



## Production of comolex fertilizers from central kyzylkum phosphorites according to phosphorus-sulfur-survey and nitrogen-phosphorus-sulfur insecticide



Kuldoshev Orifjon Ergashevich\*, Urozov Tolkin Samadovich, Tillayev Sanjar Usmonovich, Aslanov Alisher Kakhramon ogli

*Chemistry faculty, Samarkand State University, 15, University Avenue, Samarkand, 140104, Uzbekistan*

### Abstract

The article develops a new method for obtaining complex fertilizers with phosphorus-sulfur and nitrogen-phosphorus-sulfur insecticides from the central Kyzylkum phosphorites of the Republic of Uzbekistan. The moisture effect on the activation of Kyzylkum phosphorite samples in the presence of sulfur was studied. Research has shown that, as the amount of moisture in the system increases, the plant-assimilating  $P_2O_5$  portion of the activated phosphorite increases, the carbonation degree increases, and the sulfur in the mixture becomes completely hydrophilic. X-ray analysis of phosphorite samples confirmed that it contains mainly phosphate, carbonate, silicate minerals. Calcium fluoride in the obtained radiographic peaks 1.72Å, 1.824Å, 1.90Å, 1.83Å, 1.84Å, 1.87Å, 1.91Å, 1.93Å, 2.24Å, 2.62Å, 2.69Å, 2.80Å, 3.16Å, 3.45Å, 3.87Å carbonate minerals 11Å, 865Å, 2,09Å, 2.29Å, 2.267Å, 3.01Å, 3.04Å the remaining peaks are silica, quartz and showed that it is suitable for other oxides. In the derivatogram obtained by thermal analysis of fertilizer obtained from unenriched phosphorite flour four and three exothermic effects at 360°C, 406°C, 540°C, 678 °C; two and three endothermic effects at 130 °C, 821 °C; three exothermic effects were observed at 397 °C, 541 °C, 698 °C; three endothermic effects were observed at 97 °C, 140 °C, 795°C respectively, for fertilizers made from low-quality phosphorite flour. Research has led to the compact energy development and resource-saving technologies for the phosphorus fertilizers production from phosphorites. The scientific research purpose, it consists of obtaining complex fertilizers with phosphorus-sulfur and nitrogen-phosphorus-sulfur insecticides from Central Kyzylkum phosphorites.

Keywords: phosphorite, nitrogen, phosphorus, sulfur, insecticide, fertilizer, technological scheme.

### Introduction

According to scientists from the Uzbek cotton research institute, if cotton is not fertilized during the development period, the cotton yield will be only 12 quintals, if 225 kg of nitrogen, 150 kg of phosphorus and 100 kg of potassium per hectare. It has already been confirmed that the yield will reach 30-35 quintals. This is because the main nutrients needed for plants (N, P, K, S, Ca, Mg, etc.) are added to the soil at the expense of mineral fertilizers [1-6].

Currently, the mineral fertilizers production and pesticides does not fully meet the agrochemistry requirements in obtaining high yields of agricultural crops. Mineral fertilizer technology and a complex that increases the plants resistance to adverse environmental conditions in agriculture and their resistance to plant pests, spiders, and diseases, as

well as has a positive effect on increasing plant productivity fertilizer creation is a topical issue [7-10].

In addition to protecting plants, feeding them with sulfur is also an issue. Soil does not satisfy the normal growth of plants. Sulfur is essential for the growth and development of plants, along with the macronutrients needed by plants. Its deficiency leads to a spontaneous decline in crop quality and various diseases during the agricultural crops development and the expected harvest at the end of the year will not be achieved. It is recommended to treat all crops types with 2-5 times crushed or colloidal sulfur. Because sulfur is an insect repellent. However, the hydrophobic nature of sulfur reduces its effectiveness and makes it difficult to obtain sulfur chemicals [11-16].

\*Corresponding author e-mail: [qorifjon18@gmail.com](mailto:qorifjon18@gmail.com); (Kuldoshev Orifjon Ergashevich).

Receive Date: 06 September 2021, Revise Date: 24 October 2021, Accept Date: 07 December 2021

DOI: 10.21608/EJCHEM.2021.94546.4444

©2022 National Information and Documentation Center (NIDOC)

Sulfur drugs in insecticides are not harmful to humans and livestock. As sulfur insecticides are used: lime-sulfur (2:1) decoction (ISO-International Organization for standardization), sulfur talc, colloidal sulfur. However, the obtaining process of these insecticides is complicated and requires a lot of energy and money [17-21].

### Experimental

All types of phosphorite flour obtained on the basis of Central Kyzylkum phosphorites in scientific research: TC (technical conditions) 81-31:2008 unenriched phosphorite flour, TC 81-29:2008 low quality phosphorites, TC 81.2-23:2006 washed and dried phosphorite concentrate and TC 81.2-22:2006 washed with calcined phosphorite concentrates. The chemical composition of these raw materials is given in Table 1.

Also for the phosphorite samples processing were used SS 127-76 well-ground sulfuric acid, SS 4204-77 sulfuric acid, TC 6.3-74: 2002 nitric acid.

The phosphorite samples analysis and all  $P_2O_5$  forms (common, plant-soluble and water-soluble  $P_2O_5$ ), which are the main constituents of chemically activated fertilizers, determines the main quality indicators of phosphorus fertilizers.

$P_2O_5$  determination in fertilizers was carried out by photocolometric method, spectrophotometer (colorimeter photo-electric) KFK-3 at wavelength  $\lambda=450$ . The error rate of the results obtained is  $\pm 1\%$ .  $P_2O_5$  analysis in water-soluble and plant-assimilating form was determined using standard methods [22-25].

The total amount of nitrogen in the samples was determined using the Keldal method [26].

The sulfur amount in the fertilizer was determined by gravimetric method in the presence of barium chloride [27].

CaO and MgO content of raw materials and fertilizers was determined by complexometric method. In the analysis, the solutions are titrated with 0.05n trilon-B (ethylenediaminetetraacetic acid) solution in the presence of fluorescein and chromium blue indicators. The amount of CaO in the absorbing form was determined using a 0.1n hydrochloric acid

solution. Oxides such as  $Al_2O_3$  and  $Fe_2O_3$  were also analyzed using the complexometric method.

$SO_2$  content determination in samples was performed using the volumetric method. This method is based on the carbonate minerals decomposition in the sample using hydrochloric acid.

In the conducted scientific research the composition of raw materials and obtained products was studied by chemical methods as well as physicochemical (X-ray phase and thermal) methods.

X-rays of the samples were taken on a DRON-3 diffractometer with a Cu cathode voltage of 25 kV, 20 mA current, and 2 meters speed per minute. The obtained radiographs were analyzed by comparing the ASTM (American Society for Testing and Materials) American card index and the X-ray tables of minerals compiled by Mikheyev and Giller [28-32].

### Results and discussion

Central Kyzylkum phosphorites: unenriched phosphorite flour, low-quality phosphorites, washed-dried phosphorite concentrate, washed-bupHed phosphorite concentrates, as well as physical and mechanical properties of sulfur were studied. The study results are presented in Tables 2-3.

Dimensions are necessary for the design of warehouses, bunkers and transport equipment. For example, samples of unenriched and low-quality phosphorite have an average bulk density of 1.102-1.176  $g/cm^3$  at an average humidity of 1.17-1.18%, and a specific gravity of 2.089-2.117  $g/cm^3$ . When the humidity increases to 3%, their value increases by an average of 1.27 and 1.13 times, respectively. The natural slope angle in phosphorites is 40-44°, and in sulfur it is 44-45°. Their relative densities range from 2.051 to 2.731  $g/cm^3$ .

The moisture absorption rates of the raw material samples were also studied under conditions of relative humidity of 50, 85, and 100% in desiccators.

Table 1-Chemical composition of phosphorite samples, %

Components	Unenriched phosphorite flour	Low quality phosphorite flour	Washed and dried phosphorite concentrate	Washed with calcined phosphorite concentrates
$P_2O_{5com.}$	16.04-18.39	14.08-15.80	18.22-18.40	26.20-27.25
$P_2O_{5sol.}$	8.04-8.75	1.14-2.45	6.15-7.62	8.62-9.86
CaO	42.51-44.57	43.78-44.50	43.82-44.55	40.30-41.62
MgO	1.65-1.73	2.08-2.11	0.98-1.13	0.64-0.72
CO <sub>2</sub>	15.10-15.25	13.28-15.18	14.75-14.90	2.11-2.20
$P_2O_3$	2.44-2.53	3.20-3.26	1.80-1.98	1.85-2.20
SO <sub>3</sub>	2.18-3.92	1.95-2.10	2.87-3.02	2.17-2.56
F	2.11-2.32	1.42-1.75	1.97-2.30	2.24-2.82
H <sub>2</sub> O	1.17-1.50	1.17-1.51	1.24-1.32	0.20-0.50

Table 2-The granularity degree of raw materials, %

Grain size, mm	Unenriched phosphorite flour	Low quality phosphorite flour	Washed and dried phosphorite concentrate	Washed phosphorite concentrate	Sulfur
-2 - +0.5	-	-	-	1.40	-
-0.5 - +0.315	1.80	1.90	3.40	4.90	2.10
-0.315 - +0.16	28.10	32.20	39.00	32.10	7.30
-0.16 - +0.1	21.40	28.30	30.20	26.60	24.60
-0.1 - +0.063	31.20	19.50	20.70	18.20	40.10
-0.063 $\geq$	17.50	18.10	6.70	16.80	25.90
Total	100	100	100	100	100

Table 3-Physicochemical and commodity properties of Kyzylkum phosphorite samples

Phosphorite samples	Humidity, %	Density, g/cm <sup>3</sup>	Dimensional weight, g/cm <sup>3</sup>	Natural slope angle, grad.	Fluidity, second
Unenriched phosphorite flour	1.17	2.089	1.102	40	20
	2.35	2.216	1.312	42	23
	3.15	2.345	1.402	43	not fluid
Low quality phosphorites	1.18	2.117	1.176	39	20
	2.40	2.282	1.363	43	24
	3.20	2.365	1.472	44	not fluid
Washed and dried fosconcentrate	1.14	2.715	1.403	40	19
	2.25	2.810	1.574	42	22
	2.88	2.902	1.713	43	not fluid
Washed roasted phosphate concentrate	0.85	2.731	1.386	41	18
	1.50	2.886	1.508	43	20
	2.30	2.912	1.642	45	22
Sulfur	0.15	2.051	0.985	44	17
	0.28	2.122	1.075	44	19
	0.35	2.198	1.186	45	20

The moisture absorption equilibrium of the raw materials was maintained for 11 days and their value did not exceed 1.5-2.0% when the relative humidity was 50-85%. At a relative humidity of 100%, the moisture absorption of the samples is 0.98-1.0% of sulfur, 3.96% of the washed concentrate, washed and dried concentrate does not exceed 4.65%, low-quality phosphorite flour does not exceed 5.98%, unenriched phosphorite flour does not exceed 6.90%.

The sulfur activation process of phosphorite raw materials was studied in order to obtain complex insecticidal fertilizers on the basis of Kyzylkum phosphorite samples. To do this, phosphorite samples were mixed with sulfur (90%:10%)-(10%:90%) by weight and mixed in a ball mill in a laboratory for 15-

30 minutes. The amount of different states of P<sub>2</sub>O<sub>5</sub> (total, plant-soluble and water-soluble) in the obtained mixtures was chemically analyzed using certain standard methods [33-32]. Also, the hydrophilization degree (wetting) of sulfur in the mixture, the decarbonization degree, various forms of CaO were determined.

Scientific studies have shown that the phosphorus nutrients in phosphorites are insoluble in water and cannot be absorbed by plants. Unenriched phosphorite contains only 8.04% of the total P<sub>2</sub>O<sub>5</sub>, and low-quality phosphorite flour contains 1.14%. As the sulfur content in the prepared mixtures increases, the amount of plant-absorbing P<sub>2</sub>O<sub>5</sub> increases. For example, when the sulfur content of the mixture was

10, 50, and 90%, the change in absorbent  $P_2O_5$  in the mixture increased by 5.44, 42.67, and 91.42%, respectively, compared to the sulfur-free phosphorite sample. These figures are comparable to those of low-quality phosphorite shows that the amount of absorbed phosphorus (V)-oxide is 2.58, 2.42 and 0.74% higher.

The transformation of phosphate minerals into plant-assimilated forms under the influence of sulfur can be explained as follows. During the phosphorite activation with sulfur, the system interact components. Elemental sulfur undergoes modification when it interacts with minerals in phosphorite. Some of it is oxidized by atmospheric oxygen. As a result, the oxidation state of sulfur varies from  $S^0 \rightarrow S^{+4}$  to partial  $S^{+6}$ . Water vapor in the air and moisture in the system are converted to sulfite and sulfuric acid. Under the influence of a weakly acidic environment, the lattice of phosphate mineral crystals changes.

The phosphorite samples interaction with sulfur resulted in a change in the pH of the 10% mixture suspension medium (Table 4). This allows the  $P_2O_5$  in the phosphorite to be absorbed by the plant.

Chemical analysis of the obtained products showed that as the sulfur content in the mixture increases, the amount of carbon dioxide in it decreases, that is, the decarbonization level of phosphorite increases. For example, when phosphorite is activated with 10% sulfur, the decarbonization rate of the raw material is 22.35%, and when 30% sulfur is added, it increases 1.57 times. It was also observed that the sulfur content increased by 1.71 and 2.22 times, respectively, between 50% and 70%.

It is known that sulfur is a hydrophobic substance that does not mix with water, and phosphorite samples have a positive effect on its hydrophilicity. Studies have shown that when unenriched phosphorite is mixed with up to 30% sulfur and low-quality phosphorite with up to 20% sulfur, it all becomes completely hydrophilic. This is because sulfur reacts with the mineral phosphate in the presence of oxygen and moisture in the air and loses its surface activity. An increase in the amount of sulfur leads to a decrease in the hydrophilization degree. For example, when unenriched phosphorite

has a sulfur content of 40% in its mixture, 3.13% of it remains hydrophobic. As a result of changing the sulfur content to 50, 70 and 90%, 1.54, 8.50 and 22.49% of the total sulfur, respectively, are not hydrophilized.

In the presence of these samples, the hydrophilization process (wetting) of sulfur was found to be less valuable than that of the unenriched phosphorite sample. For example, when up to 20% of sulfur is added to a mixture, its hydrophilization is 100%. An increase in the amount of sulfur in the mixture leads to a decrease in the hydrophilization degree. For example, when the sulfur content of a washed and dried phosphorite concentrate mixture is 40%, 8.79% of the sulfur remains hydrophobic.

As a changing result its content by 50, 70 and 90%, 9.96, 28.63 and 42.59% of the total sulfur, respectively, do not become hydrophilic. This means that the unenriched phosphorite is 1.06, 1.24, and 1.28 times less than the flour sample, respectively.

In the presence of washed and bupHed phosphorite concentrate, the hydrophilization of sulfur is incomplete, i.e. it is 5.79-9.28% less hydrophilized with increasing sulfur content compared to the sample of washed and dried phosphorite concentrate.

This can be explained by the composition of the phosphate concentrate samples and the moisture content they normally contain. For example, when the moisture content of the washed and dried phosphate concentrate is 1.14%, the moisture content of the washed and bupHed concentrate is 1.34 times lower. This is because the phosphorite samples processing with sulfur in the presence of moisture has a positive effect on the sulfur hydrophilization [33-34].

The amount of CaO in the samples obtained was also determined in different cases. The amount of CaO absorbed increases with increasing sulfur content. For example, 1.52% of the total CaO of 44.55% of washed and dried phosphorite concentrate is plant-assimilated. When the sulfur content of the samples is 10%, 30% and 50%, the amount of absorbing CaO in the mixture increases by 3.72, 3.83 and 4.04 times, respectively.

Table 4-Changes in pH of sulfur-activated phosphorite suspensions

The pH value in the mass ratios of phosphorite and sulfur										
10:0	0:10	9:1	8:2	7:3	6:4	5:5	4:6	3:7	2:8	1:9
Unenriched phosphorite flour										
9.19	5.54	8.52	8.46	8.42	8.39	8.36	8.32	8.28	8.20	8.13
Washed and dried fosconcentrate										
8.60	5.54	8.73	8.71	8.55	8.54	8.52	8.50	8.39	8.33	8.27
Washed roasted fosconcentrate										
10.93	5.54	10.77	10.75	10.73	10.69	10.66	10.59	10.52	9.91	9.48

The activation process of washed and dried fosconcentrate, the total amount of  $P_2O_5$  (content%)  $P_2O_5$  24,40, CaO 45,56, MgO 1,03,  $CO_2$  8,47,  $P_2O_3$  1,33,  $SO_3$  3,40, F 2,32,  $H_2O$  1,14. When carried out with a sample of 1.14, it is observed that the plant absorbing  $P_2O_5$  fraction is higher. For example, in this sample, the phosphorite contains 7.90% of the  $P_2O_5$  that the plant can absorb. When the sulfur content of the mixture is 10, 50 and 90%, the value of the absorbing  $P_2O_5$  increases by 4.14, 8.07 and 11.77 times, respectively. Compared to the washed and dried phosphorite concentrate sample, which contains 18.22% total  $P_2O_5$ , the plant uptake is 2.85, 1.40 and 1.03 times higher, respectively. When the sulfur content of the mixture is 30%, its hydrophilicity is 100%.

In order to study the kinetics of the sulfur-activated process of phosphorite flour samples, a phosphorite mixture containing 30% and 70% sulfur was mixed in a ball mill for up to 120 minutes. During mixing, samples were first taken every 15 minutes and then every 30 minutes to analyze various forms of phosphorus (V) oxide, carbon dioxide content, hydrophilicity of sulfur, and different amounts of CaO.

The results showed that a sample of unenriched phosphorite flour containing 30% sulfur, after mixing for 15 minutes, 3.15% or 23.54% of the total  $P_2O_5$  containing 13.39% was converted to plant assimilation. In the sample with 70% sulfur, 4.81% or 85.14% of the total  $P_2O_5$  of 5.65% was found to be plant assimilated. These values increased to 5.83% and 5.51%, respectively, in 30% and 70% sulfur mixtures over 60 minutes. There was a further increase in the activation time of phosphorite with sulfur, with an average increase of 2.71 and 1.98% in the amount of  $P_2O_5$  assimilated at 90 and 120 minutes compared to 60 minutes.

When the sulfur hydrophilicity was 7:3, the results showed that all the sulfur in the mixture was hydrophilic. When the phosphorite ratio to sulfur is 3:7, after 15 minutes, 78.24% of the sulfur is hydrophilic, after 30 minutes, the hydrophilization rate is 88.36%. At 60, 90, and 120 minutes, the hydrophilization rate increases by 0.16, 0.80, and 1.07%, respectively.

This pattern is maintained in other samples of phosphorite. The mixing time of phosphorite in the presence of sulfur does not significantly affect the activation level of phosphorite and the hydrophilization degree of sulfur. For example, 23.16% of the total  $P_2O_5$  is converted to plant assimilation when mixed with washed phosphorite concentrate and sulfur in a ratio of 7:3 for 30 minutes. When this sample was activated four times for more than 30 minutes, the plant absorption increased by an average of 1.13-1.22 times. This means that the sulfur bulk activation process in phosphorite samples takes an average of 15-30

minutes. Increasing the activation time to 60-120 minutes slows down the conversion of phosphorus to the plant-assimilating form.

The moisture effect on the activation of Kyzylkum phosphorites by sulfur. The moisture effect on the activation of sulfur phosphorite samples in the presence of sulfur was studied [35-36]. Research has been conducted on phosphorite and sulfur mixtures with a moisture content of 4-17% with a ratio of 7:3 and 3:7. The activated samples were dried at 90-105°C for 10-15 min and their composition was chemically analyzed.

The increase in humidity resulted in an increase in the plant-assimilating form of total  $P_2O_5$  and the hydrophilization degree of sulfur, as well as the minerals decarbonization. When dried unenriched phosphorite is activated with 30% sulfur, it contains 13.31% of the total  $P_2O_5$  and 24.42% in plant-assimilating form. The decarbonization rate of the raw material in this process is 35.80%.

Scientific studies have shown that as the amount of moisture in the system increases, the plant-assimilated  $P_2O_5$  portion of the activated phosphorite increases, the degree of carbonation increases, and the sulfur in the mixture becomes completely hydrophilic.

For example, when the moisture content of the mixture increases from 4.35% to 16.67%, the phosphorite-containing plant-assimilating form  $P_2O_5$  increases by an average of 1.26 times compared to the dehydrated activated sample, and the carbonation degree increases by 1.46 times.

These changes were observed even when the sulfur content of the phosphorite was 70%. For example, when phosphorite flour is activated with sulfur after drying, 88.27% of the total  $P_2O_5$  in 5.62% of it is in plant-assimilating form. 87.21% of the total sulfur is hydrophilic. The decarbonization rate is 48.14%.

With an increase in humidity from 4.25% to 16.61%, the plant-absorbing  $P_2O_5$  fraction ranges from 92.37% to 96.48%, the hydrophilicity of sulfur from 90.62% to 100%, and the degree of carbonation of phosphorite is 53.83 increases from 59.52%.

The decomposition rate of low-quality phosphorite in the presence of sulfur and moisture is 1.06-1.14 times lower than that of unenriched phosphorite.

The effect of moisture on the activation of phosphorite by sulfur can be explained as follows. In aqueous solution, elemental sulfur formed a weakly acidic environment (pH-5.54). As mentioned above, when phosphate minerals react with sulfur, some of it is oxidized and converted to sulfite and sulfuric acids under the influence of moisture in the system. The diffusion of acid ions under the influence of moisture is better than that of the dried phosphorite sample and increases the plant absorption of phosphorus in the raw material.

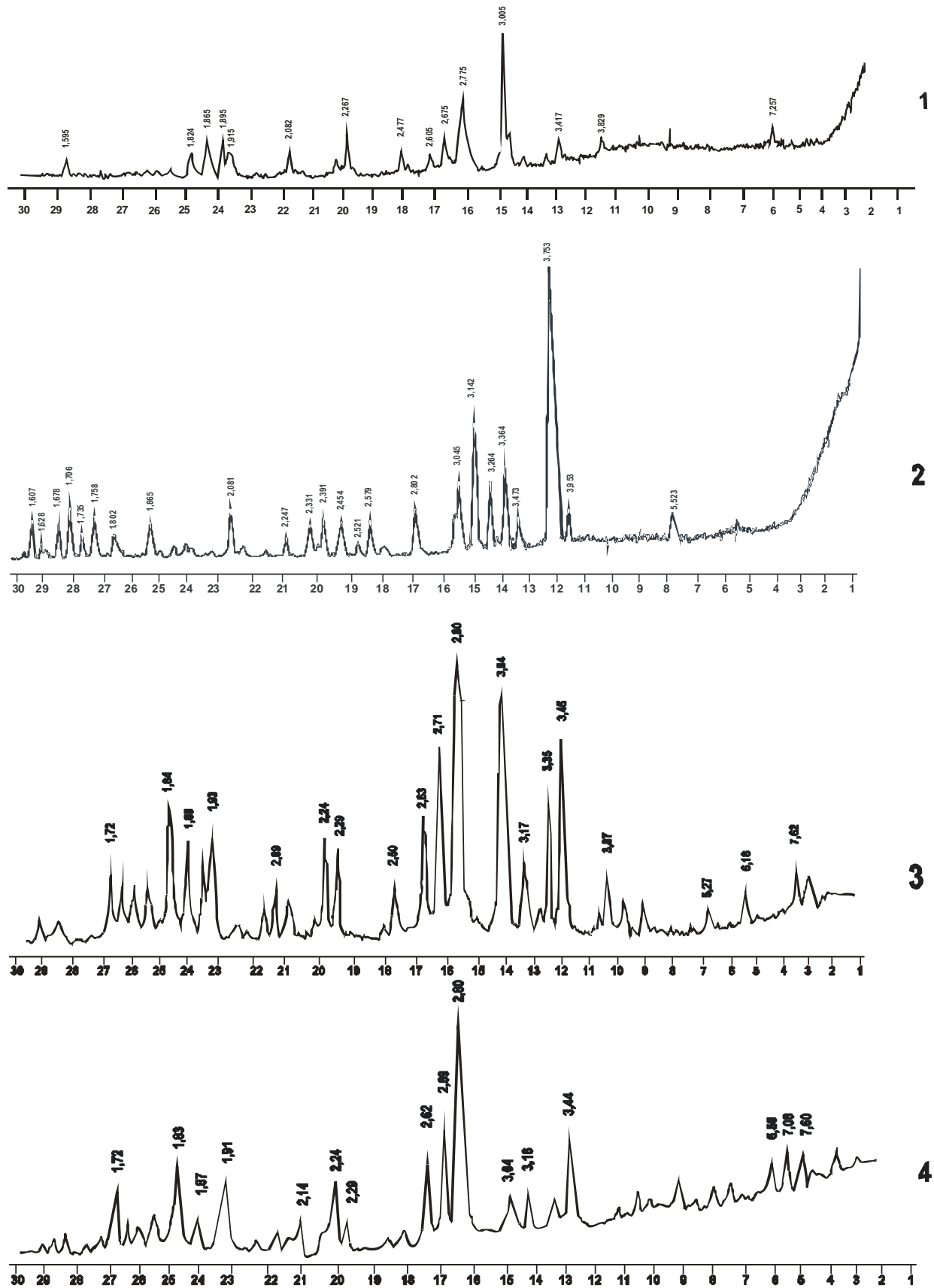


Figure 1. Radiographs of raw material samples 1- unenriched phosphorite flour; 2- oltingugurt; 3- washed and dried fosconcentrate; 4- washed roasted fosconcentrate

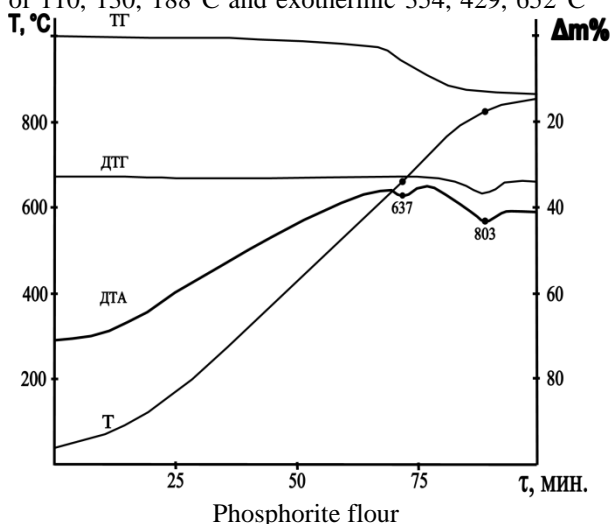
Scientific studies have shown that the decomposition of phosphate raw materials increases as the moisture content of all phosphorite samples increases with the activation of sulfur. Phosphorite, which is not enriched in washed, dried and roasted fosconcentrates, also has an average of 1.12 and 1.21 times lower decomposition levels, respectively, compared to the plant-absorbing  $P_2O_5$ , which is 1.28 and 2.23 times lower, respectively. Because this is 2.3. explained by the complex physicochemical changes in the composition of the raw material in the process of obtaining fosconcentrates, as described in the section.

X-rays and derivatograms of all types of raw materials were obtained using physicochemical methods to fully study the results of quantitative analysis. X-ray analysis of phosphorite samples confirmed that it contains mainly phosphate, carbonate, silicate minerals. The radiographs studied are shown in Figure 1.

Calcium fluoride in the obtained radiographic peaks is 1.72 Å, 1.824 Å, 1.90 Å, 1.83 Å, 1.84 Å, 1.87 Å, 1.91 Å, 1.93 Å, 2.24 Å, 2.62 Å, 2.69 Å, 2.80 Å, 3.16 Å, 3.45 Å, 3.87 Å, carbonate minerals 1.865 Å, 2.09 Å, 2.29 Å, 2.267 Å, 3.01 Å, 3.04 Å, the remaining peaks are silica, quartz and showed that it is suitable for other oxides.

Derivatograms of unenriched phosphorite flour and sulfur were obtained to compare the thermal analysis results of new varieties of fertilizers. The results are shown in Figure 2.

Two endothermic effects of 637°C and 803°C were observed in the derivatogram obtained as the thermal analysis result of phosphorite flour and mass loss is 9.80% in the first endo effect and 4.2% in the second endo effect. Three endothermic effects of 110, 130, 188°C and exothermic 354, 429, 652°C



were observed in the thermal analysis of sulfur. 6.20% of the mass obtained for analysis in the first three endo effects, 21.30% in the first exo effect at 354°C, 19.21% in the second exo effect at 429 °C and 2.15% in the last exo effect at 652 °C 'remains shown in practice.

X-ray and thermal analysis of Central Kyzylkum phosphorites and samples of fertilizers activated in the presence of sulfur. The results of X-ray phase analysis of phosphorite samples showed that their composition consists of the main components such as phosphate, carbonate, silicate. The radiographic results of the fertilizers also confirm that the phosphate raw material was converted to a plant-assimilated form when the phosphorite samples were activated in the presence of sulfur. X-rays of the substances studied are shown in Figure 3.

Fertilizer samples taken from unenriched and low-quality phosphorite samples at inter-plane distance peaks 2.33, 1.74, 1.64, 3.44 d, Å  $CaSO_4$  and  $CaSO_4 \cdot 0.5H_2O$  is characteristic for calcium sulfate in the state, while the values of dicalcium phosphate are 1.90, 2.60, 1.87, 1.72, 2.75, 3.125 d, Å.

Also in fertilizers obtained from washed and bupHed phosphate concentrate for 2.78, 2.48, 1.71 d, Å  $CaSO_4 \cdot 2H_2O$ , in 2.10, 2.61, 1.87 d, Å  $CaHPO_4 \cdot 2H_2O$  indicates the presence of peaks. X-rays show that the other diffraction lines in the product are unaffected phosphorite particles.

Thermal analysis of the obtained fertilizers was carried out in order to study the different thermal processes that occur in a certain temperature range of substances (Fig. 4).

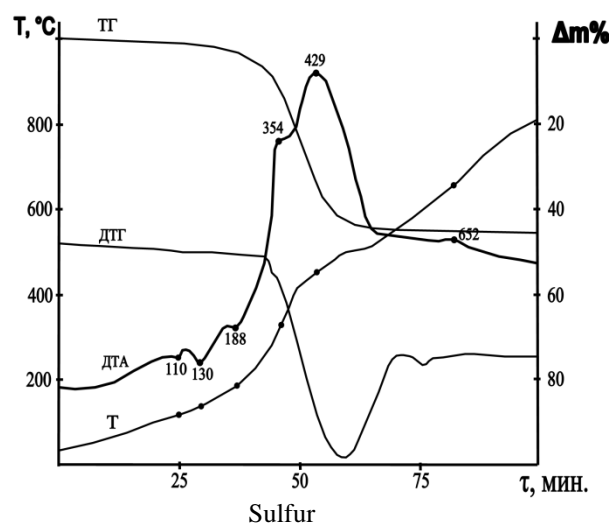


Figure 2. Derivatogram of raw materials.

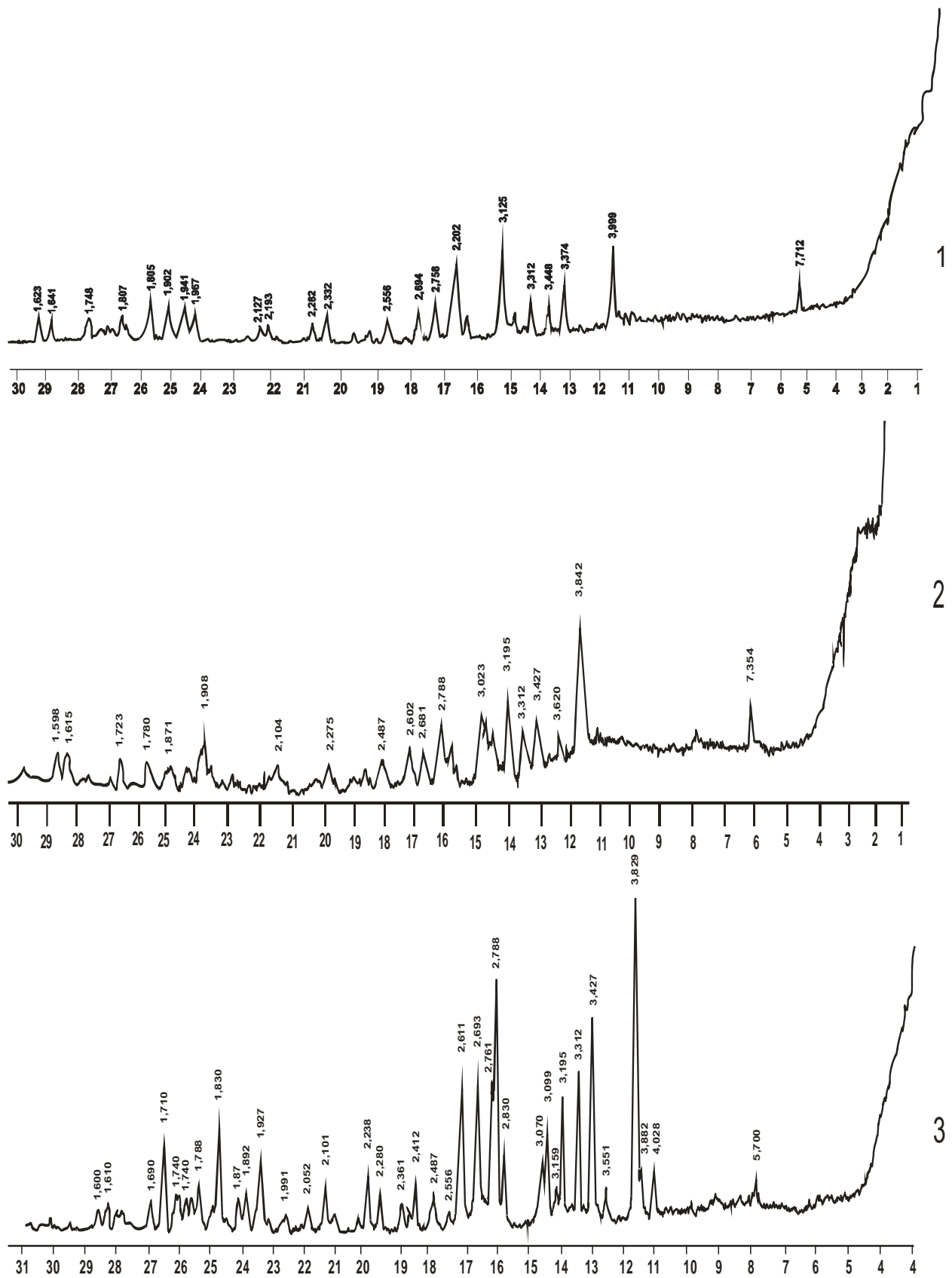


Fig. 3. Radiograph of phosphorite samples in the presence of sulfur (7: 3) activated fertilizers: 1- unenriched phosphorite flour; 2- low quality phosphorite; 3- washed and bupHed phosphorite concentrate



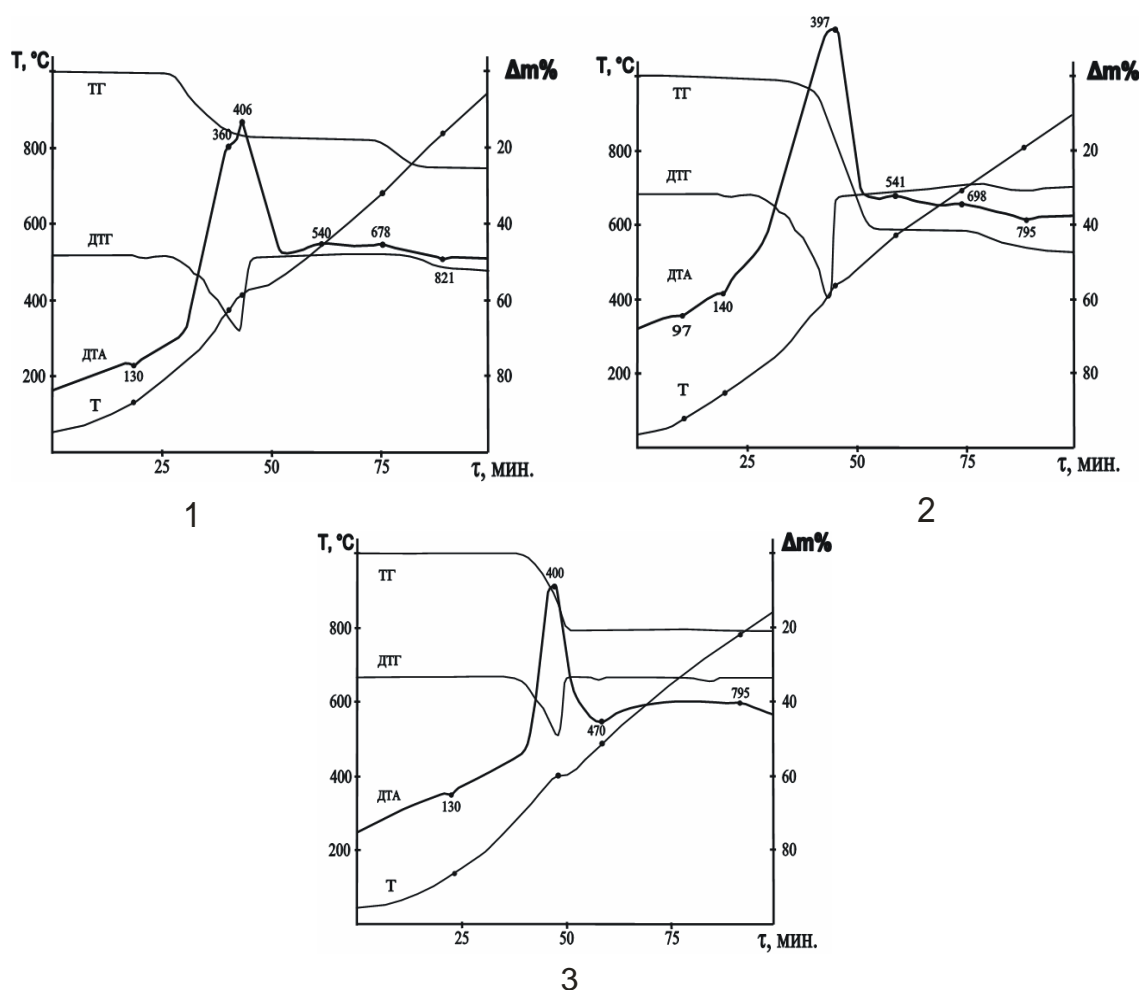


Fig. 4. Derivatogram of phosphorite samples in the presence of sulfur (7: 3): 1- unenriched phosphorite flour; 2- low quality phosphorite; 3- washed and bupHed phosphorite concentrate

The derivatogram obtained as the thermal analysis result of fertilizer from unenriched phosphorite flour has four exothermic effects at 360, 406, 540 and 678°C, and two endothermic effects at 130 and 821 °C, three for fertilizer from low quality phosphorite flour the exothermic effect was observed at 397, 541, and 698 °C, and the three endothermic effects were observed at 97, 140, 795 °C.

In addition, two exothermic effects were observed at 400 and 795°C and an endothermic effect at 130 and 470°C, respectively, in the fertilizer obtained from the washed phosphate concentrate.

The new varieties of fertilizers have important insecticidal properties for plant life. The efficiency of fertilizers storage in warehouses, transportation by various means and application in agriculture depends on their physical and mechanical properties. The granulation process of a sulfur mixture of phosphorites was studied. The granulation stage of the powder mixture was carried out in a plate granulator in the presence of water and a 45% ammonium sulfate solution. The resulting granules were dried at 80-100 °C temperature.

The physical and mechanical properties of the new fertilizer were studied using traditional methods. The moisture absorption rate of fertilizers was studied in desiccators under relative humidity conditions of 50, 85, 100%. The moisture absorption kinetics of fertilizer samples are shown in Figure 2.6.

When the relative humidity is 50%, the products do not absorb moisture. When the relative humidity is increased to 85 and 100%, the moisture absorption equilibrium of the products in the desiccators occurs on average in 9-10 days, and its values do not exceed 0,86 and 6.22%, respectively. This means that the fertilizer is not hygroscopic. They do not lose their marketability, even when stored for a long time in seasonal conditions. The above research results are the scientific basis for the phosphorite samples activation in the presence of sulfur. It is recommended to use new varieties of phosphorus-sulfur fertilizers with insecticidal properties. Because the agricultural products grown in our country are grown in different climatic and soil conditions.

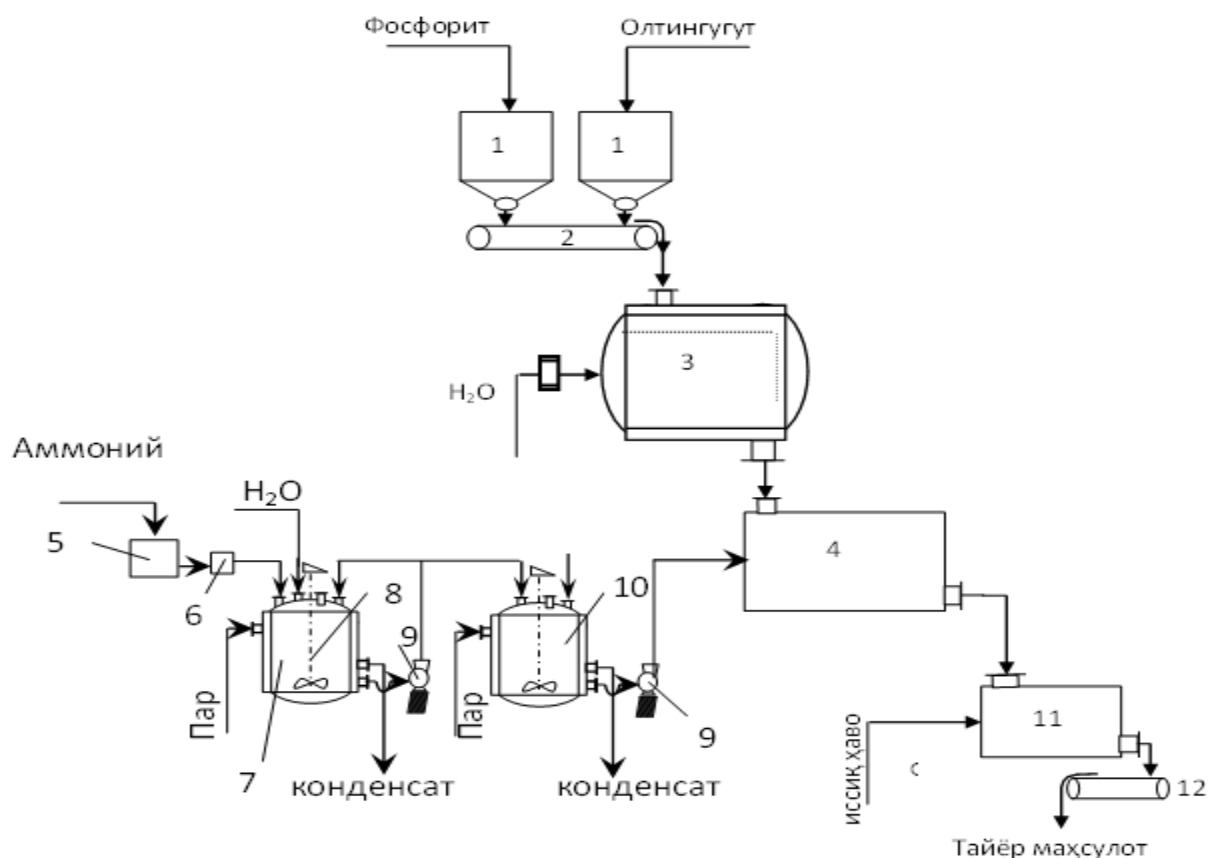


Fig.5. Technological system for the production of phosphorus-sulfur fertilizers from phosphorites

The process of activating phosphorite samples with sulfur or converting its phosphorus into a plant-assimilating form is due to moisture in the soil and in the plant body and in the leaves during irrigation. In addition, the presence of microorganisms that oxidize sulfur in the soil is much higher. Under these conditions, the elemental sulfur in the fertilizer oxidizes to form an acidic environment in the presence of moisture, which activates the undigested phosphorite. The research resulted in a compact energy and resource-saving technology for the production of phosphorus-sulfur fertilizers from phosphorites (Figure 5).

1-consumption bunkers; 2,12- conveyors; 3- mill; 4 granulating drums; 5-bunker; 6- weight scale; 7, 10 reactors; 8 mixers; 9 pumps; 11 drying drum.

The proposed technological system for the production of phosphorus-sulfur fertilizers consists of the following stages:

- receiving, storage and delivery of phosphate raw materials to the mill through the dispenser;
- reception, storage, transportation of sulfur;
- mixing and grinding of components;
- preparation of the binder solution and spraying into the granulation device through the dispenser;
- granulation and drying of products;
- storage and packaging of finished products.

Phosphate raw material and sulfur are added from the warehouse to the bunkers (1) using mechanical devices. The required amount of phosphorite and sulfur is measured using weights and sent to the conveyor belt (2) and mill (3). Water is sprayed into the mill using sprayers to reduce the amount of dust generated during components mixing and to increase the sulfur hydrophilicity in the presence of moisture. The mixture is then sent to the granulation drum (4). Ammonium sulphate solution is sprayed into the drum from several places to form granular, solid granules. Depending on the brand properties of the product, the concentration and amount of the binder chemical compound is determined. The resulting product is sent to the drying drum (5). The finished product is sent via conveyor (6) to the warehouse or packaging machine.

## 1. Conclusion

In this article, a new method of obtaining complex fertilizers with phosphorus-sulfur and nitrogen-phosphorus-sulfur insecticidal activity from the central Kyzylkum phosphorites of the Republic of Uzbekistan was developed.

The increase in humidity resulted in an increase in the plant-assimilating form of total  $P_2O_5$

and the hydrophilization degree of sulfur, as well as the minerals decarbonization.

Unenriched phosphorite contains only 8.04% of the total  $P_2O_5$ , and low-quality phosphorite contains 1.14%. As the sulfur content in the prepared mixtures increases, the amount of plant-absorbing  $P_2O_5$  increases. For example, when the sulfur content of the mixture was 10, 50, and 90%, the change in absorbent  $P_2O_5$  in the mixture increased by 5.44, 42.67, and 91.42%, respectively, compared to the sulfur-free phosphorite sample. These values were 2.58, 2.42, and 0.74% higher for the absorbed phosphorus (V)-oxide content compared to the low-quality phosphorite sample.

As all samples of phosphorite are activated by sulfur, the decomposition of the phosphate raw material increases because the moisture content increases. Phosphorite, which is not enriched in washed, dried and roasted fosconcentrates, also has an average of 1.12 and 1.21 times lower decomposition levels, respectively, compared to the plant-absorbing  $P_2O_5$ , which is 1.28 and 2.23 times lower, respectively. Because this is 2.3. explained by the complex physicochemical changes in the raw material composition in the fosconcentrates obtaining process, as described in the section.

The granulation process of a sulfur mixture of phosphorites was studied. The granulation stage of the powder mixture was carried out in a plate granulator in the water presence and a 45% solution of ammonium sulfate. The resulting granules were dried at 80-100 °C temperature.

The new varieties of fertilizers have been shown to have important insecticidal properties for plant life.

### Conflicts of interest

There are no conflicts to declare.

### References

- [1] Beglov B.M. Namazov Sh.S., Mirzakulov Kh.Ch., Umarov T.Zh. Activation of natural phosphate raw materials. –Tashkent-Urgench: Publishing house "Khorezm", 1999. –112p.
- [2] Reimov A.M. Development of technology for obtaining nitrocalcium phosphate and nitrocalcium sulfophosphate fertilizers based on the decomposition of Kyzylkum phosphorites at a reduced rate of nitric acid: Author's abstract. dis. ... Cand. tech. sciences.–T.:, 2004. –23 p.
- [3] Seitnazarov A.R. Chemical and mechanochemical activation of phosphorites of the Central Kyzyl Kum: Author's abstract. dis...cand. tech. sciences. - Tashkent, –2005. – 23 p.
- [4] Chaikina M.V. Physicochemical foundations of mechanical activation of complex phosphate-containing systems and their applied aspects: Author's abstract. diss. ... Doctor of Chemical Sciences. - Novosibirsk, 1996. – 37 p.
- [5] Mirzakulov Kh.Ch. Development of a resource-saving technology for processing phosphorites of the Central Kyzylkum Desert: Author's abstract. diss. ... Doctor of Engineering Sciences. - Tashkent, 2009. – 52 p.
- [6] Georgievsky A.F., Potashnik B.A., Mager V.O., Finogenova T.V., Avakyan Z.A. Microbiological enrichment of phosphorites - technology of the twenty-first century // GopHyi Vestnik. –1996. - Special issue. –p. 81-88.
- [7] Teryukhova R.R. The effect of phosphorus bacterial fertilizers on the biological activity of typical serozem under cotton: Author's abstract. dis. ... Cand. biol. sciences. - Tashkent, 2005. – 27 p.
- [8] Dalimova D.A. Microbiological activity of typical serozem under the influence of organomineral composts based on phosphorites of the Central Kyzyl Kum: Author's abstract. dis. ... biol. sciences. - Tashkent, 2007. – 25 p.
- [9] Shayakubov T.Sh., Ilyashenko V.Ya., Boyko V.S., Kudryashev N.S., Turanov U.T. Paleogene phosphorites of Uzbekistan // Soviet Geology. - 1982. - № 7. –p. 3-12.
- [10] Shayakubov T.Sh., Mikhailov A.S., Boyko V.S., Kudryashev N.S., Zhuravlev Yu.P. The Central Kyzylkum phosphorite-bearing region and its prospects // Geol. methods of prospecting and exploration of deposits of non-metallic minerals. Review / All-Union Research Institute of Economical Mineral Resources and Geological - exploration works. - M.: VIEMS, 1983. - 28 p.
- [11] Amirova A.M., Sokolov S.I., Narmetova N., Yusupova F.M. Sh material composition of granular detrital phosphorites of the Central Kyzyl Kum mountains // Uzbek Chem.j.-1981. №1. –p. 8-13.
- [12] Geology of phosphorite deposits, methods of forecasting prospecting/M.: Nedra (VNIIGeolnerud),-1980.-247p.
- [13] Ilyashenko V.Ya. Paleogene phosphorites of the east and south of Uzbekistan // Uzbek. geologist.j. 1966. № 4. –p.11-16.
- [14] Karzhauv T.K., Koldaev A.A. and others. New finds of phosphorites in the Paleogene sediments of WestepH Uzbekistan // Uzbek. geologist.1966. №4. - p.29-32.
- [15] Ibaidullaev N.O. New types of phosphorite occurrences in the Paleogene sediments of the Kyzylkum mountains // Uzbek. geologist.1968. №3. -p.24-29.
- [16] Popov V.S., Konov L.P. Phosphorite-bearing basins of Central Asia // Tr. Sredneaz. Research

- Institute of Geology and Mineral Raw Materials. - Tashkent, 1981. V. 3, -p. 49-60.
- [17] Linkevich V.A., Trekhin E.L., Rakhimov V.R. Leaching of the Kyzyl Kum phosphorites//XV Conf. on chemical technology of inorganic substances: Abstracts of documents. May 29-31, 1991. -Kazan, 1991. -p. 231-232.
- [18] Kuzovlov L.K., Maltseva I.I., Pugach A.N. Technology of beneficiation of granular-detrital phosphate ores of the Dzheroyskoye and Sardarinskoye deposits//Tr. Central Asia. - Tashkent. Publishing house of SAIGIMS.-issue 3.- 1981.-73-83p.
- [19] Blisovsky V.Z., Fatkhulaeva G.F., Mager V.O. The material composition of the Dzheroi-Sardara phosphorites.-V. sb: geology and material composition of non-metallic minerals in Central Asia.-Tashkent, ed. SAIGIMS.-1984. -p.19-30.
- [20] Nabiev M.N., Abdurakhmonov E, Amirova A.M. Physicochemical study of phosphorites of the Central Kyzyl Kum // JoupHal of Applied Chemistry. -1984.№4. -p. 969-973.
- [21] Boyko V.S., Shabanina N.V. Mineralogical features of granular phosphorite ores of Kyzylkum and study of their washability. // Uzbek geologist.1979. №3. -p. 84-86.
- [22] Soboleva V.S. Physics of apatite. – M.: The science, -1975. – 112 p.
- [23] Chaikina M.V., Kolosov A.S., Boldurov V.V. The question of mechanochemistry of natural and synthetic phosphates // Izvestiya SO AN SSSR, ser. -1979.-V.3, №7. - 14-19 p.
- [24] Vinnik M.M., Erbanova L.N., Zaitsev P.M. and other Methods of analysis of phosphate raw materials, phosphoric and complex fertilizers, fodder phosphates. - M.: Chemistry, 1975. - 218 p.
- [25] Pozin M.E., Kopylev B.A. and other Guide to practical training in the technology of inorganic substances. - L.: Chemistry, 1968. - p. 360.
- [26] Malakhova S.G. Temporary guidelines for the control of soil pollution. - Moscow, 1984. - 61 p.
- [27] American Card Index ASTM. Diffraction Data cards and Alphabetika land Group Numerical Index of X-Ray Diffraction Data. / Publishing House of the American Society for Testing Materials. New York. 1973.
- [28] Mikheev V.I. Radiometric determinant of minerals. In 2 volumes. - M., 1957. V.1. – 868 p.
- [29] Giller J.L. Interplanar spacing tables. In 2 volumes - M.: Nedra, 1966. – 330 p.
- [30] Urozov T.S. Obtaining insecticidal fertilizers on the basis of Kyzylkum phosphorites // Uzb. chemistry j.- № 3. 2008. – p. 74 -76.
- [31] Urozov T.S. Influence of sulfur on activation of Kyzylkum phosphorites // Uzb. chemistry j.-№ 3. 2010. – p. 98 -101.
- [32] Urozov T.S., Tadjiev S.M., Tuxtaev S. The effect of moisture on the activation of phosphorite in the presence of sulfur// Materials of the Republic. scientific and technical conf. Development of an effective technology for obtaining mineral fertilizers and agrochemicals of a new generation and their application in practice: November 25-26, 2010. – Tashkent, 2010.–p 64-67.
- [33] Urozov T.S., Tadjiev S.M., Tuxtaev S. Sulfur superphosphate// The conference actual problems of the development of chemical science, technology and education in the Republic of Karakalpakstan is dedicated to the 20th anniversary of the independence of the Republic of Uzbekistan: Nukus, 2011. – p. 84-85.
- [34] Urozov T.S., Tajiev S.M., Tukhtaev S. Splitting of reddish phosphorites with the participation of sulfate suspension//Uzb. V. - Tashkent, 2010. - № 5. - p. 30-33.
- [35] Urozov T.S., Tajiev S.M., Tukhtaev S. Khairullaev C. The influence of sulfur on the cleavage of rubella phosphorites with nitrate acid//Reports of the Russian Academy of Sciences. - Tashkent, 2010. -№4. -p. 53-56.
- [36] Urozov T.S., Tajiev S.M., Tukhtaev S. Obtaining insecticidal fertilizers N, P, S//Collection of reports of an intepHational scientific and practical conference on the topic: "Sources and water-saving technologies of reproduction from cemeteries in the agricultural system": Tashkent, 2010. – p. 256-257.