ABSTRACT

of the dissertation work of **Kozhakhmetova Aidana Maratkyzy** on the topic: **"Development of technology of obtaining prolonged action mixed fertilizer based on substandard phosphate-siliceous raw materials and TPS waste",** submitted for the degree of Doctor of Philosophy (PHD) in the specialty 6D072000 -"Chemical technology of inorganic substances"

Modern agriculture is facing global challenges — population growth, declining natural resources, and climate change. Under these conditions, the rational use of phosphorous fertilizers to increase crop yields is a priority task of science.

Kazakhstan has large reserves of phosphate raw materials from the Karatau and Chulaktau deposits. Phosphorite reserves exceed 2 billion tons, making the country one of the leading producers in Central Asia. However, most of the raw materials are low-grade, insoluble phosphates containing carbonates and silicates.

The direct use of such raw materials in agriculture is limited. Traditional processing methods (for example, the production of superphosphate by acid treatment) require high energy consumption and the use of aggressive reagents, while forming environmentally hazardous waste such as phosphogypsum. In addition, these technologies do not ensure the efficient use of low-grade raw materials.

The environmental aspects of phosphorous fertilizer production are closely linked to the UN Sustainable Development Goals, in particular SDG 2 "Ending Hunger" and SDG 12 "Responsible consumption and production". In Kazakhstan, these principles are implemented through the concept of "Green Economy" and the state program for the development of agriculture (2021-2025), aimed at reducing waste and introducing environmentally friendly technologies. However, the existing methods of processing phosphate raw materials do not fully meet these requirements.

A promising solution is the method of thermal activation of flour mixtures, in which brown coal, rocks and dolomite are added to phosphate raw materials. During heat treatment, the solubility of phosphates increases due to physico-chemical transformations without the use of acids. Brown coal acts as a reducing agent, dolomite provides an alkaline environment and a source of calcium, and silicate rocks contribute to the formation of active phases. This method not only increases the bioavailability of phosphorus, but also allows the disposal of mining waste, the volume of which in Kazakhstan reaches tens of millions of tons per year.

Thermal activation also has economic advantages — it reduces dependence on imported fertilizers and reduces production costs by 20-30%. However, the process requires an in-depth study of the kinetics of solid-phase reactions and the effect of impurities on the solubility of P_2O_5.

The features of Kazakhstani phosphorites (high content of carbonates — up to 30%) make the addition of dolomite especially effective for increasing solubility. The use of local resources, such as brown coal from the Maikube and Shubarkul deposits, further reduces production costs.

Thus, the development of technology for thermally activated pulp mixtures based on brown coal, rock waste and dolomite is an environmentally safe, economically feasible and strategically important area contributing to the sustainable development of Kazakhstan.

The purpose of the research development of technology of obtaining prolonged action mixed fertilizer based on substandard phosphate-siliceous raw materials and TPS waste.

Research objectives:

- To carry out a physico-chemical analysis of the initial components of flour mixtures (apatite raw materials, brown coal, rock dumps and dolomite) to determine their composition and properties.
- To study the effect of heat treatment temperature (100 °C, 250 °C, 400 °C, 500 °C) and exposure time (1, 2, 3 hours) on the solubility of P_2O_5in 2% citric acid.
- To investigate the decomposition processes of flour mixtures by methods of differential thermal analysis (DTA), thermogravimetry (TG) and differential thermogravimetry (DTG).
- To construct a kinetic model of the thermal activation process based on the Avrami–Yerofeyev method, to determine the reaction rate constant, the Avrami index and the activation energy.
- To evaluate the environmental and economic efficiency of the proposed thermal activation technology in comparison with traditional methods of processing phosphate raw materials.

Objects and methods of research. The objects of research are cyclone dust from the phosphorous production (new Zhambyl phosphorous plant), dolomitized carbonate-siliceous phosphate raw materials from the Aksai deposit, ash from the Ekibastuz field thermal power plant, enriched vermiculite and brown coal from the Lenger deposit, and internal overburden rocks.

Research methods: chemical analysis methods (spectrophotometry to determine the Pho_5 content), X-ray phase analysis (XFA) to determine the mineralogical composition, scanning electron microscopy (SEM) to study the morphology of particles were used to characterize the starting materials.

The thermal processes were studied using differential thermal analysis (DTA), thermogravimetry (TG), and differential thermogravimetry (DTG) on a Jupiter STA 449 F3 device (Netzsch, Germany) in the temperature range of 25-1000 °C with a heating rate of 10 °C/min.

The solubility of P_2O_5 was determined by extraction with a 2% citric acid solution followed by spectrophotometric analysis.

The Avrami–Yerofeyev model was used to analyze the kinetics of the thermal activation process. Its parameters (reaction rate constant k, Avrami index n, activation energy Ea) were calculated by linear regression.

Statistical data processing was carried out using the OriginPro 2021 program; the reliability and confidence intervals of the results were determined.

The main provisions of the thesis submitted for defense:

– Investigation of the effect of thermal activation of flour mixtures with additives of brown coal, rock waste and dolomite on the solubility of P_2O_5 at various temperatures and processing time.
– Development of a kinetic model of the thermal activation process based on the Avrami–Yerofeyev method, which made it possible to describe the mechanism of phosphate conversion and determine the key reaction parameters (rate constant, Avrami index, activation energy).
– The regularities of the dependence of the solubility of P_2O_5 on the composition of mixtures and heat treatment conditions, which contributes to the development of the theory of solid-phase reactions.
– The use of rock waste and brown coal in thermal activation processes, which opens up prospects for their use in the agrochemical industry.

The main results of the study:

– The effect of thermal activation of mixtures based on brown coal, rock waste and dolomite at various temperatures and treatment times on the solubility of P_2O_5 was systematically studied (as the temperature increases from 100°C to 500°C (from 6% to 21% in sample A and up to 23% in sample B) is explained by the conversion of phosphorus into active molds, and the processing time is from 1 to 3 hours);
– A kinetic model of the Avrami–Yerofeyev thermal activation process has been developed that describes the mechanism of phosphate transformations and makes it possible to determine the key reaction parameters (rate constant, Avrami index, and activation energy values equal to A – 7.33 kJ/mol, B – 7.59 kJ/mol, C – 9.01 kJ/mol, D – 6.72 kJ/mol, D – 6.72 kJ/mol);
– The regularities of the dependence of solubility P_2O_5 the composition of the mixtures and the conditions of heat treatment, which contributes to the development of the theory of solid-state reactions (In the temperature range of 400-500°C for pyrolysis of organic components, the decomposition of dolomite ($MgCO3 \rightarrow MgO+CO_2$) and solid-phase interactions significantly increased the solubility of P_2O_5);
– A new approach to the use of rock waste and brown coal in thermal activation processes is proposed, which opens up prospects for their use in the agrochemical industry;
- A feasibility study has been developed, which showed a production profitability of 58.7% and a payback period of 6.5 months, which confirms the practical significance of the technology.

Substantiation of the novelty and significance of the results obtained

– It was found that the high content of P_2O_5 (18.5–23%), CaO (24-24.8%), MgO (2.4–2.6%) and trace elements (Fe, Mn, Mg, S – 0.72%) in the flour mixtures of cyclone dust (65-71%), brown coal (6-8%), internal overburden (5-8%), phosphate-siliceous raw materials (5-8%), thermal power plant ash (4-8%) and vermiculite (7-10%), which confirms the raw material value and environmental expediency of their use.

– It has been shown that an increase in the processing temperature (100-500 °C) promotes the formation of calcium phosphates and silicates and increases the release of P_2O_5 by 4-5 times, which ensures a prolonged effect of the mixtures.

– As a result of kinetic analysis using the Avrami–Yerofeyev model, it was found that the mechanism of nutrient release is based on the processes of nucleation and growth. A mathematical model has been developed to optimize the composition of fertilizers.

– It is shown that the yield of tomatoes increased by 6-10%, eggplant — up to 94-98%, pepper — up to 74-95%. Samples with a high P_2O_5 content (22-23%) were found to be the most effective.

– An environmental assessment was carried out, which established that the content of heavy metals is lower than the maximum permissible concentration (Cd < 0.1 mg/kg), and the use of flour mixtures improves soil structure and reduces the risk of eutrophication.

Theoretical and practical significance of the study:

The results of the work are of high practical value for agriculture and industry. The proposed thermal activation technology increases the availability of phosphorus in low-grade phosphate ores, which makes it possible to effectively use them as fertilizers. The use of mining waste and brown coal as additives reduces production costs and promotes the disposal of industrial waste, providing a positive environmental effect. Data on the kinetic parameters of the thermal activation process can be used to optimize production modes. In addition, the developed technology can be adapted for processing other types of phosphate raw materials, which will expand the scope of its application both in Kazakhstan and abroad.

Connection with the research plan. The dissertation research was carried out within the framework of the scientific research plan of the Department "*Chemical Technology of Inorganic Substances*" of the M. Auezov South Kazakhstan University. Work related to projects: for 2016-2020 — B-16-02-03 *"Creation of alternative innovative technologies for the production of products for the synthesis of inorganic compounds from natural mineral resources and man-made waste from various industries*"; for 2021-2025 — Research and development-21-03-02 *"Development of new promising 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"*.

"At the first stage (2016-2020), methods of processing technogenic waste from phosphorus production and natural mineral resources were investigated, which served as the basis for the selection of raw materials and the study of solid-phase interaction in the framework of the thesis. At the second stage (2021-2025), research was conducted on the development of environmentally friendly fertilizers and the assessment of their impact on plant growth and productivity. These results were reflected in the dissertation regarding the development of a new nomenclature of flour mixtures, the study of kinetic patterns, the construction of a mathematical model and the development of a technological scheme. In addition, the feasibility study and analysis of the prospects for industrial implementation are consistent with the objectives of these projects to improve innovative technologies.

Thus, the dissertation research, complementing the strategic directions of the department's research plan, made a significant contribution to the implementation of its specific tasks.

The doctoral student's personal contribution to the preparation of each publication.

The author of the dissertation independently carried out experimental and analytical studies, including physico-chemical analysis, calculations and generalization of the results obtained. The author prepared and published materials on the research topic with the consulting support of scientific supervisors.

17 scientific papers have been published on the topic of the dissertation, including: 1 article in an international scientific publication included in the Scopus database; 4 articles in journals recommended by the National Research Council of the Republic of Kazakhstan; 8 articles in collections of international and national conferences; 2 patents of the Republic of Kazakhstan for a utility model were obtained, 2 THE ACT of conducting pilot tests.

1. The article "*Acquiring environmental safe mixed fertilizers containing trace elements on the basis of carbonate-siliceous dolomitized phosphate raw materials and wastes CHP"* in the *RASAYAN Journal of Chemistry* provides information on the chemical and mineralogical properties of man-made waste from industrial regions of Kazakhstan. The ash and slag wastes of the Karaganda and Ekibastuz basins, as well as the dolomitized phosphate raw materials of the Aksai deposit, are considered. The results of physico-chemical studies and characteristics of the macro- and microelement composition of waste are presented.

2. The article *"About the production of fertilizer mixture with the use of technogenic waste"* in the journal *Izvestia NAS RK* presents the results of a study of samples of phosphate raw materials and dolomite from the Aksai deposit.

3. The article *"Research of the composition of low-rated phosphorites of the Aksay deposit as a component of fertilizer"* in the journal *Izvestia NAS RK* of the National Academy of Sciences of the Republic of Kazakhstan presents the results of differential thermal and IR spectral analysis of dolomitized phosphate-siliceous raw materials of the Aksay deposit.

4. The article *"Production of fuel mixture based on broken silicon-phosphate raw material and CHPP waste*" in the journal *Izvestia NAS RK* of the National Academy of Sciences of the Republic of Kazakhstan provides data on the mineralogical and chemical properties of man-made coal mining waste and mining enterprises for the extraction of phosphate and siliceous raw materials in the Karatau phosphorous basin. The chemical and mineralogical compositions of ash and slag waste from thermal power plants formed after coal combustion in the Karaganda and Ekibastuz basins are presented.

5. The article *"Development of technology for acquiring integrated fertilizer from solid waste of production"* in the *journal Reports NAS RK* presents the results of chemical analyses of charge components to obtain a new environmentally safe nomenclature of flour mixtures.

6. The article *"Research on the production of flour mixtures based on waste from dolomitized phosphate raw materials, ashes from thermal power plants and*

coal mining" in the journal *Successes of Modern Natural Science examines man-made waste from various enterprises that can be used as raw materials in the production of fertilizers*. Data on the chemical and mineralogical properties of coal mining waste from the mining complex for the extraction of phosphate and siliceous raw materials in the Karatau phosphorous basin are presented.

The author's contribution to the preparation and publication of scientific materials is disclosed in the dissertation and confirmed by relevant publications.

The structure and scope of the dissertation. The thesis consists of 140 pages, includes 4 sections, 62 figures and 26 tables. The list of sources used includes 133 names. The appendices contain 5 additional materials.