# ANNOTATION

to the thesis of Arystanova Saltanat Dauytbekovna on the theme "Development of technology of obtaining sorbents from natural mineral raw materials for the purification of phosphorus-containing sludge", presented for the degree of Doctor of Philosophy (PhD) on the specialty 6D072000 - "Chemical technology of inorganic substances"

**Actuality of the theme of research.** At present, one of the topical issues in the development of science and technology is the processing of natural and man-made waste. In recent years, hazardous wastes from our country's production represent a serious environmental problem and to date, special attention is paid to their processing and recycling.

Due to intensive air pollution, the main focus is on restoring original state of the environment, improving environmental situation with the development of new technologies and increasing the economic efficiency of waste processing.

In support of this initiative, about 30 billion tons of economic, industrial, including 7.5 billion tons of toxic and liquid wastes were processed in Kazakhstan. At present unprocessed waste creates an acute environmental problem.

Thus, in order to improve environmental situation in the regions, it is necessary to carry out measures to ensure a step-by-step and comprehensive reduction of emissions into the atmosphere of harmful wastes, complete and comprehensive purification of waste technological gases.

The research conducted over many years has shown that in recent years the concentrations in the air of harmful substances released by phosphorous enterprises have increased.

The industrial-innovative development strategy of the country should be carried out taking into account the achievements of science and technology in the chemical industry, including in the phosphorous industry.

Technological processes associated with integrated waste processing should be aimed at obtaining finished industrial products. At the same time, the main goal is to expand the range of products, meet the needs of the domestic market and increase export potential.

The production of phosphorus is characterized by the formation of man-caused waste - phosphorus sludge, toxic dust and gaseous compounds. The main sources of air pollution with harmful substances are enterprises producing phosphorus and its compounds. Despite the fact that at the last time phosphorus production has significantly decreased, the state of the environment is still tense. Therefore, studies aimed at processing natural and man-made waste are relevant.

Despite numerous methods used for processing and utilization of phosphorus-containing sludges, they have not been widely used due to the lack of appropriate equipment and economic inexpediency. Methods for the isolation of phosphorus from the sludge differ from each other by their technological differences. Therefore, new ideas aimed at finding rational ways of extracting phosphorus from slime are indisputable.

Sorption extraction of phosphorus from sludge is based on the usage of sorbents based on local aluminosilicate minerals with a developed hydrophilic surface and mesoporosity. Such sorbents under the conditions of dynamic process are capable to absorb mineral and organic impurities that stabilize phosphorus emulsion in water. As a result, the structure of phosphorus sludge is broken and the process is accompanied by the spreading of liquid phosphorus under the action of its own gravity.

**Purpose and methods of the research.**

The purpose of the work is to prepare sorbents from local natural minerals and use them to extract phosphorus from sludge.

Advantages of the offered method, in contrast to other existing methods, are as follows:

- possibility of organizing continuous process by adding new sorbent and removing the sorbent used in the process;
- ability to process any dispersion sludge;
- possibility of processing sludge with phosphorus content <50%;
- possibility of using sorbents on the basis of local deposits of aluminosilicate minerals;

To achieve these goals, the following tasks were solved in the thesis:

-chemical and mineralogical compositions of phosphorus sludge and aluminosilicates have been determined;

- acid-alkaline properties of aluminum silicates, textural properties (identification of physical and chemical properties of primary materials)were studied;
- influence of technological additives on mechanical strength and water resistance of sorbents was studied;
- Thermodynamic modeling of systems, determination of kinetic regularities and mechanism of phosphorus separation from phosphorus-containing sludge (detection of thermodynamic and kinetic regularities of the process)were studied;
- destruction of the structure of phosphorus sludge by sorption with solid aluminosilicate sorbents was studied;
- technological scheme has been developed for the process of phosphorus extraction from phosphorus-containing sludges with sorbents obtained from solid porous aluminosilicate materials.

Based on the results of the research, possibility of isolating phosphorus from phosphorus-containing sludges with sorbents on the basis of available aluminosilicates was determined.

**Scientific novelty of the work.** The following scientific results were obtained in the thesis:

- physico-chemical and mechanical characteristics of the initial used materials are determined with modern methods of physical and chemical research;
- acid activation of the surface of sorbents, increasing their sorption capacity was carried out;

-influence of the temperature regime of heat treatment of sorbents on their strength properties was studied;

- mathematical model of the process of obtaining sorbents with method of multifactor analysis was obtained;

- thermodynamic modeling of the sorption process was studied with research of the equilibrium distribution of elements and connection, depending on the temperature and duration of the experiments;

- kinetic regularities of the sorption process and mechanism of absorption of mineral particles on the surface and pores of sorbents were studied;

-useful model to "Method of obtaining sorbents for phosphorus isolation from phosphorus sludge" was obtained (Patent for useful model 98255, published in bulletin No. 11, 15/06/2016).

**Practical significance.** As a result of the conducted researches recommendations and technological decisions on the organization of the process of phosphorus extraction from sludge with sorbents on the basis of local aluminosilicate minerals are given.

Principal technological scheme of the process of obtaining aluminosilicate sorbents and their usage for the phosphorus separation from sludge has been developed.

The developed technology allows processing main man-made waste of phosphorus production - phosphorus-containing sludge.

The obtained experimental results are confirmed with acts of semi-industrial tests implemented at LLP "Kazphosphate" Oil refinery and LLP "Kainar". The results of the work are also introduced into the educational process of the department "ChTIS" for the passage of curricular practical training.

**Objects of the research.** The objects of the research were phosphorus sludge of the enterprises producing phosphorus-LLP "Kazphosphate" NDFZ and LLP "Kainar". To obtain high-quality sorbents, we used aluminosilicate materials, such as Darbaza bentonite clays, Kulantau vermiculites and refractory clays of the Lenger deposit.

**Methods of the research.** In the course of the work, modern methods of physico-chemical studies (XRD, X-ray diffraction, SEM, DTA) and chemical analysis for determining qualitative and quantitative composition of substances were used to determine basic physicochemical and structural characteristics of raw materials.

Mathematical modeling was carried out using a program designed for multifactor experiments using regression equations.

Thermodynamic modeling of the systems inherent in this process was carried out using software package OUTKOMPU with package of documents of the sub-program HSC-5.1.

Rotinyan-Drozdov equation was used to process kinetic results.

**Subject of the study.** Obtaining sorbents from aluminosilicate minerals to isolate phosphorus from phosphorus sludge.

**Connection of work with the plan of scientific programs.** The thesis was conducted in accordance with the themes of state budgetary works of the M.Auezov South Kazakhstan State University and the department "Chemical technology of inorganic substances": B-16-02-03 "Research on the creation of

alternative-innovative technologies for the enrichment of raw materials and obtaining products of synthesis of inorganic compounds from natural ore and mineral resources and man-caused waste of various industries "and project of financing grants of the Ministry of Education and Science of the Republic of Kazakhstan №68-31 "Usage of aluminosilicate sorbents for phosphorus extraction from phosphorus-containing sludges". Research work was also carried out in the laboratory of LLP «Kaynar» and LLP «Kazfosfat» NDFZ and special scientific laboratory of the St. Petersburg State Technological Institute (Technical University) named after Lensovet.

**Basic provisions to be protected:**

- results of comprehensive study of the composition and properties of raw materials - phosphorus sludge, bentonites, vermiculites and refractory clays;
- influence of the technological regime (T,P) of the process of obtaining sorbents on their physicochemical characteristics;
- acid activation of the surface of sorbents in order to improve their sorption capacity;
- mathematical planning of experiments in the process of obtaining sorbents using program of calculation of empirical coefficients with the method of least squares.
- thermodynamic modeling of basic systems with determination of the degree of equilibrium transition of elements and compounds between reaction participants;
- kinetic regularities of the process of phosphorus separation from sludge with Rotinyan-Drozdov equation with the definition of the values of the "Appearing" activation energy. The mechanism determination of absorption of mineral particles and organic impurities with sorbents on the basis of aluminosilicate materials;
-principal technological scheme of the developed technology with techno-economic justification.

**The main results of the study.** The thesis on the development of technology of sorbents production from natural mineral raw materials for purification of phosphorus sludge has the following conclusions:

1.From the analysis of data from literature sources and experimental studies, phosphoric sludge represents phosphorus emulsion in water stabilized with mineral particles. To isolate phosphorus from sludge with stable structure, it is recommended to absorb solid mineral particles with sorbents based on highly porous aluminosilicates with a developed surface.

2.The physical and chemical characteristics of the starting materials were determined with modern methods of analysis. Main compounds and minerals that are present in the primary feedstock have been determined with methods such as XRD, DTA, X-ray, SEM and chemical analysis. Main phases of phosphorus sludge are phosphorus, anhydrate phosphorus, calcium, aluminum, magnesium and monosilicates. During the research it was found that main minerals of clay bentonite clay, vermiculite and Lenger refractory clays are montmorillonite. In addition to the basic minerals, kaolinite, hydrargite, and hydrolysates with the presence of hornblende profiles and other minerals are also found.

3. Analysis of elemental and weight compositions of aluminosilicates used in the thesis are in %: Si-22,95, Al-7,85-10,26, K-1,84-2,45, Na-0,6-1,17. The content of alkaline earth metals is from 0,62 to 1,74%. Textural features of the mud are characterized with edges 2,5-3,4 and density 0,23-0,37 g/$cm^3$. Bloating vermiculite in comparison with refractory and bentonitic clays is from 3,3 to 4,6 and bulk density of 0,32 g / $cm^3$.

4. As a result of chemical activations, the sorption capacity of sorbents was increased. The disadvantages of chemical activation can be: the cost of expensive acids reducing mechanical strength of sorbents and formation of acid waste water. With acid activation, surface ions of hydroxyl groups are replaced with ions of aluminum silicates, volumetric exchange of various organic radicals with hydrogen ions. Treatment of clay minerals with hot acids leads to increasing in their catalytic, sorption and clarifying properties.

5. Two-factor analysis method was used for mathematical modeling the processing of experimental data. The dispersion for linear and quadratic functions was determined. The equivalent mathematical model was tested by Fisher's criterion. The experimental data are adequately characterized with linear and quadratic functions of the obtained regression. Thus, mathematical modeling of the process allows obtaining maximum information with minimal experimental studies.

6. Thermodynamic modeling of systems characteristic for phosphorus separation from phosphorus sludge using silicate, aluminosilicate and aluminosilicocalcium compounds corresponding to vermiculites, bentonite and refractory clays was carried out.

General regularity for all the systems under investigation is an increase in the formation of $H_3PO_4$ as the number of moles of $H_2O$ increases and also of the gaseous compounds $PH_3$(g). For the systems $P_4$-$SiO_2$-n$H_2O$, $P_4$-CaO·$Al_2O_3$-n$H_2O$, $P_4$-CaO-n$H_2O$, $P_4$-CaO·$SiO_2$·$Al_2O_3$-n$H_2O$, $P_4$-CaO-n$H_2O$, $P_4$-CaO·$SiO_2$-n$H_2O$, $P_4$-2CaO·$SiO_2$-n$H_2O$, $P_4$-CaO·$Al_2O_3$-n$H_2O$, $P_4$-$Al_2O_3$- n$H_2O$, $P_4$-n$H_2O$ distinctive feature is the possibility of the formation of phosphoric acid and phosphine.

7. Investigations of the temperature influence from 60 to $90^0$C and duration from 30 to 150 minutes on the degree of phosphorus extraction from phosphoric sludge with sorbents on the basis of aluminosilicate minerals have shown that with increasing in the magnitudes of these factors leads to an increase in the degree of phosphorus extraction. Moreover, the maximum degree of isolation of α ends at practically 120 min. Therefore, further increase in τ is impractical.

Based on the performed studies, it can be assumed that the limiting stage of the process is the diffusion of particles of the mineral part of the phosphorus sludge onto the surface and sorbent pores. It is diffusion processes that lead to the destruction of the structure of phosphorus sludge, contributing to the isolation of pure phosphorus from it.

8. The principal technological scheme of phosphorus extraction from phosphorus sludge using aluminosilicate sorbents with specification of technical and economic indicators is presented.

**Approbation of work.** The main results of the thesis were presented at the following international conferences: "Auezov Readings-14: Innovation Potential of Science and Education of Kazakhstan in the New Global Reality" (Shymkent, 2016);"III International Conference" International Conference of Industrial Technologies and Engineering "(Shymkent, ICITE - 2015); "Internatinalization of higher education. International Conference on Industrial Technology and Technology (Brussels, Belgium,2017),"Auezov Readings-15: The Third Modernization of Kazakhstan -New Concepts and Modern Solutions" International Scientific and Practical Conference (Shymkent,2017); "IV International Conference" International Conference of Industrial Technologies and Engineering "(Shymkent, ICITE-2017); Auezov Readings-16: International Scientific and Practical Conference "The Fourth Industrial Revolution: New Opportunities for Kazakhstan's Modernization in Science, Education and Culture" (Shymkent, 2018); "Ten Steps to the Fourth Industrial Revolution: the Potential of the Development of Human Capital" International Scientific and Practical Conference (Shymkent, 2018).

**Publications.** According to the results of the research, 18 articles were published, including 5 articles in the editions of the Committee for Control in the Sphere of Education and Science of the Ministry of Education and Science of the Republic of Kazakhstan, 4 articles in highly rated rating journals (included in Scopus and Web of Science data), 9 articles at international scientific and practical conferences of the RK and far abroad. The useful model of the Republic of Kazakhstan is obtained.

**Structure and scope of the dissertation.** The thesis is presented on 152 pages of computer text, including 37 tables and 81 drawings. The thesis consists of an introduction, six chapters, conclusion, the list of used literature and applications.