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The Current State of Obtaining a New Range of Mineral Fertilizers, Fertilizer Mixtures, with the Solution of Environmental Problems

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Abstract

The proposed chapter on mixed fertilizers, related to mineral fertilizers, categorizes industrial wastes by types and ways of their processing in order to improve the environmental problems of industrial regions brief information on

- analysis of agronomic ores, their deposits location and extraction
- properties of com plex fertilizers
- the main competitive advantages of the technology for the production of fertilizer mixtures of prolonged action without an acid method
- introduced additives of natural resources and industrial waste products, improving the quality of the mixed fertilizers of prolonged action
- mechanical, mechanochemical and chemical activation of the components of the fertilizer mixture
- land cover and soils
- Technological schemes of production of fertilizer mixture
- technologies for obtaining simple and complex fertilizers
- compatibility of components of fertilizer when obtaining them from ready mineral fertilizers
- Humate-containing complex-mixed fertilizers of prolonged action

Keywords: Blend; Grinding; Mineral Fertilizer; Mixing; Mechanical Activation; Mechanochemical Activation; Phosphate Raw Materials

Introduction

At the present stage of economic development of the Republic of Kazakhstan and improvement of any state' population welfare, the issue is to improve quality and quantity of products of agrarian sector of economy. One of the main directions in solution of the above-mentioned urgent problem is development of new technical and technological solutions for production and use of mineral fertilizers, in the form of fertilizer mixtures, for agricultural vegetable, cereal and soybean crops, as well as feed additives for poultry, domestic animals and cattle.

Consumption of fertilizers in Kazakhstan per one hectare of cultivated areas of agricultural lands is 4.9 kg of fertilizers, while in sown areas in Kyrgyzstan per one hectare this figure is five times higher and is 22 kg, and in Uzbekistan - 150 kg, in Russia- 39 kg, in Belarus - 50-60 kg, in Ukraine -from 80 to 100 kg. These figures indicate that our state consumes less fertilizers per one hectare without replenishing the soil with phosphorus, potassium and nitrogen, which was taken from the soil. And in far-abroad countries - farms in Germany, France and the USA use about 400-600 kg of fertilizers per one hectare, in the Netherlands, with very small sown areas - 750 kg per one hectare. Analyzing the world market structure, it is noted that the world mineral fertilizer industry has the following characteristics:

- Direct dependence of production of nitrogen, phosphorus and potassium fertilizers on availability and uninterrupted supplies of raw materials, natural gas and coal;

- The most highly competitive market is nitrogen fertilizer market due to availability of raw materials, and the most concentrated is potassium market;

- Specificity of arrangement of capacities for production of mineral fertilizers determines their trade flows in the global market: nitrogen fertilizers are exported depending on the type, 25-40% of the world production, phosphorus fertilizers - 35-50%, and potassium fertilizers - more than 75%.

The largest fertilizer consumers are China, India, the USA, Europe, Brazil, as shown in Table 1. Analyzing raw materials and consumption in mineral fertilizers, it should be noted that China and India provide almost a third of the global demand. Therefore, prices here become milestones for other market outlets, such as Brazil, South-East Asia, etc. Such "price chain" is typical for potassium market, where long-term contracts prevail, due to the limited suppliers. Prices for nitrogen and phosphorus fertilizers are determined by seasonal factors, fluctuations in demand in regional markets and competition between suppliers. For the world mineral fertilizer market, 2016 has become one of the most difficult in the last decade. Since the investment boom in pricing policy, during peak prices, led to the introduction of a significant number of new capacities, as a result of which growth in the world production volumes significantly exceeded growth in demand. This oversupply has exerted considerable pressure on prices and profitability of production due to introduction of new production capacities in nitrogen segment in countries with cheap natural gas.

N		P		K		Total NPK	
China	34,7	China	11,3	China	5,5	China	51,5
India	17,2	India	6,9	Brazil	5,0	India	26,3
the USA	11,7	Brazil	4,6	the USA	4,2	the USA	19,8
Brazil	3,7	the USA	3,9	India	2,2	Brazil	13,3
Indonesia	3,4	Canada	0,9	Bangladesh	0,6	Indonesia	4,7
Pakistan	3,2	Indonesia	0,8	France	0,5	Pakistan	4,0
Canada	2,5	Australia	0,8	Indonesia	0,5	Canada	3,7
France	2,2	Pakistan	0,7	Poland	0,5	France	3,1

Table 1: The largest countries-consumers of mineral fertilizers (consumption volumes, million tons in the active substance).

In 2016, the main increase was recorded in the USA and Russia, which in the current situation had impact primarily on the world fertilizer producer - China, which had higher cost price of nitrogen and complex fertilizers, which forced them to reduce production volumes and suspend their expansion in the world market, due to the low prices for mineral fertilizers, as well as increase in prices for coal - the main raw materials of most Chinese producers [1]. In 2016 situation on the world market in terms of consumption decreased and sales of mineral fertilizers amounted to 250 million tons. Estimated consumption of mineral fertilizers by agriculture at the world level in 2015/2016 was slightly less than 184 million tons in the active substance. The world consumption volume of mineral fertilizers by agriculture for the first time since 2008 showed a slight decline (Table 2). The demand declined in the countries of North and Latin America, the Middle East, while consumption in South Asia, Africa and the CIS countries increased.

	Consumption volume, million tons in the active substance							Change in %					
	2013/2014	2014/2015	2015 2016	2016	2017	2018	2019	2015/2014	2015	2016	2017	2018	2019
N	109,2	110,1	109,0	107,1	106,4	106,5	107,1	0,8	-1,0	0,6	0,7	0,1	0,6
P_2O_5	41,2	41,6	42,1	45,4	46,3	45,3	46,0	1,0	1,2	1,4	2,0	-2,2	1,5
K_2O	31,2	32,4	32,6	35,9	37,4	37,0	37,4	3,8	0,6	2,0	4,2	-1,1	1,1
Total	181,6	184,1	183,7	188.5	190,1	188,8	190,5	1,4	-0,2	1,0	0,8	-0,7	0,9
Source IFA (Short-Term Fertilizer Outlook 2016-2017. 2019-2020)													

Table 2: The world mineral fertilizer agricultural consumption volumes.

The important factor for the fertilizer market is negative impact of natural phenomena - fluctuation of surface water temperature in the equatorial part of the Pacific Ocean, which had significant impact on the climate and caused drought in South-East Asia, led to reduction in production and increase in prices for palm oil, in the markets of Central America due to the rainy season for more than two months, as well as severe drought in South Africa forced farmers to postpone the time for fertilizer application, which affected the global market, but also other factors, such as crisis phenomena in the long-term trend of slowing the growth rate of demand for mineral fertilizers. If in the period of 2001-2005 the average annual growth was 2.7%, then in 2006-2010 it was 2.1%, and in 2011-2015 - 1.1% [1-7]. Data on the mineral fertilizer import volume by the world's largest producers, including the Russian Federation, is shown on the basis of the analysis in Figure 1a.

Figure 1a: The largest importers of mineral fertilizers in 2016.

In connection with the launch of new production facilities and intensification of competition in recent years, positions of suppliers have changed in the structure of the world trade. Russia is one of the three largest exporters of mineral fertilizers, but its share in the world trade declined until 2015 [4-7]. The average prices for nitrogen, phosphorus and potassium fertilizers, as well as their indicators are given in Table 3. Summarizing the above, it is possible to state that:

- In the recent years the situation on the world market has seriously become more complicated. The investment boom that began during the period of peak prices in the late 2000s led to the introduction of a significant number of new capacities;

- The oversupply exerted considerable pressure on prices and profitability of production, which is especially noticeable on nitrogen segment of fertilizer production;

- Chinese factor had a critical impact on the market: in 2015, expansion of Chinese producers of nitrogen and mixed fertilizers intensified imbalance in the market and led to a record drop in prices. However, in 2016, Chinese producers, unable to withstand competition, began to reduce production volumes of mineral fertilizers;

- Production volume of mineral fertilizers in Russia in 2015 amounted to 19.92 million tons in the active substance, which led to increase in comparison with 2014 by 1.9%. In 2016, increase in production volumes amounted to 3.7%, the total production reached a record 20.66 million tons.

	2015	2016	Change in %	2016				Change in %		
	average annual		2016/ 2015	1 qtr. 2016	2 qtr. 2016	3 qtr. 2016	4 qtr. 2016	2 qtr./ 1 qtr.	3 qtr./ 2 qtr.	4 qtr./ 3 qtr.
Nitrogen										
Ammonia, FOB South	387	236	-39%	269	274	208	190	2%	-24%	-9%
Carbamide, FOB South	271	199	-26%	209	198	183	207	-5%	-8%	13%
Ammonium citrate, FOB Black Sea	222	165	-25%	185	153	145	179	-17%	-5%	23%
KAS, FOB CIS countries	198	136	-31%	152	143	127	133	-6%	-11%	5%
Phosphorus										
DAF, FOB USA	458	345	-25%	367	351	340	324	-4%	-3%	-5%
MAF, FOB Baltic Sea	459	338	-26%	353	469	337	320	33%	-28%	-24%
TSF, FOB Tunis	303	291	-19%	328	282	282	270	-14%	0%	-4%
NPK 16-16-16, FOB CIS countries	355	283	-20%	326	308	277	254	-6%	-10%	-8%
Potassium										
spot FOB Baltics	288	232	-19%	250	235	222	185	-6%	-6%	-17%
spot FOB Vancouver	385	291	-25%	283	263	221	215	-7%	-16%	-3%

Table 3: Average prices for nitrogen, phosphorus and potassium fertilizers in 2015-2016 (dollars/ton).

One of the most important factors contributing to significant increase in the productivity of agricultural products and ensure the country's food security is increase in the production volumes and use of mineral fertilizers, including fertilizer mixtures. The share of mineral fertilizers and plant protection products is more than half of the volume of crop yields. Therefore, the use of fertilizers is one of the most powerful factors affecting both the state of soil fertility and productivity of vegetable, cereal, cereal-bean and fruit crops [4-7].

Particular importance for crops among nutrients is given to phosphorus, nitrogen and potassium, and some elements that are trace fertilizers, such as iron, magnesium, sulfur and others, are always found in any soil. However, it should be noted that introduction of high nitrogen and potassium doses, against the backdrop of deficiency of phosphorus or other trace fertilizers in soil, can lead to imbalance of soil elements and, as a result, reduce soil fertility.

Against the backdrop of negative global trends associated with continuous increase in prices for phosphate raw materials and decrease in the quality of feedstock for P_2O_5, one of the most important tasks is search for alternative methods for obtaining mineral fertilizers without acidification and increasing efficiency of their use. This will ensure introduction of new technological processes that involve transition to a closed technological cycle, full processing of technological wastes, change in the range of fertilizer products, reduction of mineral resource consumption rates while improving quality of the product, and improving environmental situation in industrial regions. The range of phosphorus fertilizers from techno genic wastes should be represented by fertilizers containing water retention substances, trace elements such as iron, manganese, sulfur, zinc, calcium, magnesium, etc., and having complex properties of positive influence on the productivity of agricultural crops and their quality. This will allow up to 60% reduce costs for their introduction and optimize mineral nutrition of plants, with simultaneous reclamation of lands.

Significant increase in prices for mineral fertilizers on the world market scale creates favorable situation for producers, and therefore the industry notes significant level of use of production capacities. The favorable situation in the price relation allows producers implement investment projects to modernize production in order to maintain competitive abilities of their products. In connection with rapid growth of the world's population and improvement of living conditions, there is increase in consumption of agricultural products in developing countries. According to the forecast of demographers [Aleinov D.P. Chemical Industry Today, 2007] by the end of this decade, the annual population growth will be about 70 million people.

Rapid depletion of agricultural lands and their extremely slow development is becoming one of the main reasons for growth in the production of mineral fertilizers. According to the IFA by 2020, extensive growth of arable lands will cease practically due to the complete depletion of natural and agricultural lands. According to the content of nutrients, fertilizers are divided into simple, containing one nutrient, and complex, containing several nutrients. Double complex fertilizers, according to their composition, are divided into three groups - nitrogen-phosphorus, nitrogen-potassium and potassium-phosphorus, triple fertilizers contain all three nutrients. Production of complex mineral fertilizers is one of the most developed segments of the chemical industry of the Republic of Kazakhstan, Russia and Belarus. Therefore, it is the use of complex mineral fertilizers that will allow up to 65-70% reduce costs for their application and optimize mineral nutrition of plants, which cannot be reduced due to the use of simple forms of fertilizers. In recent years, there is observed growing increase in the interest in the use of complex fertilizers containing sulfur, iron, magnesium and other trace elements, which play a certain role and important in plant life. They participate in movement of phosphorus and other elements in plants, activate some enzymes, accelerate formation of carbon, affect oxidation-reduction processes in plant tissues and in formation of fruits [2]. Multicomponent fertilizers containing trace elements, in addition to phosphorus, potassium and nitrogen, have positive effects on the soil poor in these elements, and on the yield and its quality. There are many ways for rational use of raw materials and secondary material resources and the most important of them are:

- Right choice of raw materials and their complex processing;
- Production wastes recycling;
- Qualitative and primary enrichment and preparation for the technological process for the use of various wastes that violate the ecological balance of industrial regions.

Choice of raw materials determines types of the used equipment, technology, duration of production cycles and affects technical and economic performance of enterprises. Modern level of production allows produce the same products from different raw materials. Right choice of raw materials allows reduce production costs with increase in its quality (Figure 1b).

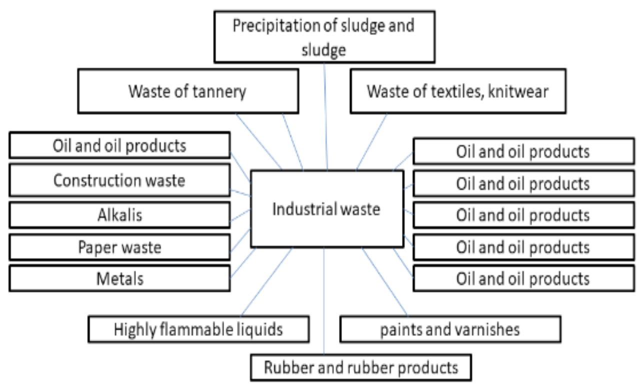


Figure 1b: Classification of industrial wastes by their types.

Complex processing of raw materials assumes application of various technological processes and expansion of nomenclature of products at the enterprises, reducing transport expenses, production costs, and also increasing profitableness of the industrial enterprises, being important economic and ecological problem. Production of mineral fertilizers is profitable and financially sustainable, since without their application fertility of soil of agricultural lands is rapidly depleted; it provides components necessary for the life of plants, which are not unlimited. This function is performed by minerals, which in 1914 Ya.V. Samoilov named agronomical ores, used to increase productivity of agriculture.

Agronomical ores are products, which contain important chemical elements favorable for growth of plants, changing soil properties, its structure, air and water regime, and also improving conditions of plant nutrition ensuring reproduction of fertility. These ores include the following minerals:

1. Ores, which are sources of the main elements of mineral nutrition of plants: phosphorus, potassium, nitrogen; secondary elements - magnesium, sulfur; trace elements – boron, molybdenum, copper, zinc, manganese, etc.

2. Ores are sources of organic substances, such as lignum fossils, sapropels, vivianite, some types of coals, mostly brown.

3. Ores are sources of elements and compounds used in the production of fertilizers: sulfur-containing raw materials, limestone, quartzite.

4. Rocks that are used for chemical land reclamation, in particular limestone, dolomite and gypsum.

5. Rocks and minerals that are used as artificial soils and to improve physical and chemical properties of soils: gravel-pebble and porous rocks such as vermiculite and zeolites.

6. Other rocks and ores that serve as mineral additives and fillers, such as fodder additives in the form of common salt, pure lime materials, fillers for toxic chemicals -talc, bentonite clays, as well as additives to prevent caking of fertilizers – vermiculite and bentonites.

Some of these minerals have polyfunctional properties. For example, sulfur is a plant food element and, at the same time, pesticide, raw material for production of sulfuric acid; limestone is used in production of fertilizers, for chemical land reclamation, magnesium sources, which allow them to be attributed to magnesium rocks. The main agronomical ores are phosphate, potassium and sulfuric, since the world mineral fertilizer industry is based on them. In the composition of agronomical ores and mineral fertilizers, phosphorus and potassium are used for plant nutrition for more than a century and a half and they are strategically significant on the global scale. The main countries where resources of the agronomical ores are concentrated and extracted:

- By apatites - Russia, Brazil, South Africa, Finland, in the future Canada and Australia;

- By phosphorites - the USA, Morocco, China, Kazakhstan, Russia, Mexico, Tunis, Iraq;

- By potassium salts - Russia, Canada, Belarus, Germany, Israel, Jordan, Thailand, and in the future Kazakhstan, Brazil, Argentina, Chile.

The Republic of Kazakhstan, like the Russian Federation, has significant and unclaimed material potential for the agronomical ores. The raw material base of the Republic of Kazakhstan by phosphate rocks is represented by explored reserves by the category $A+B+C_1$ with micrograin (82.5%) and nodular phosphorites (16.8%) of Karatau and Aktobe basins, and complex phosphorus-uranium ores (0.7%) of West and North Kazakhstan. The basis of the raw material base of the phosphoric industry of the Republic of Kazakhstan is formed by located in Zhambyl and South Kazakhstan oblasts micrograin phosphorites of Karatau basin. 45 deposits were stricken, 14 of which are the most significant. Deposits of nodular phosphorites, which constitute 17% of the total reserves of the Republic of Kazakhstan, are located in Aktobe basin - Chilisaiskoye, Bogdanovskoye, Koktobinskoye, Sholakskoye, Alginskoye, Pokrovskoye, Rodnikovskoye, Aitpaiskoye and Isetskoye, with the average P_2O_5 content of 9.6%. Considerable part of P_2O_5 in these ores exists in a lemon-soluble form; this allows them to be used as mineral fertilizers from finely ground phosphate flour.

Soil cover and ion exchange processes occurring in them

Ion exchange processes that take place in transformation of soil cover are important and undeniable and their specific manifestation in more complex soil processes has not been sufficiently studied. Ion exchange impurities themselves are mixed and their mechanism is based on description of well-developed thermodynamics that does not require knowledge of mechanisms of processes, but only possession of initial and final state of ion-exchange systems in soil [Pinkovskiy D.L., p. 98].

Systematic studies of ion-exchange absorbing capacity of soils and interest in soil-exchange processes is based on the fact that they have significant influence in soil formation and its functioning. So, for example, in the 2nd century BC Aristotle noted ability that soil prevents peeling sea water during filtration process. One of physicists-chemists and soil scientist K.K. Gedroits, founder of modern soil chemistry, characterizes the ion-exchange capacity of soil with the following expression: “This kind of absorption capacity of soil plays particularly important role in all soil processes and at the same time, it is the most studied”.

The ion-exchange absorption capacity of soil is its functional property, and realized by this ability ion exchange process is universal physicochemical mechanism, regulating redistribution of ions between surface of soil particles and soil solution. These processes occur in the period of external changes in the composition of solid and liquid soil phases as a result of natural and anthropological impacts of terrain relief, climatic conditions, presence of living organisms in soil and human activities. Influence of these factors on the basis of molecular level was developed at the beginning of the last century by K.K. Gedroits, D. Hissink, W. Kelly, and A. Zigmund, who revealed ion-exchange-chemical theory of formation of saline soils occurring in three stages:

- Soil enrichment by sodium absorbed from the soil solution due to the ion-exchange processes, as well as changes in the dispersion and solubility of soil components;
- Sodium leaching (desorption) from soil under the influence of changed external conditions, such as increase in the amount of precipitation;
- Soda formation and soil alkalization due to the exchange reaction of absorbed sodium by calcium from $CaCO_3$ present in soil.

These last two stages lead to leaching of highly disperse and dissolved soil components from the upper horizons, which lead to the formation of specific profile of saline soils, especially in cotton-growing regions of South Kazakhstan. Changes in the composition of exchangeable cations and influence on the physical properties of soil lead to the change in the surface layer properties of soil particles. This can lead to the change in dispersion, peptizability, aggregate state of soil susceptibility, its structure and water-physical characteristics, as well as its physical state. The existing set of methods for obtaining complex and compound mineral fertilizers containing 2 or more nutrients are widely studied in the works of such scientists and practitioners, as Pozin M.Ye., Kopylev B.A., Sokolovsky A.A., Kochetkov V.N., Evenchik S.D., Brodsky A.A., Beremzhanov A.A., Moldabekov Sh.M., Zhantasov K.T., Bugenov Ye.S., Dzhusipbekov M.Zh., Nabiyev M.N., Usmanov S., Serazetdinov D.Z., Karmyshev A.A., Kononov A.V., Yakhantov Ye.L., Petropavlovskiy I.A., Dormeshkin O.B., Kramarev and many others. Extraction leaching of phosphates since the middle of the last century has been directed mainly to acid decomposition of raw materials with sulfuric, phosphoric, hydrochloric and nitric acids. Obtaining of mineral fertilizers through acid is one of the main directions to this day.

Advantages of technology for obtaining fertilizer mixtures with acid-free method

Acid decomposition of phosphate raw materials, mainly sulfuric acid, is characterized by considerable expenditure of material and energy resources, as well as formation of heavy tonnage wastes in the form of phosphogypsum, the problem of utilization of which is still not completely solved at present. Fertilizer mixtures are complex compound fertilizers produced by individual orders of agro-companies – have not yet managed to gain popularity among agrarians. Lack of possibility to conduct qualitative soil analysis, without which fertilizer mixtures are almost useless to buy, put agrarians to a nonplus, which is affected by unacceptable price of fertilizer. According to producers of fertilizer mixtures, the future is precisely behind these fertilizers, since combining their composition it is possible to choose optimal composition for any lands. This allows increase yields in several times, as well as increase resistance of plants to climatic conditions. Due to their ecological properties and effectiveness on agricultural plants, quality dry fertilizer mixtures are not inferior to similar brands of complex fertilizers, where all components are in the same granule, so their use, taking into account needs of a particular field and culture, can exceed standard complex fertilizers.

The world experience shows that due to the wrong culture of fertilization in soil up to 30% of them are brought in as ballast. Agrochemists have found that the greatest efficiency of multicomponent fertilizers is manifested when they are balanced by fertilizer elements (P, K, N) and introduced into soil at the optimum ratio based on the cartogram of a particular field for a certain agricultural crop. Technological fertilizer mixtures by the cost of fertilizer elements and their introduction into soil of sown areas do not exceed the cost of separately imported and adequately introduced simple fertilizers on the basis of which they have development perspective. At present, agricultural production passed into private hands, so, efficiency of spent funds for fertilization became more urgent.

Despite small volume of sales, production and consumption of fertilizer mixtures, Russian specialists forecast increase in domestic sales in 2017 to 120-150 thousand tons. In addition, if fertilizer mixtures containing trace elements are used, then it will be possible to increase efficiency of crop production by 20-30%, since complex fertilizers with micro additives are widely used in the world practice in addition to traditional mixtures from nitrogen, phosphorus and potassium. Kemira, Kargel, Arvi, Masarik are among the world leaders in the production of fertilizer mixtures. In the world practice, fertilizer mixtures are used for more than 60 years. For example, in Germany and Holland, from 40 to 60% of all fertilizers are fertilizer mixtures, in the USA - 70-80%, in European countries- 10-15%, in the Eastland- 15-20%, and in Ukraine- 10% [4-5].

The assortment of produced fertilizer mixtures is very diverse, in the countries of Western Europe, it counts dozens of varieties, in the USA this figure is more than 3000, but the most common varieties are just dozens of varieties of mixed fertilizers. The main competitive advantages of the technologically mixed fertilizers is that:

- mixtures prepared using concentrated fertilizers contain fertilizer elements in easily accessible form and quantities that require climatic conditions and biological characteristics of agricultural crops, they have good physical and chemical properties, they are environmentally safe;

- a wide variety of various NPK ratios allows ensure optimal nutrition depending on soil properties, planned crop, culture characteristics;
- phosphorus accessibility in technological mixtures is almost 2 times higher in comparison with superphosphate;
- costs for delivery and application of mixtures in comparison with simple fertilizers are reduced by 2-3 times;
- total cost cutout when using technological mixtures can be up to 50%;
- price per unit of the active substance is 20-30% cheaper in comparison with simple fertilizers;
- high concentration of granulated macro elements are not hygroscopic, do not cake and have good aerodynamic features when applied;
- high availability for plants

To date, price for fertilizer mixture in the Russian Federation fluctuates within 12-16 thousand rubles or 55-85 thousand KZT per ton, and in the Republic of Kazakhstan 1 ton of complex compound fertilizers is from 50 to 60 thousand KZT. Therefore, fertilizer mixture development in the Republic of Kazakhstan and in particular fertilizer mixtures with trace elements is unquestionable.

Phosphorites of Karatau basin are difficult to enrich, therefore ore containing not less than 24.5 P_2O_5 is subject to the acid treatment for water-soluble fertilizers. Complex and alternative composition of Karatau basin phosphorites and presence of impurities in them complicate their direct processing to phosphoric acid by the extraction method. The main mineral of phosphorite is fluorocarbonatepatite, there are also other minerals in the form of quartz, chalcedony, and also field spar, in the ore mass. Carbonate varieties of phosphorite contain calcite and dolomite. According to [Belov V.I. and Tushina A.M.], P_2O_5 content is significantly lower in the samples of phosphate fines compared to the samples of lump phosphorite. Qualitative characteristics and reserves of phosphate ores and phosphorus-containing rocks are given in Table 1. Significant content of alumina impurities in phosphate fines is explained by the fact that alumina minerals contained in enclosing rocks are passed to the breeze extraction when breaking as they have lower density.

In addition, phosphate fines contain less fluorine than lump phosphorus. These authors explain that by the lower content of fluor apatite in phosphate fines compared to lump phosphorite. Fe_2O_3 content in phosphate fines is higher than its content in lump phosphorite. Increased content of Fe_2O_3 and alkalis in phosphate fines predetermines its comparatively low melting temperature. Tabyldiyev K.T. also notes characteristic decrease in P_2O_5 content with decrease in the size of phosphorite particles. Table 2 gives data on chemical composition of samples of phosphate fines of various granulometric compositions. In phosphorite, phosphate is connected with carbonate minerals ($CaCO_3$) in the form of carbonate- or hydroxylapatite (francolite, kurskite) $Ca_3P_2O_8 \cdot xCaCO_3 \cdot yCa(OH)_2$. Quartz ($SiO_2$) and clay rocks ($A1_2O_3$, Na_2O, K_2O) also pass into the small fraction of raw material. Calcium fluoride CaF_2 is closely connected with phosphate substance and not passed to the fines during crushing, therefore phosphate grains contained in phosphate fines have free fluorine. Therefore, according to Zhantasov K.T. and others [Technological instrumentation of yellow phosphorus production, 2014], total amount of phosphate fines, depending on chemical-mineralogical composition and physicochemical properties of phosphorites of various Karatau basin deposits, substandard in granulometric composition and low-grade by chemical composition, is more than 60% from the volume of mined phosphate ore. The simplest method for obtaining mineral fertilizers is mechanical processing of phosphorites by fine grinding, which allows obtain phosphate flour, as a finished product or initial product for chemical processing. The phosphate flour is a powdery, highly dusty product, very uncomfortable in transportation and application. This leads to its large losses, and also has insufficient accessibility in most soils. As a result, the phosphate flour production is currently very limited.

The second method is acid processing of natural phosphate raw materials, which is the most common and studied method. Acids used in phosphorus extraction are sulfuric, phosphoric and nitric acid, as well as their mixtures. However, natural phosphorites, which do not contain significant amount of impurities of calcium and magnesium carbonates, iron and magnesium compounds, are suited for the acid processing. These impurities complicate acid treatment processes of Phosphorites, increase losses of P_2O_5 and deteriorate fertilizers. In the acid processing, there are very significant drawbacks associated with formation of large-tonnage phosphogypsum wastes.

The third method is electro-thermal processing of natural phosphorites by reduction of phosphates by carbon in the presence of quartzite, it allows process natural phosphate raw materials of low quality. At that, obtained phosphoric acid and phosphorus salts and fertilizers on its basis have better qualities than in the acid processing of phosphorites due to the absence of impurities of inorganic compounds of silicon, calcium, magnesium, iron, fluorine, aluminum, and other alkali metals in phosphorus. The disadvantage of this method is possibility of processing natural phosphate raw materials only with a certain granulometric composition. _The fourth method is thermochemical processing of natural phosphate raw materials. It allows obtain thermal-alkali phosphates by sintering or fusing phosphorites with alkali products, as well as hydrothermally. However, this method has not found wide industrial application due to the deficit of soda for alkali decomposition of phosphates, as well as poor quality of fertilizers obtained hydrothermally.

The hydrothermal method consists in thermal treatment of phosphate raw materials in the presence of water vapors and silica with obtaining of defluorinated phosphates [Zhdanov Yu.A., M., Chemistry, 1979, 240 p].

Use of thermal phosphates on acid soils is not inferior to superphosphate. Introduction of thermal and fused phosphates into industrial practice of production is constrained mainly due to the huge energy costs for creation of high temperatures and very cumbersome and material-intensive equipment (tubular furnaces, etc.) are required for that. Therefore, such fertilizers are produced in small quantities, and defluorinated phosphates are used mainly as fodder products [Wolfkovich S.I. and others. Hydrothermal processing, M.-L., Chemistry, 1964, 172 p]. Brief review of industrial methods for processing phosphate raw materials for fertilizer production allows conclude that existing methods are not yet effective for processing low grade by chemical and granulometric composition phosphorites [8-16].

In the light of the above, the problem of developing new efficient energy and resource-saving technologies for complex phosphorus-containing fertilizers based on involvement of cheaper phosphate raw materials in fertilizer production becomes especially urgent. In addition, use of phosphate fines accumulated in dumps, use of acid-free method is ecologically and economically advantageous for complex and complex-mixed processing of phosphate raw materials in order to reduce cost of fertilizers [8-10,14-16].

In many countries in the world in recent decades, interest in obtaining activated forms of natural phosphates as a source of phosphorus for plant nutrition has increased noticeably. There are two main ways for activating phosphorites:

- Incomplete (partial) decomposition by mineral acids;
- Acid-free activation of various salts by mechanical, mechanochemical or combined methods [17,18].

Analysis of known methods and preliminary studies have shown that the most effective method can be method of acid-free mechanochemical activation of natural phosphorites, in particular phosphate fines, it will allow improve economic and environmental performance in production of complex phosphorus-containing fertilizers with high agrochemical efficiency. Wolfkovich S.I. and others [Hydrothermal processing of phosphorites for fertilizers and fodder phosphates], as well as Sadyrova A.T., Kalauova A.S. [Chemical Journal of Kazakhstan 2012, No. 4, p. 174-198] outline the main development concepts for the processing of Karatau basin phosphorites and principles for creation of non-waste technologies. The non-waste production technology creation is based on:

- The principle of systemic nature, according to which each separate process or technology is considered as element of more complex production system or element of ecological and economic system;
- The complexity of using primary and fuel-energy resources.

In this connection, development of new universal method suitable for processing of poor phosphate ores and techno genic wastes of mining and industrial complex is very relevant for today. The promising method is the method of mechanical activation, which allows process almost any phosphate raw materials, it does not require scarce acids, high temperatures, and complex instrumental designs. This allows place such production in places close to the mines, or directly at places of consumption, in order to reduce the range of transportation of raw materials or finished products, contributing to the obtained fertilizers profitability improvement.

On the basis of the foregoing, the main theoretical background, state of the problem of solids' mechanochemical activation and mechanical chemistry of natural phosphates in particular are of great interest. Active systematic studies conducted for a long time by a number of authors [Temuujin J., Kochetkov S.P., Chaikina M.V. and Paudert R.], have shown that the method of mechanical activation of phosphate raw materials is considered as a promising way for increasing efficiency of production and application of phosphoric and complex fertilizers. The method of mechanical activation is of particular importance for processing of phosphate ores, substandard in chemical composition and poor enrichment.

Qualitative characteristics of phosphate ores and phosphorus-containing rocks of Karatau basin and chemical composition of different granulometric composition phosphate fines samples are given in Tables 4 and 5 respectively.

Item	Balance phosphate ores, %		Off-balance phosphate ores, %		Phosphate-silica rocks, %		Phosphated silica, %	
	limits	averages	limits	averages	limits	averages	limits	averages
P_2O_5	15,0-30,0	23,5	15,0-23,0	17,5	5,0-15,0	11	0,5-8,0	4,0
CaO	25,0-50,0	42,5	25,0-40,0	30,0	12,0-30,0	20,0	1,6-16,0	8,0
MgO	0,5-7,0	3,5	0,5-6,0	3,0	0,5-3,5	2,0	0,2-0,3	1,6
SiO_2	5,0-35,0	15,0	15,0-45,0	30,0	40,0-70,0	50,0	65,0-95,0	80,0
CO_2	2,5-15,0	8,0	3,0-13,0	7,0	1,0-8,0	5,0	1,0-6,0	3,0
R_2O_3	0,5-3,0	1,5	1,0-3,0	2,0	1,5-8,0	4,0	0,5-2,5	1,0
K_2O+Na_2O	0,5-1,5	1,0	0,5-1,5	1,0	0,5-1,5	2,0	0,5-1,5	1,0
Reserves (in % from the total deposit)	60		13		8		19	

Table 4: Qualitative characteristics of phosphate ores and phosphorus-containing rocks of Karatau basin.

Mechanoactivation of phosphate ores in planetary mills allows turn 80-90% of the phosphoric substance into readily soluble forms and obtain ready fertilizers. The corresponding data are given in the work of V.V. Boldyrev and others [Reports of Academy of Sciences of the USSR, 1997] according to the mechanical activation of phosphate ores of various types and compositions it is shown that even from such hardly soluble ores such as Karatau basin phosphorites and Khibinsky apatite, 75-85% of phosphate turn to soluble forms in 2% lemon acid.

In connection with the problem of developing the acid-free method for obtaining phosphoric fertilizers, effect of the mechanical activation on the physicochemical properties of phosphate and apatite was investigated in more detail. Chaikina M.V. and others showed that apatite and phosphorites solution rate in weak acids as a result of the mechanical activation substantially increases.

Granulometric composition, mm	Chemical composition, %									
	P_2O_5	SiO_3	CaO	MgO	$A1_2O_3$	Fe_2O_3	F	SO_3	K_2O+Na_2O	loss on ignition
+5,0	24,86	16,71	39,11	2,04	1,87	1,72	2,78	0,86	0,49	9,47
5-3,0	23,51	17,05	39,21	1,35	1,86	2,41	2,70	1,31	0,55	10,05
3-1,0	22,99	17,91	38,56	1,74	1,60	2,57	2,43	1,20	0,77	10,07
1-0,5	22,01	21,06	34,56	1,72	1,93	2,40	1,97	1,61	1,29	11,45
0,5-0,1	20,80	21,51	33,40	2,80	1,98	2,70	1,80	1,31	1,48	12,40
-0,1	20,58		32,74	2,72	1,59	2,33	1,71	1,79	1,50	13,04

Table 5: Chemical composition of different granulometric composition phosphate fines.

According to Chaikina M.V., in the mechanical activation process, apatite decomposes into amorphous trisubstituted calcium phosphate - α-$Ca_3(PO_4)_2$ (high-temperature form of tricalcium phosphate) and fluorite. Apatite melting temperature is 1900K, and α-tricalcium phosphate melting temperature is 2050K. This indicates that during indentation after the mechanical activation process the substance was in excited state. Fluor apatite solubility in the citric acid solution was studied by Lyakhov N.Z. and Chaikina M.V. in 1991, [p. 84-89] and the complex of heterogeneous reactions is given:

$$Ca_{10}(PO_4)_6F_2 + 6C_6H_8O_7 \rightarrow 3Ca_3(C_6H_5O_7)_2 + 6H_3PO_4 + CaF_2 \quad (1.1)$$

$$Ca_{10}(PO_4)_6F_2 + 4C_6H_8O_7 \rightarrow 2Ca_3(C_6H_5O_7)_2 + 3\ Ca(H_2PO_4)_2 + CaF_2 \quad (1.2)$$

$$Ca_{10}(PO_4)_6F_2 + 2C_6H_8O_7 \rightarrow Ca_3(C_6H_5O_7)_2 + 6CaHPO_4 + CaF_2 \quad (1.3)$$

The presented data show that the third reaction flows with the mechanical activation with a higher probability. The essence of the phosphate flour mechanical activation consists in fine grinding carried out in special grinders - activators, which are characterized by high-energy intensity. This process in accordance with the work of Reent O.G. and others provides a very intense effect on the phosphorite particles and leads to some deformation of its crystal structure, increasing its degree of amorphousness, specific surface and significant increase in the phosphate solubility by almost 2 times in 2% citric acid.

- Mechanical activation, i.e. ultrafine grinding, is carried out in energy-intensive grinding units of:

- Impact action - impact-centrifugal mills, jet mills, disintegrators;

- Abrasive action -roll mills;

- Combined impact-abrasive action- vibrating mills, attritors, planetary mills, etc.

Sokolov A.S. showed that almost 80% of the yield increase from the use of standard phosphate flour is provided by its fine fraction -0.1 mm, of class of about half in the phosphate flour by weight. Effectiveness of the other half of the phosphate flour, consisting of larger particles of class +0.1 mm, is very low and when applied to soil provides only 20% of the total yield increment, which is the goal of the first part of the work carried out in 2012-2014. Tiossen P.A. notes that fertilizer that has good effect, both in the initial application period and after long residence time in soil, can be obtained by mixing superphosphate with tribophos -mechanically activated natural phosphate. In the post-Soviet period, researchers of Research Institute for Fertilizers and Insectofungicides Yanishchevsky F.V. and others (Agrochemistry, 1989, No. 7, p. 8-17) carried out studies with various samples of phosphate flour obtained from all exploited and promising phosphorite deposits of the former USSR. As a result of research, universal indicator of agrochemical efficiency of phosphorites (ПАЭФ) has been developed:

$$PAEF = \frac{PPP}{1000} + \frac{P_2O_5лр}{P_2O_5общ} + \frac{CO_3^{2-}}{PO_4^{3-}}, \quad (1.4)$$

Where:

PPP - loss on ignition, %;

- Relation characterizing isomorphous anion substitution

PO_4^{3-} for CO_3^{2-} - ion in the crystal latitude of phosphate.

Zhitov V.V. (1986, No. 4, p. 21-23) indicates that tests of activated and non-activated phosphorites on soils of Irkutsk oblast showed that dispersed phosphorites must be introduced first of all in soil with acid reaction and low content of mobile phosphorus. It has been established by investigations that, in the year of application of mechanically activated phosphorites, fairly strong aftereffect with 20% increase in barley yield was provided in meadow-carbonate slightly alkali soil. Nisanbayev G.M. and others (Ufa, 2010, V.2, p. 128-132, 2010, part 3, p. 61-64) received organic-mineral fertilizer by mechanochemical activation of phosphorite with poultry wastes. Study of its properties has shown that slowly soluble condensed phosphate compounds are formed in the activation products.

Nisanbayev G.M. and others (2010, No. 4, (10), part 4, p. 115-116) revealed that during mechanochemical activation of phosphorites, in the presence of poultry wastes, content of water- and lemon-soluble forms of P_2O_5 increases from 0.35% and 27.20% to 4.83% and 62.53% respectively. It is established that phase composition of the products obtained is characterized by the fact that, in addition to fluor apatite and hydroxydapatite, it contains hydrophosphate, diphosphate and calcium polyphosphate. Alteyev T. (Shymkent, 2010, 31 p.) presents results of studies on disintegration mechanoactivation of phosphate concentrate and use of activated phosphate flour in preparation of extraction phosphoric acid. As a result of generalization of the conducted analytical studies of published works on mechanoactivation of phosphate raw materials, it can be stated that mechanoactivation of natural phosphate raw materials:

- Increases phosphorites reactivity;

- Increases content of soluble forms of P_2O_5 in the activation product;

- Reduces fluorine content;

- Gives possibility of using activated natural phosphates as fertilizers.

In addition, it was found that use of chemical reagents in mechanochemical activation affects improvement of physicochemical properties of phosphates' solubility. Development of competitive industries in the chemical phosphorous branch industry, including production of complex mineral fertilizers, is one of the priority areas for industrial and innovative development. In the Republic of Kazakhstan, production of phosphorus, phosphoric and phosphorus-containing fertilizers is based on the world's largest Karatau basin phosphorite deposits and is export-oriented industry with over 70% of chemical products (excluding petrochemicals) and provides 2/3 of the total volume of the chemical industry in Kazakhstan. The total reserves and predicted resources of Karatau basin phosphorites are estimated at more than 15 billion tons of ore (3.5 billion tons in terms of P_2O_5) and occupy the fourth place in the world.

X-ray study of natural phosphate fines was performed on Bruker AXS X-ray diffractometer (Germany). Decoding of diffract grams is carried out automatically using EVA software. Diffractogram of the phosphate fines and printout are shown in Figure 1a.

As a result of study, the following mineralogical composition of the phosphate fines is established:

Basic crystal phases of the phosphate fines:

- Fluor apatite $Ca_5(PO_4)_3F$;
- Hydroxyapatite $Ca_5(PO_4)_3(OH)$;
- Francolite $CaF(Ca,C)_4[(P,C)(O,OH,F)_4]_3$;
- Quartz α-SiO_2;
- Dolomite $CaMg(CO_3)_2$.

The phosphate fines are characterized by pronounced oolitic-granular structure with predominance of phosphate cement, intensive development of carbonate cement (dolomite), locally turned to quartz cement. The results of the investigation of microstructure and elemental composition of the phosphate fines by scanning electron microscopy and microroentgen spectral analysis using JSM-6490LV (JEOL, Japan) scanning electron microscope are shown in Table 6.

Si	Al	Ca	Mg	P	Fe	Na	K	Mn	Ti	F	S
10,63	2,06	25,35	1,58	9,81	1,91	0,22	1,14	0,15	0,04	2,28	0,33

Table 6: Content of elements when scanning the phosphate fines sample, mass %.

Mechanochemical activation of phosphate fines

Scientists of M.O. Auezov South Kazakhstan State University, the Republic of Kazakhstan, jointly with Belarusian State University of the Republic of Belarus, carried out research on the mechanical activation of low-grade by chemical composition and substandard by granulometric composition phosphate fines of Zhanatas deposit. Determination of available (lemon-soluble) form of phosphorus was carried out in accordance with GOST 20851.2, by dissolving of citric acid in 2% solution. Content of available form of phosphates was determined in accordance with the indicated standard by the differential colorimetry method of phosphorus-vanadium-molybdenum complex on KFK-2MP photoelectric colorimeter.

Experimental studies were carried out under the follbowing conditions. Control samples of the phosphate fines were ground in a ball mill to the fineness of grinding of the material passing through a sieve with a mesh size of 0.16×0.16 mm, i.e. up to the standard fineness of grinding of the phosphate flour. Mechanical activation of the phosphate fines was carried out in “Activator-4” planetary mill (CJSC “Activator”, Russia) with different activation time. After the mechanical activation, properties of the activated phosphate fines were analyzed and compared with the initial (not activated) sample, ground in the ball mill to the fineness of the standard grinding of the phosphate flour [3]. The results of the study on dependence of phosphorus pentoxide lemon-soluble form content in the phosphate fines on the time of mechanical activation are given in Table 7. Analysis of Table 4 shows that increase in the content of P_2O_5 available form indicates significant effect of the mechanical activation on the phosphorites reaction with 2% citric acid. The maximum effect achieved with the mechanical activation of the phosphate fines consists in increasing the content of P_2O_5 lemon soluble form 17.61% to 53.15%.

Material	Activation time, min	Total content of P_2O_5, %	Content of lemon-soluble form of P_2O_5, %	
			absolute	relative
Phosphate fines	-	20,91	4,52	17,61
	5	20,89	9,76	46,63
	10	20,93	11,01	52,62
	15	20,92	11,08	52,94
	20	20,91	11,12	53,15

Table 7: Data on the mechanical activation of Zhanatas phosphate fines.

The results of the conducted studies indicate rather high efficiency of the mechanical activation of the phosphate fines, leading to significant increase in the content of phosphorus pentoxide available form in it and indicate significant increase in the quality of the mechanical activation of the phosphate fines compared to the standard phosphate flour. Increase in the content of P_2O_5 available form indicates that the mechanically activated phosphate fines can become effective component of complex phosphorus-containing fertilizers [3-19].

At the next stage, investigations of the mechanochemical activation processes and dependence of the phosphate fines mixture with ammonium sulfate on the content of phosphorus pentoxide lemon-soluble form and on their different ratios were carried out. Ammonium sulfate, byproduct of caprolactam production according to GOST 9097, was used in the research. Ammonium sulfate contains 21% of nitrogen, and the total P_2O_5 content in the phosphate fines is 20.89%. These values for the content of nitrogen and phosphorus pentoxide allow calculate P_2O_5:N ratio: in the mixture of the phosphate fines and ammonium sulfate. The mechanochemical activation time was 10 minutes. The results obtained during the mechanochemical activation of the mixture of the phosphate fines and ammonium sulfate are given in Table 8.

Analysis of Table 8 shows that the best result is obtained with 1:1 component ratio. The results of the experimental studies indicate high efficiency of the mechanochemical activation of the mixtures containing the phosphate fines and ammonium sulfate, which leads to significant increase in P_2O_5 available form content. Diffractogram and thermograviogram of the phosphate fines of Zhanatas deposit are shown in Figures 2 and 3.

Activated mixture	Ammonium sulfate share in the mixture, %	Total P_2O_5 content in the phosphate fines, %	P_2O_5 lemon-soluble content in the mixture, %	
			absolute	relative
Phosphate fines + ammonium sulfate	10	20,92	10,19	54,13
	20	20,91	10,01	59,89
	30	20,93	9,27	63,25
	40	20,92	8,38	66,73
	50	20,91	7,13	68,16

Table 8: Dependence of phosphorus pentoxide lemon-soluble form content during the mechanochemical activation of the mixture of the phosphate fines and ammonium sulfate.

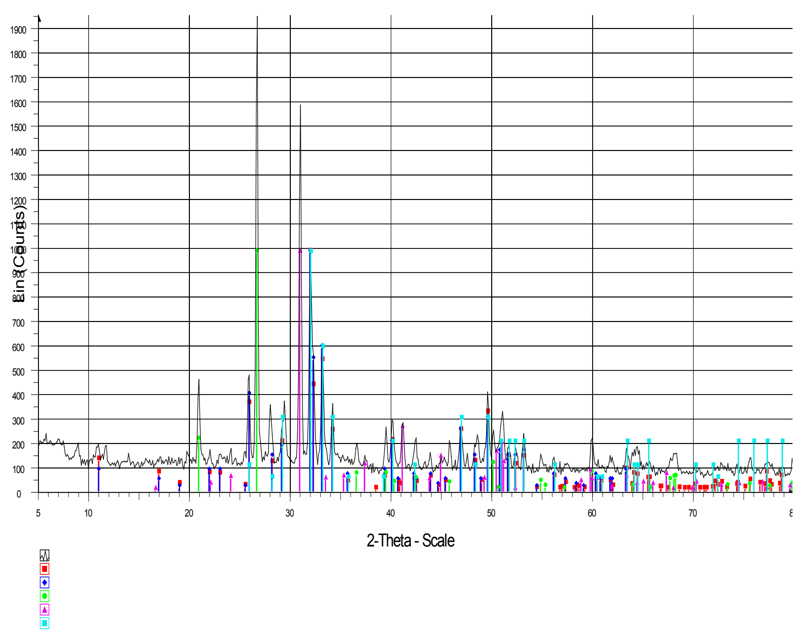


Figure 2: Diffractogram of the phosphate fines of Zhanatas deposit.

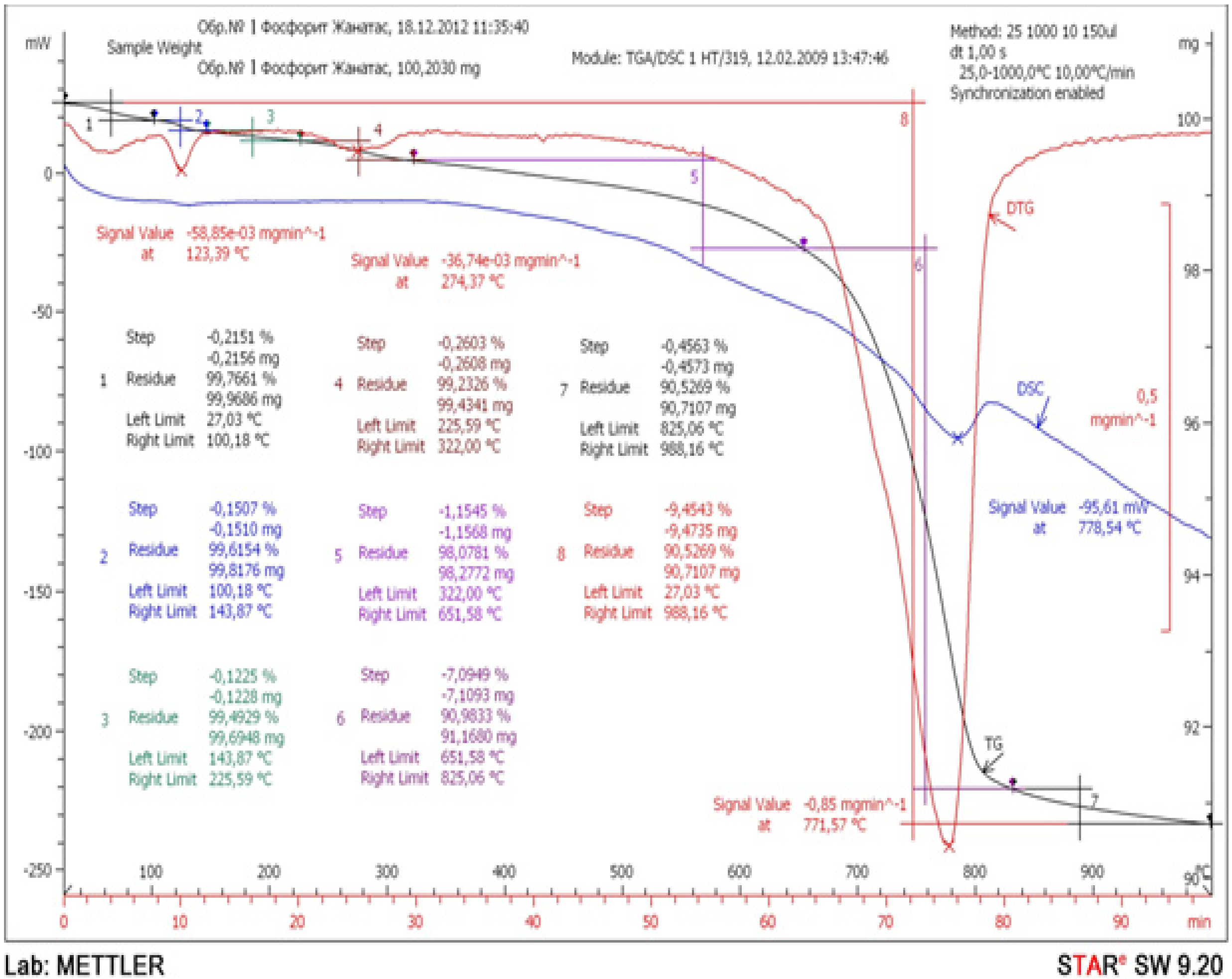


Figure 3: Thermograviogram of the phosphate fines of Zhanatas deposit.

The phosphate fines grinding process intensification

With the fine grinding of mineral raw materials, the smallest particles of the ground material aggregate with each other and form lumps, and also adhere to the milling bodies and internal armor plates of mills with a strong layer and further the grinding stops. Under these conditions the fine grinding process conditions sharply worsen and further grinding of the material becomes technically and economically impractical, since becomes excessively energy consuming. Use of grinding aids - special additives of surface-active substances (surfactants) causes clearing of dispersed particles' aggregation and adherence when grinding the mineral raw materials. Analysis of scientific and patent literature showed a great deal of very scant information about use of surfactants for grinding the phosphate raw materials.

In order to increase the grind ability and reduce energy consumption, influence of special additives, surfactants- the grinding aids on the grinding processes of natural phosphoric mineral raw materials was studied. In the process of the research, the phosphate fines of less than 5 mm class and grinding aids of various nature - triethanolamine and thermochemically treated soap stock, were used as starting materials. The problem of caking of mineral fertilizers is urgent scientific and technical task, since expensive imported technical products are used for these purposes. Development and introduction of effective and affordable anti-clodding agent will allow reduce the costs of production, storage and use of mineral fertilizers.

Therefore, in our method of phosphorite grinding, it is recommended to use soap stock, the thermochemical treatment product, in amount of 0.05-0.10% as a grinding aid. The soap stock is a byproduct of production of vegetable oils from renewable plant raw materials and is a slightly soluble in water homogeneous mass of brown color. The soap stock is heated to a temperature of 55-60 °C to increase its fluidity. 5% solution of NaOH (caustic soda) is prepared in a metal container, besides prepared from galvanized or aluminum material. After complete dissolution of the caustic soda, the solution is heated to 70-80 °C and the heated soap stock is poured in the solution in portions by a slip stream at the rate of 250 kg (on the main substance basis) per one cubic meter of the caustic soda solution with a constant mixing of the solution. The heated mixture is passed through ultrasonic disperser for complete dissolution of the soap stock. The process of its dissolution must be carried out in a reactor equipped with a heated jacket, with intensive mixing of the solution for 1.5-2 hours. In the thermochemical treatment process, in interaction of the caustic soda and soap stock, there are formed sodium salts of carboxylic unsaturated fatty acids, such as linoleic, oleic, palmitic, which are surface-active substances that penetrate into micro cracks of grains, and appearing at that in the micro cracks propping strains lead to adsorption reduction in strength (the Rehbinder effect) of the grinded material. Forming a uniform monomolecular layer on the surface of the grinded particles, they lead to decrease in the adhesive force between the dispersed particles, prevent their adhesion and aggregation during the grinding process, increasing the grindability and dispersability of the grinded phosphorite [4]. Characteristics of the grinded phosphorite granulometric composition using the soap stock are presented in Table 9.

Particle size, mm	Special particle yield, mass %			
	view and content of the grinding aid, mass %			
	nitric-acid ammonia	product of thermochemical treatment of the soap stock		
	0,05	0,05	0,075	0,10
More than 0,1	24	19	19	19
0,1-0,071	8	3	3	3
0,071-0,04	47	56	57	57
0,04-0,03	12	15	15	15
0,03-0,02	6	5	4	4
Less than 0,02	3	2	2	2

Table 9: Characteristics of the granulometric composition of the phosphorite grinded with additives of various grinding aids.

Analysis of Table 9 allows conclude that the soap stock introduction as the grinding aid significantly reduces content of coarse particles with fraction more than 0.1 mm from 24% to 19%, with size of 0.1-0.071 mm from 8% to 3%, and increase yield of fine particles with class of 0.071-0.04 mm from 47% to 57%, under the same grinding conditions, or shortens the phosphate raw materials grinding time with the same parameters of the grinded material dispersed composition. Besides, the soap stock introduction forms on the surface of the dispersed phosphorite particles monomolecular layer of a hydrophobic surfactant forming thin hydrophobic non-wetting cover which prevents moisture absorption from the environment and thus eliminates clumping and caking of powdered (pulverized) phosphorite and phosphorus-containing mineral fertilizer. As is seen from Table 10, use of the thermochemical treatment product, the soap stock, during the phosphorite grinding provided sharp reduction and removal of phosphorus-containing material caking from 97.8 to 100%.

Material	The soap stock consumption, kg/t	Breaking force, KPa	Caking reduction, %
Dispersed phosphorite (phosphate flour)	-	0,023	-
	0,05	0,0005	97,8
	0,075	0,0003	98,7
	0,10	0,00	100

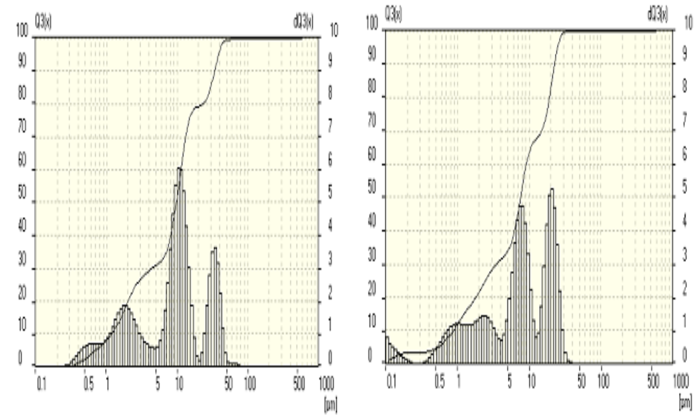
Table 10: The phosphate flour caking indicators.

To determine the caking, the phosphate flour or mineral fertilizer is kept in a heat chamber for 240 hours in a cylindrical capacity at a pressure of 15 KPa with a cyclic temperature change from 20°C to 60°C [5].

Physicochemical processes carried at the phosphate fines' mechanochemical activation

Mechanical and mechanochemical methods of activation of solids in grinding machines - activators have recently been increasingly used. With the help of these methods, it is possible substantially intensify many heterogeneous chemical processes that are limited by kinetics of interfacial interaction and diffusion in the solid phase: dissolution of hardly soluble substances, solid-phase reactions, etc. Development of studies on the regularities of such processes led to the emergence of a new science -mechanochemistry. Many researchers argue that over ground substance can be characterized as activated, and consider fine grinding of substances as a process of their activation. It must be noted that simple grinding of materials in a conventional ball mill does not allow achieve goals facing mechanical and mechanochemical activation, therefore, ball mills use only free impact and abrasive mechanical actions. In conventional ball mills, the only force through which the grinding process is carried out is gravitation with acceleration of 1g. This limits the mill efficiency, as at high speeds of rotation, the centrifugal force brings milling bodies to be constantly retained against the inner surface of the drum grinding unit, i.e. mill. This problem can be eliminated by using an activator mill, exemplified by planetary and some vibrating mills. When carrying out comparative tests on the mechanical activation of apatite (phosphate), a clear advantage of the planetary mill compared to the vibrating mill is established.

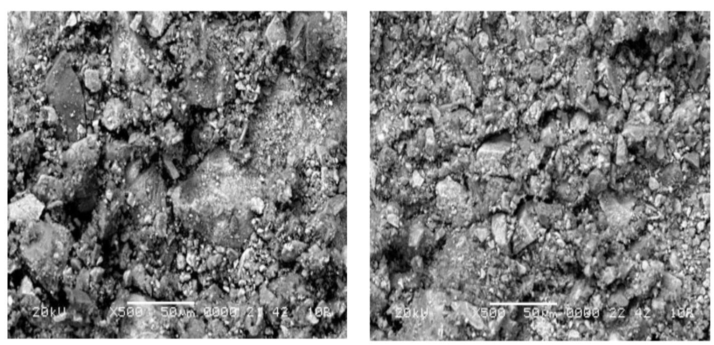
In the activator planetary, as well as centrifugal-elliptic mills, three mechanical actions are simultaneously forced: impact, shear and abrasion. These mills are called planetary because their drums rotate both around their own axis and around the common axis, like planets in the solar system. Due to this, large accelerations are achieved, up to 100g, as a result of which not only finer grinding occurs, but also defects in the crystal structure of the material appear. The results of the studies of the activated phosphate fines' dispersed composition and particle sizes on "Analizette 22" laser analyzer (MicroTecFritsch GmbH, Germany) are presented in Figure 4a and b.



a b

Figure 4: Dispersion spectra of the control sample (a) and mechanically activated phosphate fines (b).

Show that the mechanically activated phosphorite sample is a polydispersed material, in which a finely dispersed fraction from 0.5 to 10 μm is a significant fraction, whereas in a non-activated control sample of finely ground phosphate flour, a fraction of 5-50 μm predominates. Investigations of the non-activated and mechanically activated phosphate fines' dispersed particles morphology were carried out using "JSM-5610 LV" scanning electron microscope equipped with "EDX JED-2201" (JEOL, Japan) chemical analysis system. The obtained images of the electron-microscopic structure are shown in Figure 5.



a b

Figure 5: Electron microscopic images of the control sample (a) and mechanically activated phosphate fines (b), enlargement x500.

As a result of comparison of the given photomicrographs, it is noted that there are no coarse grains on the photomicrograph of the mechanically activated phosphorite fines sample (Figure 5b), as in the activation process, their average size decreased by more than 2 times compared to the non-activated sample (Figure 5a) and the largest grains have a size of 15×30 µm. This is due to the grinding efficiency of coarse grains during the mechanical activation of the material.

Amorphization and change in the dispersed particles morphology, where formless particles of indefinite configuration predominate in the sample of the mechanically activated phosphate fines, and particles with more pronounced flat faces, i.e. particles in the form close to prismatic or polyhedral bodies are present in the initial sample of the non-activated phosphate fines. By the dispersed composition and by studying the microstructure of the sample of the mechanically activated phosphate fines, it is possible to judge about partial amorphization, as well as possible deformation in the crystal structure of fluorocarbonapatite in the mechanochemical activation process. Based on the generalization of the results of the complex physicochemical studies, we proposed mechanism for the processes that occur during the mechanoactivation of the phosphate fines, the essence of which is:

- first, increase in P_2O_5 lemon-soluble form content in the mechanically activated mixture of the phosphate fines and ammonium sulfate is not only due to increase in the degree of dispersion and increase in the specific surface, but also due to increase in the number and area of the contacting regions between the activated particles;

- second, accumulation of various kinds of defects on the surface of phosphate substances and in their volume leads to increase in the reactivity of the phosphate substance to the solid-phase interaction with ammonium sulfate.

A flow of the reaction at the point solid-phase interaction of the phosphate substance and ammonium sulfate during the mechanochemical activation can be presented by the following scheme:

$$3(NH_4)_2SO_4 + Ca_3(PO_4)_2 \rightarrow 2(NH_4)_3PO_4 + 3CaSO_4 \downarrow$$

In addition to the above, in the mechanoactivation process, the phosphorite particle surface is amorphized, this is due to the fact that amorphization in the phosphate material structure is a consequence of plastic deformation of crystals during the mechanoactivation. A higher content of P_2O_5 available form in the overground mechanically activated phosphorite in comparison with the non-activated phosphorite is also a consequence of formation of particles on the thin amorphous layer surface. The amorphous layer formation reduces the phosphate substance density and significantly increases its reactivity.

Creation of pilot plant for production of mechanically activated fertilizer mixture of prolonged action "ZHAMB-70"

Based on the results of the research and developed technologies, experimental industrial technological line with production capacity of 0.5 t/h of fertilizer mixture has been created, its general view is shown in Figure 6. The main equipment of the pilot plant is a drying drum rotary furnace, centrifugal elliptical mill (CEM) "Activator C500", two-shaft bladed mixer, packing unit, screw pelletizer - mixer and machine for sticking the packing.

Figure 6: General view of the pilot plant.

Technological process for production of mechanically activated complex multicomponent phosphoric fertilizer mixtures "ZHAMB-70" consists of the following operations, shown in Figure 7. The dried phosphate fines, together with ammonium sulfate, are fed from bunkers calibrated by dosers into a 2-shaft blade mixer, and then dried from the surface moisture in a drying drum furnace, which is also used, if necessary, for calcination of raw materials in order to remove gaseous compounds, in particular CO_2, and increased moisture of the material, fed to the CEM "Activator C500", where it is mechanically activated with grinding to a fraction of less than 50 µm in the presence of the soap stock. The ground phosphorus-containing material is then mixed with other components of the fertilizer mixture at a customer's request. The fertilizer mixture, consisting of phosphate fines and ammonium sulfate, produced and tested by experimental batches (grades "A", "B" and "C") of complex NP fertilizers, NPK fertilizers, NPK-humate-containing fertilizers of prolonged action, containing potassium in the form of potash, brown coal and expanded enriched vermiculite, corresponds to the developed and introduced standard ST 2425-1958-01-ГП-002-2014 "Complex-mixed mineral fertilizer of prolonged action ZHAMB-70" and "Change 1" to it, as well as standard ST 9990- 1958-TOO-001-2015 "Complex phosphoric-nitrogen-sulfur mineral fertilizer "KMU-HT".

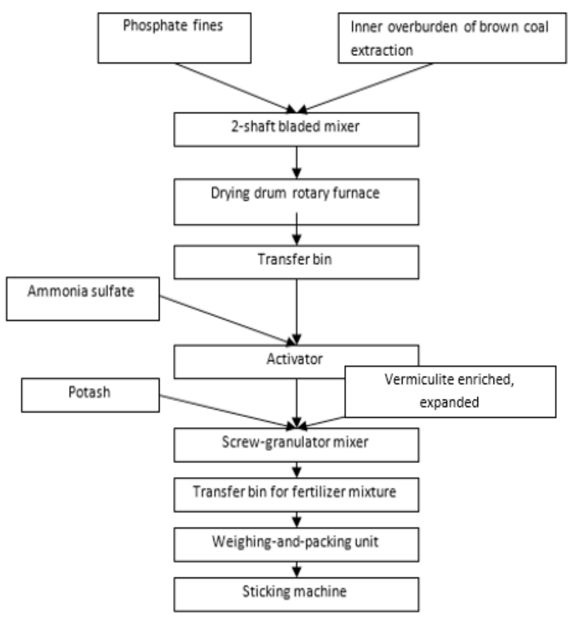


Figure 7: complex multicomponent phosphoric fertilizer mixtures "ZHAMB-70".

In addition, introduction of complex mineral fertilizers - fertilizer mixtures - was carried out at the leased by the Republican state enterprise on the right of economic management M. Auezov South Kazakhstan State University in the rural district "Zhaskeshu", Tulkubas district, cotton-sowing fields of LLP "Mart" of Ordabasy district and in sown areas leased by the peasant farm "Zhantas", on the outskirts of Shymkent city [6]. Soil cover of sown areas of these farms is flat, grayish, fixed to the hydromorphic series - meadow. The soils contain from the surface about 0.4% humus, the amount of which decreases with the profile depth. The cation exchange capacity is small and leaves about 4-5 eq/100 g, calcium predominates in the absorbed complex composition. The reaction of the medium is strongly alkali, and the soils are practically not saline.

The following genetic horizons are distinguished in the morphological structure:

A - 10-15 cm in thickness, light gray, dry, slightly compacted, not firmly-lumpy- dusty, permeated with plant roots, transition to the horizon;

B1 - 20-25 cm in thickness, brownish-light-gray, slightly compacted, not firmly-lumpy-dusty, with plant roots. In the upper horizon, gross form of nitrogen is about 0.01%, phosphorus is about 0.02%. Soil-forming rocks are layered-alluvial deposits of various mechanical composition, most often with predominance of loamy layers in the upper part.

The climate of South Kazakhstan oblast is sharply continental. Summer is dry, hot and long. Winter period is short, strong fluctuations in air temperature are observed. The oblast region refers to the desert-steppe zone, which covers pre-mountainous, mountainous areas of Tien Shan spurs. The absolute minimum of winter temperature reaches -20°C. The hottest months of a year are July and August, the maximum long-term air temperature in this period reaches +44°C or more.

The experiments were carried at:

- LLP "SKSU", Zhaskeshu village, Tulkubas district, over 1.0 ha area;
- On cotton-sowing fields of LLP "Mart", located in Ordabasy district;
- On sown areas leased by "Zhantas" peasant farm on the outskirts of Shymkent city, over 0.25 ha area.

Prior to conducting the research of mineral fertilizers in experimental field conditions, when planting various crops, in particular corn, sunflower, tomatoes, carrots, soybeans and cotton, samples were made containing a certain amount of ingredients of the fertilizer mixture listed in Table 11.

Sample with the phosphate component	P_2O_{5total}	Available Lemon-soluble	Nitrogen	K_2O	Humate	Vermiculite	Sulfur
Sample 1 68%	17,2	5,39	0,9	4,8	5,1	10	2
		5,42					
Sample 2 64%	17,7	6,42	0,8	4,8	5,4	10	3
		5,48					
Sample 3 59%	14,2	5,9	0,2	5,7	5,9	12,5	3
		5,4					
Sample 4 59%	13,6	5,4	0,2	6,0	5,8	12,5	3
		4,9					
Sample 5 100%	20,7	6,49					
		5,87					

Table 11: Average chemical composition of samples by the main components (in %).

Analysis of Table 11 shows that the average P_2O_{5total} content is more than 15%, including (in %) $P_2O_{5avail.}$ and lemon-soluble 5.9 and 5.4 respectively; nitrogen from 0.2 to 0.9; potassium in terms of K_2O 5.3; humates about 5.6; vermiculite 11.25 and sulfur 2.75. These ratios and average composition of the samples were used in the analysis of changes in the content of sanitary epidemiological, toxicological and radiological compounds in tomatoes, carrots, corn and soybeans and soil in 2015, 2016 and 2017. The application of fertilizers to the soil was carried out before sowing and planting the studied agricultural crops - tomatoes, carrots, beans, eggplant and bell pepper in "Zhantas" peasant farm in the period from 13 May to 9 July 2015.

Determination of changes in growth and quality of crops was carried out according to the developed experimental design matrix. The objects of the research used in LLP "SKSU" were corn, sorghum and sunflowers of LLP at SKSU, Zhaskeshu, on the upper terrace of the Arys river, according to the following scheme of experience: 1. Control background; 2. Sample No. 1; 3. Sample No. 2; 4. Sample No. 3; 5. Sample No. 4; 6. Sample No. 5. In the period from 13 May to 14 May 2015, seeds of corn, sunflower and sorghum were planted on the sown areas of Zhaskeshu, and cotton was planted on 19 May 2015, at the section of LLP "Mart" of Ordabasy district.

The experiment was laid in six variants, the area of each plot is $30m^2$. The accounting area is $15m^2$. All agrotechnical measures are carried out according to the generally accepted methodology. The field emergence was determined by the accounting method, at 10-linear meters, three replications in all experiments. The seeding rate of corn is 18 kg/ha, sorghum is 15 kg/ha and sunflower is 13 kg/ha at the seeding depth of 6-7 cm. Full sprouts were obtained in 7 days. To determine the field emergence in each plot, 10-linear meters of area were placed for accounting, in three replications. It should be noted that providing plants with nutrients in the early period is very decisive in increasing yield and improving its quality. During the vegetation period, records and observations (according to the methods for carrying out field and vegetation experiments of Soyuz NIHI, 1983) were carried out:

- Height of the main stalk of plants by development phases;
- Formation of fruiting branches and fruit organs by development phases;
- Sampling of plants for chemical analysis by phases;
- Selection of harvest samples for chemical analysis.

Static processing of the actual material was carried out according to B.A. Dospekhov methodology (1979). Testing of fertilizers on the sown areas allowed obtain significant increase in the output of agricultural crops, by 10-20%, the data of which are given in Table 12.

Culture	Harvesting from one m^2 of the sown area (kg) for the period of experiments from August to 9 October 2015					
	Control	Sample No. 1	Sample No. 2	Sample No. 3	Sample No. 4	Sample No. 5
1	2	3	4	5	6	7
Corn	5,39	6,16	6,74	6,14	6,24	6,34
Sorghum	39,83	43,76	49,09	45,50	48,50	48,96
Sunflower	2,41	2,57	2,65	2,87	2,83	2,67
Tomatoes	36,7	44,47	49,09	45,17	48,53	49,03
Bean	1,82	1,95	2,34	2,08	2,53	2,10
Carrot	2,85	3,20	3,35	3,15	3,50	3,25
Bell pepper	7,0	7,9	9,8	7,5	10,3	8,8
Eggplants	8,1	9,3	11,5	8,9	12,4	10,8
Raw cotton	3,14	3,52	3,62	3,56	3,73	3,47

Table 12: Harvesting using "ZHAMB-70" fertilizer (samples 2-6) and without fertilizers.

In all samples of agricultural products and plant stems carried out in the testing laboratory for chemical quality control of food products of the Belarusian State Technological University, Minsk, HCCH (α-β, γ-isomers), were determined in accordance with GOST 30710-2001, quality indicators 0.5. Content of radionuclides in all samples of corn and carrot: uranium-137 and strontium-90 contain less than 64.5 c/kg in cesium-137 and less than 20.0 in strontium-90, with values of quality indexes by the Technical regulatory legal acts 80 and 100 c/kg, respectively, and determined by the MBISNO 1481-2011, on the basis of GOST, it is concluded that the tested samples meet the requirements of the technical regulations of the Customs Union 021/2011. Table 13 shows the results of the field experiments of the developed complex fertilizers' agrochemical efficiency carried out jointly with the staff of Kazakh Research Institute for Soil Science and Agrochemistry on fields of "Ketebai" production cooperative in Makhtaaral district of South Kazakhstan oblast.

Variants of experiments	Accounting of raw cotton yield, c/ha				Increase in yield	
	I sample	II sample	III sample	average value	c/ha	%
Control	17,5	16,8	17,9	17,4	-	-
"A" grade sample	22,4	21,6	22,8	22,2	4,8	27,5
"B" grade sample	24,2	25,0	24,0	24,4	7,0	40,2
"C" grade sample	25,4	25,3	25,5	25,4	8,0	46,0

Table 13: Biological accounting of raw cotton yield, c/ha.

Use of complex fertilizers has positive effect on the yield of cotton and allows increase the yield of raw cotton to 22.2-25.4 c/ha, with increase in the yield of 4.8-8.0 c/ha. The following results were achieved by the research:

- Use of mechanical and mechanochemical activation of low-grade phosphate fines in activator grinding plants allows increase content of available (lemon-soluble) form of P_2O_5 from 17.61% to 53.15% and 68.16% respectively. This is due to the physicochemical changes in the dispersed composition and in the fine structure of the phosphate fines;

- Use of the soap stock as a surfactant allows intensify phosphorite grinding processes and reduce caking of the obtained mineral fertilizers;

- New innovative technologies for energy- and resource-saving acid-free processing of low-grade phosphate fines into complex mineral fertilizers with the use of mechanical and mechanochemical activation methods were developed. The novelty and international level of the developed technical solutions are confirmed by four innovative patents of the Republic of Kazakhstan No. 29121, No. 29132, No. 30649, No. 31226 and Eurasian patent No. 023417 for inventions;

- In the process of introduction, experimental batches of the mechanically activated complex phosphoric and phosphorus-containing NP-, NPK-, NPK-humate-containing fertilizers - prolonged action fertilizer mixtures – were developed;

- During field experiments of agrochemical efficiency of the developed complex mineral fertilizers obtained on the basis of mechanically activated phosphate fines, increase in the yield of raw cotton from 17.4 c/ha to 22.2-25.4 c/ha was achieved, this provide increase in the yields of 4.8-8.0 c/ha.

- Technical and economic efficiency of the developed technologies is caused by decrease in the costs for production of complex mineral fertilizers and consists KZT 22,257.50 per 1 ton of the production.

Thus, as a result of the carried out research, innovative energy and resource-saving acid-free technologies for production of fertilizer mixtures, which allow process substandard phosphate raw materials in the mechanically activated complex fertilizers that do not require sulfuric and nitric acids for their use and do not require complex production equipment, have been developed and introduced.

Non-use of chemical acids and absence of solid and liquid wastes allow place such production in places close to sources of raw materials (in mines) or directly at places of consumption, in order to reduce the radii of transportation of raw materials or finished products. This will contribute to the economy of the fertilizers produced. The world market of mineral fertilizers has been developing rapidly since the early 1960s and has contributed to the growth of agriculture, due to which the world consumption of fertilizers has increased almost fivefold in less than thirty years.

Significant increase in prices for mineral fertilizers on the world market scale creates favorable situation for producers, and therefore the industry notes significant level of use of production capacities. The favorable situation in the price relation allows producers implement investment projects to modernize production in order to maintain competitive abilities of their products. In connection with rapid growth of the world's population and improvement of living conditions, there is increase in consumption of agricultural products in developing countries. This led to general increase in the welfare of the population; however, soil fertility is not increased, although the requirements for the quality of agricultural products are constantly growing.

Rapid depletion of agricultural lands and their extremely slow development is becoming one of the main reasons for the growth of production of mineral fertilizers. By 2020, extensive growth of sown areas will cease practically due to the complete depletion of natural and agricultural lands. Therefore, in recent years there is growing rise in interest in the use of complex fertilizers containing sulfur, iron, magnesium and other trace elements, which play a certain role and important in plant life. Multicomponent fertilizers containing trace elements, in addition to phosphorus, potassium and nitrogen, have positive effects both on the soil poor in these elements, and on the yield and quality in general. However, traditional technology for obtaining complex mineral fertilizers, based on the acid decomposition of phosphate raw materials with sulfuric acid, is characterized by considerable expenditure of material and energy resources, as well as formation of heavy tonnage waste in the form of Phosphogypsum, the problem of utilization of which has not yet been fully resolved.

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