the production of products of the synthesis of inorganic compounds from natural ore and mineral resources and technogenic waste of various industries" for 2016-2022 and NIR-21-03-02 "Development of new promising technologies and improvement of traditional technologies for the production of inorganic products, environmentally friendly fertilizers and plant growth stimulants based on mineral raw materials and man-made waste" for 2021-2025.

Research objects. Phosphate-siliceous slates of the Zhanatas deposit, low-grade phosphorites of the Akzhar and Chilisai deposits; enriched phosphate concentrates, acetate solution.

Research methods. During the chemical analysis, photometric, gravimetric and titrimetric research methods were used. A scanning electron microscope was used to determine the element-weight composition and microstructure of the samples. The mineralogical composition was determined using a metallographic microscope, and infrared spectroscopy was performed using an IR-Fourier device. X-ray diffraction analysis was carried out on a Bruker D8 diffractometer (Germany) on the basis of JSC "Institute of Metallurgy and Enrichment", part of K.Satpayev KazNRTU. Thermodynamic analysis of the processes of enrichment of low-grade phosphorites with acetic acid was carried out on a modern, multifunctional software package HSC 9.3, based on the principle of maximum entropy and minimization of Gibbs energy. Statistical and mathematical processing of the experimental data obtained was carried out in the Statistics Online application.

Purpose and objectives of the study. Development of a scientifically based technology of acetic acid enrichment of substandard phosphate raw materials and waste of the phosphorus industry on phosphorus oxide (V) based on the study of their material composition.

To achieve the purpose, the following scientific tasks were solved:

- analysis of methods of enrichment of substandard phosphate raw materials based on well-known scientific publications and patent research;
- based on chemical analysis, element-weight, IR spectroscopic, X-ray diffraction and mineralogical analyses to establish the material composition of phosphate-siliceous slates of the Zhanatas deposit, low-grade phosphorites of the Akzhar and Chilisai deposits;

- study of chemistry and thermodynamic justification of the processes of enrichment of substandard raw materials and waste of the phosphoric industry with acetic acid;

- determination of optimal regime parameters of enrichment processes, study of the kinetics of processes, statistical and mathematical processing of experimental data;

- development of a schematic diagram of the enrichment process, conducting a feasibility study;

- description of the physico-chemical properties of enriched concentrates and by-products, assessment of their suitability;

- study of the regeneration process of acetate solutions formed during the enrichment of substandard raw materials and waste of the phosphoric industry with the help of sulfuric acid, determination of optimal regime indicators.

Scientific novelty:

- for the first time, the regularities of the process of acetic acid enrichment of substandard raw materials (Akzhar, Chilisai phosphorites) and waste (phosphate-siliceous slates) by phosphorus oxide (V) have been established. As a result of experimental studies, it was found that the content of total P_2O_5 increased to 20.04% in phosphate-siliceous slates, to 22.19% in Akzhar phosphorites, to 25.58% in Chilisai phosphorites;

- it was found that as the temperature and time increase, the reaction rate decreases by 2-3 times. This is explained by the fact that acetate salts formed in the pulp as a result of the interaction of carbonates in the composition of phosphate raw materials with acetic acid have a significant diffusion resistance to the process under study. The "apparent" activation energy of the process of acetic acid enrichment of phosphate raw materials for three types of raw materials is 24.5 kJ/mol, 19.7 kJ/mol and 23.3 kJ/mol, respectively, and based on these values, it is established that the process under study is limited by external diffusion;

- the chemistry of the processes used in the basis of acetic acid enrichment of substandard raw materials and waste of the phosphorus industry has been identified and thermodynamically substantiated;

The main statements submitted for defense:

- the material composition of phosphate-siliceous slates of the Zhanatas deposit, low-grade Akzhar and Chilisai phosphorites;

- chemistry and thermodynamics of processes taking place in the acetic acid enrichment of substandard raw materials and waste of the phosphorus industry;

- established optimal regime parameters of acetic acid enrichment processes, kinetics of processes, results of statistical and mathematical processing of experimental data;

- developed schematic diagram, feasibility study of the enrichment process;

- studied physico-chemical properties of enriched concentrates and by-products, assessment of their suitability;

- the chemistry of the regeneration process of acetate solutions formed in the process of acetic acid enrichment with the help of sulfuric acid, certain optimal regime parameters of this process.

Practical significance:

- a cost-effective technology of acetic acid enrichment of phosphate-siliceous slates of the Zhanatas deposit, low-grade phosphorites of the Akzhar and Chilisai deposits has been developed;

- it is established that the enrichment process takes place at low temperatures and within a short period of time;

- the suitability of concentrates obtained as a result of enrichment for the production of phosphorus and phosphorus-containing products has been evaluated;

- the process of regeneration of acetate solutions using sulfuric acid was studied for the first time, the mechanisms of chemical reactions were established and thermodynamically substantiated.

- based on the results of the conducted research, a patent for a utility model was obtained.

The degree of reliability and approbation of the results.

The reliability of the results obtained is confirmed by the use of modern laboratory equipment, proven research methods, as well as methods of statistical processing of experimental data. Approbation of the process of enrichment of substandard raw materials and waste of the phosphorus industry with acetic acid was carried out in the form of experimental laboratory tests conducted in the scientific laboratory of the Zhambyl branch of Kazphosphate LLP (NDFZ).

Publications on the topic of the work.

Scientific articles published in journals included in the Web of Science / Scopus database:

1. Beneficiation of phosphate-siliceous slates via acetic acid // International Journal of Chemical Reactor Engineering (De Gruyter). – 2021. – Vol. 19, №11. – P. 1187-1195.

2. Review of methods and technologies for the enrichment of low-grade phosphorites // Reviews in Inorganic Chemistry. – 2022.

Scientific articles published in publications included in the list of the Committee for Control in the Field of Education and Science of the Ministry of Education and Science of the Republic of Kazakhstan:

1. Қаратау фосфориттерінің жарамдылығы төмен шикізаты мен қалдықтары өндірістік тауарлы шикізат ретінде // Қ.И. Сәтбаев атындағы ҚазҰТЗУ Хабаршысы. – 2020. – №1(137). – Б. 664-668.

2. Review of methods for enrichment of phosphate raw materials in the world // Bulletin of the Karaganda University, Chemistry Series. – 2020. – №2(98). – P. 92-96.

3. Recovery of used acetic acid via sulfuric acid // Bulletin of the Karaganda University, Chemistry Series. – 2020. - №4(104). – P. 149-162.

In the proceedings of the conference:

1. Resource Indicators of Phosphate Raw Materials in the World // Proceeding VII International Conference «Industrial Technologies and Engineering» (ICITE – 2021) (Shymkent: M. Auezov South Kazakhstan University, 2021. – 10-11 November 10-11. – Vol. 1. – P. 60-62.

Structure and volume of the thesis.

The thesis consists of 137 pages, including 4 sections, contains 61 figures and 60 tables, 154 sources of used literature, 4 appendixes.