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STUDY OF THE PROCESS OF OBTAINING NITROGEN-PHOSPHORUS FERTILIZER FROM WASTE OF PHOSPHORITE MINING INDUSTRY

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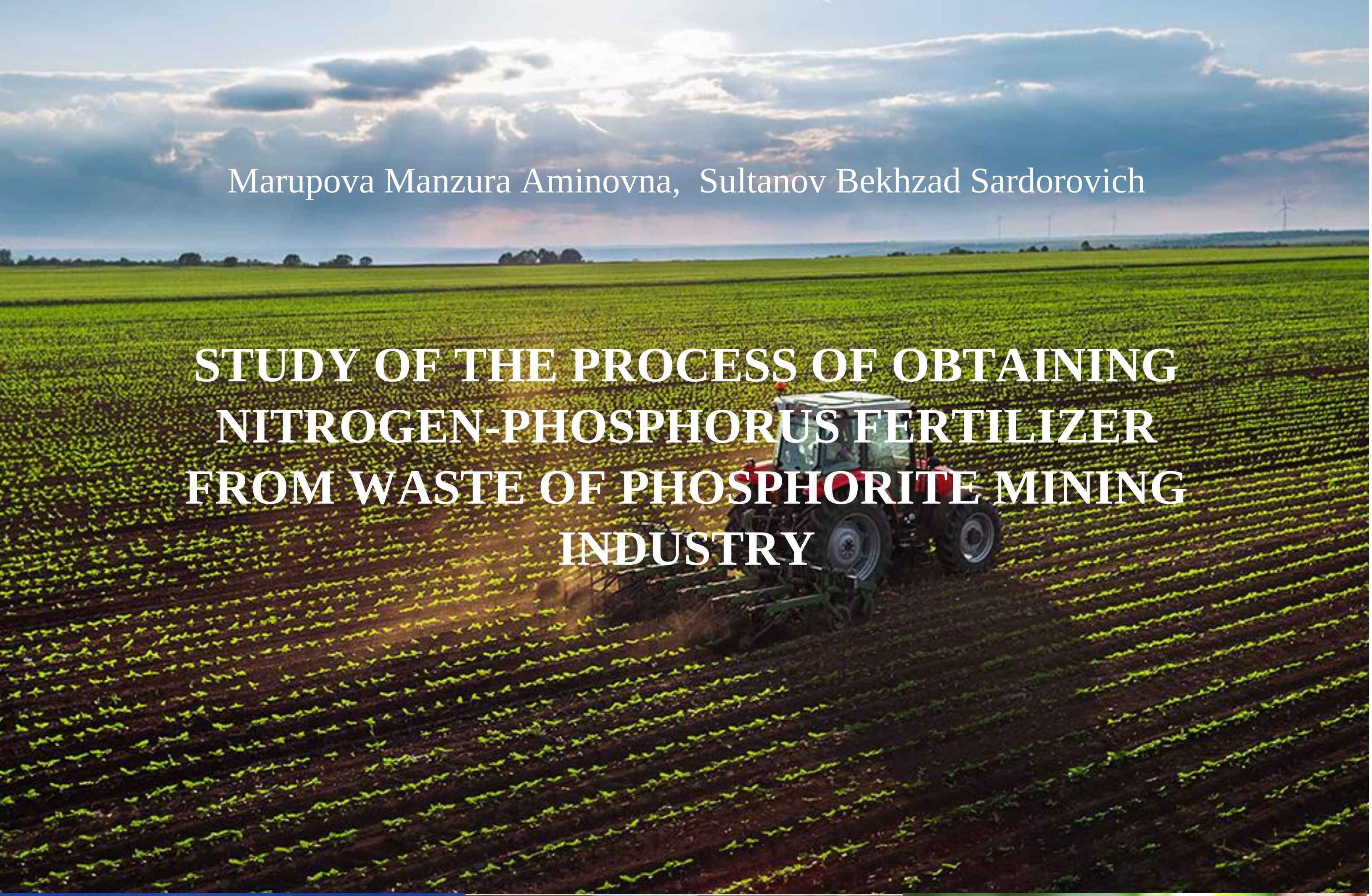

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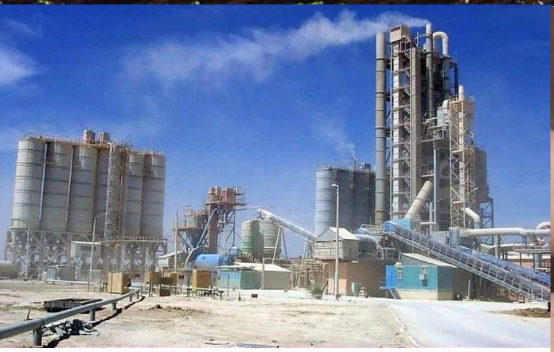

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STUDY OF THE PROCESS OF OBTAINING NITROGEN-PHOSPHORUS FERTILIZER FROM WASTE OF PHOSPHORITE MINING INDUSTRY

MONOGRAPH

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Marupova M.A., Sultanov B.S. Study of the process of obtaining nitrogen-phosphorus fertilizer from waste of phosphorite mining industry. Monograph.

In this monograph, the processing of mineralized mass (MM) of phosphorites of the Central Kyzylkum from the waste of the Kyzylkum phosphorite plant with extraction phosphoric acid (EPA), neutralized with ammonia with a pH of 1.2 to 2.2, was studied. In this case, the mass ratio of partially ammoniated EPA to MM varied from 100 : 15 to 100 : 50 at an interaction time of 30 min and a temperature of 60°C. It has been found that if the pH value of EPA and the mass ratio of partially ammoniated EPA to MM is lower, then the values of usable and aqueous forms of P_2O_5 are accordingly less.

The monograph is intended for scientists and specialists working in fields of chemistry and technology of mineral fertilizers, agrochemistry and soil science, as well as for bachelor's and master's students studying the above specialties.

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CONTENT

INTRODUCTION

The most important sector of the economic development of our country, as in many countries, is agriculture. Since Uzbekistan exports and imports mineral fertilizers, the role of producing enough quality single-sided as well as complex fertilizers for a successful harvest is directly related to the level of the country's economy. Therefore, both the provision of agriculture with mineral fertilizers and the possibility of increasing the export of mineral fertilizers to the world market depend on the situation on the world market. Population growth and reduction of cultivated areas in the world lead to an increase in demand for mineral fertilizers, which is one of the leading factors in the growth of prices for these products.

Currently, the world's largest producers of mineral fertilizers are China, which occupies more than 25% of the global market, India (about 13%), the USA (about 10%) and Russia (about 8%). In recent years, the US share of the global fertilizer market has been gradually declining. The world market of mineral fertilizers includes three main segments of nitrogen, phosphorus and potash fertilizers. The share of nitrogen fertilizers is approximately 59%, phosphorus - 24% and potash - 17% of the world market [1].

High demand for nitrogen fertilizers is due to quality characteristics (nitrogen is the main component of protein) and availability. The raw materials for them are mainly natural gas, oil and coal. Therefore, enterprises from about 60 countries are engaged in the production of nitrogen fertilizers. A significant part of them is located in Latin America and the Middle East. The competitive advantages of these countries are the relatively low cost of labor, a large number of reserves and a high level of hydrocarbon production.

The situation on the market of phosphate fertilizers is as follows: more than 175 countries are consumers, only 30 countries produce phosphate raw materials, and about 40 countries are producers of phosphoric acid and its products. The basis for their production are phosphorites and apatite ores, and the deposits do not have a geographical concentration. At the beginning of 2019, the estimated need of agriculture in Uzbekistan for mineral fertilizers amounted to 395 thousand tons, including nitrogen - 221 thousand tons, phosphorus - 162 thousand tons, potash - 12 thousand tons. Currently, the production of phosphate and potash fertilizers provides only about 30% of demand (2019) [1].

Therefore, the "Strategy of Action in Five Priority Directions for the Development of the Republic of Uzbekistan for 2017-2021" was put forward, among the tasks of which is the modernization and accelerated development of agriculture. According to the Decree On Measures for the Accelerated Development of the Chemical Industry of the Republic of Uzbekistan [2], the President instructed to increase the production of phosphorus, polyvinyl chloride and caustic soda, for which the task was set to build two plants, and Ammophos-Maxam JSC was instructed to produce 20 tons more phosphoric fertilizers, polyvinyl chloride, caustic soda - by 75 thousand tons, methanol - by 300 thousand tons, nitric acid - 500 thousand tons at Navoiazot JSC, ammonia with a capacity of 660 thousand tons, carbamide - 577.5 thousand tons at Navoiazot JSC, modern polymer wallpaper - 7.8 million units at JSC "Ferganaazot" with the attraction of foreign direct investment.

It should be noted that the global intensification of agricultural sectors leads to an ever-increasing consumption of mineral fertilizers, in particular, phosphorus-containing ones. When using phosphorus-containing fertilizers, the quality indicators of agricultural crops are improved, and their resistance to adverse climatic conditions also increases.

World experience in the production of phosphorus-containing fertilizers shows that the annual increase in capacity and the range of finished products leads to the depletion of high-quality natural phosphate raw materials. In the current situation, it is expedient to involve low-grade phosphorites in the industrial production, the reserves of which are practically inexhaustible. But the main difficulty in processing this type of raw material is that they have distinctive features in terms of mineralogical, chemical and fractional composition, which create difficulties in their processing by traditional methods [3].

In the agro-industrial sector of the Republic of Uzbekistan, the state of production of phosphate fertilizers for growing cotton and the restoration of its traditional supplies to Russian enterprises is characterized as unsatisfactory for both countries. The production facilities for the processing of phosphate raw materials created in the Republic of Uzbekistan turned out to be cut off from the deposits of phosphate raw materials located in the Republic of Kazakhstan (Karatau), the supply of which to Uzbekistan ceased for various reasons.

At the same time, on the territory of the Republic of Uzbekistan, there are deposits of phosphate raw materials with a low content of the main substance P_2O_5 and a rather high content of chlorine and carbonate admixtures, the development of which requires large capital investments. Under the current conditions, the solution of strategic tasks of restoring the production of phosphate fertilizers in the Republic of Uzbekistan based on the use of its own raw materials and new technologies for its extraction, enrichment and processing is a priority area of research and development.

Relevance of the research topic

The need of agriculture in Uzbekistan is provided with nitrogen, phosphorus and potash fertilizers by 100%, 33% and 59%, with their annual production in the amount of 839.58; 145.33 and 168.47 thousand tons in terms of 100% nutrients, respectively, and the need for them grows correspondingly with population growth [1]. The most difficult situation has developed with the production of phosphorus-containing fertilizers. Firstly, there is not enough raw material for their production, since the Kyzylkum phosphate ore is classified as “poor” containing 10-18%

phosphorus oxide, and these resources are decreasing from year to year. The reason is exacerbated by the lack of high-quality phosphate raw materials, while the need for agriculture in phosphate fertilizers is 746 thousand tons per year of 100% P_2O_5 [4].

Whereas all three chemical enterprises currently operating in the republic: JSC "Ammophos-Maxam", "Samarkandkimyo" and "Kokand Superphosphate Plant" annually produce about 135-140 thousand tons. per year of phosphate fertilizers in the form of 100% P_2O_5. This is due to the close relationship with the low quality of the original ore. At the same time, over 10 million tons of mineralized mass (12-14% P_2O_5) have accumulated in dumps at the Kyzylkum phosphorite plant - off-balance phosphorite ore, which is a waste of the process of enrichment of phosphorites that can also be used as a raw material for the production of nitrogen-phosphorus fertilizers.

The Kyzylkum Phosphorite Plant annually produces 716 thousand tons of washed calcined concentrate with 26% P_2O_5 (WCC-26) from 1875 thousand tons of phosphorite ore with an average content of 17.12% P_2O_5. The release of off-balance ores with the status of mineralized mass (12-14% P_2O_5) and sludge phosphorite (10-12% P_2O_5) into the dump is 42% of the original ore or 134.77 thousand tons of waste in terms of 100% P_2O_5 [4]. Under the conditions of an acute shortage of phosphate raw materials, it can also be involved in the production of phosphorus-containing fertilizers.

In a world with depleted reserves of high-quality deposits of natural phosphates, moreover, the extraction of which is becoming increasingly difficult and expensive, manufacturers of phosphate fertilizers have begun to focus on the processing of low-grade, especially carbonate-phosphorite ores (15-20% P_2O_5), which account for two thirds of the world's reserves. [4].

To do this, it is necessary to substantiate the relevant scientific and technical solutions, including the involvement in the technology of ammophosphate fertilizers of low-grade phosphorites of the Central Kyzylkum (CK) as a secondary raw material; establishing the optimal mode of concentration of extractive phosphoric acid by the evaporation method; finding the optimal conditions for obtaining double superphosphate and concentrated nitrogen-phosphorus fertilizer based on the interaction of low-grade phosphorites of evaporated EPA using a cyclic decomposition method.

Certain results have been achieved in the republic in the field of unilateral phosphorus (simple and enriched superphosphates) and complex fertilizers (ammophos, PS-Agro, ammonium sulphate phosphate, suprefos, Ammonium Phosphate fertilizer, NPK based-fertilizer) based on acid processing of phosphorites by CK. The third direction of the Action Strategy of the Republic of Uzbekistan has set forward tasks for the period of 2017-2021 to come up with high-tech processing industries especially for the production of high-quality finished products based on utilization of local raw materials [2].

In this regard, the development and implementation of a rational and economic solution that ensures the maximum degree of use of raw materials, the reduction of mineral acids and waste is an urgent problem. In this aspect, one of the promising methods can be considered a cyclic method of processing CK phosphorites with one stripped off EPA into concentrated phosphorus and nitrogen-phosphorus fertilizers, which are necessary for application both for autumn plowing and for sowing and feeding plants.

This monograph to a certain extent serves to fulfill the tasks stipulated in the Decrees of the President of the Republic of Uzbekistan PP-3236 dated August 23, 2017 "On the program for the development of the chemical industry for 2017-2021" and PP-3983 dated October 25, 2018 "On measures to accelerate development of the chemical industry of the Republic of Uzbekistan”, in Decree UP-4947 dated February 7, 2017 “Action strategy in five priority areas of the Republic of Uzbekistan in 2017-2021”, as well as other legal documents adopted in this area.

The purpose of the study is to identify the optimal conditions for obtaining highly concentrated nitrogen-phosphorus fertilizers by phosphoric acid processing of mineralized mass with the status of "off-balance ore" obtained during the enrichment of phosphorites at the Central Kyzylkum Combine.

The objectives of the study are to study the process of interaction of phosphorites with a low content of phosphorus (V) oxide with partially ammoniated EPA to obtain ammophosphate in various ratios of the reagent to phosphorus and the acidity of the medium.

The object of study is low-grade phosphorites of CK, EPA, sulfuric acid, monocalcium phosphate, ammonia, mother liquor, phosphogypsum, and ammophosphate.

The subject of the study is the process of phosphoric acid processing of waste phosphorites of the Central Committee into ammophosphate using partially ammoniated EPA.

The theoretical and methodological basis of the study was the work of domestic scientists on the enrichment of phosphate raw materials and the production of nitrogen-phosphorus fertilizers, as well as the contributions of foreign researchers in this area. The basis of this study is a comprehensive analysis and a systematic approach to the study of the topic under consideration. When conducting research and presenting the material, general scientific methods were applied: theoretical and methodological analysis of literary sources, empirical research methods in the form of observation, experiment, description, measurement and comparative analysis. Chemical and physicochemical research methods were carried out: X-ray, IR spectroscopic, electron microscopic and optical emission spectroscopy with inductively coupled plasma (OES with ICP).

The use of these methods, as well as the analysis of the factual material, made it possible to ensure the objectivity of the findings and results.

The scientific novelty of the research is as follows: The optimal mass ratio of EPA : PR and pH of EPA was found at which an ammophosphate fertilizer was obtained with the highest content of digestible and water-soluble forms of P_2O_5, which has good physical, chemical and commercial properties.

The practical results of the study are as follows: A technology has been developed for obtaining ammophosphate fertilizer by involving a weak solution of ammoniated EPA and low-grade phosphorites without the stage of ammophosphate pulp evaporation on ammophos equipment.

The theoretical and practical significance of the study is that the development of the technology of ammophosphate fertilizers will make it possible to involve poor phosphorites in industrial production, while reducing the cost of deficient sulfuric acid by 20-25% and thereby increase the gross volume of concentrated phosphate fertilizers and meet the needs of agriculture for making under autumn plowing, with sowing and top dressing. This technology reduces raw materials and energy resources: sulfuric acid - by 15%, fuel - by 15%, phosphate raw materials - by 2%. The ecological situation of production is improving due to the reduction of phosphogypsum waste by 15%, the almost complete elimination of ammonia losses. Replacing 1_5% P_2O_5 of phosphoric acid with P_2O_5 of phosphorite in ammophosphate leads to positive technical and economic indicators.

Approbation of the research results

The results of this study were reported and discussed at the republican scientific and practical conference on strategic chemical problems held at the National University of Uzbekistan named after Mirzo Ulugbek in 2021, as well as at the republican scientific and practical conference on strategic issues of chemistry of complex compounds and analytical chemistry held at Termez State Pedagogical University in 2022

Publication of research results. On the topic of the monograph, a scientific article was published in the Russian journal Universum: technical sciences, 2022.

CHAPTER I. LITERATURE REVIEW

1.1. Natural phosphates, apatites and phosphorites

Phosphorus is a common element in nature. Its content in the earth's crust (clarke) is 0.08-0.12% (by weight) or about 0.07% of the total number of atoms in the earth's crust [3] . Due to the high activity of elemental phosphorus and its oxides, it forms minerals that are sparingly and sparingly soluble in water. More than 200 minerals [4] containing phosphorus are known. Of these, minerals of the apatite group, which are part of phosphate ores or phosphates, are of the greatest industrial importance. Natural phosphates, called agronomic ores, are the feedstock for the production of phosphorus compounds - elemental phosphorus, phosphoric acid, mineral fertilizers, feedstuffs, polyphosphates, etc.

Natural phosphorus ores from different deposits differ in their physical and chemical properties depending on the mineralogical composition, structure and content of impurities. They are divided into two main types - apatite and phosphorite. The phosphorus substance in both types of raw materials are minerals of the apatite group with the general formula $3M_3(PO_4)2*MX2$, where M is calcium, and X is fluorine, chlorine, and the OH group. Calcium, which is part of the phosphate part of the molecule, can be isomorphically replaced by strontium, rare earth elements, sodium; ion $PO_4{}^{3-}$ - ions $SO_4{}^{2-}$, $SiO_4{}^{4-.}$ The natural mineral as a variety contains fluorapatite, small amounts of chlorapatite and hydroxyl apatite.

Apatite ores contain minerals: nepheline $(Na,K)AlSiO_4$, pyroxenes - aegirine $NaFe(SiO_3)2$ and others, titanomagnetite Fe_3O_4 $FeTiO_3$, ilmenite $FeTiO_3$, sphene $CaTiSiO_5$. Pure fluorapatite Ca, feldspars, mica and others. $5F(PO_4)_3$ contains 42.23% P_2O_5, 55.64% CaO and 3.77% fluorine. In addition to minerals of the apatite group, phosphate ores contain other minerals - impurities. The most common in nature is calcium fluorapatite $3Ca_3(PO_4)_2{\cdot}CaF_2$ or $Ca_5(PO_4)_3F$, as well as hydroxyapatite $3Ca_3(PO_4)_2 \cdot Ca(OH)_2$ or $Ca_5(PO_4)_3OH$. Hydroxylapatite is found in the bones of animals.

In apatite ores, the main phosphorus-containing mineral is calcium fluorapatite and, in small amounts, hydroxylapatite and other forms of isomorphic substitution. Fluorapatite in the ore is in the form of translucent irregular crystals, slightly colored in green and yellow-green. The grains are sometimes shaped like hexagonal prisms. Apatites consist of large crystalline particles characterized by the absence of polydispersity and microporosity. The composition of chemically pure calcium fluorapatite is as follows: 42.23% P_2O_5, 55.64% CaO, 3.77% fluorine. Due to partial isomorphic substitution, natural pure mineral contains on average 40.7% P_2O_5 and 2.8–3.4% fluorine [5].

Phosphorites are characterized by fine crystalline structure, high polydispersity and porosity of particles. At the same time, the microstructures of the phosphate substance of various phosphorites are very diverse. The phosphate occurs both as a coagulated near-amorphous gel and in a distinctly crystalline form, although there are numerous intermediate groups. For example, relatively large and well-crystallized particles with a size of 1–2 microns predominate in the Karatau phosphorites, while particles with a size much smaller than 1 micron and very high porosity predominate in the Estonian Kingisepp phosphorites [5, 6].

Apatite ores, in addition to apatite, contain minerals: nepheline $(Na, K)AlSiO_4 \cdot nSiO_2$, pyroxenes - aegirine $NaFe(SiO_3)_2$ and others, titanomagnetite $Fe_3O_4 \cdot FeTiO_3 \cdot TiO_2$, ilmenite $FeTiO_3$, sphene $CaTiSiO_5$, feldspars, black mica, eudialyte . The amount of phosphate minerals in the earth's crust is no more than 0.75%. About 95% of phosphorus is in the earth's crust in the form of apatites, which are present in almost all igneous rocks in an extremely dispersed state and rarely form accumulations of industrial importance [7].

Large apatite deposits are of magmatic passage. There are hydrothermal formations of apatite, i.e., released from hot aqueous solutions. Apatite was also formed during the contact of magma with limestones. Phosphorite deposits arose as a result of the precipitation of phosphates from sea water. There are also formations of phosphorites close to francolite associated with hydrothermal solutions. Deposits of phosphate ores are located on almost all continents of our planet. They are divided into exogenous and endogenous. The first group includes deposits of a sedimentary nature, formed as a result of weathering of phosphorite-bearing rocks and apatites. Endogenous deposits are igneous in nature and are represented by carbonatite and apatite ores. The largest deposits of phosphate ores are located in Morocco (approximately 40% of all known reserves), as well as in China, North Africa, the USA, Mongolia, Jordan, South Africa, Vietnam, Peru and Algeria [1,6].

For the industrial production of phosphorus-containing fertilizers, only phosphate ores are used, which are classified according to their P_2O_5 content into the following rocks [3]:

1. very rich (more than 35% P_2O_5)
2. rich (28-35% P_2O_5)
3. medium quality (18-25% P_2O_5)
4. poor (10-18% P_2O_5)
5. very poor (5-10% P_2O_5)
6. phosphate-containing (0.5-5% P_2O_5).

Since the average content of phosphorus anhydride in the ores of Central Kyzylkum is 12 percent, it can be seen from the classification of ores that domestic ores fall into the category of "poor" requiring effective enrichment to obtain high-quality phosphorus-containing fertilizers.

1.2. Characteristics of phosphorites of the Central Kyzylkum and methods of their enrichment.

Phosphorites of the Central Committee are the main phosphate-raw material base of Uzbekistan for the production of phosphorus-containing fertilizers. Granular phosphorites of the Central Committee were studied by many scientists in the second half of the 1950s [6, 8]. In 1953-1955. M.E. Egamberdiev first discovered phosphorites in the Paleogene deposits of the Central Kyzylkum region [8]. On the recommendation of the scientist for further study of this raw material, in 1974, special geological exploration and scientific research was resumed with the establishment of a wide distribution of granular phosphorites in the explored area. Promising areas have been determined, the parameters, material composition and technological properties of ores have been studied.

The phosphorite content of the territory of western Uzbekistan was studied by the expedition "Khimgeolnerud" of the MG RUz, PGO "Kyzylkumgeologiya" and research organizations (IG and GAN RUz, SAIGIMS, VNIIgeolnerud, GIGHS, etc.). According to [7], in the Upper Cretaceous, Paleocene, and Eocene deposits, several industrial types of phosphorite ores have been identified: granular (African type), nodular (Chilisai), and halyno-gravel (Floridian).

According to the geological assessment, it has been established that phosphate layers occur at depths from 0 to 280 m, as a result of which it is possible to extract phosphorite ores, both by open and underground methods. In addition, they are characterized by a small thickness (0.3-0.8 m), their number in the formation varies from 1 to 7 [8]. The area of the Kyzylkum phosphorite-bearing basin occupies about 65 thousand km.

However, the industrial phosphorite content covers only 5% of this area, however, the predicted reserves of phosphorites with an average total thickness of their layers of 2.5 m are 16.25 billion tons or 1.95 billion tons of $P2O_5$ (with an average content of $P2O_5$ - 12%) [9].

The results of prospecting work testify to the discovery and study of marly granular phosphorite ores in the Kyzylkum on an area of 3000 sq. m. If we take into account that the calculated resources of phosphorites to a depth of 300 m are 10 billion t, approximately 2 billion t P_2O_5, then at depths available for open mining (up to 60 m), 1000-1200 million tons of ore or 200-240 million tons of phosphorus pentoxide [10; S. 10-16].

To date, four main deposits of granular phosphorites have been identified in the explored areas of the Central Kyzylkum basin, the so-called Jeroi-Sardara, Northern Dzhetymtau, Tashkura and Karakata. The reserves of these deposits have been identified in the bowels to a depth of 50 m and they are suitable for open-pit mining, the predicted share of which is more than 50% of P_2O_5 in the explored area. The total reserves of granular phosphorites are estimated at 10 billion tons of ore.

Among the estimated phosphorite deposits, the Jerooy-Sardara deposit can be attributed to the most promising. Among the 6 calcareous-clay deposits, two 1 and II are of industrial importance, the thickness of which is 0.2-1.2 m. Between them there is a marly layer with a thickness of 8-12 m. reservoir (60%), with a content of 20.93% P_2O_5. and in the 1st this indicator has 17.09% P_2O_5. In total, the forecast ore resources are estimated at 2.9-3.0 billion tons (550 million tons of P_2O_5).

In the Northern Dzhetymtau, only one layer is developed with a thickness of 0.8-1.5 m with an average content of 20.25% P_2O_5 and, in terms of technological characteristics, it is quite consistent with the Jeroy-Sardara field. Currently, it is listed on the balance sheet of the State Committee for Geology, it is not being developed, but the object has been prepared for industrial development.

The explored reserves of phosphorite ore of the Tashkurinskoye deposit were found in two layers 0.3-1.2 m thick with a content of 13-24% P_2O_5. In the indicated layers of the reservoir, the predicted resources of the deposit are 1100 million tons of ore or 200-250 million tons of P_2O_5.

The Karakata field consists of two sections - Aznek and Ayakuduk. The predicted reserves of raw materials are estimated at 600-650 million tons of P_2O_5 or 3000-3500 million tons of ore. Down to a depth of 60 m, it is 55-60 million tons of P_2O_5 (320 million tons of ore).

Granular phosphorites of the Central Committee are predominantly loose argillaceous-calcareous polymineral rock consisting of phosphatized shells of foraminifers, pteropods less than 1 mm in size, oolites, pseudoliths, fragments of pelecypod shells, gastropod nuclei, bone fragments, fish scales, etc. The polymineral rock itself is cemented with clay-carbonate cement and the P_2O_5 content in it varies from 15 to 26.7% [11, 12]. In these phosphorites, carbonate minerals have three forms: relics of calcite preserved from replacement by phosphate inside phosphatized shells - “endocalcite”; cement calcite - “exocalcite”; carbonate groups isomorphically included in the crystal lattice of the phosphate mineral [13].

The phosphate grain is represented by fluorocarbonate apatite (francolite) with a unit cell -4.0% CO_2 and up to 3% SO_3, isomorphically included in its crystal structure [14].

These two types of minerals - francolite (fluorocarbonate apatite) and calcite, together make up from 75 to 95% in the mass of raw materials. Calcite is characterized by close and deep intergrowth with the phosphate mineral. In phosphate grains, it composes both the pelitic fraction and unsubstituted valves of the fauna, which makes it very difficult to isolate carbonates. Its effective release from phosphorite ores is possible only by roasting them, followed by quenching with an ammonium chloride solution [8; S.84-86]. Such behavior of calcite in the composition of raw materials in the structure of the phosphate mineral was not found even in phosphorites similar to it from the deposits of the African-Arabian phosphorite province, processed at the enterprises of Morocco, Algeria, Tunisia, Jordan, Israel, Egypt and Iran, containing 20-30% P_2O_5 into commercial concentrates with 30-35% P_2O_5 [15; pp.7-12. 16; S. 17-20].

The composition of cement also includes another important component - a clay substance. The clay substance is characterized by a polymineral composition consisting of hydromica (21-87% fraction), montmorillonite (0-86%) and kaolinite (2-15%). In the total amount of clay minerals in the ore is 5-25%. The process of their isolation from cemented faunas with calcite can be carried out partially by washing or dry scrubbing before firing. Gypsum and hydrogoethite are always present as accompanying minerals in oxidized phosphorite ores, and organic matter up to 4% and pyrite up to 1% in non-oxidized ores. The ore of the Jerooy-Sardara deposit has the following mineral composition, (wt.%): francolite - 56.0; calcite - 26.5; quartz - 7.5 - 8.0; hydromicaceous minerals and feldspars - 4.0 - 4.5; gypsum - 3.5; goethite - 1.0; zeolite <1.0; organic matter - about 0.5 [17].

The average sample of the Jerooy-Sardara deposit contains (wt. %); 16.2 P_2O_5; 46.2 CaO; CaO: P_2O_5 = 2.85; 17.7 CO_2; 0.6 MgO; 2.9 (Fe_2O_3 + Al_20_3); 1.5 (K_2O+Na_2O); 2.65 SO_3; 1.94 F; 7.8 insoluble residue. This type of raw material is not suitable for acid processing in order to obtain from it qualified types of phosphorus-containing fertilizers. Therefore, it is necessary to enrich it. First you need to get rid of excess carbonates.

In world practice, the flotation method of enrichment operates. Flotation enrichment of apatite raw materials is successfully used in operating companies of the world, such as Brazil, South Africa and Finland with initial content of 4-5% P_2O_5 to obtain concentrates containing 36-39% P_2O_5 [18]. However, attempts at flotation enrichment did not lead to positive results. Although the works [19-21] show the possibility of enrichment of phosphorites with CC by the flotation method. Soap stock, an intermediate product of the oil and fat industry, was used as a flotation agent. The low recovery factor of the concentrate in the range of 60-65% and the use of scarce raw materials for detergents is the main disadvantage of this work [22; S.82-83, 23; 26 p.].

As an alternative to the above method, a chemical enrichment method using both inorganic and organic acids can also be cited. The method is based on the selective dissolution of carbonates.

Several works are devoted to this direction [24, p.3-7: 25, p.64-66; 26, pp. 10-13; 27, pp. 51-54; 28; 29, 20 s]. Thus, concentrated (57-59%) nitric acid was used to enrich phosphorites with CK. The developed method consists in the treatment of phosphorite with nitric acid with a concentration of 45-60%, taken in an amount of 90-110% of the stoichiometric norm required for the decomposition of calcium carbonate, for 10-15 minutes, followed by repulpation with a circulating solution containing 5-25% $Ca(NO_3)_2$, at a mass ratio of phosphate raw materials to $Ca(NO_3)_2$ solution equal to 1 : (2.0-3.5), settling the resulting nitrophosphate suspension for 5-10 min, washing the precipitate with water and drying the product. The disadvantages of this method are the low yield of the main component P_2O_5 in the phosphoconcentrate (56-65%), the non-filterability of the acid suspension and the formation of a large volume of acid effluents containing calcium nitrates and phosphates, which requires additional costs for its processing into solid fertilizers.

The authors of these works continued their research in search of ways to improve the process of chemical enrichment and eliminate losses of P_2O_5 in the liquid phase [30; pp.79-86, 31; pp. 26-34, 32; S. 51-54].

P_2O_5 losses are prevented by the use of gaseous ammonia in a system consisting of monocalcium phosphate and calcium nitrate. The following reaction takes place in this system:

$Ca(H_2PO4)_2 + Ca(NO_3)_2 + NH_3 = 2CaHPO_4 + 2NH_4NO_3$

The resulting dicalcium phosphate precipitates, and the extracted phosphorus is practically returned to the composition of the phosphorite concentrate. For enrichment were taken two types of phosphate rock composition (wt.%): 16.33-17.52 P_2O5, 47.13-47.53 CaO; 15.23-17.23% CO_2; 1.24-2.OO SO_2; CaO: P_2O_5 = 2.71 and 2.89, respectively, HNO_3 58.78% concentration. The norm of HNO_3 was taken as 40, 45, 50 and 60% in terms of CaO. Processing of phosphate raw materials (PR) with nitric acid was carried out for 25–30 min. The temperature of the reaction mass was maintained at 40 °C. After decomposition, the resulting nitrocalcium phosphate pulp was repulped with a 5–20% solution of calcium nitrate at various weight ratios of PR:$Ca(NO_3)_2$=1:(2–3) solution for 3–4 minutes.

Then the nitrocalcium phosphate solution was ammoniated with gaseous ammonia to a pH value of 3 in order to exclude the transition of P_2O_5 into the solution, then the liquid and solid phases were separated by filtration. Next, the resulting wet phosphorite concentrate was washed with water at a mass ratio of PR: H_2O = 1: 1.5. Wet phosphoconcentrates were dried at 100°C. Depending on the norm of HNO_3, the pH of the medium, the weight ratio of the PR: solution $Ca(NO_3)_2$, the concentration of $Ca(NO_3)_2$ (5-20%), the amount of wash water and its temperature (20-80°C) were obtained phosphorus concentrates with P_2O_5 content from 22.58 to 25.88% and from 24.03 to 27.14% with a calcium module from 1.83 to 1.47 and from 1.82 to 1.44, respectively. The research results show that the greater the amount of calcium nitrate solution and the higher the water temperature, the higher the degree of washing the latter from phosphoconcentrate increases from 93.04 to 94.78% and from 89.34 to 95.97%, respectively.

In order to bring to the minimum content of calcium nitrate in phosphoconcentrate in [33; S.279-285] offers three-time washing, simulating the washing of phosphogypsum in the production of EPA. The conditions of the experiment are the same, but differ in that to ensure the mobility of the pulp, a part of the 7.16-16.83% washing solution of calcium nitrate, returned from the first stage, was added to the original phosphorite. As the results of studies on a three-fold washing scheme of wet phosphorus concentrate at a ratio of PR: solution Ca (NO_3) 2 \u003d 1: (1.60; 2.29; 2.97) and a norm of HNO_3 - 50%, a phosphorus concentrate is formed with a content of P_2O_5 25 .90-26.1 1%; CaO 39.94-41.13%; CO_2 2.29-2.34% CaO: P_2O_5 = 1.53-1.59 and the degree of washing 96.52-98.92% $Ca(NO_3)_2$.

In the chemical enrichment of phosphate raw materials, the limiting factor is phase separation. Therefore, in [34; P.57-62] presents a detailed study of the process of filtering nitrocalcium phosphate suspension obtained on the basis of the decomposition of phosphorite flour composition (wt.%): 17.52% P_2O_3; 47.53% CaO; 15.23% CO_2 and CaO:P_2O_5 = 2.71 nitric acid 58.78% concentration at 40 °C for 25-30 minutes. followed by neutralization with gaseous ammonia to a pH value of 3, repulpation with a 10% solution of calcium nitrate at a weight ratio of PR: solution Ca $(NO_3)_2$ = 1: 2.5 for 3-4 minutes.

And to improve the pulp filtration rate, 0.1 was added to the neutralized nitrocalcium phosphate suspension; 0.2; 0.3; 0.4 and 0.5% aqueous solutions of various coagulants, such as Gipan-UM, aluminum sulfate, PC-2-3, K-9 and polyacrylamide (PAA). Among them, PAA with a concentration of 0.1 and 0.2% turned out to be the most effective (the filtration rate of the nitrocalcium phosphate suspension was 785.96 to 1028.8 kg/m 98% P_2O_5; 40.83-40.90% CaO; 2.28% CO2; CaO:P_2O_5=1.57-1.58. The degree of washing $Ca(NO_3)_2$ from the phosphoconcentrate is in the range of 97.26-97.83%.

Based on the above, the nitric acid method of phosphorite enrichment requires strict technological control when washing commercial phosphorus concentrate from calcium nitrate at certain ratios of PS: H_2O, maintaining the water temperature to the required value, and using expensive filtration reagents, which in turn creates unfavorable conditions for large-tonnage production.

Of scientific and practical interest is [35; pp.111-112. 36; pp. 121-124, 37; S.5-11, 38; pp.5-11, 39; P.15-23] nitric acid enrichment of phosphorites of the Central Committee using an organic solvent - ethanol to leach the resulting calcium nitrate from nitrocalcium phosphate pulp. The peculiarity of this method lies in the regeneration of ethanol and its return to the technological cycle. The essence of the developed technology consists in the decomposition of phosphorite flour of the CC composition (wt.%): 16.60-18.22 P_2O_5; 47.13-47.80 CaO; 14.90-17.23 CO_2 and $CaO:P_2O_5$ = 2.59-2.84 with 58.78% nitric acid, followed by leaching of calcium nitrate with ethyl alcohol (EA) with a concentration of 96%. The rate of nitric acid varied from 30 to 60% of the stoichiometry for the decomposition of CaO in the raw material and the weight ratio PR: EA = 1: (3-10). Phosphorite was treated with nitric acid for 20–30 min. at a temperature of 40°C. After decomposition, a thick nitrocalcium phosphate pulp is obtained, which was repulped with alcohol for 3-4 minutes, after which the contents were separated into liquid and solid phases by vacuum filtration. Wet precipitates were dried at 100 °C. So, when enriched with nitric acid with its norm of 30-45% of the stoichiometry and the ratio of PR: EA from 1: 3 to 1:10, the content of P_2O_5tot in the phosphorus concentrate increases from the initial 16.60% from 21.62 to 23.74%, and the content of CO_2 decreases from the initial 17.23% from 7.62 to 4.26%. At the same time, the degree of decarbonization of phosphate raw materials increases from 60 to 82%. The calcium module in this case decreases from the original 2.84 to 1.95 - 1.60.

The same authors proposed a method for neutralizing a nitrate-phosphate-alcohol suspension with ammonia (up to pH = 3) before separating it into liquid and solid phases, which prevents the transition of P_2O_5 into the liquid phase [40; S.37-40.41; pp. 114-121, 42; 70-80, 43]. The optimal conditions for the enrichment of raw materials were: HNO3 norm - 50%; PR : EA = 1: 5; pH = 3. Under these conditions, a phosphoconcentrate was obtained with the following composition (wt %): P_2O_5tot 26.20; CaOtot 38.25; CO_2 2.80 and CaO:P_2O_5=1.46. Such a concentrate meets the requirements of sulfuric acid extraction to obtain EPA. After the alcohol is distilled off, a concentrated nitroammonium-calcium solution is obtained containing 50% $Ca(NO_3)_2$ and 3% NH_4NO_3. However, the disadvantages of these studies are the use of a flammable liquid - alcohol, sealing of equipment is required, a large weight ratio of PR : EA and a low degree of calcium nitrate washing from phosphoconcentrate.

According to the results of [44; S.96-107, 45; S.573-586, 46; pp. 133-141. 47; pp. 41-48, 48; pp. 286-292, 49; 1459-1461, 50; P. 113-119] of world survey studies, chemical enrichment of carbonate phosphorites is possible with the use of organic acids, such as acetic, lactic, formic and succinic. Seitnazarov A.R. et al. systematically studied the process of enrichment of phosphorites with CK by acetic and formic acids [51; pp. 12-18; 52; S.215-221]. The optimal conditions for conducting the enrichment process were found: the acid rate is 11% of the stoichiometry for the decomposition of $CaCO_3$ in the raw material, the ratio S : L = 1 : 8, the temperature is 25°C, the mixing time is 30 min. It is shown that from ordinary phosphorite flour with a content of 16.33% P_2O_5; 17.23% CO_2; CaO : P_2O_5 = 2.89, you can get a concentrate with a content of 25.58% P_2O_5tot, 4.24% CO_2 and a calcium module of 1.66. Such a concentrate can be successfully processed by acid extraction into any type of phosphorus-containing fertilizers.

In any case, a reliable way to remove CO_2 and organic matter from carbonate phosphorites is thermal. Calcined roasting of phosphorites in rotating horizontal drums and in fluidized bed furnaces at a temperature of 800-950 °C is widely used in Algeria, Tunisia, Israel and Morocco [53; S.226-230]. In contrast to flotation, the yield of concentrate by thermal roasting is 90% with a content of 31% or more P_2O_5 [54; pp. 49-52, 55; pp. 15-19, 56: pp. 44-52, 57; pp. 387-407; 58; S. 35-42]. After roasting at 680-980°C, the ore is treated with water or salt solutions (sea water can be used) and calcium hydroxide is separated.

In 2001, the thermal method of enrichment of phosphate raw materials of the Central Committee was introduced into production at the Kyzylkum Phosphorite Plant (KPP). The finished thermal concentrate with a content of 28% P_2O_5 was sent to the Almalyk and Samarkand plants, now Ammophos-Maksam JSC and Samarkandkimyo JSC, for the production of ammophos. However, the content of chlorine in the concentrate in the range of 0.12-0.18% caused corrosion and failure of the equipment of enterprises. Manufacturers were faced with the question of reducing the chlorine content in raw materials to its permissible concentration (0.04% C1) [59; 460 p].

According to the Decree of the first President of the Republic of Uzbekistan I.A. Karimov No. PP-420 dated July 18, 2005, an industrial plant was built at KPP to wash phosphorite ore from chlorine. Starting from 2007 to 2014, KPP produced three types of phosphorite products: 400 thousand tons per year of washed calcined phosphorus concentrate (WCC) with a content of 27-28% P_2O_5; 200 thousand tons per year of washed dried phosphorus concentrate (WDC) with a content of 18-19% P_2O_5 and 200 thousand tons per year of ordinary phosphate rock with a content of 16-17% $P2O_5$. WDC served as a raw material in the production of simple ammoniated superphosphate at the Kokand superphosphate plant, and nitrocalcium phosphate fertilizer was produced from ordinary phosphorite flour at

Samarkandkimyo JSC. WCC is a raw material for the production of ammophos, suprephos and ammonium sulfate phosphate.

In 2014, within the framework of the project "Expansion of the existing production for the enrichment of phosphorite raw materials" on the basis of KPP, according to the new technological scheme, the production capacity of WCC was increased from 400 thousand tons to 716 thousand tons per year with an average content of P_2O_5 of at least 26%. However, the currently functioning technological scheme of enrichment at KPP cannot be considered rational. Since the new enrichment scheme does not provide for the associated production of WDC and ordinary phosphate rock. And the increase in the concentration of P_2O_5 in the WDC (26% P_2O_5) compared to its concentration in the original ore (17.58%) by only 8.42% occurs against the background of a significant loss of P_2O_5 (134.77 thousand tons of P_2O_5 or 42% of the original P_2O_5 in ore) with enrichment tailings with the status of "off-balance ore". Of these, 9.6% occurs during dry sorting at the site of the ore control station, 28.3% during hydrosorting and 4.1% at the stages of drying and roasting. This is, respectively, a mineralized mass (12-14% P_2O_5). sludge phosphorite (10-12% P_2O_5) and pulverized fraction (18-20% P_2O_5). To date, more than 10 million tons of mineralized mass and more than 4 million tons of slurry phosphorite have already been accumulated. However, there is no effective technology for enrichment and processing of waste phosphorites into finished fertilizers.

With the accumulation of factual and scientific material on the nature of distribution, geological and technological types and features of the phosphate mineral, various methods and options for ore enrichment are proposed [60]:

1) mechanical enrichment methods based on the use of differences in the physical and granulometric characteristics of phosphate and carbonate minerals. The most common variants of this method are the following: reduction of the

calcium module by averaging the quality of the ore in the process of mining and removing the main part of carbonates by screening (with a favorable granulometric characteristic of the ore);

2) flotation methods for the separation of phosphate minerals (search and synthesis of new reagents, development of special reagent regimes and technological schemes);
3) radiometric enrichment methods based on the use of chemical elements to separate the atomic and nuclear properties that manifest themselves when interacting with various types of radiation (photometric, X-ray luminescent, neutron absorption, and others; separation or separation of ore into technological grades, as a rule, in a lumpy state);
4) thermal enrichment methods based on ore roasting followed by hydration and removal of calcium and magnesium oxides by washing or pneumatic classification;
5) chemical enrichment methods based on different rates of decomposition of the carbonate and phosphate parts of phosphate rock (ore, concentrate, intermediate) in mineral acids or acidic salt solutions;
6) combined methods of enrichment with various combinations of the above methods and options.

Phosphorites of the Central Kyzylkum differ sharply in their mineralogical and chemical composition from their foreign counterparts. Phosphorites of the largest deposits of the African-Arabian phosphorite province processed at the enterprises of Morocco, Algeria, Tunisia, Jordan, Israel, Egypt and Iran contain 20-30% P_2O_5, and commercial concentrates 30-35% P_2O_5. This type of raw material is easily enriched by the thermal method, according to which, after firing at 680-980^o C, it is treated with water or saline solutions (sea water can also be used), followed by the separation of calcium hydroxide.

However, the close interspersing of calcite mineral with small phosphate faunas makes ore from phosphorites of Central Kyzylkums difficult to enrich by known methods. In this case, ore with a high content of carbonates (up to 17% CO_2) from 2005 to 2014 and up to today at the Kyzylkum phosphorite Combine is processed according to the current combined technological line of dry and wet screening of phosphorite in class 5 mm with the withdrawal of a fraction of +5 mm into the dump (off-balance ore with a content of 12-14% P_2O_5), which is 9.6% of the initial ore; deslamation of the flow of -0.5 mm in three steps on hydrocyclones [61]. Desliming is carried out along the boundary grain of 0.02 mm. At the same time, poor sludge is removed into the dump, and a fraction of -0.5 +0.02 mm is prepared as a concentrate (the content of P_2O_5 is 23-25%), then the stages of filtration of the washed concentrate with washing from chlorine are followed; drying of the washed concentrate to a humidity of less than 7%, sent to the firing department to obtain a washed burnt concentrate with a yield of 58% of the initial ore (25-26% P_2O_5), at which 4.1% of the pulverized fraction (18-20% P_2O_5) is formed in the form of waste; sludge thickening, return of clarified water (thickener drain), removal of condensed sludge in the amount of 28.3% of the total, so-called slurry phosphorites (8-10% P_2O_5) in the tailings pond.

Based on the above, it can be seen that the volume of waste is about 42%, of which off-balance ore - mineralized mass reaches 13 million tons. Due to the shortage of phosphate fertilizers in the Republic, this type of waste can become an alternative to get out of the most acute situation. At the same time, the issue of choosing methods for its processing becomes the most relevant. The fact is that the existing traditional methods of processing this ore, such as nitric acid and sulfuric acid, are not acceptable. But if the raw material is unconventional, then it is also necessary to find an unconventional approach for it, which will become classic over time.

1.3. Kyzylkum phosphorite complex.

As follows from the message of Uzkimyosanoat JSC [1], the Kyzylkum phosphorite complex is included in the list of affiliates of the Uzbek chemical industry. Uzkimyosanoat JSC owns 100% of the shares in the new subsidiary business company, the Qizilqum fosforit kompleksi limited liability company.

The first line of a modern mining and processing complex in Kyzylkum with an almost completed production cycle - from operational exploration to the production of phosphorite raw materials was commissioned by the Navoi Mining and Metallurgical Combine in 1998. The decision of the government of Uzbekistan in the first decade of independence to protect the domestic phosphorus industry from the supply of phosphorites from Kazakhstan's Karatau can be attributed to the disadvantages of decentralization in Central Asia. This step, according to experts, resulted in a loss of quality for the Uzbek chemical industry and a significant decrease in the production of phosphorus fertilizers [10]. In Uzbekistan, they are produced by three enterprises – Almalyk JSC "Ammophos – Maxam", JSC "Kokand superphosphate Plant" and JSC "Samarqandkime". The key market player with a share of more than 90% is Almalyk Ammophos, which has been producing phosphorus fertilizers since 1969 [1].

According to official data [2], the production of phosphorus fertilizers (in terms of 100% nutrients) in 2017 decreased by 4.6 times compared to 1991 – from 551.1 thousand tons to 119 thousand tons last year. A major accident in February 2014 at the main producer of phosphorous fertilizers, Almalyk OJSC Ammophos-Maxam, made its contribution, when more than three thousand tons of chemicals leaked as a result of a welding seam rupture in the sulfuric acid warehouse of the enterprise. Uzbekistan's demand for this type of fertilizers, according to experts, is at the level of 700 thousand tons [1]. The high cost and low quality of local phosphorus fertilizers is due, according to experts, to the decentralization of the production of phosphorus fertilizers at the expense of local raw materials.

No data on the total costs involved in the construction of the Kyzylkum phosphorite complex built by the Navoi MMC due to gold mining is available to public. The first line of a large mining and processing complex, which currently employs 800 people, was commissioned in 1998 [17]. Problems immediately arose. It turned out that there is an increased content of chlorine in locally produced fosmuk. It destroys the equipment of chemical plants adapted for Karataus phosphorites [62].

Over 2000-2005, according to official data, a sharp decline in the phosphate-based fertilizer production in Uzbekistan. In 2000, 116.7 thousand tons were produced, in 2005 – 101.2 thousand tons [1]. It was necessary to create a combined scheme for the enrichment of phosphorous ores. Then an additional 10 million euros were added to the construction costs of the apparently expensive KPP. For this money, the German company INGINEERING DOBERSEK GmbH supplied ore washing equipment, which reduced the chlorine content in the concentrate to 0.04 percent [20]. Installations for washing chlorides from phosphoric ore with a capacity of 400 thousand tons of washed burnt phosphor concentrate (for the production of ammophos) and 200 thousand tons of washed dried phosphor concentrate (for the production of superphosphate) have been used at the KPP since 2007 [16]. This circumstance did not significantly increase the productivity of Uzbek chemical enterprises. Suffice it to say that in three years – 2010, 2011 and 2012 Uzbekistan produced a little more than 440 thousand tons of phosphorus fertilizers – significantly less than in 1991 (551.1 thousand tons) [19]. In 2014, the phosphorite industry needed additional funds to expand production that amounted to about $ 60 million, of which about $ 30 million has been allocated to the State Enterprise "Navoi MMC".

1.4. Existing and alternative methods of phosphoric acid processing of phosphate raw materials for phosphoric fertilizers

Traditional methods of processing phosphate raw materials into one-sided phosphoric fertilizers are based on the use of phosphoric and sulfuric acids. Among unilateral phosphoric fertilizers, double superphosphate is more promising, as a ballast-free concentrated phosphoric fertilizer obtained by phosphoric acid decomposition of natural phosphates. Depending on the quality of phosphate raw materials and phosphoric acid, double superphosphate contains 42-55% P_2O_5 and about 90% of it is in a water-soluble form (60; 216 p., 61; 32 p.62; 13 p.]. Double superphosphate is most effective when applied under winter plowing. It should be noted that in 1980 the world production of double superphosphate accounted for 16% of the total amount of phosphorus-containing fertilizers, but today this figure has decreased to 6% [60; 216 p., 63]. The reason for such a decrease in the production rate of double superphosphate is due to a sharp decrease in the quality of phosphate raw materials and the lack of a more modern technology for drying and granulation of the finished product.

The main suppliers of high-quality phosphate raw materials on the world market are the USA, Morocco, China and Russia [64; 457c.. 65; 25g p., 66; 354 p., 67; pp. 752-757, 68; pp.6-11]. However, the reserves of rich phosphate raw materials are being depleted, mining and processing it is becoming more difficult and more expensive. Intensive exploitation of deposits leads to their depletion, which creates a critical situation for producers for further development and supply of mineral fertilizers [6; pp.22-37, 59; 460 p.]. Phosphate raw materials with a content below 30% P_2O_5 practically do not enter the international market, and raw materials containing less than 32% P_2O_5 find only limited sales.

It is known from practice that the traditional methods of processing natural phosphates into double superphosphate are the following: chamber, chamber-flow,

flow and retour [60; 216 p., 61; 327 p., 69; 336 p., 70; 29 p., 71; 235 p.]. These methods differ in the concentration of phosphoric acid used, and accordingly, the technical and hardware design of the main stages. The above methods are based on high-quality phosphate raw materials.

According to the selected technological parameter of a particular method, the decomposition of phosphates is carried out in thickening and non-thickening modes. The thickening mode of processing phosphate raw materials is applicable for chamber and chamber-flow methods, and not thickening for in-line.

When decomposing phosphate raw materials by the chamber method, apatite concentrate or rich phosphorites and phosphoric acid with a concentration of 52-54% P_2O_5 are used with its consumption rate of 100-105% of the stoichiometric for the formation of monocalcium phosphate. The decomposition of phosphate raw materials by phosphoric acid takes place in a mixer for 57 minutes at 60-65 ° C. Next, the pulp enters the superphosphate chamber, where the process of crystallization of calcium dihydrophosphate begins. The subsequent decomposition of phosphate raw materials is carried out in the aging warehouse. Here the superphosphate mass is shoveled from time to time and cooled from 80 to 40 °C. The duration of storage aging depends on the type of raw materials, which is 15-30 days for apatite concentrate, and 6-8 days for phosphorites. In the process of warehouse aging of a product based on apatite, the decomposition coefficient of Kraz. it is 77-80%, whereas for phosphorite products this indicator reaches 80-85% [60; 216 p., 71; 235 p.].

Thus, the matured powdered superphosphate with the composition: P_2O_5usb - 46%; P_2O_5avb - 8%; H_2O - 13% and P_2O_5usb - 42%; P_2O_5avb - 6%; H_2O - 9%, respectively, obtained on the basis of apatite and phosphorite raw materials, is neutralized with limestone or ammonia before or after granulation. The neutralization and granulation process is carried out in drum granulators and ammonizer granulators, followed by drying and sieving of the finished product on screens. After the completion of the process, the granular double superphosphate has 2.5% P_2O_5avb, 3% H_2O and 41-44% P_2O_5usb in its composition with a relative content of 90% relative to its total form.

The chamber-flow method for producing double superphosphate differs from the chamber method with the exception of warehouse maturation, where acidic superphosphate enters immediately for granulation and drying. According to this method, easily degradable phosphorites are processed in a high-speed mixer (15-30 seconds) and further decomposed in a superphosphate chamber with phosphoric acid concentration of 48-50% P_2O_5 and 85% stoichiometric norm at a temperature of 95-105 ° C for 70-90 minutes. Then the cut-out superphosphate is fed into the granulator drum, where retour and water are additionally introduced to moisten the charge to 13-15% moisture. Dried granules are classified and neutralized from 8.5% to 3.5% P_2O_5.

Recently, the in-line method of producing double superphosphate using phosphoric acid with concentrations of P_2O_5 of 28-36% and BGS (drum-granulator-dryer), SBDG (spray-boiling dryer-granulator) and "spherodizer" devices has become widespread. Drying and granulation of the product are combined in them, which makes it possible to decompose secondary raw materials up to 80-85% in a short time. The in-line method for producing double superphosphate using the BGS apparatus includes the process of decomposition of phosphate raw materials with phosphoric acid in reactors with mixing devices, where the process temperature is maintained at 65-75 ° C for 60-90 minutes. Such pulp is easily pumped by pumps to the spray devices of devices designed for granulation and drying of the product. Dried acid granules with a content of 6-8% P_2O_{5avb}. are neutralized, cooled, and then sent to the warehouse.

In any method of obtaining double superphosphate, depending on the type of raw material, the product contains: P_2O_5tot. 45-56%, P_2O_5usb 42-50%, P_2O_5aq38- 42%, P_2O_5avb 2.5-5.0%; H_2O 3-4%.

However, all the mentioned methods have their drawbacks. So, for the chamber method, warehouse maturation is necessary, which requires significant costs for structures,. labor and energy consumption for repeated periodic shoveling of the product with the release of large amounts of toxic fluoride gases. Therefore, this method is excluded from the production node in almost all countries of the world. The disadvantages of the chamber-flow method, first of all, include low productivity and the need to use only easily degradable phosphorites, since not all types of raw materials are acceptable for this technology. The flow method using BGS and other types of devices has a number of limitations due to the use of relatively pure phosphoric acid. But most importantly, both chamber and tubeless methods after the classification process of acidic products require additional conditioning of intermediate products with ammonia or limestone. The connection of an additional technological line for the improvement of commodity properties complicates and hinders the increase in the production of double superphosphate.

The most common method of processing phosphates into double superphosphate is considered to be retour (Dorr-Oliver process), which uses phosphoric acid with a concentration of 37-39% P_2O_5 [70; 29 p., 71; 235 p.]. According to this method, easily degradable Moroccan, Syrian and Tunisian phosphorites decompose with phosphoric acid at lower stoichiometric norms of the latter. The technological scheme includes three mixers followed by mixing the pulp in a two-shaft paddle mixer-granulator, which also receives retour in the amount of 13-15 tons per 1 ton of finished product. On average, the granular material passes through the paddle mixer 13-15 times, and due to this, after drying, the product granules have a very high strength (more than 5-6 MPa versus 2-3 MPa according to chamber, chamber-flow and in-line methods). Phosphorite in mixers decomposes by 80-85%, and at the outlet of the drying drum this indicator increases to 94% (against 75-85% by chamber, chamber-flow and in-line methods). At the same time, the free acidity of the product does not exceed 2-3%, so no additional stage is required - neutralization. It should also be noted that the composition of the double superphosphate of the foreign brand "45-15" corresponds to 45% P_2O_5, 15% CaO with pH = 1-3 [70; 29 p.].

The main disadvantage of the "Dorr-Oliver" method is the high retroactivity associated with mechanical and thermal energy costs for fractionation and return of small granules, as well as the complexity of the technological process.

Based on the above, the rate of decomposition of natural phosphates by phosphoric acid at the initial stage of the process is relatively high, but over time it abruptly decays [60; 216 p.]. This phenomenon is especially pronounced when poor phosphorites interact with extraction phosphoric acid from the same raw material, since it is considered unsuitable for the production of double superphosphate. To intensify the decomposition process, the use of stronger acids - sulfuric, nitric and hydrochloric - has been proposed as an additive [72; pp.43-49, 73; pp. 1425-1428].

The paper [72; pp. 43-49] shows the results of the introduction of double superphosphate technology at the Dzhambul plant using Karatau phosphorites and at the Gomel Chemical Plant using apatite concentrate by replacing part of phosphoric acid with sulfuric acid. At the same time, the optimal norm of phosphoric acid was 85% of stoichiometry, and the weight ratio of sulfuric acid to phosphoric acid was 0.1-0.2. It was found that at ratios of H_2SO_4:H_3PO_4, less than 0.15-0.2 (depending on the total acid norm), the degree of decomposition by acid mixtures exceeds the degree of decomposition of phosphorite by phosphoric acid alone, and at ratios greater than 0.15-0.4 - vice versa. This dependence is explained by the increased content of H_2SO_4 in the mixture, which in turn leads to the formation of large amounts of small crystals of calcium sulfate, which are deposited on the surface of phosphate grains [74; pp. 113-115].

At the Gomel Chemical Plant, apatite concentrate and most (~ 80% of the total consumption) of phosphoric acid enter the first section of a four-shaft continuous mixer. Sulfuric acid is mixed with the remaining part (~ 20%) of phosphoric acid and this mixture is fed into the third section of the mixer. As a result, sulfuric acid mainly reacts with the monosubstituted calcium phosphate present in the solution. Such a sequence of reagent supply allows to avoid crystallization of calcium sulfate on phosphate grains and thereby accelerate the decomposition of apatite already at the stage of mixing it with acids and during the chamber aging of the product [75; pp. 670-672]. One of the drawbacks of this work is the relative dilution of the double superphosphate by SO_4 and NO_3 ions, which worsen its physico-mechanical and marketable properties.

The authors of the work [76; p. 8; 77; p.259-260] studied in detail the complex effect of impurities present in phosphate raw materials on the decomposition of phosphates by phosphoric acid by multivariate regression analysis. The raw materials for the experiment were Kovdorsky apatite concentrate (Russia), phosphorite concentrates Lao-Kai (Vietnam), Kingisepp (Russia), Jebel Onk (Algeria), Chilisaya (Kazakhstan), Eastern (Syria), Kuribga (Morocco), Shra-Huertana (Tunisia), Gafsa (Tunisia) with an average content 24-36% P_2O_5. The study of the effect of impurities on the degree of decomposition of phosphates was carried out at 60 ° C using an EPA containing 28% P_2O_5; 0.3% CaO; 1.8% F; 0.9% Fe_2O_3; 0.7% $A1_2O_3$ under the conditions of a flow method. The granulometric composition corresponded to a 20% residue on a 0.0074 mm sieve. The norm of phosphoric acid was 85% of the stoichiometry calculated for the formation of calcium dihydrophosphate, taking into account the decomposition of impurities contained in the raw materials. The degree of decomposition of Kr phosphate in the pulp was determined 2 hours after the start of the experiment and calculated as the ratio of the amount of P_2O5 passed into the solution to the initial amount of P_2O_5 in phosphate. Further, the obtained pulps were dried at. 105 °C to a humidity of 1.5-2.0% and the degree of decomposition of phosphate in the product was calculated. The obtained analysis data indicate a high reactivity of Gafsa phosphorites (95%), Shra-Ueran (92%), Kuribga (92%) and low- Kovdorsky apatite concentrate (75%). A double superphosphate was obtained from Tunisian phosphorite depending on the aging time at a temperature of 45° C with and normal EPA - 90% of stoichiometry. It is shown that when the product matures with a shelf life from the initial to 20 days, the degree of decomposition of phosphorite ranges from 74 to 85%, respectively. Under the above conditions, the double superphosphate contains P_2O_5tot. 48.7%; P_2O_5usb 46.9%; P_2O_5aq. 45.9%; P_2O_5avb 3.9%; H_2O 3.8%.

In [78; 48 p.], structural changes of the lifting-blade nozzles in the BGS apparatus made it possible to intensify the process of phosphate decomposition. It is established that the optimal norm of phosphoric acid for the decomposition of Kingisepp phosphorite is 72-80 mass parts of P_2O_5 acid per 100 mass parts of phosphorite. Under this condition, the pulp before entering the BGS apparatus contains 13-14.5% P_2O_5avb., and the dried product contains P_2O_5avb. does not exceed 7%. It was revealed that an increase in the content of free acidity to 15% or more led to a violation of the granulation regime. This work deserves special attention because a part of the Kingisepp phosphorous (10-15%) is replaced by a hard-to-decompose apatite concentrate in the in-line method for producing double superphosphate. As the results of the analysis show, when apatite is introduced into an EPA containing 27-30% P_2O_5, in an amount that ensures the concentration of CaO in solution within 1-3%, the degree of its decomposition will be close to 100%, and the resulting solution can be neutralized with Kingisepp phosphorite to obtain a double superphosphate composition (wt.%): P_2O_5tot. 48.6-50.28; P_2O_5usb

44.7-47.18; P_2O_5avb 4.42-6.0; H_2O 2.0-2.4. The essence of the experiment is as follows: EPA with a concentration of 26.3% P_2O_5, 2.0% SO_3; 1.6% F and 0.09% CaO is mixed with apatite concentrate in a ratio of 1.3-1.4:1 for 1 hour at a temperature of 60-70 °C and the resulting suspension is separated by filtration. The cake is sent to the extractor, and the filtrate containing P_2O_5 is shared. 31.5%; SO_3 0,3%; CaO 3.1%; $Fe_2O_3$0.4%; $A1_2O3$ 0.8; F 1% is processed by Kingisepp phosphorite flour at a rate of 72 m.h. P_2O_5 to obtain double superphosphate.

A long maturation time, a low degree of decomposition of raw materials and the performance of the BGS apparatus are the disadvantages of the developed technology.

One of the ways to increase the use of phosphate raw materials is the liquid-phase circulation technology of double superphosphate. The present technology differs significantly from traditional methods in that phosphate raw materials, regardless of their quality and chemical and mineralogical composition, decompose with an excess rate of phosphoric acid. The essence of the cyclic method consists in the decomposition of phosphate raw materials with 3-5 times the amount of phosphoric acid, followed by the crystallization of monocalcium phosphate, its separation from the mother liquor, neutralization of acid monocalcium phosphate (MCP), sulfatization of the mother liquor, separation of phosphogypsum and the return of acid to the production cycle. At the same time, the maximum opening of the phosphate mineral is ensured up to 98-99% and the production of double or triple superphosphate with a content of 50-59% P_2O_5.

The whole process proceeds in a liquid-phase, i.e. non-thickening mode similar to the flow, but at high concentrations of phosphoric acid (40-65% P_2O_5), and on the other hand, in relation to the chamber or chamber-flow method, differing only in the use of high 300-800% norms of acid reagent. The advantage of cyclic technology is that it becomes possible to obtain high-quality double superphosphate from almost any type of phosphate raw materials based on its phosphoric-sulfuric acid processing in the same cycle.

According to the authors [60; 216 p.], the issue of intensification of the process of obtaining double superphosphate is acceptable only when it is possible to use the SBDG apparatus and circulation of a recycled phosphoric acid solution. The recycling of working solutions in the technology of many salts creates conditions for the separation of salts in a more concentrated commercial form and the exclusion of energy-intensive processes of solution evaporation and salt drying from the technology of their production. The principles of cyclic technology are of particular relevance in the production of salts consumed on a large scale and in many areas of agriculture [79; 400 p.]. It is shown that in order to ensure energy saving, the use of recycling is effective in the technology of the following salts: potassium, zinc, copper sulfates; sodium, potassium, magnesium, barium, manganese, lead, aluminum nitrates: sodium, potassium, lithium, calcium phosphates; sodium and ammonium thiosulfates; ammonium, potassium, barium.

In the author's certificate [80], the process of obtaining double superphosphate based on the decomposition of apatite concentrate (39.4% P_2O_5) with phosphoric acid with a concentration of 45% P_2O_5 at a rate of 300-400% of stoichiometry for the formation of WCC was investigated. Conducting the process at a temperature of 60 ° C for 2 hours ensured the degree of decomposition of phosphate raw materials up to 91-96%. According to this method, the pulp saturated with WCC and a small amount of unreacted apatite is divided into two parts. Part of this pulp, after separation from the liquid phase to form a solid phase - acidic WCC, is neutralized with ammonia or limestone at 80 ° C for 30 minutes, resulting in a double superphosphate (mass. %): 57.50 P_2O_5tot, 56.3 P_2O_5usb., 49.2 P_2O_5aq. and 57.54 P_20_5tot, 56.21 P_2O_5usb, 52.70 P_2O_5aq. accordingly. The rest, together with the mother liquor from the first part, is treated with 55% sulfuric acid to regenerate phosphoric acid in order to return the latter to the cycle.

Kingissep flotation concentrate (28.9% P_2O_5) was decomposed by both thermal and extraction phosphoric acid with a concentration of 55-65% P_2O_5 at their norms of 400-600% of stoichiometry, followed by crystallization and filtration of anhydrous WCC [81.P. 1445-1450]. The decomposition process lasted 1-1.5 hours at 110-130 ° C, which provided a fairly complete (up to 95-98%) opening of phosphate raw materials. The process of circulating a recycled phosphoric acid solution with the addition of fresh phosphoric acid (58.3% P_2O_5) up to 5 cycles was studied and a positive assessment of crystals in the form of spheroidal accretions with an average diameter of 70 microns was given. After 5 cycles of the process, the separated solid phase was subjected to ammonization and a double superphosphate of the composition (wt. %): 51-54 P_2O_5tot; 50-52.5 P_2O_5usb; 39- 50.7 P_2O_5aq.; 13-14 CaO; 2.0-5.9 N and 0-8 P_2O_5avb.

According to the patent [82], a method for obtaining double superphosphate by a cyclic method is proposed, including decomposition of apatite concentrate with a mixture of fresh thermal acid (TPA) with a concentration of 53% P_2O_5 or EPA with a concentration of 48% P_2O_5 with a circulating mother liquor (58-60% P_2O_5), pulp filtration, return of the mother liquor to the cycle and neutralization of the product precipitate. The decomposition reaction is carried out at 60 ° C for 3 hours. Then the pulp is evaporated to a liquid phase concentration of 58-60% P_2O_5 at 90-110 ° C, and is delayed for 1-4 hours with the transfer of single-water WCC ($Ca(H_2O_4)_2$-H_2O) in the product to anhydrous ($Ca(H_2O_4)_2$ form. The last one from 8.6-10.5% free P_2O_5. is neutralized with chalk and a double superphosphate of the composition (wt. %): 59.8-59.0 P_2O_5usb, 2.8-3.0 P_2O_5avb, 2.8-3.0 H_2O.

In contrast to [82], in order to reduce the time of the decomposition process, a cyclic method has been developed [83], which provides for evaporation not of a suspension of a single-water WCC, but a mixture of a circulating mother liquor (55.7-59.6% P_2O_5) and fresh EPA (49-50% P_2O_5) to 63-65% P_2O_5. As a result, the resulting evaporated mixture is sent to the processing of apatite (39.4% P_2O_5) or Kingissep (28% P_2O_5) flotation concentrate at a rate of 300% of stoichiometry. According to the authors, the combination of the decomposition of phosphate raw materials and the crystallization of anhydrous WCC reduces the duration of the technological cycle to 1-2.5 hours instead of 4-7 [82]. The precipitate of anhydrous WCC with 8,7-10% P_2O_5avb., separated from the mother circulating solution, is neutralized with chalk and a double superphosphate containing 56-59.3% P_2O_5usb, and 1,8-3,0 P_2O_5avb is obtained.

In [84; pp. 170-176], the mode of decomposition of apatite TPA concentrate with a P_2O_5 content from 40.4 to 42.04% at a rate from 333 to 694/o from stoichiometry in closed and open cycles was investigated. The contact time of the reagents was 60 minutes at 100-115 °C. After the process was completed, the pulp was evaporated to a concentration of 53% P_2O_5, and then cooled at 40 ° C for 1.5 hours. The essence of the evaporation is to increase the decomposition coefficient of apatite concentrate from 84-89 to 93-98%, respectively. The obtained crystals of acidic WCC contain 53.87-55.69% P_2O_5 tot, 53.45-55.41% P_2O_5aq, and 21.05-24.01% P_2O_5avb.

In [78; 48 p.], the prospects of a recirculating method for obtaining triple superphosphate of the composition P_2O_5 are substantiated. 55.5%; P_2O_5 tot 55.0%; P_2O_5avb.2.5%. Apatite concentrate and evaporated EPA containing (wt. %): 63.1 P_2O_5; 0.25 CaO; 1.5 R_2O3; 0.04 MgO; 4.1 SO3; 0.2 F. This includes the preliminary mixing of a part of the mother liquor and EPA, the separation of the calcium sulfate precipitate, the decomposition of phosphate, the crystallization of WCC, the separation of the product from the mother liquor and the return of the phosphoric acid solution to the mixing and decomposition stage.

Kazakh researchers have shown the principal possibility of processing low-quality phosphorites of the Chilisai and Karatau deposits into double superphosphate by a cyclic method [85; pp. 107- 112. 86; pp.34-38]. Chilisai phosphorite with a content of 17.72% P_20_5, 5% CaO decomposes with thermal phosphoric acid with a concentration of 40-41% P_2O5 at its rate of 450-550% of stoichiometry in the temperature range of 90-95°C for 40 minutes, followed by separation of the insoluble residue from saturated solutions of WCC by filtration [86; pp.34-38, 87, 18 s].

The resulting filtrate is cooled at 40 ° C for 90 minutes in order to crystallize WCC, and the mother liquor is treated with 100% H_2SO4 (92-93%) at 50-60 ° C and a duration of 15-20 minutes. to obtain phosphoric acid, which is returned again to the phosphorite decomposition cycle. After neutralization of acidic WCC with a free content of 28.7-31.3% H_3PO4 with ground limestone, a double superphosphate of the composition (wt. %): 51.50 P_2O_5tot, 49.30 P_2O_5usb, 47.20 P_2O_5aq., 0.70 P_20_5avb and 2.80 moisture.

In [88; pp.60-64, 89; pp. 183-190], a graphical calculation is proposed to find optimal conditions for the decomposition of substandard phosphorites of the Karatau basin of the Kokjon and Koksu deposits with thermal phosphoric acid with a concentration of 40% P_2O_5, with its norm of 450-500% of stoichiometry in a non-thickening liquid-phase regime according to a recirculation scheme. The contact time of the components was 50-60 minutes. at 90-95^{o}C, followed by filtration of the reaction mass from the insoluble residue (decomposition coefficient 99.0-99.5%), cooling of the filtrate at 40 ° C for 90 minutes, regeneration of the mother liquor by sulfuric acid extraction, mixing it with fresh thermal phosphoric acid and returning to the cycle for decomposition of the subsequent batch of phosphate raw materials [%: pp. 11-15]. Neutralization of acidic WCC was carried out with ammonia water and calcium oxide. Chemical composition of the finished product (mass. %): 54.28 P_2O_5tot.; 52.53 P_2O_5usb; 52.14 P_2O_5avb. 3.01 P_2O_5usb., 3.54 N and 54.53 P_20_5tot; 51.11 P_2O_5usb, 51.13 P_2O_5avb. , 97 P_2O_5avb. accordingly [90; 145 p.].

One of the possible directions of direct processing of low-grade phosphorites without their enrichment may also be the hydrochloric-phosphoric acid decomposition process with the recycling of the mother liquor when obtaining WCC [91; pp.65-69].

In these works, the method of processing phosphorous flour of the Polpinskoye deposit of composition (mass. %): 15.50 P_2O_5; 27.40 CaO; 0.96 MgO; 3.29 Fe_2O3; 3.80 Al_2O_3; 5.00, n.o. 43.03 (including 36.4 SiO_2) using phosphoric acid in the conditions of recycling of hydrochloric-phosphoric acid mother liquor to obtain WCC. The mother solution containing calcium chloride, after separation of the WCC, is mixed with phosphoric acid introduced into the process and, in the form of a so-called "circulating solution", returns to the decomposition stage, while hydrochloric acid is regenerated. A distinctive feature of this technological approach is the crystallization of WCC together with an insoluble residue, which passes into the finished product. After washing, the resulting product has the composition: P_2O_5tot. 38.6-39.0%; P_2O_5usb. 38.1-38.5%; P_2O_5aq. 33.2-33.7%; P_2O_5avb. 0.3-0.5%; CaO 14.4%; MgO 0.3%; Cl 0.8-1.1%; Fe_2O_3 2,0%; $A1_2O_3$ 2,3% [90; 16 p.]. Optimal conditions of the decomposition process have been identified: temperature 40 ° C, decomposition duration 20 min, phosphoric acid norm 110%, at which Kraz is at least 97.3%.

According to the proposed method [92], double superphosphate is obtained by decomposition of natural phosphate with a mixture of phosphoric and hydrochloric acids at a ratio of HC1: (CaO + P_2O_3) phosphate equal to 0.76-3.62 at a temperature not higher than 50 °C for 60 minutes. The resulting pulp is cooled to 25 ° C for 3-4 hours, the precipitate, which is monocalcium phosphate, is filtered out, and the mother liquor containing hydrochloric acid is returned to the process for decomposition of another portion of phosphate. At the same time, the authors managed to obtain a double superphosphate with a content of 51.56-54.6% P_2O_5 with a total ratio of CaO:P_2O_5= 0.394. In all the proposed variants of the study, the degree of decomposition of phosphate was 98.2-99.8%. It is concluded that the advantage of the cyclic method is manifested in cases when the raw materials are not subjected to additional enrichment and do not require significant resource and energy costs for their processing, which leads to a reduction in the cost of the target product by 1 ton of 100% P_2O_5. The essence of the processes of obtaining phosphorus fertilizers consists in the conversion of the indigestible form of P_2O_5 in the raw material into a form assimilable for plants in the product. An alternative to non-traditional methods of obtaining phosphorus-containing fertilizers from poor phosphate raw materials is its chemical activation. The essence of this process is the processing of raw materials with phosphoric acid, but in much smaller quantities than is required for the complete decomposition of phosphorites. In this case, the so-called undecomposed or partially decomposed phosphates are formed. These works began to develop after realizing the fact that rich phosphate raw materials are becoming increasingly scarce, and such fully water-soluble highly concentrated phosphorus-containing fertilizers as ammophos and double superphosphate are becoming more expensive.

Studies on the production of activated types of phosphoric fertilizers based on the decomposition of low-grade phosphate raw materials at reduced phosphoric acid consumption rates were carried out in [93; from 27-99; pp. 30-31. 94; pp. 7-12]. Three variants of technological schemes for obtaining a new phosphorus-containing fertilizer - calcium dimonophosphate containing a mixture of mono- and dicalcium phosphate have been developed. The technology has been tested on the processing of the yellow type of phosphate raw materials: Vyatka-Kama (21.522.5% P_2O_5 and

6.2-6.9% R_2O_3), Yegoryevsky (20% P_2O_5 and 11% R_2O_3). The Chilisai (17.1% P_2O_5 and 4.7% R_2O_3) deposits, as well as the residual metasomatic type of the Ashinsky deposit (22.5% P_2O_5). The product contained 31-43% P_2O_5 at C = 70-80%. From an agronomic point of view, calcium dimonophosphate has certain advantages over other phosphorus fertilizers, since its ratio of P_2O_5 aq: P_2O_5usb is in the range of 0.4-0.7, which allows plants to absorb nutrients more evenly during the growing season, growth and maturation and provides a more effective aftereffect of fertilizer.

In the 90s of the last century, specialists of the NGO "Minudobrenia", NGO "NIIHIMMASH", NIIFA, Mendeleev Moscow Art Institute developed a resource-saving technology for the production of nitrogen-phosphorus fertilizer called "Ammophosphate" [90, 16 s, 94; 56 p.]. Phosphate components in the ammonium phosphate are mainly monoammonium phosphate, dicalcium phosphate, in a smaller amount, monocalcium phosphate, and as impurities, it also contains highly basic calcium phosphates such as hydroxyl fluorapatite. The technology includes the decomposition of phosphorite in excess of EPA (150-300%) at a reagent ratio of 0.15 wt.h. P_20_5 from phosphorite per 1 wt.h. P_20_5 from EPA; neutralization of phosphate pulp with ammonia gas to pH 3.0 - 3.5; granulation and drying of the product in the BGS apparatus. The production of a new fertilizer is carried out using the equipment of the ammophos workshops [94; 51 p.].

The technology of ammonium phosphate based on Karatau phosphorites was introduced at the Dzhambul superphosphate plant in Kazakhstan, at the Chardzhou Chemical Plant in Turkmenistan, and at the Almalyk Chemical Plant in Uzbekistan. At the Balakovo software "Mineral Fertilizers" in Russia, this method was introduced using Khibiny apatite concentrate. According to TU No. 113-08-552-84, the ammonium phosphate from Karatau phosphorites contains 39% P_2O_5 and 5% N

[120]. Ammonium phosphate based on apatite concentrate contains 47.0% P_2O_5 and 8.4% N [95; pp.50-56].

This technology solves the problem of involving in the production of almost all types of phosphates from various deposits, which reduces raw materials and energy resources: sulfuric acid - by 15%, fuel - by 15%, phosphate raw materials - by 2%. The environmental situation of production is improving due to a 15% reduction in phosphogypsum waste, and the almost complete elimination of ammonia losses. The replacement of 15% P_2O_5 phosphoric acid with P_2O_5 phosphorite in ammonium phosphate leads to positive technical and economic indicators. The technology of ammonium phosphate is carried out by a non-welding method, which greatly simplifies the hardware and technological scheme of the process and reduces the metal consumption of production. The technological line excludes four-body vacuum evaporators with circulation pumps, tanks and auxiliary equipment.

According to the author's certificate [82], a method is proposed to improve the quality of the product to a content of 44.9% P_2O_5 tot. compared with the known method with a content of 39.0% P_2O_5, described in [91] and increasing the process manufacturability due to evaporation of phosphate pulp before granulation. To do this, 20 kg of phosphorite with the composition (mass.%): 27.41 P_2O_5; 44.14 CaO; 2.21 MgO; 3.80 CO_2; 2.48 F; 14.84 n.o. decompose 100 kg of apatite EPA containing (wt.%): 26.16 P_2O_5; 0.32 CaO; 1.40 R_2O_3; 1.18SO_3 at 50 °C for 3 hours. The resulting pulp in an amount of 118 kg is neutralized with gaseous ammonia to a pH value of 3.7 and subjected to evaporation to a humidity of 30%. Then 90 kg of evaporated ammonium phosphate pulp is mixed with 200 kg of retour, granulated and dried. After drying, 267 kg of product is obtained with a humidity of 67 kg and a composition (wt. %): 44.9 P_2O_5 total; 44.0 P_2O_5usb.; 27.8 P_2O_5aq.; 6.2 N.

The patent [82] describes a method for increasing the productivity of the process, which includes the decomposition of poor phosphate raw materials with phosphoric acid in the presence of sulfuric acid at a mass ratio of H_2SO_4:P_2O_5, equal to (1.0-0.5):1 and the mass ratio of H_3PO_4:CaO, MgO, R_2O_3 in phosphate equal to (0.9-2.2): 1.0, followed by neutralization of phosphate pulp acids with ammonia. The ammonium phosphate pulp is pretreated with a retour taken in the ratio of pulp to retour equal to (2.5-20) with a retour particle size of 0.2-2.0. It was found that the structure of the phosphate component in the pulp and the size of the crystals sharply differ from the initial state. Their surface is etched with acid, and the dimensions do not exceed several microns, which is the reason for the assimilation of the phosphate component in the soil.

Based on the results of laboratory studies [96; 31 p.], the technological parameters of the process were clarified and experimental production lines were installed at the Almalyk Chemical Plant and at the pilot plant of the NPO "Minudobreniya". The results of industrial tests have shown that when Karatau phosphorites are decomposed with an excess of EPA with a concentration of 19-21% P_2O_5, the process proceeds without thickening of the phosphate pulp. The degree of extraction of phosphoric anhydride from phosphorite is 90-95%. Pumping phosphate pulps with a pump into the BGS apparatus did not cause technical difficulties. The resulting fertilizer contained 38-40% P_2O_5, including 25-28% water-soluble form; 4-6% nitrogen and 1-1.5% H_2O.

In [94; 19 p. the issue of activation of the ores of the Karatau basin by various phosphorus-containing solutions is considered. It was found that the degree of activation is influenced by the duration of treatment (30-90 min), the ratio of L:S from 2:1 to 7:1 and the degree of neutralization of the phosphorus-containing solution (pH from 0.65 to 5). Under optimal conditions, two types of ammonium phosphate were obtained, grade "A", containing 45-46% P_2O_5tot.; 40-41% P_2O_5usb.; 34-36% P_2O_5aq.; 7-9% N and grade "B" of the composition 38-39% P_2O_5tot.; 31-32% P_2O_5usb.; 27-28% P_2O_5aq.; 4-5% N.

It is shown that, along with a high content of nutritional components, ammonium phosphate is also characterized by non-compressibility, moderate hygroscopicity, high strength of granules, good flowability and dispersibility. Ammophosphate is suitable for bulk storage and can be used in dry form for the preparation of concentrated PK, NP and NPK mixtures with different ratios of nutrients [86; pp.68-70, 97; pp.29-39]. The ammonium phosphate is intended for use as a complex nitrogen-phosphorus fertilizer in agriculture. The agrochemical efficiency of ammophosphate is equivalent to ammophos and double superphosphate and can be used in various soil and climatic zones for all agricultural crops [96 p.35-41]. The analyzed materials indicate the acceptability of the technology of ammonium phosphate for poor phosphorites of the CC.

1.5. Phosphoric acid processing of Kyzylkum phosphorites for ammonium phosphate fertilizers.

For the production of complex and concentrated phosphorus-containing
the main reagent of fertilizers is EPA, which causes a large consumption of scarce sulfuric acid. Thus, to obtain 1 ton of P_2O_5 in the form of ammophos from Kola apatite concentrate requires 2.5 - 2.7 tons of H_2SO_4 , and from Karatau phosphorites - 3.5-3.7 tons. In the production of ammophos from washed burnt concentrate of CC phosphorites with a calcium modulus of 1.9-2.0, the consumption of sulfuric acid is even more - 4.3-4.4 tons. The amount of phosphogypsum thrown into the dump increases by the same amount.

In the works of Asamov D.D. et al. [98], the principal possibility of obtaining phosphorus-calcium fertilizer with a high content of the relative digestible form of phosphorus and calcium from unenforced phosphate raw materials and washed concentrate is shown. The optimal conditions for conducting the process are: 100-120% EPA norm from stoichiometry for the formation of dicalcium phosphate, temperature - 60-80 °C pH — 2.9-3.67. The authors also developed an intensive technology for obtaining PR fertilizers by decomposing Kyzylkum phosphorites first with sulfuric acid, and then by decomposing phosphate raw materials with extraction phosphoric acid. The developed technologies of phosphorus-calcium and PS-fertilizers have been tested in industrial conditions at JSC "Ammophos-Maxam" with the release of experimental batches of products.

Kanoatov H.M., Seitnazarov A.R. et al. [99,100] studied the possibility of obtaining activated single phosphorus fertilizers based on the interaction of various types of poor Kyzylkum phosphorites at a reduced EPA rate. For the activation of phosphate raw materials, an unpeeled (18.69% P_2O5) and evaporated EPA (29.05 - 46.00% P_2O_5) was used. The compositions of the phosphorus fertilizers obtained were determined. It is shown that an increase in the fraction of phosphorite in a mixture with EPA, i.e. a decrease in the weight ratio of P_2O_5 EPA : P_2O_5 PR has a significant effect on the relative content of the digestible form of phosphorus. The content of the total and digestible amount of phosphorus pentoxide in fertilizers, depending on the concentration of the initial EPA, the type of phosphate raw materials and the ratio of P_2O_5 EPA : P_2O_5 PR, varies between 30.18 - 47.46 and 19.00 - 41.93%, respectively.

In [101], the process of activation of Kyzylkum phosphorites by a mixture of EPA and H_2SO_4 in the range of weight ratios of P_2O_5 in acid to P_2O_5 in raw materials from 1:0.3 to 1:1 and P_2O_5 in acid to H_2SO_4 (monohydrate) was investigated from 1:0.25 to 1: 0.5. It was found that the addition of sulfuric acid increases the content of digestible and water-soluble forms of P_2O_5 and CaO in the products. The technology of obtaining concentrated phosphorous fertilizers based on phosphorites of CK and EPA has been tested on a model installation with the establishment of the main technological parameters of the process. The material balance of production has been compiled. Chemical and radiographic! the methods of analysis established the approximate salt composition of the fertilizer.

In [102], the process of obtaining activated phosphorus-containing fertilizers by the interaction of various types of CK phosphorites with partially ammoniated extraction phosphoric acid from Karatau phosphorites was studied in detail. It is shown that the decomposition of highly carbonized phosphate raw materials by phosphoric acid is accompanied by abundant foaming. A significant reduction in pricing is achieved in the case of using a pre-ammoniated EPA-having a pH-2. It is established that the elimination of pricing allows for two-stage phosphoric acid decomposition of phosphorite. The first stage - decarbonization of phosphate raw materials is carried out in a heterogeneous process with a minimum amount of liquid phase flowing in a screw mixer reactor. The second stage - additional decomposition of decarbonized phosphorite is carried out in a conventional reactor. Depending on the experimental conditions, it is possible to obtain a nitrogen-phosphorus-calcium fertilizer containing from 33-38% P_2O_5tot, 4-8% nitrogen and 11.56 to 21.12% CaO. The relative content of the digestible and water-soluble forms of P_2O_5 in fertilizers ranges from 89-96 and 52-72%, respectively.

Sattarov T.A. et al. studied in detail the process of obtaining ammonium phosphate fertilizers based on the decomposition of CK phosphorites by extraction phosphoric acid [103]. To conduct laboratory experiments, the authors used various types of phosphate raw materials from the Jeroy - Sardarinsky deposit; ordinary phosphorous flour, thermal concentrate, chemically enriched concentrate, pulverized fraction. As an acid reagent, the EPA of Almalyk OJSC "Ammophos" of the composition (wt.%) was taken: 21.45 P_2O_5; 0.77 CaO; 0.89 MgO; 0.51 Fe_2O3; 1.33 $A1_2O_3$; 1.78 F 0.50.The mass ratio of EPA : PR is taken in the range of 100: (5-30). The duration of the decomposition process was 45 minutes. The content of the digestible form of P_20_5 in phosphate pulp in relation to the total form of P_20_5 remains high at all EPA: PR ratios. The same is observed for the content of the water-soluble form of P_2O_5. As a percentage, this value lies in the range of 83.77-98.50% for ordinary phosphorite flour, 68.67- 97.57% for thermal concentrate, 84.24-99.02% for the pulverized fraction and 84.27-99.17% for chemically enriched concentrate.

According to the authors, this indicates that CK phosphorites decompose fairly well with phosphoric acid to form digestible phosphates. Further, the authors subjected acid phosphate pulps to neutralization with gaseous ammonia to pH values of 3.10-4.40 and drying. The composition of ammonium phosphate fertilizers varies depending on the conditions of their production (weight %) P_2O_5 tot. from 43.27 to 49.85%; from 43.30 to 50.10%; from 40.11 to 50.36; from 43.80 to 50.25; P_2O_5.usv. from 34.55 to 48.69; from 34.64 to 49.02; from 32.50 to 49.38; from 31.08 to 47.60; P_2O_5 aq. from 24.60 to 43.00; from 25.43 to 45.34; from 26.24 to 46.48; from 24.40 to 42.41; nitrogen from 4.74 to 10.40; from 4.86 to 9.58; from 4.92 to 8.97; from 4.97 to 9.78, respectively, for phosphorite flour, pulverized fraction, chemically enriched concentrate and thermal concentrate.

Taking into account the consumption of phosphoric acid per 1 ton of 100% P_2O_5 and the content of digestible and water-soluble P_2O_5 handicap in the final product, the authors recommend obtaining ammonium phosphate fertilizers from all types of CC phosphorites at EPA ratios:PR equal to 100:(15-20).

In order to intensify the decomposition of phosphate raw materials, the same authors [170- C 57-62. 171; p.57-61, 172; p.65-68] carried out the process by adding a small amount of sulfuric acid to the EPA. To conduct the study, the same types of phosphorites of CK and EPA were used as in the preparation of ammonium phosphate fertilizers. Sulfuric acid used as an additive had a concentration of 93.52%. The proportion of sulfuric acid was from 3 to 7, the proportion of phosphorite in relation to the mass fraction of EPA was from 10 to

25; from 10.44 to 26.11; from 10.06 to 25.16; from 8.75 to 21.88 for ordinary phosphorite flour, pulverized fraction, chemically enriched concentrate and thermal concentrate, respectively.

Experimental data show that with an increase in the addition of sulfuric acid, the Cr of phosphate raw materials increases. So, with a mass fraction of phosphorite flour 15 and with mass fractions of sulfuric acid 3, 5 and 7, the Kr are equal to 64.27, 68.20 and 70.95%, respectively. The highest Kr. phosphorite flour - 81.31%, pulverized fraction - 87.85%, chemically enriched phosphoconcentrate - 92.07% and thermoconcentrate - 68.73% is observed with mass fractions of EPA : H_2SO_4: PR, equal to 95:5:10; 95:5:10,44; 95:5:10.06 and 95:3:8.75 respectively. The excess acidity of the obtained pulps was neutralized with ammonia.

The composition of sulfoammophosphate fertilizers obtained under the found optimal experimental conditions is as follows (wt.%): for ordinary phosphorite flour (EPA: H_2SO_4:PR = 93:7:20 and 93:7:25) P_2O_5tot. 38.60 - 40.02; P_2O_5usb. according to the trilon B 31.68- 34.71; P_2O_5 aq. 23.04 - 25.73; N 5.22 - 6.50; for the pulverized fraction. (EPA: H_2SO_4:PR = 93:7:20.89 and 93:7:26.11) P_2O_5tot 38.27 - 39.74; P_2O_5usb. according to the trilon B 31.67 - 34.56; P_2O_5 aq. 24.90 - 27.31; N 5.85 - 6.20; for chemically enriched phosphoconcentrate (EPA:H_2SO_4:PR = 93:7:20,13 and 93:7:25,16) P_2O_5tot 37.35 - 38.92; P_2O_5usb. according to the trilon B 31.51 - 34.49; P_2O_5aq. 26.79 - 30.27; N 5.32 - 6.33; for thermal concentrate (EPA: H_2SO_4:PR = 93:7:17.51 and 93:7:21.88) P_2O_5 in general. 40,90- 41,09; P_2O_5usb. according to the trilon B 28.77 - 31.61; P_2O_5 aq,. 22.90 - 24.88; N 5.24 - 6.15.

These authors also systematically studied the decomposition processes of Kyzylkum phosphorites of EPA with the addition of nitric acid [104]. The decomposition of phosphorites was carried out at a mass ratio of EPA:PR for an ordinary from 100:30 to 100:60, for a dusty fraction from 100:30.4 to 1'00:60.7 and for a thermal concentrate from 100:20.7 to 100:41.4. The HNO_3 norm varied from 15 to 40% of the stoichiometry on the CaO. The content of the water-soluble and digestible form of phosphorus according to trilon B in the activated nitroams obtained.monophosphate fertilizers under the optimal conditions found fluctuates, respectively, in the range of 59.71 - 66.27 and 77.72 - 88.27% of the total P_2O_5. The main technological parameters of the process of obtaining all types of ammonium phosphate fertilizers have been worked out at the laboratory model plant and experimental batches of products for agrochemical tests have been released. A technological scheme has been developed for the recommended fertilizers and the material balance of production has been compiled.

Scientific results indicate the value of ammonium phosphate fertilizers and the possibility of obtaining from poor phosphorites, which are Kyzylkum. From these positions, slow-acting fertilizers that release macronutrients evenly and gradually are the most preferable for irrigated agriculture [108].

1.6. Conclusion on the literary review

Reserves of high-quality ores are steadily being depleted, and it is becoming more difficult and more expensive to extract and process them. The current situation leads to the need for an increasing appeal to the poor phosphate-raw material base. In this regard, the decisive technical and economic factor in the phosphate industry is the successful enrichment of poor phosphate, in particular phosphate-carbonate ores, whose reserves make up two thirds of the world's reserves. Phosphorites of the Central Committee can be attributed to this type of raw material. Kyzylkum phosphorite consists mainly of calcite, fluorocarbonate apatite and a small amount of clay mineral. But because of the close germination of phosphate .of a mineral with "calcite" and a high value of the calcium modulus, CC phosphorites are not amenable to flotation and are not suitable for sulfuric, nitric and hydrochloric acid extraction of phosphoric acid to obtain standard highly concentrated and water-soluble fertilizers such as ammophos and double superphosphate.

For the processing of poor phosphorite ores, which are phosphorites of the Central Committee, it is necessary to develop effective technologies that require knowledge of the physico-chemical and technological features of the enrichment processes, or direct acid processing of phosphorites of various nature, chemical and mineralogical composition.

Scientists and specialists of NIIHIMMASh, NIIFA, Mendeleev Moscow Art Institute have developed a technology for obtaining a new nitrogen-phosphorus fertilizer - ammonium phosphate. It is important that the consumption of sulfuric acid for the production of 1 ton of P_2O_5 in the form of ammonium phosphate is 10-15% lower compared to ammophos, and the degree of use of phosphate raw materials is 1.0-1.5% higher. The production of ammonium phosphate from Karatau phosphorites has been mastered at the Dzhambul superphosphate plant in Kazakhstan, at the Charzhou Chemical Plant in Turkmenistan, at Almalyk OJSC Ammophos in Uzbekistan, and from the Khibiny apatite concentrate at the Balakovo Mineral Fertilizers Plant in Russia. It is necessary to master the technology of ammonium phosphate fertilizers based on CC phosphorites.

CHAPTER 2. RESEARCH METHODS AND TECHNIQUES.

2.1 Objects and methods for conducting experiments.

To conduct a study on the production of ammophosphate fertilizers, high-carbonate phosphorites of the Central Committee were used - ordinary phosphate rock (OPR), pulverized fraction (PF), washed dried concentrate (WDC), mineralized mass (MM), washed calcined phosphorous concentrate (WCC) and chemically enriched phosphate concentrates (CEC) , the compositions of which are given in Table 2.1, as well as EPA, obtained by the dihydrate method from the WCC of phosphorites of the Central Committee, composition (wt.%): 20.5 P_2O_5; 0.28 CaO; 0.66 MgO; 0.51 Fe_2O_3; 0.80 AI_2O_3; 2.98SO_3; 1.05 F; 0.1Cl.

Table 2.1. The chemical composition of phosphorites of the Central Kyzylkum used to obtain ammophosphate.

Types of phosphorites	Content of components, wt. %									CaO: P_2O_5
	P_2O_5	CaO	MgO	Fe_2O_3	$A1_2O_3$	F	CO_2	H_20	% by limit. acid	
1	2	3	4	5	6	7	8	9	10	11
High-carbonate						phosphorites				
OPR	17,20	46,22	1.75	1,05	1.24	2,00	16,00	7,691	18.50	2.69
PF	18,54	44,72	0,80	0,80	0,95	2,22	14.80	8,54	20.71	2.41
WDC	18,22	47,28	0,99	0,60	1,18	2,29	14,90	6.81	17,80	2.60
MM	14,68	40,80	0,53	1,37	1,17	1,85	12,80	11,89	16.41	2.78
				phosphate concentrates						
WCC	27,26	53,36	0,61	0,51	1,30	2,91	2,41	5,95	12.24	1.96
CEC	26,55	41,62	1,36	0,93	1,86	2,37	2,89	9,45	44,71	1.57

CEC was obtained by the method of [118; p. 5-10.], by the interaction of OPR with 57.87% nitric acid at a rate of 50% of stoichiometry on CaO, followed by the release of calcium nitrate.

2.2 Methodology of chemical and physico-chemical analyses of raw materials and obtained products.

Laboratory experiments were carried out on an installation consisting of a tubular glass reactor equipped with a screw stirrer driven by a motor. The required amount of EPA was stirred by the reactor and ammoniated with ammonia gas to the pH value 1,2; 1,5; 1,7, 1,8, 2,0, 2,2 and 2.5. After reaching the pH, the calculated amount of phosphate raw materials was added to the partially ammoniated acid obtained with intensive stirring (the rotation speed of the agitator is 250-300 rpm). The temperature of the reaction mass was maintained at 60 ° C using a contact thermometer. After the phosphorite dosage, the contents in the reactor were kept for 30 minutes. Then the obtained pulps were dried in a thermostat at 90-100 ° C.

Chemical analysis of dried products was carried out according to the generally accepted method [110].

Determination of phosphates (total, usable and aqueous forms of P_2O_5) was carried out by differential photometric method. The method is based on the formation of a yellow-colored phosphor-vanadium-molybdenum complex and photometric measurement of the optical density of this complex at a wavelength of X = 430-450 nm relative to a reference solution containing a known amount of P_2O_5. The usable form of P_2O_5 was calculated using solubility in both 2% citric acid and 0.2M solution of trilon B, while the amount of usable form of CaO was determined only by citric acid.

Calcium and magnesium were determined by the complexometric method [111]. The method involves a color change of the indicator (fluorexone for the determination of calcium and acid chromium dark blue for the estimation of magnesium) during the interaction of calcium and magnesium ions with trilon B.

Sulfates were determined by the weight method [112.]. The method is based on the precipitation of sulfates with barium chloride in an acidic medium and subsequent weighing of the precipitate.

The content of iron and aluminum oxide was determined on the basis of the complexometric method [113]. The method is based on titration of iron with 0.0125 M solution of trilon B in the presence of sulfosalicylic acid as an indicator and reverse titration of the excess of trilon B with a solution of zinc sulfate to determine aluminum in the presence of xylene orange indicator.

The free form of P_2O5 in the products was determined by the potentiometric method on the I-130M ionometer with an electrode system of ESL 63-07, EVL-1M3.1 and TKA-7 electrodes with an accuracy of 0.05 pH units. This method is based on titration of an alkali solution (0.1 N NaOH solution) to pH 4.0 [114.].

The fluorine content in the raw material was determined by ionometric method [115]. The method is based on measuring the concentration of fluorine in a solution using a fluoride selective electrode without prior extraction of fluorine.

The amount of carbon dioxide in phosphate raw materials and products was determined by the volumetric method [116]. The method is based on the decomposition of carbonates with 10% hydrochloric acid and the determination of the volume of carbon dioxide released when absorbed by a 40% solution of caustic potassium.

The moisture content in solid samples was determined by drying in a drying cabinet to a constant mass at a temperature of 100-105 ° C. The pH of solutions and suspensions was determined by the electromechanical method [117]. The pH value of a 10% aqueous suspension of the products, after their hourly agitation, was determined on an H-130M ionometer.

Total nitrogen was determined by the method [118]. The method is based on the reduction of nitrate nitrogen to ammonia by the Devard alloy, followed by distillation of ammonia and its titrometric determination.

The granulation of wet phosphate masses was carried out during the drying process by the rolling method.

The X-ray analysis of phosphogypsum was studied on a DRON-3 diffractometer with filtered (Fe) radiation mode: I = 25-30mA, U-30kV, Vdetect = 2^o/min, Vdifr.tape = 600 mm/hour, measurement limit - $4x10^2$ imp/sec, t = 0.5 sec, slots: 1x4x1 mm. The survey area is 2θ=3-820 for the initial samples.

The IR spectra of the sample were recorded on a PERKIX-ELMER IR Fourier spectrometer (Japan) in the form of tablets with KBr in the area of 400-4000 cm^{-1}. Decoding of radiographs was carried out using a database [119], carrying bands of IR spectra was carried out using reference literature [120].

The component composition of the W samples was determined by the OES with the ICP. The OES method with ICP is based on the emission of a certain wavelength for each element, where the release (emission) of absorbed energy occurs depending on the concentration of the element. The plasma here serves to transfer the element under study to an excited state. When an element goes into a normal state, it emits (releases) the absorbed energy E =hv. The wavelength is measured in nm.

The method of quantitative determination of micro- and macroelements by the OES method with ICP is as follows: 0.5000-0.0500 g of the test substance is weighed on analytical scales and transferred to Teflon autoclaves. Then 3 ml of concentrated nitric acid (pure) and 2 ml of hydrogen peroxide (pure) are poured into autoclaves. Next, the autoclaves are closed and placed on a Berghoff microwave decomposition device with MWS-3+ software or a similar type of microwave decomposition device. The decomposition program is determined based on the type of the substance under study, the degree of decomposition and the number of autoclaves (up to 12 pcs.) are indicated. When the decomposition is finished, the contents in autoclaves are placed to a 50 ml volumetric flask in which the volume is brought to the mark with 2% nitric acid. The determination of the test substance is carried out on an OES device with the Optima-2400DV ICP (USA) or a similar device of an optical emission spectrometer with inductively coupled argon plasma. In the determination method, the optimal wavelength of the micro- or macroelement being determined is indicated at which it has the maximum emission. In the construction of the sequence of analyses, the amount in mg and the degree of its dilution in ml are indicated. After receiving the data, the device automatically calculates and enters in mg/kg or mcg/g the true quantitative content of the substance in the test sample.

In order to establish the shape, size and nature of the distribution of substances in the composition of the ICP sediment, electron microscopic studies were carried out. Electron microscopic studies were carried out on a BS 242E electron microscope (Tesla, Czech Republic). The samples were sprayed with a vacuum VUP-5 installation using a carbon replica method. After spraying, the samples were dissolved in hydrochloric acid (HCl) at a concentration of 5-10%. The samples were then washed in distilled water, followed by purification in alcohol. The replica was mounted (caught) on a mesh object holder, and after drying it was viewed on an electron microscope.

The chemical composition of the water-insoluble part of the ammonium phosphate fertilizers has been determined. In the composition of the water-insoluble part of fertilizers, the presence of a large amount of the digestible form of P_2O5 and CaO and a high degree of decarbonization of phosphate raw materials confirms the fact that the phosphate mineral was subjected to acid activation during the processing of raw materials with partially ammoniated EPA. At the same time, the structure of a phosphate mineral in a water-insoluble precipitate differs significantly from its structure in the initial phosphate raw material, since its grains are etched with acid, have a porous structure and are 15-30 times smaller in size than the original one.

All this contributes to the conversion of the indigestible form of P_2O_5 in the raw material into the form of P_2O_5 assimilable for plants in a water-insoluble precipitate. It should be noted that when highly carbonized Kyzylkum phosphorites interact with partially ammoniated EPA, intensive decarbonization occurs. Intensive release of CO_2 destroys the structure of the phosphate mineral, also contributing to its activation.

The salt composition of NP fertilizers was determined by X-ray and IR spectroscopic analysis methods. It is shown that the salt composition of fertilizers mainly consists of ammonium dihydrophosphate, calcium hydro- and dihydrophosphates, as well as partially activated and undecomposed phosphorites.

CHAPTER III. AMMONIUM PHOSPHATE FERTILIZERS BASED ON THE ACTIVATION OF KYZYLKUM PHOSPHORITES WITH PARTIALLY AMMONIATED EPA.

3.1 Reaction of unenforced high-carbonate phosphorites of Central Kyzylkums with partially ammoniated extraction phosphoric acid.

The variable parameters were the pH of the acid and the mass ratio of partially ammoniated EPA to phosphate raw materials (PR) [78.95]. When phosphate raw materials interact with partially ammoniated phosphoric acid , the following reactions occur:

$CaO + 2H_3PO_4 = Ca(H_2PO_4)_2 + H_2O$

$CaO + H_3PO_4 = CaHPO_4 + H_2O$

The general picture of the interaction of highly carbonized CC phosphorites with partially ammoniated EPA is similar to that given in [78, 95,98] for Karatau phosphorites. The difference is only in the absolute values of the degree of decomposition of phosphate raw materials. With a 30-minute interaction at a temperature of 60 °C, we observe the following patterns for all types of phosphorites studied: the lower the pH of the acid and the higher the EPA : PR ratio, the greater the value of the degree of decarbonization of raw materials.

In the case of using OPR at pH = 1.2 and the ratio of EPA : PR = 100 : 50, the degree of decarbonization is 82.8%, whereas at pH = 2.5 and the same ratio of EPA: PR, it reaches a value of only 68.77%. At EPA: PR = 100 : 20 and pH = 1.2, it is 95.11%, and at pH = 2.5 - 83.03%. Only with EPA:PR = 100:15 and pH = 1.2 we have almost complete decarbonization - 98.05%, and at pH = 2.5 it is 86.32%. At pH = 2.5 and EPA : PR = 100 : 15 - 91.82%, and at EPA : PR = 100 : 50 - 65.01% (Fig.3.1).

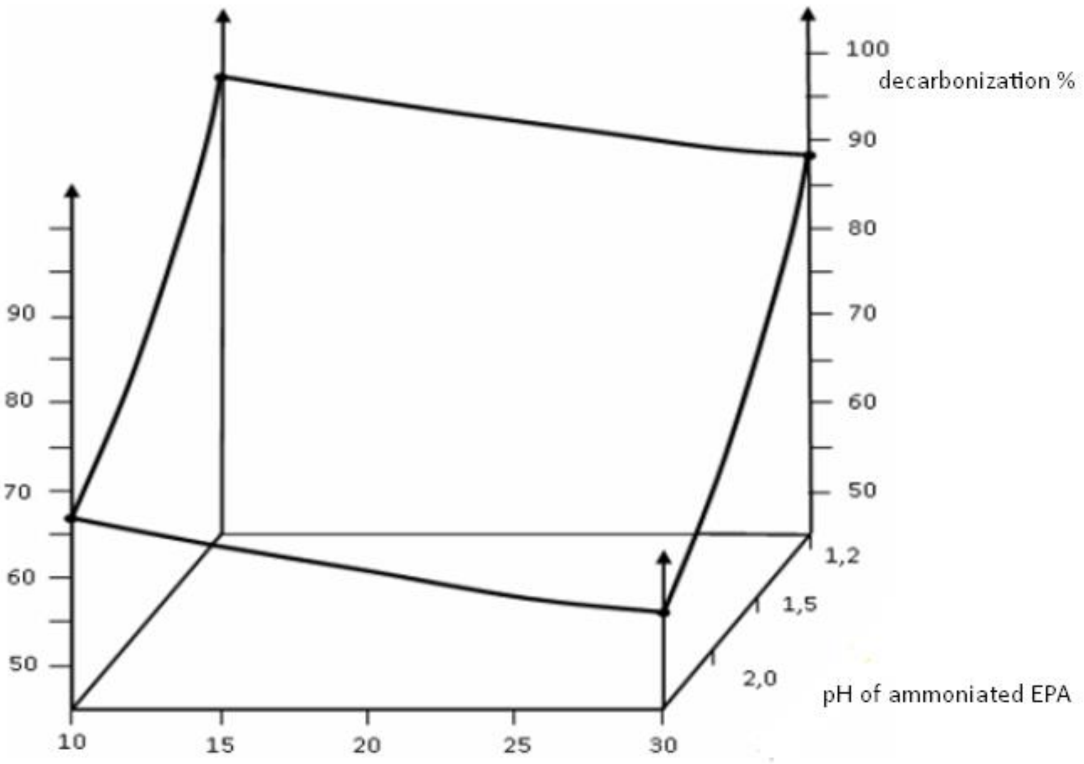

Fig.3.1 - dependence of the change in the degree of decarbonization of the mineralized mass on the pH of EPA and the mass ratio EPA: PR

Exactly the same pattern has been established with respect to the relative content of the form P_2O_5 digested by citric acid in fertilizers. For phosphorite flour at pH of acid 1,2 and EPA: PR = 100 : 15 P_2O_5usb: P_2O_5tot = 98.6%, and with EPA: PR = 100 : 50 - 80.01%. The relative content of digestible and aqueous forms of P_2O_5 in fertilizers based on Kyzylkum phosphorites, depending on the pH of EPA and EPA : PR are shown in Figure 3.2. The main factor affecting the composition of fertilizers is the mass ratio of EPA : PR. With the same pH value of EPA equal to 1.2 and a decrease in the ratio of EPA : PR from 100:15 to 100: 50 leads to a decrease in the relative content of the water-soluble and digestible form of P_2O_5 in 2% citric acid and 0.2 M solution of Trilon B in fertilizers from 76.79 to 34.89; from 72.86 to 29.90; from 98.60 to 80.01; from 92.16 to 72.27, from 86.51 to 61.48 and from 81.86 to 56.13%, respectively, for OPR and WDC. The composition of fertilizers is also influenced to a certain extent by the pH value of partially ammoniated EPA. For example, an increase in the pH of EPA from 1.2 to 2.5 with a ratio of EPA : PR = 100 : 15 contributes to a decrease in the products of P_2O_5aq : P_2O_5tot and P_2O_5usb : P_20_5tot for trilon B from 76.79 to 67.46; from 72.86 to 63.67; from 86.51 to 82.02 and from 81.86 to 76.15%, respectively, for ordinary phosphate flour and washed dried concentrate. Similar patterns are observed when using PR and MM.

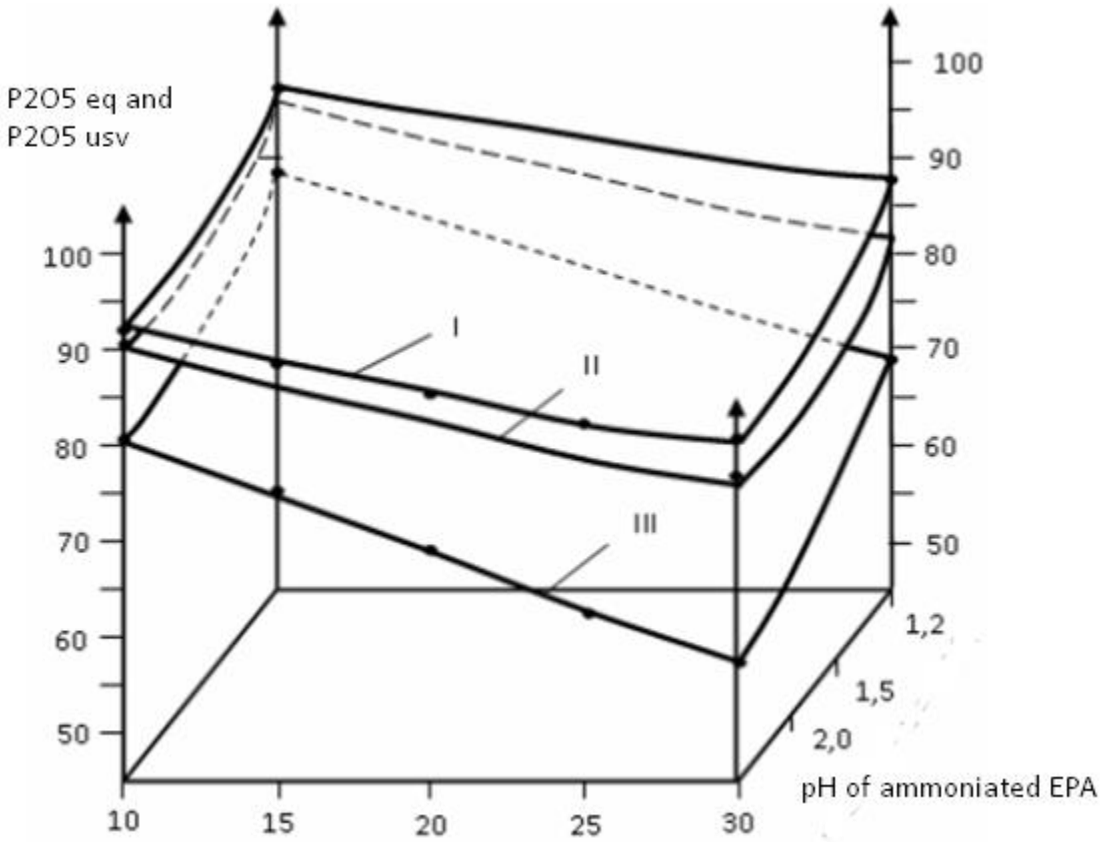

Fig. 3.2- Dependence of the change in the assimilable and water-soluble forms of P_2O_5 in ammophosphate fertilizers on the pH of EPA and the mass ratio of EPA : PR. I - P_2O_5usb. according to citric acid, II - P_2O_5usb. according to Tr. B, III - P_2O_5aq.

The water-soluble forms of P_2O_5 and CaO in fertilizers prove the presence of calcium dihydrophosphate in them. The excess of the digestible form of P_2O_5 and CaO over the water-soluble form indicates the formation of calcium hydrophosphate and an activated form of fluorapatite in the products. At high acid pH values and low EPA ratios. The aqueous and digestible forms of P_2O_5 in the products are formed as a result of the decomposition of calcium carbonate by phosphoric acid. And only at low pH values and a high EPA: PR ratio, the activation of the phosphate mineral also occurs.

Laboratory studies on the production of ammonium phosphate fertilizers were carried out in laboratory conditions at a temperature of 60 °C for 30 minutes. The mineralized mass (MM) was used as a raw material – the waste of the Kyzylkum processing complex of the composition (mass. %): P_2O_5tot - 14.68; CaO tot – 40.80; MgO – 0.53; Fe_2O_3 – 1.37; Al_2O_3 – 1.17; F-1.85; CO_2 – 12.80, NO – 11.89 and extraction phosphoric acid composition (wt. %): 20.5 P_2O_5; 0.28 CaO; 0.66 MgO; 0.51 Fe_2O_3; 0.80 Al_2O_3; 2.98 SO_3; 1.05 F; 0.1 Cl. The variable parameters were the pH of the acid from 1.2 to 2.0 and the mass ratio of partially ammoniated EPA to MM from 100:15 to 100:50. Interaction time 30 min temperature 60 ºC. When phosphate raw materials interact with partially ammoniated phosphoric acid , the following reactions occur:

$CaO+2H_3PO_4 \rightarrow Ca(H_2PO_4)_2+H_2O$ and $CaO+H_3PO_4 \rightarrow CaHPO_4+H_2O$

After completion of the decomposition process, the reaction mass was dried at a temperature of 85-90 ° C with simultaneous pelletizing by rolling. Dried fertilizer samples were analyzed for the contents of various forms of P_2O_5, CaO and nitrogen according to the method [93].

The usable form of P_2O_5 was evaluated by solubility in both citric acid (2%) and 0.2M solution of trilon B, whereas the amount of usable form of CaO was calculated only by citric acid. Nitrogen was determined by the distillation method on a Kjeldaglia flask. The results of the studies are shown in the table. As can be seen from the table, with a 30-minute interaction at a temperature of 60 ℃, we observe the following patterns for all types of phosphorites studied: the lower the pH of the acid and the higher the ratio of partially ammoniated EPA: MM, the greater the value of the assimilable and aqueous forms of phosphorus. To establish the effect of the pH of partially ammoniated EPA on the relative assimilable by citric acid, trilone B and aqueous forms of $P2O_5$, the mass ratio 100:15; 100:20; 100:25; 100:30; 100:35; 100:40 and 100:50 was conventionally designated by dividing 100 by 15-50 as 6.67; 5.0; 4.0; 3.33; 2.5 and 2, respectively (Fig. 3.3 and 3.4). Note that the correct 5 curves belong to the relative usable form P_2O_5 by citric acid, and the lower one belongs to trilon B.

Table 3.3. Composition of ammonium phosphate fertilizers based on ammoniated EPA and MM

Mass ratio part. Ammo. EPA: MM	pH pulp after decompose	pH 10% suspension	Chem. Content of dried product, %							
			P_2O_5 tot.	P_2O_5 free in 2%-citric.a	P_2O_{5usb} in 0,2M. tril.B	P_2O aq.	CaO tot..	$CaO_{usb.}$ in 2%-citric. ac	CaO aq.	N_{tot}, %
1	2	3	4	5	6	7	8	9	10	11
part. Amm. Up to pH = 1,2 EPA (P_2O_5 –17,35 %, N–1,86 %)										
100 : 15	2,21	2,89	40,06	36,34	31,95	27,98	12,87	10,04	5,51	3,62
100 : 20	2,36	3,19	38,25	33,82	29,31	25,04	15,85	12,16	5,25	3,38
100 : 25	2,67	3,46	36,58	31,34	27,01	22,13	17,91	13,36	4,99	3,07
100 : 30	2,94	3,67	35,04	29,12	24,31	19,28	19,96	14,22	4,56	2,97
100 : 35	3,31	3,74	34,11	27,57	22,08	16,84	21,87	15,25	3,97	2,58
100 : 40	3,45	4,03	33,07	25,29	19,78	13,78	23,49	15,54	3,40	2,47
100 : 50	-	4,47	31,34	21,94	17,26	9,39	26,48	16,35	2,64	2,24
Part. Amm. upto pH = 1,5 EPA (P_2O_5 –16,74 %, N–2,13 %)										
100 : 15	2,56	3,23	39,71	35,62	31,24	27,29	12,76	9,74	5,14	4,48
100 : 20	2,85	3,32	37,69	32,80	28,59	23,98	15,63	11,69	4,92	3,99
100 : 25	3,33	3,57	35,56	30,03	25,76	20,79	17,68	12,74	4,57	3,76
100 : 30	3,57	3,89	34,43	28,11	23,59	18,50	19,88	13,66	3,78	3,45
100 : 35	-	4,23	33,58	26,62	21,40	15,82	21,70	14,35	3,32	3,17
100 :	-	4,46	32,51	24,17	18,94	13,22	23,34	14,83	2,88	2,98

40										
100 : 50	-	4,81	30,81	21,18	16,73	8,78	26,29	15,60	2,01	2,57
Part. Amm. upto pH = 1,7 EPA (P_2O_5 –16,49 %, N–2,27%)										
100 : 15	2,89	3,30	38,87	34,38	30,27	26,24	12,67	9,34	4,59	4,79
100 : 20	3,29	3,62	36,78	31,55	27,34	22,59	15,56	11,21	4,31	4,36
100 : 25	3,58	3,84	35,04	29,20	25,11	19,62	17,59	12,26	3,46	4,01
100 : 30	-	4,17	33,73	27,04	22,53	17,34	19,64	13,03	3,06	3,64
100 : 35	-	4,38	32,42	24,94	20,27	14,52	21,60	13,75	2,61	3,37
100 : 40	-	4,65	31,56	22,91	18,11	11,98	23,22	14,17	2,18	3,21
100 : 50	-	4,89	30,42	19,88	15,91	8,42	25,85	14,67	1,72	2,73
part. Amm. upto pH = 2,0 EPA (P_2O_5 –16,07 %, N–2,50 %)										
100 : 15	3,16	3,73	37,34	32,46	28,44	24,54	12,54	8,82	4,10	5,20
100 : 20	3,67	3,99	35,62	29,83	25,88	20,94	15,41	10,53	3,66	4,67
100 : 25	3,87	4,24	33,76	27,24	23,33	18,12	17,44	11,36	2,61	4,35
100 : 30	-	4,61	32,56	25,27	21,27	15,82	19,47	12,12	2,24	4,05
100 : 35	-	4,78	31,48	23,34	19,07	13,02	21,38	12,79	1,71	3,86
100 : 40	-	4,97	30,73	21,45	17,29	11,01	23,06	13,08	1,43	3,52
100 : 50	-	5,35	29,62	18,43	15,23	7,63	25,66	13,25	1,07	3,19
part. Amm. upto pH = 2,2 EPA (P_2O_5 –15,72 %, N–2,70 %)										
100 : 15	3,37	3,71	36,05	30,91	27,25	23,01	12,44	8,53	3,75	5,47
100 : 20	3,89	4,15	34,72	28,70	24,91	20,01	15,28	9,97	3,12	5,12
100 : 25	-	4,52	33,09	26,24	22,64	17,23	17,23	10,74	2,36	4,70
100 : 30	-	4,73	32,13	24,42	20,76	14,19	19,29	11,33	1,84	4,48
100 : 35	-	4,99	31,15	22,66	18,61	12,05	21,20	11,88	1,41	4,19
100 : 40	-	5,21	30,28	20,51	16,83	9,56	22,85	12,37	1,14	3,84
100 : 50	-	5,74	29,15	17,52	14,74	7,10	25,53	12,61	0,77	3,51

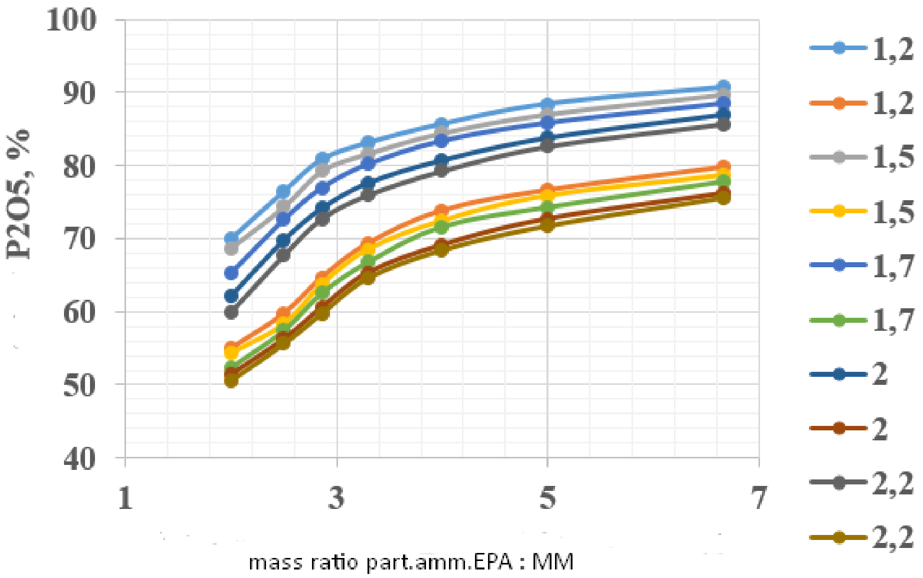

Fig.3.3. Influence of pH of PAEPA and mass ratio of PAEPA to MM. Here on the left is P205 usb.

It follows from the figure that an increase in pH and a decrease in the mass ratio from 6.67 to 2.0 contributes to a decrease in the relative digestible forms of phosphorus from 90.71 to 60.01 and from 79.76 to 50.57%, respectively, for citric acid and trilone B. While the relative aqueous form of P_2O_5 decreases from 69.84 to 24.36%.

In agriculture, the most valuable phosphorus-containing fertilizers are those in which ratio of P_2O_5 aq : P_2O_5 tot is 50 percent or more. Thus, the optimal values for production of such fertilizers can be considered the following: for OPR the pH of partially ammoniated EPA - 1.2-1.5; ratio of EPA : MM is 100:(15-30). Composition of fertilizers (wt. %): P_2O_5 tot - 34.43-40.06; P_2O_5usb. by citric acid - 28.11-36.34; P_2O_5usb. by tril. B - 23.59-31.95; P_2O_5aq. - 18.50-27.98; CaOtot - 12.76-19.96; CaOusb. - 9.74-14.22; CaOaq. - 3.78-5.51; P_2O_5usb. by citric acid: P_2O_5tot. - 81.64-90.71; P_2O_5usb. by tril. B : P_2O_5 total - 68.52-79.76; P_2O_5 aq : P_2O_5 tot - 53.73-69.84; N- 2,97-4,48. The strength of the fertilizer granules is at least 3 MPa.

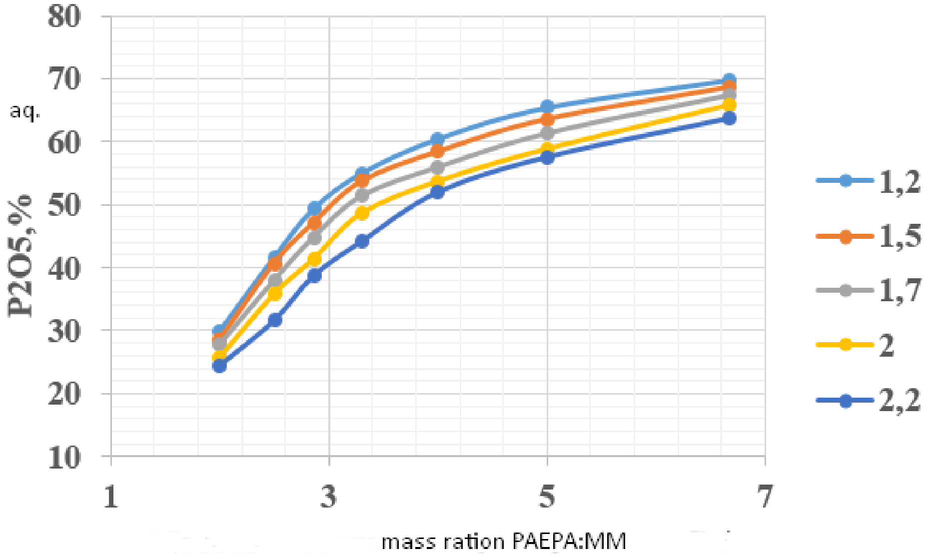

Fig.3.4. Influence of pH of PAEPA and mass ratio of PAEPA to MM

Thus, based on the data obtained, it can be concluded that the mineralized mass, under the found optimal conditions, lends itself well to chemical activation with the formation of assimilable calcium phosphate compounds. Studies of the process of chemical interaction of MM phosphorites of the Central Kyzylkum with partially ammoniated EPA showed the possibility of processing highly carbonized and unenriched phosphate raw materials to obtain a fertilizer containing nitrogen, phosphorus and calcium in its composition.

3.2 X-ray and IR spectroscopic studies of ammonium phosphate fertilizers and their water-insoluble part.

X-ray and IR spectroscopic methods of analysis were used to determine the approximate salt composition of ammonium phosphate fertilizers and their water-insoluble part [111: p.87- 91]. The results of the X-ray examination showed that the diffractograms of fertilizers and their water-insoluble part obtained on the basis of OPR, MM, PF and WDC are very similar to each other. Therefore, we decided to give X-ray images of samples of ammonium phosphate fertilizers and their water-insoluble part obtained only on the basis of OPR (Fig. 3.5.-3.7).

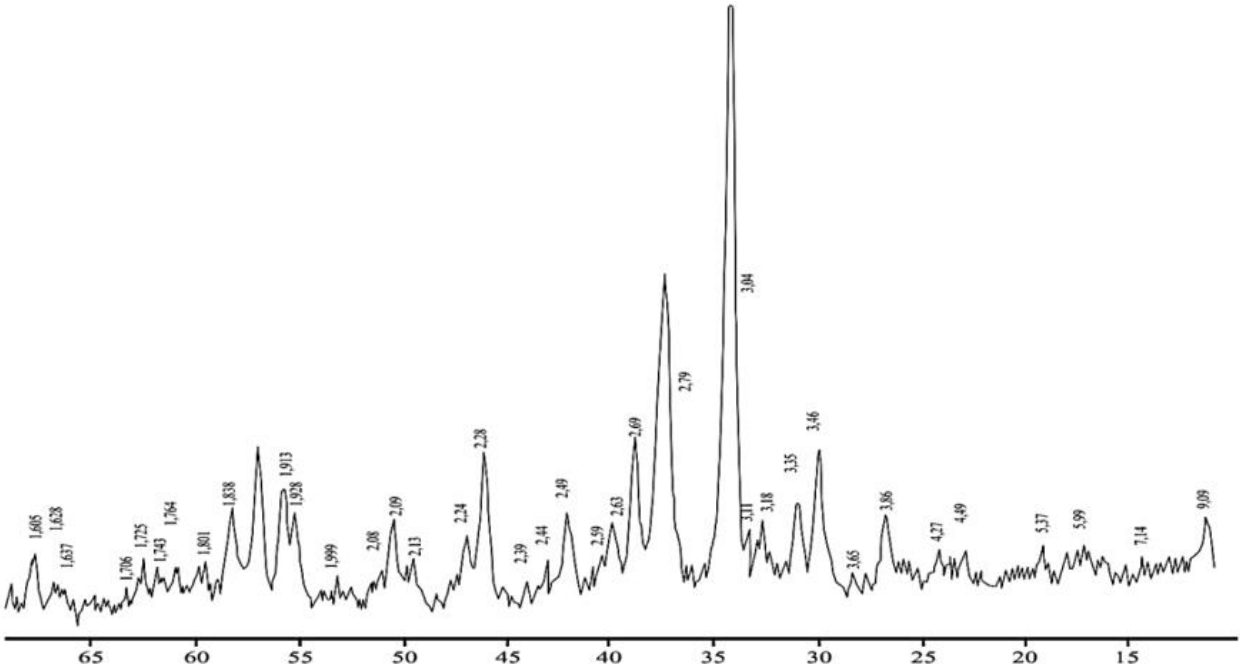

Fig. 3.5 - Radiograph of mineralized mass

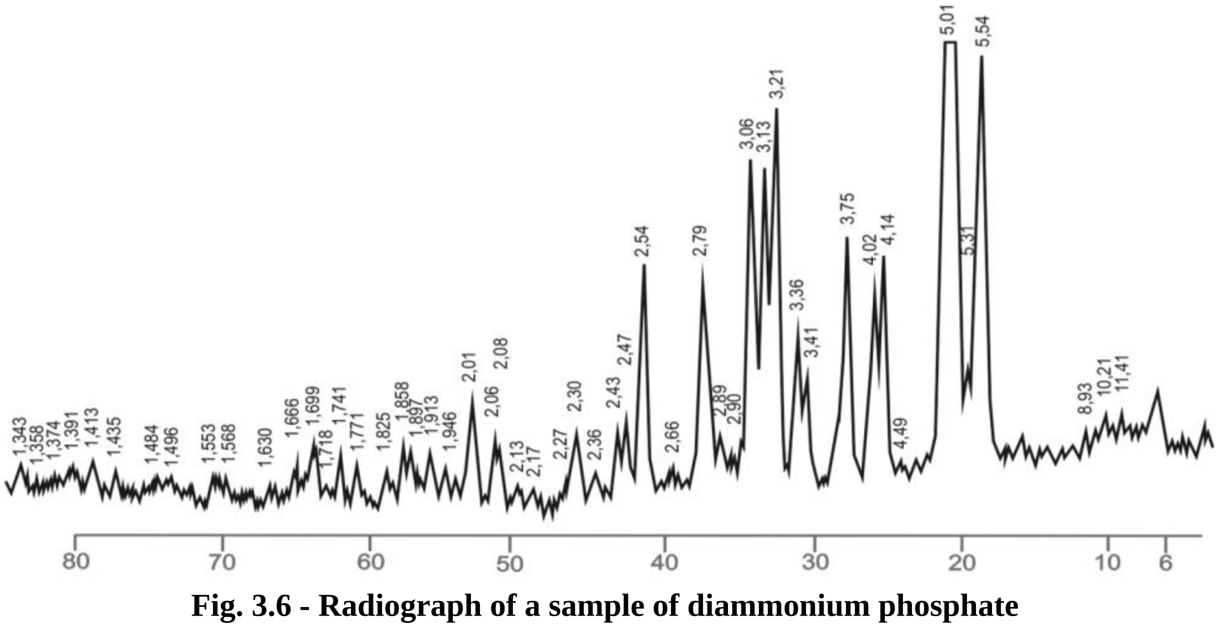

Fig. 3.6 - Radiograph of a sample of diammonium phosphate

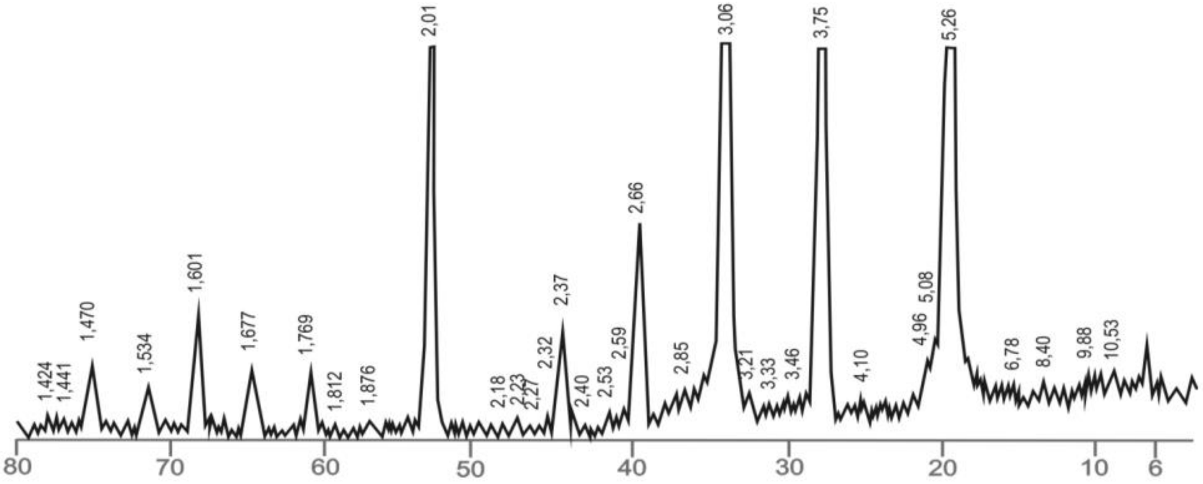

Fig. 3.7- X-ray pattern of a sample of monoammonium phosphate

Almost all diffractograms of fertilizers have clear interplane distances characteristic of ammonium dihydrophosphate 5,31 - 5,35; 3,76-3,77; 3,07 - 3,09; 2,65-2,67; 2,01 A, fluorocarbonatapatite 3,45 -3,47; 3,16-3,18; 2,80; 2,81; 2,70; 2,71; 2,62-2,64; 1,93; 1,94; 1,77; 1,75 A, calcium hydrophosphate 7,63-7,69; 4,26 - 4,29; 3,01-3,03; 2,24-2,28; 2,13; 2,14 and calcium dihydrophosphate is 2.97; 2.98; 1.79; 1.60 A. They only differ among themselves in the intensity of interplanar distances. The higher the pH value of the ammoniated acid and its amount for processing phosphate raw materials are taken, the more intense the peaks belonging to ammonium dihydrophosphate appear. The diffractograms of the water-insoluble part almost completely lack the interplane distances characteristic of ammonium dihydrophosphate (5,31-5,35; 3,76; 3,77; 3,09; 2,65-2,67 A) and calcium dihydrophosphate (2.97; 2.98; 1.79; 1.60 A). At the same time , peaks clearly appear 3,45; 3,46; 3,16-3,18; 2,80: 2,70; 2,71 A related to fluorocarbonatapatite, 4,29; 4,27; 4,25; 3,04-3,07; 2,24; 2,13; 2,14 A - to calcium hydrophosphate. Diffractograms of fertilizers and their water-insoluble part also show weak interplane distances of 2.50-2.52; 2.28; 2.29 A, which are characteristic of calcite. There are no interplane distances of 2.10 and 1.90 A in them, since when phosphorites interact with partially ammoniated EPA, the main part of calcite undergoes decomposition to form calcium dihydro- and hydrophosphates. X-ray studies show that the water-insoluble part of ammonium phosphate fertilizers mainly consists of undecomposed fluorocarbonatapatite, calcite, calcium hydrophosphate. A comparative analysis of the radiographs of the initial phosphate raw materials and the insoluble part of the ammonium phosphate fertilizers shows that some interplane distances characteristic of phosphorite, after its treatment with acid, largely shift in the direction of decrease or increase. In our opinion, this is due to changes in the structure of the phosphate mineral as a result of decarbonization and decomposition of the initial phosphorite EPA.

The absorption bands 1100, 1405, 1410, 1415, 1460 cm, which belong to ammonium dihydrophosphate, are clearly visible on the infrared spectra of ammonium phosphate fertilizers obtained on the basis of decomposition of phosphorites of partially ammoniated EPA at different mass ratios of EPA: PR and pH of EPA. The presence of water-insoluble calcium hydrophosphate in the composition of fertilizers is confirmed by the absorption bands 1220, 1660, 1680 cm^{-1}.

The absorption bands of 565, -0 cm may be attributed to calcium dihydrophosphate. Bands of lower intensity - 880 and 890 cm^{-1} indicate a small residual calcite content after the decomposition of phosphate raw materials EPA. Absorption bands are clearly visible on the IR spectrs of fertilizers 565, 570, 1050, 1080, 1100, 1460 cm^{-1} show the presence of fluorocarbonatapatite, which indicates incomplete decomposition of the raw materials. Thus, the data of X-ray and IR spectroscopic analyses are in good agreement with each other.

The process of obtaining ammonium phosphate by chemical activation of various types of Kyzylkum phosphorites with partially ammoniated EPA at weight ratios EPA : PR = 100: (15-50) and pH intervals of ammoniated EPA 1,2-2,5 was studied.

The dependence of the change in the degree of decarbonization of phosphate raw materials and the relative content of the digestible form of P_2O_5 on the ratio of EPA : PR and pH of EPA is established.

The chemical composition of the water-insoluble part of the ammonium phosphate fertilizers has been determined. In the composition of the water-insoluble part of fertilizers, the presence of a large amount of the digestible form of P_2O_5 and CaO and a high degree of decarbonization of phosphate raw materials confirms the fact that the phosphate mineral was subjected to acid activation during the processing of raw materials with partially ammoniated EPA. At the same time, the structure of a phosphate mineral in a water-insoluble precipitate differs significantly from its structure in the initial phosphate raw material, since its grains are etched with acid, have a porous structure and are 15-30 times smaller in size than the original one. All this contributes to the conversion of the indigestible form of P_2O_5 in the raw material into the form of P_2O_5 assimilable for plants in a water-insoluble precipitate. It should be noted that when highly carbonized Kyzylkum phosphorites interact with partially ammoniated EPA, intensive decarbonization occurs. Intensive release of CO_2 destroys the structure of the phosphate mineral, also contributing to its activation. The salt composition of NP fertilizers was determined by X-ray and IR spectroscopic analysis methods. It is shown that the salt composition of fertilizers mainly consists of ammonium dihydrophosphate, calcium hydro- and dihydrophosphates, as well as partially activated and undecomposed phosphorites.

CONCLUSION

As a result of all this, the interaction of off-balance ores of CK phosphorites with partially ammoniated EPA was investigated at a wide range of weight ratios of EPA: PR (100: 15-50) and pH of ammoniated EPA (1.2-2.5). The compositions of ammonium phosphate fertilizers were determined, the degree of decarbonization of phosphate raw materials and the relative contents of the digestible and aqueous forms of P_2O_5 were calculated. It is shown that the activation of phosphorites, i.e. the conversion of the form of P_2O_5 that is not digested in them into the digestible form, occurs when they are treated with an ammoniated solution of phosphoric acid. Both the fertilizer itself and its water-insoluble part have high concentrations of the digestible forms of P_2O_5 and CaO, having a prolonged effect. The products consist of monoammonium phosphate, mono- and dicalcium phosphate, activated fluorocarbonatapatite. Thus, this approach partially solves the problem of involving low-grade phosphorites in the production of concentrated phosphorus fertilizers.

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APPENDIX

ЎЗБЕКИСТОН РЕСПУБЛИКАСИ
ОЛИЙ ВА ЎРТА МАХСУС ТАЪЛИМ ВАЗИРЛИГИ

МИРЗО УЛУҒБЕК НОМИДАГИ ЎЗБЕКИСТОН
МИЛЛИЙ УНИВЕРСИТЕТИ

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ВОПРОС ИСПОЛЬЗОВАНИЕ НИЗКОСОРТНЫХ ФОСФОРИТОВ КЫЗЫЛКУМА В АЗОТНОФОСФОРНЫЕ УДОБРЕНИЯ

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В мире с истощением запасов качественных залежей природных фосфатов и добыча, которых становится всё сложнее и дороже, производители фосфорных удобрений начали ориентироваться на переработке низкосортных, особенно карбонатно-фосфоритовых руд (15-20% P_2O_5), объем которых составляет две трети мировых запасов. Для этого необходимо обосновать соответствующие научно-технические решения, в том числе вовлечение в технологию аммофосфатных удобрений низкосортных фосфоритов Центральных Кызылкумов (ЦК) в качестве вторичного сырья; установление оптимального режима концентрирования экстракционной фосфорной кислоты (ЭФК) методом упаривания; нахождение оптимальных условий получения двойного суперфосфата и концентрированного азотнофосфорного удобрения на основе взаимодействия низкосортных фосфоритов упаренной ЭФК с применением циклического метода разложения.

Технология аммофосфата на основе фосфоритов Каратау была внедрена на Джамбульском суперфосфатном заводе в Казахстане, на Чарджоуском химическом заводе в Туркменистане, и на Алмалыкском химическом заводе в Узбекистане. На Балаковском ПО «Минудобрения» в России данный способ внедрен с применением хибинского апатитового концентрата. Согласно ТУ № 113-08-552-84 аммофосфат из фосфоритов Каратау содержит 39% P_2O_5 и 5% N. Аммофосфат на основе апатитового концентрата содержит 47.0% P_2O_5 и 8.4% N.

Данная технология решает задачу вовлечения в производство практически всех видов фосфатов различных месторождений, что сокращает сырьевые и энергетические ресурсы: серной кислоты – на 15%, топлива – на 15%, фосфатного сырья – на 2%. Улучшается экологическая обстановка производства за счет сокращения на 15% отхода фосфогипса, практически полной ликвидации потерь аммиака. Замена 15% P_2O_5 фосфорной кислоты на P_2O_5 фосфорита в аммофосфате приводит к положительным технико-экономическим показателям.

Процесс исследование аммофосфатных удобрений были проведены в лабораторных условиях при температуре 60 ºС в течение 30 мин. В качестве сырья была использована минерализованная масса (ММ) – отход Кызылкумского обогатительного комплекса состава (масс. %): $P_2O_{5\text{общ.}}$ – 14,68; $CaO_{\text{общ.}}$ – 40,80; MgO – 0,53; Fe_2O_3 – 1,37; Al_2O_3 – 1,17; F-1,85; CO_2 – 12,80, н.о. – 11,89 и экстракционная фосфорная кислота состава (вес. %): 20,5 P_2O_5; 0,28 CaO; 0,66 MgO; 0,51 Fe_2O_3; 0,80 Al_2O_3; 2,98 SO_3; 1,05 F; 0,1 Cl. Варьируемыми параметрами были pH кислоты от 1,2 до 2,0 и массовое соотношение частично аммонизированной ЭФК к ММ от 100:15 до 100:50. При взаимодействии фосфатного сырья с частично аммонизированной фосфорной кислотой протекают следующие реакции:

$$CaO+2H_3PO_4 \rightarrow Ca(H_2PO_4)_2+H_2O \text{ и } CaO+H_3PO_4 \rightarrow CaHPO_4+H_2O$$

При 30-минутном взаимодействии при температуре 60^0С мы наблюдаем следующие закономерности для всех видов исследованных фосфоритов: чем ниже pH кислоты и выше соотношение ЭФК : ММ, тем больше значение степени декарбонизации сырья. Для ММ оптимальными значениями можно считать pH ЭФК - 1,2-1,5; ЭФК : ММ = 100: (15-30). Состав удобрений (масс. %): $P_2O_{5\text{общ.}}$ - 34,43-40,06; $P_2O_{5\text{усв.}}$ по лим. к-те - 28,11-36,34; $P_2O_{5\text{усв.}}$ по трил. Б - 23,59-31,95; $P_2O_{5\text{водн.}}$ - 18,50-27,98; $CaO_{\text{общ.}}$ - 12,76-19,96; $CaO_{\text{усв.}}$ - 9,74-14,22; $CaO_{\text{водн.}}$ - 3,78-5,51; $P_2O_{5\text{усв.}}$ по лим. к-те: $P_2O_{5\text{общ.}}$ - 81,64-90,71; $P_2O_{5\text{усв.}}$ по трил. Б : $P_2O_{5\text{общ.}}$ - 68,52-79,76; $P_2O_{5\text{водн.}}$: $P_2O_{5\text{общ.}}$ - 53,73-69,84; N- 2,97-4,48.

Таким образом, исследована возможность получения нетрадиционного азотнофосфорного удобрения – аммофосфата путем разложения забалансовой руды частично аммонизированной фосфорной кислотой из фосфоритов Центральных Кызылкумов.

ЎЗБЕКИСТОН РЕСПУБЛИКАСИ
ОЛИЙ ВА ЎРТА МАХСУС ТАЪЛИМ ВАЗИРЛИГИ

ТЕРМИЗ ДАВЛАТ УНИВЕРСИТЕТИ
ЎЗБЕКИСТОН МИЛЛИЙ УНИВЕРСИТЕТИ

АКАДЕМИК А.Ғ.ҒАНИЕВ ВА АКАДЕМИК Н.А.ПАРПИЕВ ХОТИРАСИГА БАҒИШЛАНГАН

“КОМПЛЕКС БИРИКМАЛАР КИМЁСИ ВА АНАЛИТИК КИМЁ ФАНЛАРИНИНГ ДОЛЗАРБ МУАММОЛАРИ”

РЕСПУБЛИКА ИЛМИЙ-АМАЛИЙ КОНФЕРЕНЦИЯСИ

МАТЕРИАЛЛАРИ ТЎПЛАМИ

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Термиз

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ИСПОЛЬЗОВАНИЕ НЕКОНДИЦИОННОГО ФОСФОРИТА ДЛЯ ПОЛУЧЕНИЯ КОМПЛЕКСНОГО АГРОХИМИКАТА - АММОФОСФАТА

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В связи того, что наблюдаеця резкий рост населения на планете (к 2050 численность населения достигнет 9 млрд) потребность к фосфорным удобрению неуклонно растет с каждым годом в среднем 2,5%. А это составляет 1 млн тонн 100% P_2O_5 в среднем. Известно, что минеральные удобрения играют важную роль для получения высоких урожаев, примерно 55% и сокращения значительных затрат на человеческий труд. Однако не все виды фосфатного сырья подходят к переработке с целью получения концентрированных фосфорных удобрений как аммофос, диаммофос, простой и двойной суперфосфат, а также NP и NPK-удобрения на их основе. Для этого необходимо фоссырье с содержанием не менее 32% P_2O_5, из которого можно получить любое фосфорное удобрение с хорошими технико-экономическими показателями. Однако, такие виды сырья исчерпываюця, и добыча их становиця все сложнее и дороже год за годом. Поэтому в мире наблюдаеця тенденция ориентироваться производителей фосфорных удобрений на переработку низкосортных, особенно карбонатно-фосфоритовых руд (15-20% P_2O_5), объем которых составляет две трети мировых запасов.

В данной ситуации альтернативой к традиционным фосфорным удобрениям можно отнести аммофосфатное удобрение, получаемое практически из низкосортных карбонатных зернистых (14-18% P_2O_5) и пластовых фосфоритов (18-22% P_2O_5).

Лабораторные исследования по получению аммофосфатных удобрений были проведены в лабораторных условиях при температуре 60ºС в течение 30 мин. В качестве сырья была использована рядовая фосфоритовая мука (РФМ) - отход Кызылкумского обогатительного комплекса состава (масс. %): $P_2O_{5\text{общ.}}$ - 17,20; $CaO_{\text{общ.}}$ - 46,22; MgO - 1,75; Fe_2O_3 - 1,05; Al_2O_3 - 1,24; F-2,00; CO_2 - 16,00, н.о. - 7,69 и экстракционная фосфорная кислота состава (вес. %): 20,5 P_2O_5; 0,28 CaO; 0,66 MgO; 0,51 Fe_2O_3; 0,80 Al_2O_3; 2,98 SO_3; 1,05 F; 0,1 Cl. Варьируемыми параметрами были pH кислоты от 1,2 до 2,5 и массовое соотношение частично аммонизированной ЭФК к РФМ от 100:15 до 100:50. При взаимодействии фосфатного сырья с частично аммонизированной фосфорной кислотой протекают следующие реакции:

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При 30-минутном взаимодействии при температуре 60°С мы наблюдаем следующие закономерности для всех видов исследованных фосфоритов: чем ниже рН кислоты и выше соотношение ЭФК : РФМ, тем больше значение степени декарбонизации сырья.

В сельском хозяйстве наиболее ценными фосфорсодержащими удобрениями считаюця те, в которых $P_2O_{5\text{водн.}}$: $P_2O_{5\text{общ.}}$ составляет 50 и более процентов. Установлено, что оптимальными значениями можно считать РФМ рН ЭФК - 1,2-2,0; ЭФК : ФС = 100 : (15-35) состав удобрений (масс. %): $P_2O_{5\text{общ.}}$ - 33,58-41,36; $P_2O_{5\text{усв.}}$ по лим. кис-те - 28,44-40,78; $P_2O_{5\text{усв.}}$ по трил. Б - 22,85-35,78; $P_2O_{5\text{водн.}}$ - 18,31-31,76; $CaO_{\text{общ.}}$ - 14,11-24,78; $CaO_{\text{усв.}}$ - 10,32-17,35; $CaO_{\text{водн.}}$ - 5,18-7,69; $P_2O_{5\text{усв.}}$ по лим. к-те: $P_2O_{5\text{общ.}}$ - 84,69-98,60; $P_2O_{5\text{усв.}}$ по трил. Б: $P_2O_{5\text{общ.}}$ - 68,05-86,51; $P_2O_{5\text{водн.}}$: $P_2O_{5\text{общ.}}$ - 54,53-76,79; N- 2,73-5,16. Прочность гранул удобрений составляет не менее 3 МПа.

Таким образом, проведенные исследования доказали получить комплексного агрохимиката, аммофосфата, из низкосортного фосфорита Кызылкума. Полученные продукта соотвецтвуют ТУ № 113-08-552-84, где аммофосфат из фосфоритов Каратау содержит 39% P_2O_5 и 5% N.

ИККИЛАМЧИ ХИНОЛИН АМИНЛАРИНИНГ МАСС СПЕКТРЛАРИ ТАҲЛИЛИ

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Хинолин бирикмалари азотли гетероциклик бирикмаларнинг муҳим синфларидан бири ҳисобланади. Ҳозирги кунда *quinine, chloroquine* каби дори воситаларини яллиғланишга, саратонга, микробларга, астма касаллигига қарши қўлланилиб келинётганлиги хинолин бирикмалари турли хил биологик фаолликларга эга эканлигидан далолат беради. Адабиёт маълумотлари таҳлилидан маьлум бўлди, таркибида амин гуруҳлар сақлаган бирикмаларнинг биологик фаолликлари нисбатан юқори бўлиши мумкин [1].

Шуларни инобатга олган ҳолда аминодубаминни ароматик альдегидлар билан маҳсулотдарини биологик фаолликиги ўрганиш мақсадида 4 та коньюгатларнинг икки босқичли синтези ўтказилди [2].

Синтез қилиб олинган моддаларнинг тузулиши ИҚ, ^{1}H ва ^{13}С ЯМР усуллар ёрдамида исботланди ҳамда уларнинг масс спектрлари таҳлили молекуляр ионлардан ташқари 265 ва 219 ионли фрагментлари нисбатан барқарор эканлигини кўрсатди. Биз буни 2- [4’,5’-Метилендиокси-2′-(N-3’’-гидрокси-4’’-

АКАДЕМИК А.Ғ. ҒАНИЕВ ВА АКАДЕМИК Н.А. ПАРПИЕВ ХОТИРАСИГА БАҒИШЛАНГАН

“КОМПЛЕКС БИРИКМАЛАР КИМЁСИ ВА АНАЛИТИК КИМЁ ФАНЛАРИНИНГ ДОЛЗАРБ МУАММОЛАРИ”

РЕСПУБЛИКА ИЛМИЙ - АМАЛИЙ КОНФЕРЕНЦИЯСИДАГИ ФАОЛ ИШТИРОКИ УЧУН

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ПЕРСПЕКТИВНОСТЬ ПЕРЕРАБОТКИ НЕКОНДИЦИОННОГО ФОСФОРИТА КЫЗЫЛКУМА НА АММОФОСФАТНОЕ УДОБРЕНИЕ

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PERSPECTIVITY OF PROCESSING OUT OF CONDITION KYZYLKUM PHOSPHORITE FOR AMMOPHOSPHATE FERTILIZER

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АННОТАЦИЯ

Изучен процесс переработки минерализованной массы (ММ) фосфоритов Центральных Кызылкумов отхода Кызылкумского фосфоритового комбината экстракционной фосфорной кислотой (ЭФК), нейтрализованной аммиаком с pH от 1,2 до 2,2. При этом массовое соотношение частично аммонизированной ЭФК к ММ варьировали от 100 : 15 до 100 : 50 при времени взаимодействии 30 мин и температуре 60 °С. Установлено, что чем ниже значение pH ЭФК и ниже массового соотношение частично аммонизированной (ЧА) ЭФК к ММ, тем ниже значения относительных усвояемых и водных форм P_2O_5. В связи того, что для растений необходимо использовать удобрения не ниже относительной водной формы P_2O_5 50% оптимальными значениями можно считать pH ЧАЭФК - 1,2-1,5; ЧАЭФК : ММ = 100: (15-30). Состав удобрений (масс. %): $P_2O_{5\text{общ.}}$ - 34,43-40,06; $P_2O_{5\text{усв.}}$ по лим. к-те - 28,11-36,34; $P_2O_{5\text{усв.}}$ по трил. Б - 23,59-31,95; $P_2O_{5\text{водн.}}$ - 18,50-27,98; $CaO_{\text{общ.}}$ - 12,76-19,96; $CaO_{\text{усв.}}$ - 9,74-14,22; $CaO_{\text{водн.}}$ - 3,78-5,51; $P_2O_{5\text{усв.}}$ по лим. к-те: $P_2O_{5\text{общ.}}$ - 81,64-90,71; $P_2O_{5\text{усв.}}$ по трил. Б : $P_2O_{5\text{общ.}}$ - 68,52-79,76; $P_2O_{5\text{водн.}}$: $P_2O_{5\text{общ.}}$ - 53,73-69,84; N- 2,97-4,48. Прочность гранул удобрений составляет не менее 3 МПа.

ABSTRACT

The process of processing the mineralized mass (MM) of phosphorites of the Central Kyzylkum from the waste of the Kyzylkum phosphorite plant with extraction phosphoric acid (EPA), neutralized with ammonia with a pH of 1.2 to 2.2, was studied. In this case, the mass ratio of partially ammoniated EPA to MM varied from 100 : 15 to 100 : 50 at an interaction time of 30 min and a temperature of 60°C. It has been established that the lower the pH value of EPA and the lower the mass ratio of partially ammoniated EPA to MM, the lower the values of relative digestible and aqueous forms of P_2O_5. Due to the fact that for plants it is necessary to use fertilizers not lower than the relative aqueous form P_2O_5 of 50%, the optimal values can be considered pH of partially ammoniated EPA - 1.2-1.5; partially ammoniated EPA: MM = 100: (15-30). The composition of fertilizers (wt.%): $P_2O_{5\text{tot.}}$ - 34.43-40.06; $P_2O_{5\text{deg.}}$ according to citric acid - 28.11-36.34; $P_2O_{5\text{deg.}}$ EDTA - 23.59-31.95; $P_2O_{5\text{aq.}}$ - 18.50-27.98; $CaO_{\text{tot.}}$ - 12.76-19.96; $CaO_{\text{deg.}}$ - 9.74-14.22; $CaO_{\text{aq.}}$ - 3.78-5.51; $P_2O_{5\text{deg.}}$ by citric acid: $P_2O_{5\text{tot.}}$ - 81.64-90.71; $P_2O_{5\text{deg.}}$ by EDTA : P2O5tot. - 68.52-79.76; $P_2O_{5\text{aq.}}$: $P_2O_{5\text{tot.}}$ - 53.73-69.84; N- 2.97-4.48. The strength of fertilizer granules is at least 3 MPa.

Ключевые слова: фосфорит, экстракционная фосфорная кислота, минерализованная масса, частичная аммонизация, аммофосат.

Keywords: phosphorite, extraction phosphoric acid, mineralized mass, partial ammonization, ammophosate.

Как известно Кызылкумские фосфориты месторождений Джерой-Сардара, Северный Джетымтау, Ташкура и Караката в отличие от своих аналогов Североафриканских фосфоритов и фосфоритов Ближнего Востока значительно отличают по специфике и текстуре минеральных составляющих и их расположением в самой природной руде. Руда в основном состоит из трех видов минералов: фосфаты из морских фаунов, кальцит с тремя разновидностями – эндокальцит, экзокальцит и изоморфнозамещенный; глинистые минералы, это гидрослюды (21-87% фракции), монтмориллонита (0-86%) и каолинита (2-15%) [1-3]. Исходя из этого представлен минеральный (мас.%): франколит – 56,0; кальцит – 26,5; кварц – 7,5 - 8,0; гидрослюдистые минералы и полевые шпаты – 4,0 - 4,5; гипс – 3,5; гетит – 1,0; цеолит < 1,0; органическое вещество – около 0,5 и химический состав (мас.%): 16,2 P_2O_5; 46,2 CaO; CaO: P_2O_5 = 2,85; 17,7 CO_2; 0,6 MgO; 2,9 (Fe_2O_3+Al_2O_3); 1,5 (K_2O+Na_2O); 2,65 SO_3; 1,94 F; 7,8 нерастворимого остатка усредненной пробы фосфорита [3]. Из практики известно, что такое сырье никак не поддается обогащению и получить на его основе стандартных фосфорных удобрений как аммофос, диаммофос, простой и двойной суперфосфат со знаком качество [4]. Попытки обогащения сырья химическим методом для удаления карбонатов в виде нитратов, хлоридов и ацетатов кальция не вышли из лабораторных рамков. Например, в работе [5-7] предлагается разложение Кызылкумского фосфорита HNO_3 58,78%-ной концентрации при ее норме от 40 до 60% в пересчете на CaO. Обработку фосфатного сырья (ФС) азотной кислотой проводили в течение 25-30 мин при 40°С согласно уравнению:

$$Ca_5(PO_4)_3F+CaCO_3+8HNO_3 = 4Ca(NO_3)_2+Ca(H_2PO_4)_2+CaHPO_4+HF+CO_2 + H_2O \quad (1)$$

После разложения полученную нитрокальцийфосфатную пульпу репульпировали 5-20%-ным раствором нитрата кальция при различных весовых соотношениях ФС:раствор $Ca(NO_3)_2$ = 1:(2-3) в течение 3-4 минут.

Затем нитрокальцийфосфатный раствор аммонизировали газообразным аммиаком до значения pH 3, для предотвращения потер водорастворимой P_2O5 в монокальцийфосфате ($Ca(H_2PO_4)_2$):

$$Ca(H_2PO_4)_2 + Ca(NO_3)_2 + NH_3 = 2CaHPO_4 + 2NH_4NO_3 \quad (2)$$

Далее происходит разделение реакционной суспензии на жидкую и твердую фазы разделяли путем фильтрации с последующей отмывкой нитрата кальция:

В результате образуется фосфоконцентрат с содержанием P_2O_5 25,90-26,11%; CaO 39,94-41,13%; CO_2 2,29-2,34% CaO: P_2O_5 = 1,53-1,59 и степенью отмывки 96,52-98,92%$Ca(NO_3)_2$.

Однако, наиболее лучшим методом обогащения карбонатных фосфоритов является термический, что и было внедрено в 2001 г, а далее было модернизировано в 2007 и 2014 гг на Кызылкумском фосфоритовом комбинате (КФК). Схема включает сухое грохочение, отмывка от хлора, мокрое обесшламывание и удаление CO_2 методом обжига при 950-1000 ºС [4].

Однако, ныне действующую технологию обогащения на КФК нельзя считать рациональной, т.к. в схеме обогащения повышение концентрации P_2O_5 в мытый обожженный концентрат (МОК-26% P_2O_5) всего на 8,42% по сравнению с его концентрацией в исходной руде (17,58%) происходит на фоне значительной потери P_2O_5 с хвостами обогащения со статусом «забалансовая руда» (134,77 тыс. т P_2O_5 или 42% от исходного P_2O_5 в руде). Из них 9,6% происходит при сухой сортировке на площадке рудоконтрольной станции, 28,3% при гидросортировке и 4,1% на стадиях сушки и обжига. Это, соответственно, минерализованная масса (12-14% P_2O_5), шламовый фосфорит (10-12% P_2O_5) и пылевидная фракция (18-20% P_2O_5). На сегодняшний день уже накоплено свыше 14 млн. т минерализованной массы и более 4 млн. т шламового фосфорита. Однако отсутствует эффективная технология обогащения и переработка отходных фосфоритов в готовые удобрения.

В данной ситуации альтернативой к традиционным фосфорным удобрениям можно прилагаться к технологии аммофосфата, приемлемая практически всем видам сырья как низкосортным карбонатным зернистым (14-18% P_2O_5), так и пластовым фосфоритам (18-22% P_2O_5).

Технология аммофосфата на основе фосфоритов Каратау была внедрена на Джамбульском суперфосфатном заводе в Казахстане, на Чарджоуском химическом заводе в Туркменистане, и на Алмалыкском химическом заводе в Узбекистане. На Балаковском ПО «Минудобрения» в России данный способ внедрен с применением хибинского апатитового концентрата. Согласно ТУ № 113-08-552-84 аммофосфат из фосфоритов Каратау содержит 39% P_2O_5 и 5% N. Аммофосфат на основе апатитового концентрата содержит 47.0% P_2O_5 и 8.4% N.

По данной технологии сокращается сырьевые и энергетические ресурсы: серной кислоты – на 15%, топлива – на 15%, фосфатного сырья – на 2%. Улучшается экологическая обстановка производства за счет сокращения на 15% отхода фосфогипса, практически полной ликвидации потерь аммиака. Замена 15% P_2O_5 фосфорной кислоты на P_2O_5 фосфорита в аммофосфате приводит к положительным технико-экономическим показателям.

Цель настоящего исследования показать возможность переработки забалансовой руды в аммофосфатное удобрение экстракционной фосфорной (ЭФК), нейтрализованной аммиаком.

Лабораторные исследования по получению аммофосфатных удобрений были проведены в лабораторных условиях при температуре 60 ºС в течение 30 мин. В качестве сырья была использована минерализованная масса (ММ) – отход Кызылкумского обогатительного комплекса состава (масс. %): $P_2O_{5общ.}$ – 14,68; $CaO_{общ.}$ – 40,80; MgO – 0,53; Fe_2O_3 – 1,37; Al_2O_3 – 1,17; F-1,85; CO_2 – 12,80, н.о. – 11,89 и экстракционная фосфорная кислота состава (вес. %): 20,5 P_2O_5; 0,28 CaO; 0,66 MgO; 0,51 Fe_2O_3; 0,80 Al_2O_3; 2,98 SO_3; 1,05 F; 0,1 Cl. Варьируемыми параметрами были pH кислоты от 1,2 до 2,0 и массовое соотношение частично аммонизированной ЭФК (ЧАЭФК) к ММ от 100:15 до 100:50. Время взаимодействия 30 мин температура 60 ºС. При взаимодействии фосфатного сырья с частично аммонизированной фосфорной кислотой протекают следующие реакции:

$$CaO + 2H_3PO_4 \rightarrow Ca(H_2PO_4)_2 + H_2O \text{ и}$$
$$CaO + H_3PO_4 \rightarrow CaHPO_4 + H_2O$$

После завершения процесса разложения реакционную массу подвергли сушке при температуре 85-90ºС с одновременным гранулированием методом окатывания. Высушенные образцы удобрений анализировались на содержания различных форм P_2O_5, CaO и азота согласно методике [10]. Усвояемую форму P_2O_5 определяли по растворимости как в 2 %-ной лимонной кислоте, так и в 0.2М растворе трилона Б, усвояемую форму CaO – только по лимонной кислоте. Азот определяли дистилляционным методом на колбе Къелдалья. Результаты исследований приведены в таблице.

Таблица 1.

Состав аммофосфатных удобрений на основе аммонизированной ЭФК и ММ

Массовое соотношение ЧАЭФК : ММ	pH пульпы после разложения	pH 10%-ной суспен	Химический состав высушенного продукта, %							
			$P_2O_{5общ.}$	$P_2O_{5усв.}$ в 2%-лим. кислоте	$P_2O_{5усв.}$ по 0,2М. трил.Б	$P_2O_{5вод.}$	$CaO_{общ.}$	$CaO_{усв.}$ в 2%-лим. кислоте	$CaO_{вод.}$	$N_{общ}$, %
1	2	3	4	5	6	7	8	9	10	11
Частично аммонизированная до pH = 1,2 ЭФК (P_2O_5 –17,35 %, N–1,86 %)										
100 : 15	2,21	2,89	40,06	36,34	31,95	27,98	12,87	10,04	5,51	3,62
100 : 20	2,36	3,19	38,25	33,82	29,31	25,04	15,85	12,16	5,25	3,38
100 : 25	2,67	3,46	36,58	31,34	27,01	22,13	17,91	13,36	4,99	3,07
100 : 30	2,94	3,67	35,04	29,12	24,31	19,28	19,96	14,22	4,56	2,97
100 : 35	3,31	3,74	34,11	27,57	22,08	16,84	21,87	15,25	3,97	2,58
100 : 40	3,45	4,03	33,07	25,29	19,78	13,78	23,49	15,54	3,40	2,47
100 : 50	-	4,47	31,34	21,94	17,26	9,39	26,48	16,35	2,64	2,24
Частично аммонизированная до pH = 1,5 ЭФК (P_2O_5 –16,74 %, N–2,13 %)										
100 : 15	2,56	3,23	39,71	35,62	31,24	27,29	12,76	9,74	5,14	4,48
100 : 20	2,85	3,32	37,69	32,80	28,59	23,98	15,63	11,69	4,92	3,99
100 : 25	3,33	3,57	35,56	30,03	25,76	20,79	17,68	12,74	4,57	3,76
100 : 30	3,57	3,89	34,43	28,11	23,59	18,50	19,88	13,66	3,78	3,45
100 : 35	-	4,23	33,58	26,62	21,40	15,82	21,70	14,35	3,32	3,17
100 : 40	-	4,46	32,51	24,17	18,94	13,22	23,34	14,83	2,88	2,98
100 : 50	-	4,81	30,81	21,18	16,73	8,78	26,29	15,60	2,01	2,57
Частично аммонизированная до pH = 1,7 ЭФК (P_2O_5 –16,49 %, N–2,27%)										
100 : 15	2,89	3,30	38,87	34,38	30,27	26,24	12,67	9,34	4,59	4,79
100 : 20	3,29	3,62	36,78	31,55	27,34	22,59	15,56	11,21	4,31	4,36
100 : 25	3,58	3,84	35,04	29,20	25,11	19,62	17,59	12,26	3,46	4,01
100 : 30	-	4,17	33,73	27,04	22,53	17,34	19,64	13,03	3,06	3,64
100 : 35	-	4,38	32,42	24,94	20,27	14,52	21,60	13,75	2,61	3,37
100 : 40	-	4,65	31,56	22,91	18,11	11,98	23,22	14,17	2,18	3,21
100 : 50	-	4,89	30,42	19,88	15,91	8,42	25,85	14,67	1,72	2,73
Частично аммонизированная до pH = 2,0 ЭФК (P_2O_5 –16,07 %, N–2,50 %)										
100 : 15	3,16	3,73	37,34	32,46	28,44	24,54	12,54	8,82	4,10	5,20
100 : 20	3,67	3,99	35,62	29,83	25,88	20,94	15,41	10,53	3,66	4,67
100 : 25	3,87	4,24	33,76	27,24	23,33	18,12	17,44	11,36	2,61	4,35
100 : 30	-	4,61	32,56	25,27	21,27	15,82	19,47	12,12	2,24	4,05
100 : 35	-	4,78	31,48	23,34	19,07	13,02	21,38	12,79	1,71	3,86
100 : 40	-	4,97	30,73	21,45	17,29	11,01	23,06	13,08	1,43	3,52
100 : 50	-	5,35	29,62	18,43	15,23	7,63	25,66	13,25	1,07	3,19
Частично аммонизированная до pH = 2,2 ЭФК (P_2O_5 –15,72 %, N–2,70 %)										
100 : 15	3,37	3,71	36,05	30,91	27,25	23,01	12,44	8,53	3,75	5,47
100 : 20	3,89	4,15	34,72	28,70	24,91	20,01	15,28	9,97	3,12	5,12
100 : 25	-	4,52	33,09	26,24	22,64	17,23	17,23	10,74	2,36	4,70
100 : 30	-	4,73	32,13	24,42	20,76	14,19	19,29	11,33	1,84	4,48
100 : 35	-	4,99	31,15	22,66	18,61	12,05	21,20	11,88	1,41	4,19
100 : 40	-	5,21	30,28	20,51	16,83	9,56	22,85	12,37	1,14	3,84
100 : 50	-	5,74	29,15	17,52	14,74	7,10	25,53	12,61	0,77	3,51

Как видно из таблицы при 30-минутном взаимодействии при температуре 60^0С мы наблюдаем следующие закономерности для всех видов исследованных фосфоритов: чем ниже pH кислоты и выше соотношение ЧАЭФК : ММ, тем

больше значение усвояемых и водных форм фосфора. Для установление влияния pH ЧАЭФК на относительных усвояемых по лимонной кислоте, трилону Б и водных форм P_2O_5 массовое соотношение 100:15; 100:20; 100:25; 100:30; 100:35; 100:40 и 100:50 условно обозначили делением 100 на 15-50 как 6,67; 5,0; 4,0; 3,33; 2,5 и 2 соответственно (рис. 1 и 2). Отметим, что верные 5 кривые принадлежат относительным усвояемым форма P_2O_5 по лимонной кислоте, а нижнее – трилону Б.

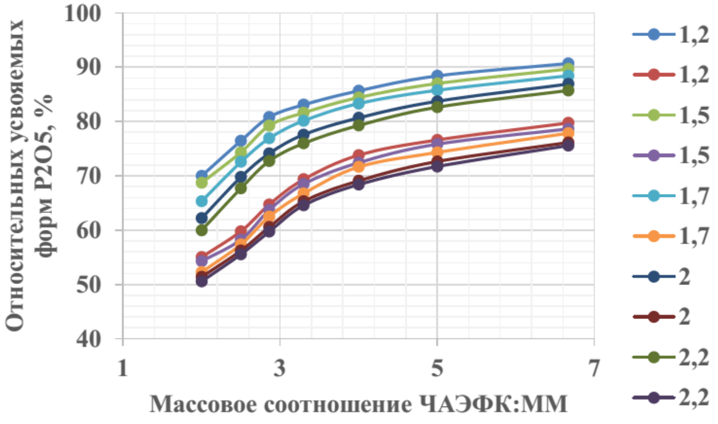

Рисунок 1. **Влияние pH ЧАЭФК и массового соотношение ЧАЭФК к ММ**

Из рисунка следует, что увеличение pH и снижение массового соотношение от 6,67 до 2,0 способствует снижению относительных усвояемых форм фосфора от 90,71 до 60,01 и от 79,76 до 50,57% соответственно по лимонной кислоте и трилону Б.

Тогда как относительная водная форма P_2O_5 снижается от 69,84 до 24,36%.

В сельском хозяйстве наиболее ценными фосфорсодержащими удобрениями считаются те, в которых $P_2O_{5водн.}$: $P_2O_{5общ.}$ составляет 50 и более процентов.

Таким образом оптимальными значениями можно считать pH ЧАЭФК - 1,2-1,5; ЧАЭФК : ММ = 100: (15-30). Состав удобрений (масс. %): $P_2O_{5общ.}$ - 34,43-40,06; $P_2O_{5усв.}$ по лим. к-те - 28,11-36,34; $P_2O_{5усв.}$ по трил. Б - 23,59-31,95; $P_2O_{5водн.}$ - 18,50-27,98; $CaO_{общ.}$ - 12,76-19,96; $CaO_{усв.}$ - 9,74-14,22; $CaO_{водн.}$ - 3,78-5,51; $P_2O_{5усв.}$ по лим. к-те: $P_2O_{5общ.}$ - 81,64-90,71; $P_2O_{5усв.}$ по трил. Б : $P_2O_{5общ.}$ - 68,52-79,76; $P_2O_{5водн.}$: $P_2O_{5общ.}$ - 53,73-69,84; N- 2,97-4,48. Прочность гранул удобрений составляет не менее 3 МПа.

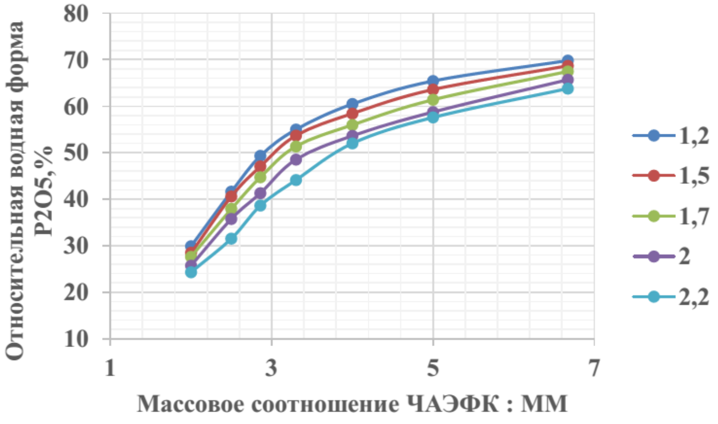

Рисунок 2. **Влияние pH ЧАЭФК и массового соотношение ЧАЭФК к ММ**

Таким образом, на основе полученных данных можно заключить, что минерализованная масса, при найденных оптимальных условиях хорошо поддается химической активации с образованием усвояемых кальциевофосфатных соединений. Исследования процесса химического взаимодействия ММ фосфоритов ЦК с частично аммонизированной ЭФК показали возможность переработки высококарбонизированного и необогащенного фосфатного сырья с получением удобрения, содержащего в своем составе азот, фосфор и кальций.

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И.С. Степанов

Москва
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ABBREVIATIONS

MM – mineralized mass

EPA – extraction phosphoric acid

CK – Central Kyzylkum

PR – phosphate raw

PAA – polyacrylamide

EA – ethylalcohol

tot – total

S – solid phase

L – liquid phase

KPP – Kyzylkum phosphorite plant

WCC – washed calcined phosphorous concentrate

WDC – washed dried phosphorous concentrate

avb – available

usb – usable

aq – aqueous

MCP – monocalcium phosphate

OES – optical emissions spectroscopy

ICP – inductively coupled plasma

SBDG – spray-boiling dryer granulator

TPA – thermal phosphoric acid

OPR – ordinary phosphate rock

PF – pulverized fraction

CEC – chemically enriched phosphate concentrate

IR – infra red

PAEPA – partially ammoniated extraction phosphoric acid

rpm – rotation per minute

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