

Article

Acid-Free Processing of Phosphorite Ore Fines into Composite Fertilizers Using the Mechanochemical Activation Method

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Abstract: The relevance of involving substandard raw materials for the production of composite phosphorus-containing fertilizer production is significant due to the problem of providing food products for the growing population of the Earth. The main raw materials for phosphorus and composite phosphorus-containing fertilizer production are natural phosphate ores—phosphorites. However, in the process of mining and crushing, ~55–60% phosphorite ore fines are formed—a fraction of less than 10 mm, which is unsuitable for traditional processing into composite phosphorus-containing fertilizers. This article presents the results of physicochemical studies of the substandard fine fraction of phosphorite ore and the results of the studies of the possibility of their direct processing into phosphorus and composition of phosphorus-containing fertilizers using methods of mechanical and mechanochemical activation in the “Activator 4” planetary mill. The findings of the studies performed confirm the rather high efficiency of phosphorite ore fines’ mechanical activation and phosphorite-containing mixtures’ mechanochemical activation, which make it possible to significantly increase the content of assimilable phosphorus pentoxide P₂O₅ in composite phosphorus-containing fertilizers. The proposed innovative technology has fundamental differences from existing technologies, since the mechanochemical activation of a mixture of phosphorite ore fines and functional components will allow for direct acid-free and waste-free processing into phosphorus and composite phosphorus-containing mineral fertilizers.

Keywords: composite phosphorus-containing fertilizers; phosphorite ore fines; physical and chemical studies; mechanochemical activation; environment protection; engineering; technological scheme



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1. Introduction

The global scale of the mineral fertilizers market is steadily developing and its volume has reached almost \$80 billion. The development of the mineral fertilizers world market is characterized by stable growth, which is caused by an increase in the population of the Earth, an increase in the need for food products, a global trend towards a reduction in the resources of sown areas, and an increase in requirements for the quality and volume of agricultural products. All these factors, in turn, require an increased return on sown areas, which, to a certain extent, can be ensured by increasing the volume of production and the application of mineral fertilizers. The global market of mineral fertilizers includes three main segments—nitrogen, phosphorus and potash fertilizers; the share of nitrogen fertilizers is 59%, phosphorus 24% and potash 17% of the world market [1].

According to the IFA (International Fertilizers Association) forecasts, there is a steady upward trend in the global demand for mineral fertilizers. While growing crops for plant nutrition, phosphate fertilizers are of paramount importance. Phosphorus affects the development of the plant root system, which in turn performs the main function in providing nutrients necessary for plant growth and productivity [2–5].

The raw materials for the phosphate fertilizers manufacture are natural phosphate ores—phosphorites and apatites, while apatites are less common in the world [6–10]. Phosphorites are of sedimentary origin; their main constituents are calcium phosphate $\text{Ca}_3(\text{PO}_4)_2$ and fluorapatite $\text{Ca}_5(\text{PO}_4)_3\text{F}$. The composition of phosphorite ores, in addition to phosphate raw materials, includes quartz, dolomite, clay impurities, limestone, etc.

Kazakhstan takes fourth place in terms of phosphate raw materials reserves in the world. Kazakhstan has more than 4 billion tons of recoverable funds of phosphorite ores and over 15 billion tons of predicted reserves [11–14].

The Karatau phosphorite ore basin is one of the largest in the world and is located in Southern Kazakhstan, covering an area of 2500 km² (Figure 1). The center for the development of phosphorite ores is the city of Zhanatas. A total of 45 phosphorite deposits have been identified in the territory of the Karatau phosphorite ore basin. The largest fields being developed are Zhanatas, Kok-Zhon, Koksou, Aksai, Sholaktau, Himmelfarb, Ushbas, Tiesai, and Akzhar. Among them, Zhanatas is the largest deposit in the Karatau basin.



Figure 1. The Karatau phosphorite ore basin on the map of Central Asia (indicated by a red circle).

According to the authors of works [15,16], phosphorite ores of the Karatau basin are mainly represented by phosphorites with a granular and microgranular structure. At the same time, the phosphate substance of phosphorites is represented by fluorapatite, as well as isomorphic varieties of fluorapatite—francolite and kurskite.

The phosphorites of the Karatau basin, along with phosphate grains, also contain non-phosphate grains: quartz, feldspars, mica, etc. However, their content does not exceed 3–5% in the total mass of ore [16].

Phosphorite ores of the Karatau basin have a heterogeneous and complex mineralogical composition. They are characterized by a variety of forms of mineral bonds with each other, while the presence of inclusions of carbonate, siliceous and other impurity components in phosphate makes it difficult to separate rocks by mineralogical composition [16].

In the process of crushing, mining, subsequent classification, around 55–60% of all mined phosphorite raw materials pass into phosphorite ore fines—pieces of less than 10 mm. These pieces are not applicable for chemical processing into extraction phosphoric acid by chemical composition. On the other hand, they are not applicable for electrothermal processing into thermal phosphoric acid in terms of grain composition. In addition, there has been a steady trend towards a decrease in the P_2O_5 content in phosphorite ore. For these reasons, tens of millions of tons of phosphorite ore fines have been stored in the dumps of mining enterprises for more than forty years. Therefore, the processing of phosphorite raw materials' fines into mineral fertilizers is an important task related to environment, science, technics and economics.

During the crushing and subsequent classification of phosphorite ore, less durable mineral impurities of the ore pass into the resulting phosphorite ore fines; therefore, the fine of phosphorite ore is characterized by a lower content of phosphate substance.

Traditional technologies for the processing of phosphorite ore into phosphate fertilizers are characterized by the formation of a large amount of solid mineral (phosphogypsum) waste and liquid chemical effluents [17,18].

Phosphorite from the Karatau basin deposits has its own physicochemical and mineralogical features, due to the microgranular structure and mutual intergrowth of minerals, which make it difficult to process them by known methods [16].

These circumstances predetermine the need for the development of new environmentally friendly technologies that make it possible to involve phosphorite ore fines as low-grade phosphorite raw materials in the production of phosphorus-containing fertilizers [19–42].

The relevance and significance of the research performed in this work lie in the fact that the proposed innovative technology has fundamental differences from the existing traditional technologies for processing phosphorite ore, since mechanochemical activation will allow direct acid-free and waste-free processing of substandard phosphorite ore into phosphorus and composite phosphorus-containing mineral fertilizers.

2. Materials and Methods

2.1. Origin and Characteristics of the Materials Used

The object of the study is the phosphorite ore fines, which are formed in the process of crushing and classifying the phosphorite ore of the Zhanatas deposit in the Karatau basin.

The manufacture of phosphorus and phosphorus-containing fertilizers in Kazakhstan is based on the biggest deposits of phosphorites in the Karatau basin. It is an export-oriented industry, taking more than 70% of the total export of chemical products (excluding petrochemicals). It covers 2/3 part of the whole output of the Kazakhstan's chemical industry [14].

Within the Karatau basin, 45 phosphorite deposits were identified. The main deposits of industrial reserves of the Karatau basin (about 80%) are located in five main mines—Zhanatas, Kok-Jon, Tiesai, Aksai, Chulaktau. They are characterized by a large extent by the presence of productive layers and are estimated to be 1.2 billion tons. The Karatau phosphorites are difficult to enrich, thus, phosphorite ore containing at least 24.5% P_2O_5 is used at acid processing for the extraction of phosphoric acid and water-soluble fertilizers. However, a significant part (more than 40%) of the Karatau phosphorites has a low average content of P_2O_5 in the range of ~17.5%, which implies the need to develop new technologies to involve low-grade phosphorite raw materials in the production of phosphorus-containing fertilizers.

The phosphorite ore of the Karatau basin is divided into two main categories:

- phosphorite ore with a content of at least 24.5% P_2O_5 , suitable for chemical processing for the extraction of phosphoric acid;
- phosphorite ore with a content of at least 20% P_2O_5 , suitable for electrothermal processing to obtain phosphorus and thermal phosphoric acid.

Karatau basin deposits are characterized by significant fluctuations in the R_2O_5 content in the phosphorite ore. The author of the work [43], depending on the content of the main chemical components (P_2O_5 , CaO, MgO, SiO_2 , Al_2O_3 , CO_2) in the ore, classifies phosphorite ore into the following varieties and industrial types given in Table 1. With a P_2O_5 content of less than 21%, phosphorite ore belongs to poor (off-balance sheet) ore.

Table 1. Main types of phosphorite ores of Karatau basin deposits.

Types of Phosphoritic Ore	Content of Main Components in Ore, %					
	P_2O_5	CaO	MgO	SiO_2	Al_2O_3	CO_2
rich (phosphorite) ore	29–32	43–47	2–3	10–15	0.6–0.8	4–6
carbonate ore	28–30	43–48	1–2	10–15	1–1	6–8
carbonate-siliceous ore	21–23	37–40	3–4	19–25	1–2	2–6
siliceous ore	21–23	36–39	-	30–32	-	-
poor (off-balance sheet) ore	19–21	32–40	3–4	26–28	1–2	5–7

In addition, the main difference in the Karatau basin phosphorites is the presence of magnesium oxide in the phosphorite ore, the sources of which are dolomite $CaMg(CO_3)_2$ and magnesium silicates—talc $Mg(OH)_2Si_4O_{10}$, serpentine $Mg_3(OH)_4Si_2O_5$, mixed silicates of magnesium and calcium—tremolite $Ca_2Mg(OH)_2(Si_4O_{11})_2$, and diopside $CaMg(SiO_3)_2$. Magnesium phosphates are highly soluble in solutions of phosphoric acid H_3PO_4 , which makes it difficult to obtain a concentrated extraction of phosphoric acid H_3PO_4 from phosphate ore with a high magnesium content.

The choice of ammonium sulfate as a nitrogen-containing component of composite fertilizers is due to the low cost and availability, since ammonium sulfate is a by-product in the production of caprolactam.

2.2. Physicochemical Methods of Analysis of Phosphorite Ore Fines Samples

X-ray studies of the phosphorite ore fine sample were performed on an X-ray diffractometer “Bruker AXS” (Karlsruhe, Germany). The diffraction reflections were interpreted automatically using the EVA software package of a “Bruker AXS” X-ray diffractometer.

Thermogravimetric studies of the phosphorite ore fines were performed using a modern thermoanalytical system “TGA/DSC-1/1600 HF” from “Mettler Toledo Instruments” (Greifensee, Switzerland), which is a device with combined differential thermographic analysis and differential scanning calorimetry.

The arrangement analyzes and measures thermodynamic data and also registers mass changes in the material samples in the temperature interval from 25 to 1600 °C.

Studies of the phosphorite ore fines’ microstructure and chemical elemental composition were carried out with scanning electron microscopy and X-ray microanalysis using a “JSM-6490LV” scanning electron microscope from “JEOL” (Tokyo, Japan).

The analysis of the dispersed composition and size of the particles to be ground was carried out using the “Analyzette 22” laser analyzer from “MicroTec Fritsch GmbH” (Idar-Oberstein, Germany).

IR spectroscopic studies were performed using an IR-Fourier spectrometer “Nexus TM E.S.P” from “Thermo Nicolet” (Madison, WI, USA).

The content of the citrate-soluble form of phosphates in the phosphorite ore fines samples of fine phosphorite ore was determined using the method of differential colorimetry of the phosphorus–vanadium–molybdenum complex on a “KFK-2MP” photoelectrocolorimeter (JSC “Zagorsk Optical-Mechanical Plant”, Sergiev Posad, Russia) at a wavelength (λ) equal to 440 nm, founded on a change in the light transmission of the resulting yellow complex.

2.3. Methods of Mechanical and Mechanochemical Activation

The mechanical activation of phosphorite ore fines and mechanochemical activation of a mixture of phosphorite ore and ammonium sulfate were carried out in a high-energy planetary mill "Activator 4" (Figure 2) with 4 steel drums simultaneously rotating both around their own axis and around the central axis of the mill. The drum volume is 1000 cm^3 , the diameter of grinding balls is 10 mm, and the rotation speed of the drums around a common axis is 600 rpm. The drums and grinding balls are made of alloy steel (Fe-Cr). The weight ratio of grinding balls and crushed material is 10:1. The mechanical activation time was 5, 10, 15 and 20 min.



Figure 2. General view of the planetary mill "Activator 4".

In order to study the acid-free production of nitrogen-phosphorus fertilizers, the mechanochemical activation of a mixture of phosphorus fines and ammonium sulfate was carried out. The content of ammonium sulfate by weight in the activated mixture ranged from 10% to 50%.

3. Results and Discussion

3.1. Results of Complex Physical and Chemical Studies

X-ray studies of the phase composition of the phosphorite ore fines samples were performed using an X-ray diffractometer "Bruker AXS" (Germany). The diffractogram of the phosphorite ore fines and instrument printouts of crystalline phases have been shown in Figure 3.

On the diffractogram of the phosphorite fines, the vertical axis reflects the X-ray intensity values in the pulses (counts) and the horizontal axis reflects the diffraction angle values of the 2θ (2θ).

When decoding diffractograms, the radiometric identification of crystalline phases and minerals is carried out by determining the inherent values of interplanar distances d (hkl) and intensity I (hkl) of X-ray peaks. In this work, diffractogram decoding was carried out automatically using the EVA software complex of the Bruker AXS X-ray diffractometer.

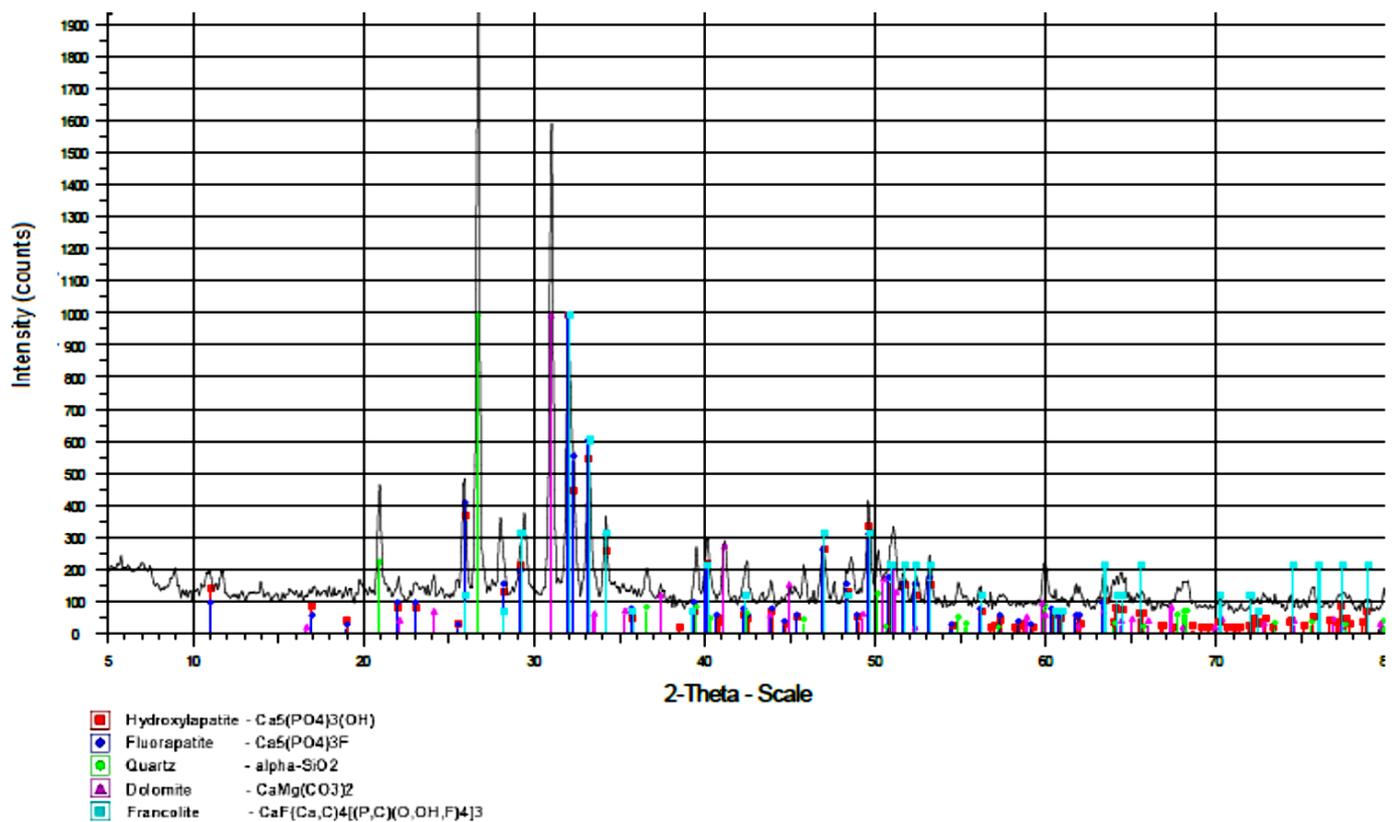


Figure 3. Diffractogram of the phosphorite ore fines.

The X-ray study's result shows the mineralogical composition of the phosphorite ore fines was established, in which the main crystalline phases are:

fluorapatite $\text{Ca}_5(\text{PO}_4)_3\text{F}$; francolite $\text{CaF}(\text{Ca,C})_4[(\text{P,C})(\text{O,OH,F})_4]_3$;

hydroxidapatite $\text{Ca}_5(\text{PO}_4)_3(\text{OH})$; dolomite $\text{CaMg}(\text{CO}_3)_2$; quartz $\alpha\text{-SiO}_2$.

Thermogravimetric studies of the phosphorite ore fines were carried out using a modern thermoanalytical system "TGA/DSC-1/1600 HF" ("Mettler Toledo Instruments", Switzerland) in the temperature interval from 25 to 1000 °C.

The resulting thermogravigram of the phosphorite ore fines is shown in Figure 4.

The result of the thermogravimetric studies of the phosphorite ore fines samples revealed three endothermic effects: 1–123.4 °C; 2–274.4 °C; 3–771.6 °C.

The first endoeffect is caused by the loss of physically bound moisture from phosphorite samples, the second endoeffect is caused by the loss of chemically bound moisture, the third endoeffect is due to the thermal decomposition of the carbonate component of fine phosphorite ore (dolomite).

Small endothermic effects occurred on the DTG curve at 119–124 °C and were caused by the removal of adsorption moisture from the samples of the phosphorite ore fines (mass loss ~0.2%), and the big endothermic effect at 771.5 °C was caused by thermal decomposition of dolomite. The carbonate component of phosphorite, according to the reaction, was as follows:



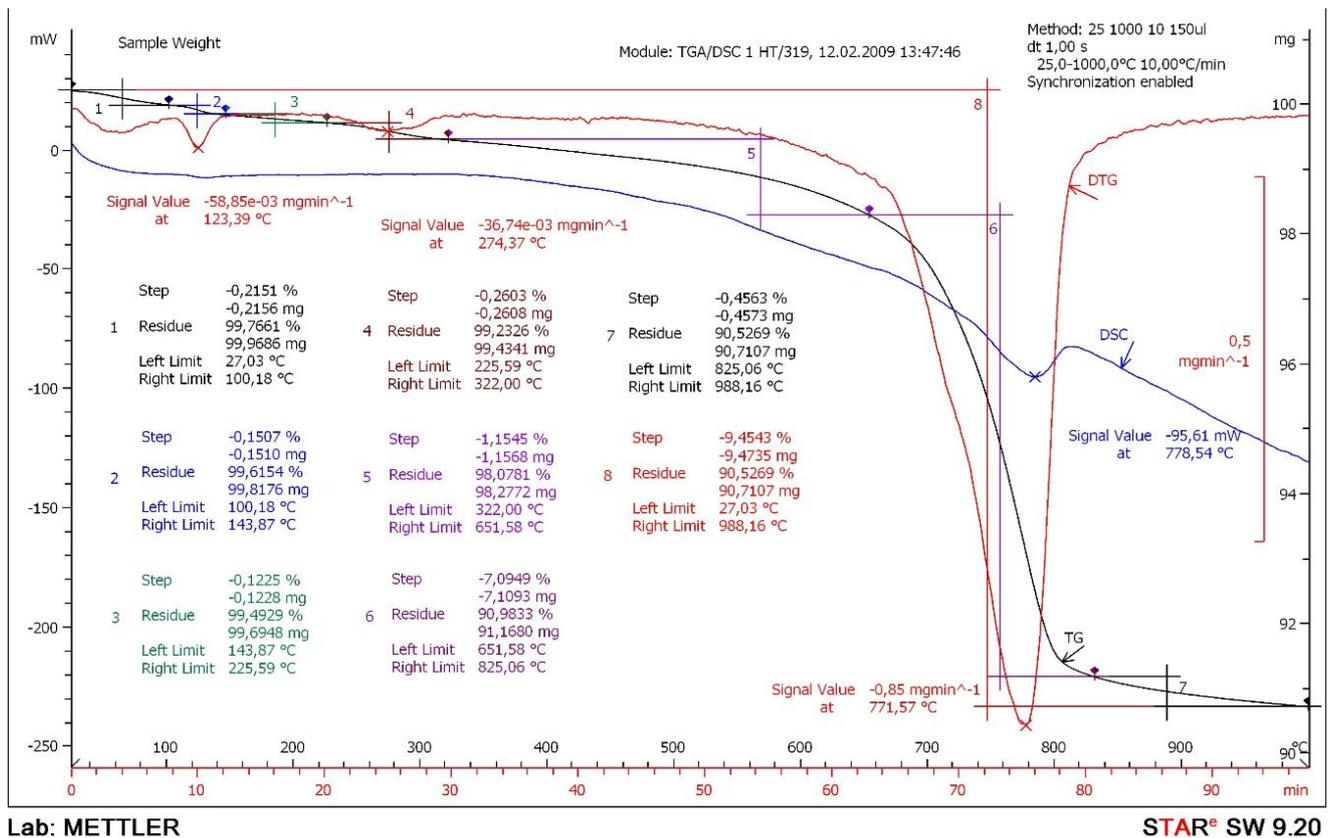
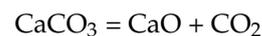
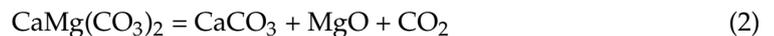


Figure 4. Thermogravigram of the phosphorite ore fines.

Two distinct endothermic effects are observed on the thermogravigrams at ~770 °C and at ~920 °C, indicating a stepwise course of the reaction of thermal decomposition of dolomite:

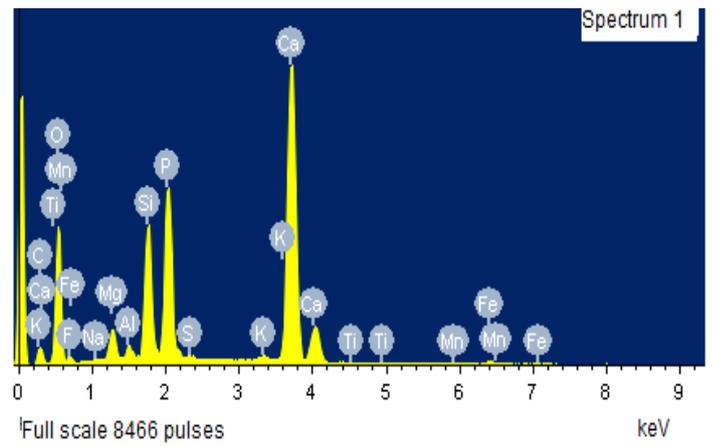
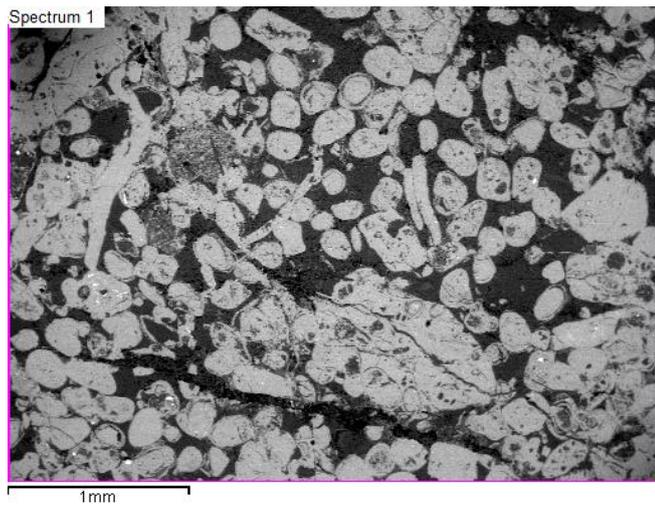


The investigation results of the phosphorite ore fines' microstructure and chemical elemental composition using electron microscopy and X-ray microanalysis are shown in Figure 5a–e and in Table 2.

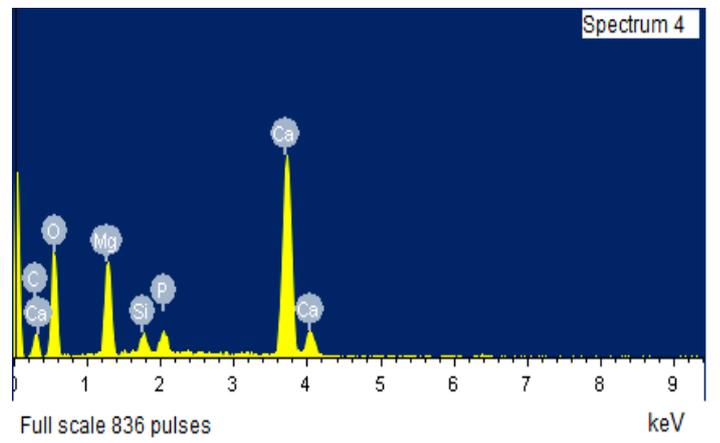
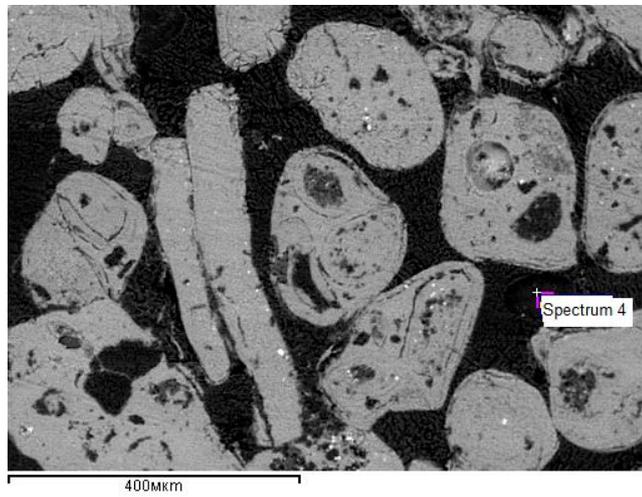
As a result of the study of the microstructure and elemental chemical composition, it was established that the phosphorite ore fines contain minerals of calcium phosphate (spectrum 5), dolomite (spectrum 4), quartz (spectrum 6) and clay minerals (spectrum 2).

Thus, as can be seen from the results of complex physical and chemical studies, the predominant phase in the structure of phosphorite ore fines is calcium phosphate in the form of fluorocarbonate apatite, while calcium is also present in the composition of dolomite. Silicon is present mainly in the form of quartz.

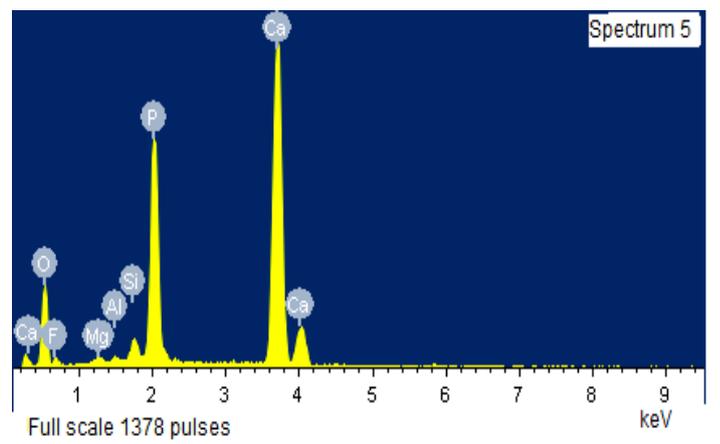
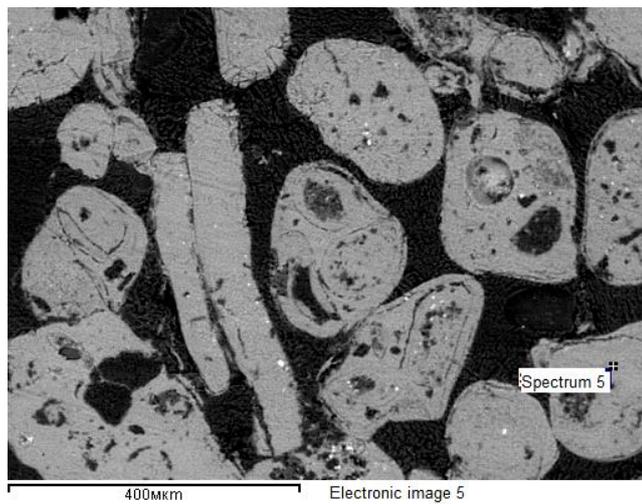
Electron microscopic studies of the distribution of the main chemical elements P, Ca, Mg, Si, F using energy dispersion X-ray spectroscopy in the mapping mode showed the predominant presence of fluorine-containing calcium phosphate, with dolomite and quartz also in close germination (Figure 6).



(a)



(b)



(c)

Figure 5. Cont.

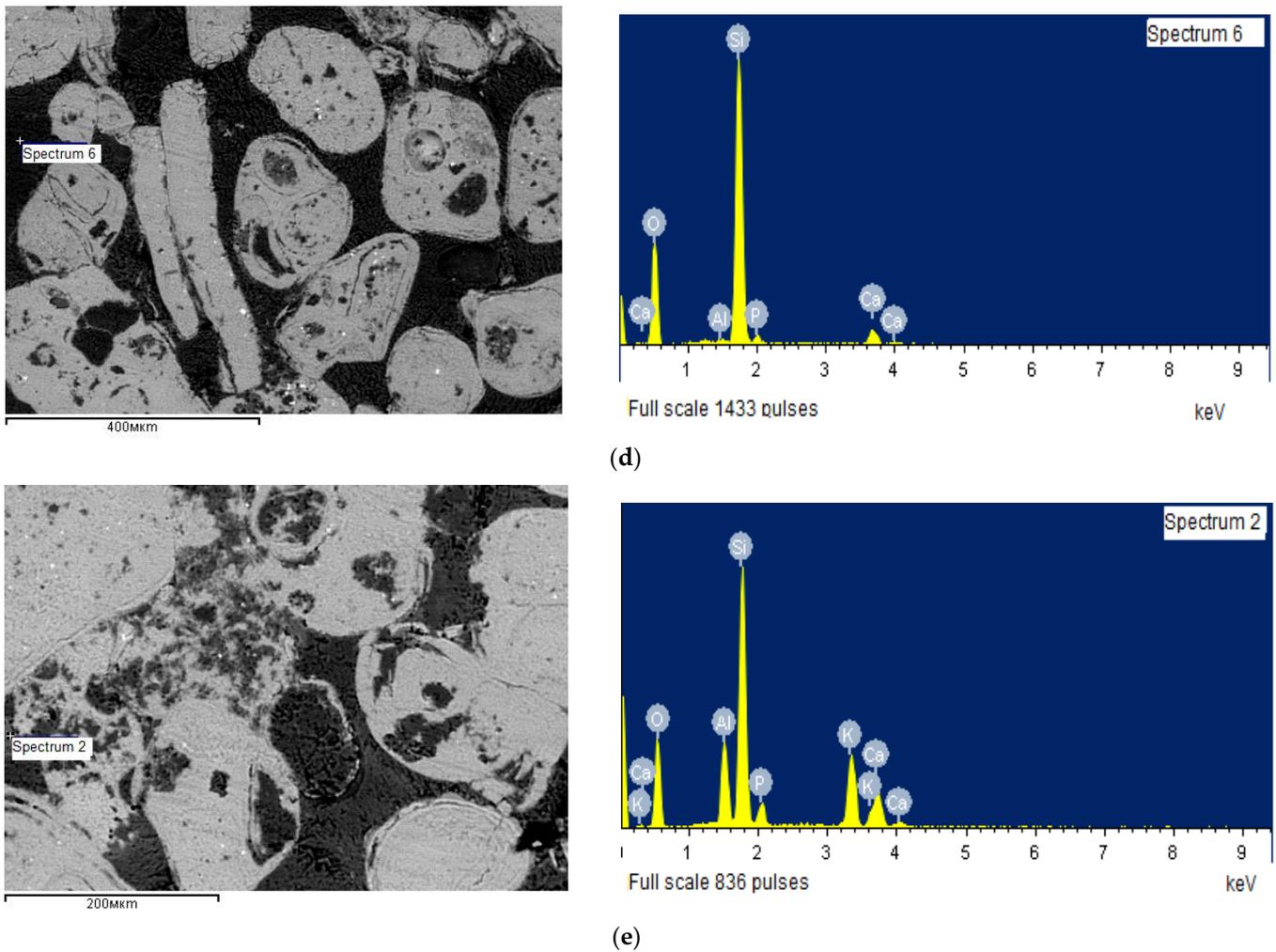


Figure 5. Enlarged electronic image of the microstructure and the content of elements in the structure of the phosphorite ore fines, wt.% (at points “Spectrum 1, 2, 4, 5, 6”). (a) Microstructure and elemental composition of the phosphorite ore fines (“Spectrum 1”). (b) Microstructure and elemental composition of the phosphorite ore fines (“Spectrum 4”). (c) Microstructure and elemental composition of the phosphorite ore fines (“Spectrum 5”). (d) Microstructure and elemental composition of the phosphorite ore fines (“Spectrum 6”). (e) Microstructure and elemental composition of the phosphorite ore fines (“Spectrum 2”).

Table 2. Content of chemical elements in phosphorite ore fines according to spectra, % wt.

Spectrum No.	Si	Al	Ca	Mg	Mn	Na	K	P	Fe	Ti	S	F
Spectrum 1	10.64	2.05	25.36	1.57	0.16	0.21	1.13	9.82	1.92	0.03	0.34	2.25
Spectrum 2	25.76	7.48	6.11	-	-	-	11.74	3.52	-	-	-	-
Spectrum 4	1.52	0.25	33.43	15.01	-	-	-	2.62	-	-	-	-
Spectrum 5	1.17	0.27	37.75	0.35	-	-	-	17.30	-	-	-	3.82
Spectrum 6	41.06	0.51	4.50	0.33	-	-	-	2.14	-	-	-	-

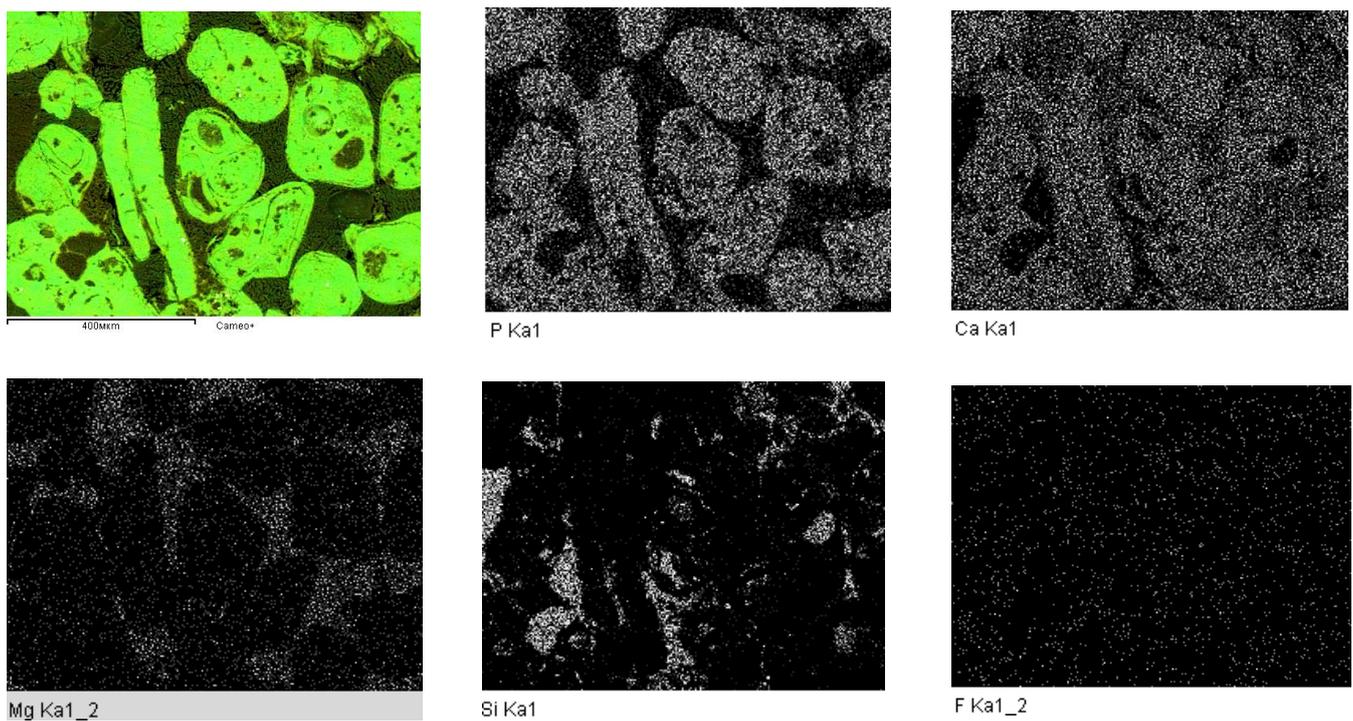


Figure 6. Mapping of the main chemical elements in the structure of phosphorite ore fines.

The results of complex physical and chemical studies using X-ray phase analysis, thermogravimetric analysis, chemical elemental analysis, and electron-microscopic studies are consistent with each other and make it possible to determine with a high reliability the mineralogical composition of phosphorite ore fines.

Processing the phosphorite ore fines into activated phosphate flour using mechanochemical activation using an “Activator 4” planetary mill, while changing the activation time, were studied.

Through the fine grinding of the phosphorite ore fines in ball mills, the simplest phosphate fertilizer is obtained—phosphate flour. However, phosphate flour is a low-efficiency fertilizer due to the low solubility of the phosphate substance.

At the same time, phosphorite flour has the following advantages:

- phosphorite flour is produced using a simple technology that excludes the formation of large-tonnage production waste—phosphogypsum and chemical effluents;
- phosphorite flour is produced from available phosphate raw materials—phosphorites;
- phosphorite flour, unlike water-soluble fertilizers, is a slowly soluble fertilizer with a long period of action.

The properties of activated phosphorite flour were compared with non-activated phosphorite flour obtained via grinding in a ball mill.

The analysis of dispersed composition and size of milled particles of mechanoactivated phosphorite flour was carried out on a “Analizette 22” laser analyzer of “MicroTec Fritsch GmbH” (Germany). The results of the study compared to the non-activated phosphorite flour ground in a conventional ball mill are presented in Figure 7.

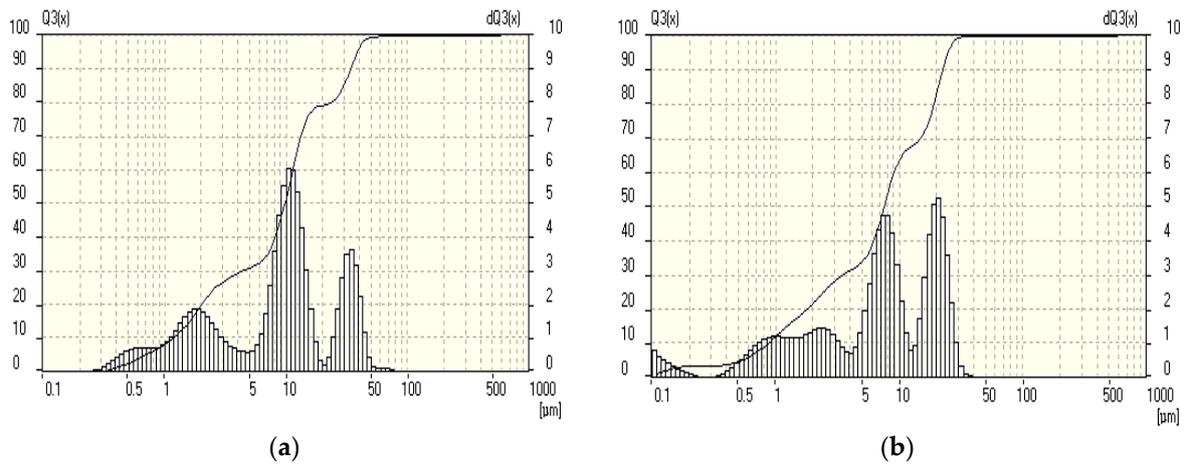


Figure 7. Dispersion spectra of non-activated (a) and mechanoactivated (b) phosphorite flour.

A sample of mechanically activated phosphorite flour is a polydisperse material in which a significant part is a fine fraction of 0.5–10 μm , while a fraction of 5–50 μm prevails in the non-activated phosphorite flour. The results of the study of the dispersed composition confirm the high efficiency of the mechanical activation of phosphorite ore fines. The results show a significant increase in fine particle content in mechanoactivated phosphorite flour compared to standard milling phosphorite flour.

The results of IR spectroscopic studies of samples of inactive and mechanoactivated phosphorite flour using an IR-Fourier spectrometer “NexusTM E.S.P” from “Thermo Nicolet” (USA) are presented in Figure 8.

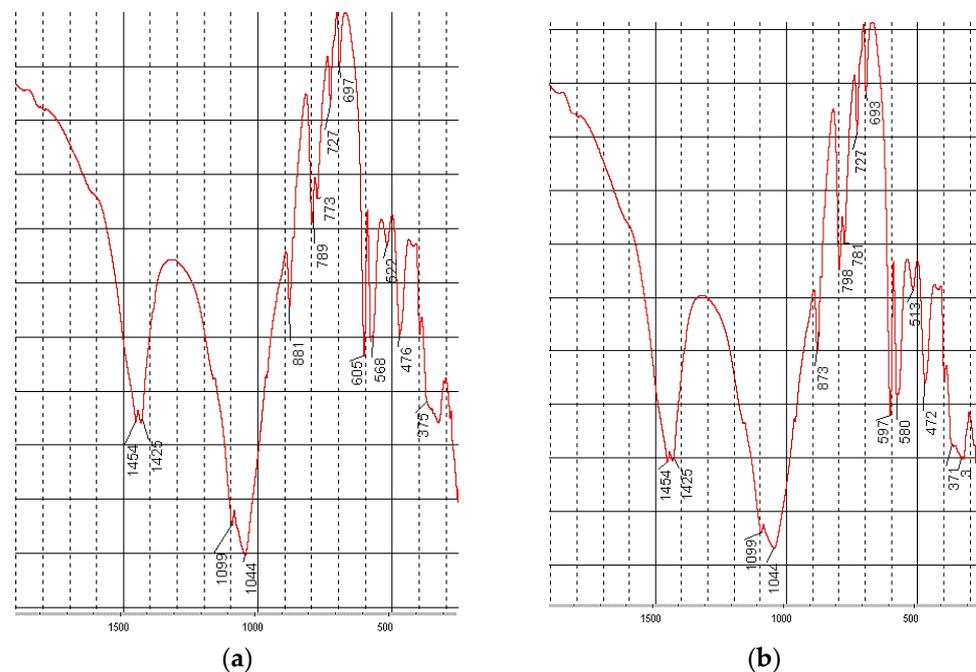


Figure 8. IR spectra of non-activated (a) and mechanically activated (b) phosphorite flour.

Characteristic frequencies (wavenumbers, cm^{-1}) of vibrations of fluorocarbonate apatite, calcium and magnesium carbonates, and quartz appear on IR spectra of samples of non-activated and activated phosphorite flour.

On IR spectra, frequencies 605 and 568 cm^{-1} correspond to deformation oscillations of the PO_4^{4-} —group in a sample of non-activated phosphorite flour, and frequencies of 597 and 580 cm^{-1} are characteristic of a sample of mechanoactivated phosphorite flour.

On IR spectra, frequencies 1454, 1425 cm^{-1} correspond to the valence oscillations C-O of dolomite bond, and frequencies 789, 727, 375 cm^{-1} correspond to deformation oscillations of CO_3^{2-} —groups.

On IR spectra of frequency 773, 693, 522, 476, 375 cm^{-1} correspond to OH^- —group of clay minerals as impurities in phosphorite composition.

By comparing the IR spectra in the frequency range of 250–2000 cm^{-1} , significant changes were established in the nature of the spectra corresponding to the deformation fluctuations of the PO_4^{4-} —groups for samples of non-activated and mechanoactivated phosphorite flour. The IR spectra show a shift of frequencies 605 and 568 cm^{-1} corresponding to the deformation oscillations of the PO_4^{4-} —groups in the sample of non-activated phosphorite flour to the frequency region 597 and 580 cm^{-1} in the sample of mechanically activated phosphorite flour. When comparing the IR spectra, changes were revealed in the oscillatory spectra of the PO_4^{4-} —groups that suggest that during mechanical activation, the crystal lattice of fluorocarbonate apatite, the main mineral of phosphorite, is deformed.

The assignment of the IR band is confirmed in the authors' work [44], in which the Ichang (China) were studied using infrared spectroscopy. Infrared spectroscopy was carried out in the spectral band of 450–4000 cm^{-1} using on device Perkin-Elmer-FT-1730 (Waltham, MA, USA).

Samples of non-activated and mechanoactivated phosphorite flour were studied using energy-dispersive X-ray spectroscopy (Figure 9). Intense secondary X-ray signals inherent in Ca, Si, O, P, Mg, Al elements are observed on the energy dispersion spectrum of the non-activated phosphorite flour (Figure 9a). The energy dispersion spectrum of mechanically activated phosphorite flour (Figure 9b) shows a significant decrease in the intensity of secondary X-ray signals, which, in our opinion, indicates a corresponding decrease in the content of minerals in crystalline form in which the elements Ca, Si, O, P, Mg, Al are present.

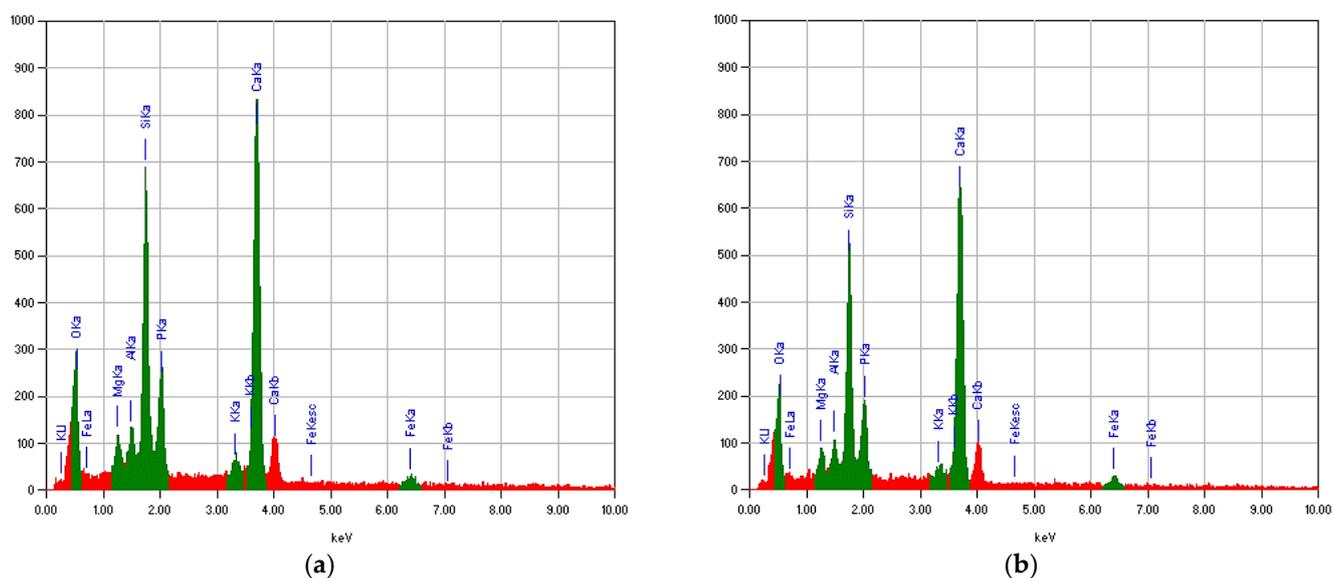


Figure 9. Energy dispersion spectra of samples of non-activated (a) and mechanoactivated (b) phosphorite flour.

Through comparing the energy dispersion spectra of the non-activated and mechanoactivated phosphorite flour, it can be seen that the intensity of the secondary X-ray signals is significantly attenuated, indicating possible changes in the crystal structure of the phosphate minerals as a result of mechanical activation of the phosphorite flour.

In the process of the mechanical activation of phosphorite flour in the activator mill, as a result of intensive action of grinding balls on the powder material, it is possible to observe the effect of amorphizing on the surface of the ground particles and deformation

changes in the crystal structure of fluorocarbonate apatite, as a result of which the content of P_2O_5 in a soluble form in phosphorite flour increases.

Morphology studies of dispersed particles of non-activated and mechanically activated phosphorite flour were carried out using a scanning electron microscope “JSM-5610 LV” from “JEOL” (Japan). The obtained electron microscopic images of samples of phosphorite flour are shown in Figure 10.

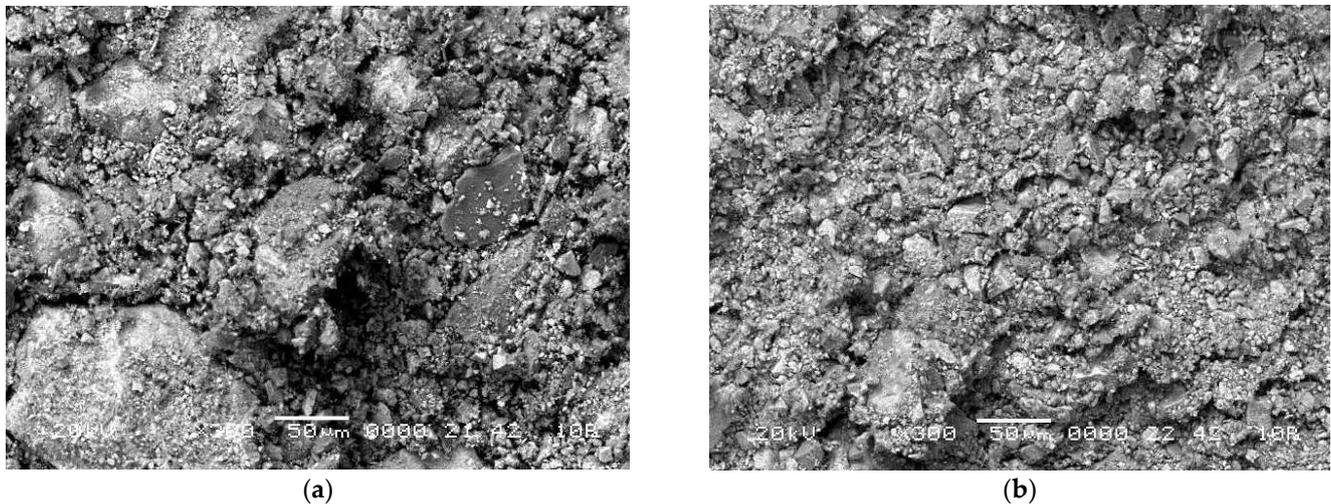


Figure 10. Electron microscopic images of non-activated (a) and mechanically activated (b) phosphorite flour ($\times 300$).

Figure 10 shows significant differences in the morphology and size of dispersed particles of non-activated and mechanoactivated phosphorite flour. Thus, particles reaching a size of up to $200\ \mu\text{m}$ are observed in a sample of non-activated phosphorite flour (Figure 10a). At the same time, such relatively large particles are absent in the sample of mechanoactivated phosphorite flour, and dispersed particles with a size of less than $50\ \mu\text{m}$ prevail (Figure 10b).

In the sample of mechanoactivated phosphorite flour, a change in the morphology of crushed dispersed particles is observed—formless particles of an indeterminate configuration prevail here, while in the sample of non-activated phosphorite flour there are particles with more pronounced flat faces, that is, there are particles approaching prismatic and polyhedral bodies in shape.

In the process of mechanical activation of phosphorite flour in an activator mill, as a result of intensive versatile action of grinding balls on the ground material, deformation changes in the crystal structure of the phosphate mineral may also occur, resulting in an increase in the content of P_2O_5 in a soluble form in phosphorite flour.

The authors’ work [45] also shows that the formation of an amorphous phase in rocks during their mechanical activation is an important aspect of increasing the reactivity of the crushed dispersed material. For such systems, this reactivity is determined via surface activity. Obviously, this is due to the transition of the potential energy accumulated by the rock due to mechanical activation into free surface energy.

3.2. Results of Experimental Studies

The results of studies of the content of the citrate-soluble form of phosphorus pentoxide in phosphorite ore fines, depending on the duration of mechanical activation, are presented in Table 3.

Table 3. The results of mechanical activation of the phosphorite ore fines.

Activated Material	Activation Time, min	Total Content of P ₂ O ₅ in the Phosphorite Ore Fines, %	Content of the Citrate Soluble form P ₂ O ₅ , %	
			Absolute	Relative
Phosphorite ore fines	-	20.92	4.53	17.63
	5	20.91	9.78	46.65
	10	20.92	11.03	52.66
	15	20.92	11.09	52.95
	20	20.91	11.13	53.18

From the results shown in Table 3, it can be seen that with mechanical activation of the phosphorite ore fines, the relative content of the citrate-soluble form of P₂O₅ increases more than three times from 17.63% to 53.18%.

Increasing the mechanical activation time to more than 20 min does not lead to a significant increase in the content of the lemon-soluble form of phosphate, so in further experiments the mechanical activation time was taken to be 20 min.

Processing the phosphorite ore fines into composite phosphorus-containing fertilizers using methods of mechanochemical activation were studied.

Experimental studies of the dependence of the content of the citrate-soluble form of P₂O₅ in mixtures of the phosphorite ore fines and ammonium sulfate on their ratio of components and parameters of mechanochemical activation were carried out.

In conducted research, a by-product of the production of caprolactam, ammonium sulfate, was used. This ammonium sulfate contains up to 21% of nitrogen, and in the phosphorite ore fines, the content of phosphorus pentoxide P₂O₅ is 20.92%. These indicators for the content of nitrogen and phosphorus pentoxide make it possible to determine the N:P₂O₅ ratio in complex nitrogen–phosphorus fertilizer obtained using the mechanochemical activation of a mixture of the phosphorite ore fines and ammonium sulfate.

The results acquired during the mechanochemical activation of a mixture of the phosphorite ore fines and ammonium sulfate are shown in Table 4.

Table 4. Dependence of the citrate-soluble form of P₂O₅ content during mechanochemical activation of a mixture of the phosphorite ore fines and ammonium sulfate.

Activated Mixture	The Proportion of Ammonium Sulfate in the Mixture, %	Total Content of P ₂ O ₅ in Fine of Phosphorite Ore, %	The Content in the Mixture of Citrate-Soluble form of Phosphorus, %	
			Absolute	Relative
Phosphorite ore fines and ammonium sulfate	10	20.91	10.09	53.61
	20	20.92	10.01	59.83
	30	20.92	9.72	66.39
	40	20.91	8.83	70.41
	50	20.92	7.36	70.36

From the data in Table 4, it is seen that the mechanochemical activation of a mixture of the phosphorite ore fines and ammonium sulfate leads to an increase in the assimilable phosphorus concentration in the nitrogen–phosphorus fertilizer gained.

3.3. Discussion

One of the effective ways for direct waste-free and energy-saving processing of the phosphorite ore fines into phosphorus and phosphorus-containing composite mineral fertilizers can be the use of mechanical and mechanochemical activation methods. Mechanical and mechanochemical activation is carried out in special activator-type mills.

Recently, mechanical and mechanochemical activation methods have been increasingly used in the process of grinding solids in special activator-type mills.

In activator-type mills, an equivalent dispersed fine-grinding product can be obtained in a shorter time and with less electrical energy consumption. Conventional ball mills have a low efficiency in finely grinding solids, since they use only free impact and abrasion mechanical effects of steel balls (grinding bodies) on the ground material. In ball mills, the only force by which the grinding process is carried out is gravity at the acceleration of the free fall of steel balls equal to 1 g. This limits the efficiency of the mill because at high rotational speeds the centrifugal force causes the steel balls (grinding bodies) and the ground material to constantly press against the inner surface of the mill drum.

The efficiency in finely grinding solids can be greatly improved by using other high energy-intensive mill designs; planetary mills and centrifugal-elliptical mills are examples of such mills. Conventional ball mills have low efficiency in finely grinding solids, since they use only free impact and abrasion mechanical effects of steel balls (grinding bodies) on the ground material.

In highly energized activator-type mills, three mechanical actions are simultaneously forced: shock, shear and abrasion. These mills are also called planetary because their drums orbit both their own axis and their common axis, similar to planets in the solar system. Due to this, high accelerations up to 100 g are achieved in the mill, and as a result, not only fine grinding is achieved, but also the appearance of defects in the crystalline structure of the material, as well as partial amorphization of the surface layer of the ground particles. The intensity of effects of grinding bodies in activator-type mills can be ten times higher than their effects in ball mills, in which impacts occur only due to the acceleration of the free fall of steel balls equal to 1 g. At the same time, in ordinary ball mills, only two mechanical actions can occur at the same time: impact and abrasion [46].

A schematic representation of the grinding and activation processes in mills, which differ both in design and in the principle of mechanical effects on the crushed material [47], is shown in Figure 11.

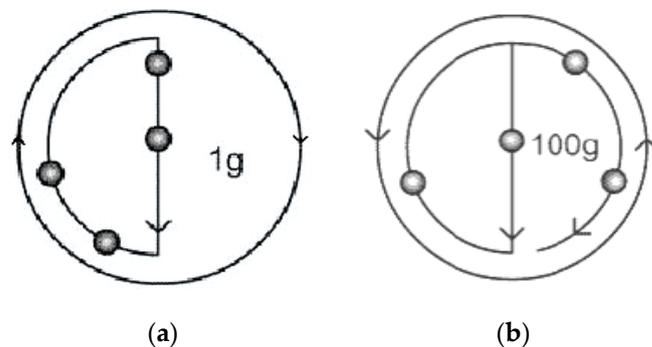


Figure 11. Diagrams of the movement of grinding media during grinding in mills of various types [47]. (a) in a ball mill; (b) in a planetary mill “Activator 4”.

In activator-type mills, along with fine grinding, deformation changes occur in the fine structure of the solid due to the partial transition of crystalline compounds into amorphous ones, an increase in the degree of defectiveness of the crystal structure, the accumulation of internal energy reserves and an increase in the reactivity of the solid. Mechanochemical activation is, in fact, also fine grinding as with mechanical activation, but carried out in conjunction with various solids that act as chemical reagents during solid-phase reactions on the surface of the crushed particles. Using the mechanical activation and mechanochemical activation methods, it is possible both to finely grind solids, and to significantly intensify many heterogeneous chemical processes that are limited by the kinetics of interphase interaction and diffusion in the solid phase, i.e., the dissolution of difficult-to-dissolve substances, solid-phase reactions, etc. The development of studies of the laws of such processes has led to the emergence of a new science—mechanochemistry [48].

In recent decades, active scientific studies of physicochemical transformations in the process of mechanical and mechanochemical activation of inorganic substances have been carried out.

The authors of work [49] believe that the formation of an amorphous phase in silicon-containing rocks upon their mechanical activation contributes to an increase in the reactivity of the finely dispersed material and this ability is determined via surface activity. Due to the mechanical activation of the surface of the raw material being ground, the stored potential energy is converted to free surface energy.

The mechanical activation of the silicon-containing rock destroys its layered crystal lattice to release silicon and magnesium oxides, which via solid phase reaction may react with each other to form serpentine group minerals.

Mechanical activation using long-term high-energy grinding in a planetary ball mill leads to a significant increase in mechanical stresses and defects in the grain structure of crushed substances [50].

By studying the phosphorite concentrates of Tunisia, Estonia, Uzbekistan and Kazakhstan before and after mechanical activation in a planetary mill, it was found that with an increase in the specific surface area, the solubility of phosphorus in them increased [51]. Mechanical activation in a planetary mill is more effective in the case of sedimentary phosphorites and less effective in the case of magmatic phosphorites.

The author of the work [52] believes that intensive mechanical impacts on the crystal structure of phosphates lead to the deformation of the crystal lattice and an increase in reactivity.

During mechanical activation after 60 min of a high-intensity grinding of phosphate concentrate, a higher 85% degree of amorphization of fluoroapatite was achieved [51,53].

Mechanochemical treatment is an efficient and ecological method of processing low-grade phosphorite raw materials for mineral fertilizers [54]. The results of studies using the chemical extraction method in 2% citric acid showed an increase in phosphorus solubility for 7.76–13.67 times. IR spectroscopic analysis showed that in apatite there is an isomorphic substitution of SO_3^- on the PO_4^{3-} and the $\beta\text{-Ca}(\text{PO}_3)_2$ is formed with better phosphorus solubility. It was found that a significant increase in the solubility of phosphorus in slightly acidic soil is due to an increase in the reactivity of low-grade phosphorite raw materials during mechanochemical activation.

The authors of several papers [55–58] have shown that significant structural changes occur in the process of mechanochemical activation, leading to an increase in reactivity and an improvement in the solubility of mechanochemically activated substances.

The author of work [59] describes several states of the substance that occur during impact while grinding in a mill, and gives a model of the process that occurs when the crushed particles collide (Figure 12). The author points out that mechanical impact causes a complex combination of deformation-structural, thermal and chemical processes leading to the occurrence and development of defects in the structure of the crushed solid, its partial amorphization and rapid local heating at the impact site. At the same time, breaks of chemical bonds occur during the formation of a fresh surface and short-lived active centers appear on it. In addition, the emission of electrons, photons, ions and the formation of an electrostatic charge may occur.

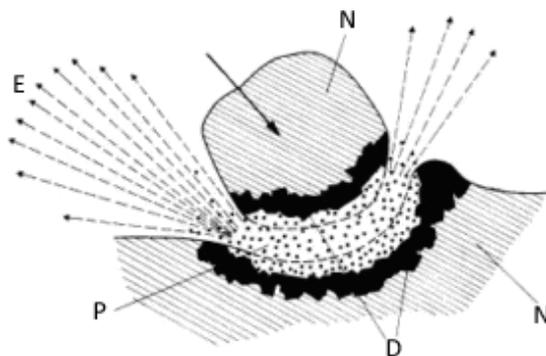


Figure 12. Zones of states when particles collide during their grinding [56,59]. D—deformed structure zone, E—exoemission zone, N—natural structure zone, P—“triboplasma” zone.

According to the author of work [60], due to the impact of the grains against each other during grinding, the energy concentration occurs in a microscopically small area of the surface. As a result, a thin melt layer and even a high energy plasma-like substance can be formed in this local area for a very short period of time. This condition was called triboplasma (from the Greek “τριβος”—friction).

The destruction of solid and brittle bodies, to which most inorganic minerals belong, differs in a number of features. In the process of grinding during mechanical activation, the internal energy accumulated by the crushed substance causes an increase in potential chemical activity, which results in increased reactivity, and a decrease in the temperature of solid-phase interaction, thermal dissociation and other physicochemical phenomena.

The authors of work [61] show the correlation between the dispersion of reacting particles and the rate of solid-phase reaction—the smaller the particle size, the higher the reaction rate.

The application of mechanical activation techniques, leading to the creation of an active state in a solid, is a promising direction for increasing the potential chemical activity.

Studies of the relationship between deformation changes in the crystal structure and the reactivity of inorganic substances have established that the rate of solid-phase (topochemical) reactions is strongly influenced by the nature of the resulting defects, both on the surface and in the volume of the crystal structure of substances [62].

Summarizing the results of the analysis of published works, it can be noted that mechanochemical activation has its own characteristic patterns and, in general, is developing as an independent promising direction in the technology of composite mineral fertilizers [63,64].

Also, the agrochemical, ecological, and economic efficiency of involving low-grade phosphorite raw materials in the production of phosphorus-containing fertilizers may significantly increase.

The studies have shown that when using the mechanochemical activation of phosphorite ore fines together with a solid nitrogen-containing additive of ammonium sulfate, it is possible to obtain composite phosphorus-containing fertilizers using acid-free technology.

The performed investigation results became the basis for the development of a technological scheme for the production of composite nitrogen–phosphorus–potassium containing NPK fertilizers, using also expanded vermiculite to ensure a prolonged action of the resulting fertilizers (Figure 13).

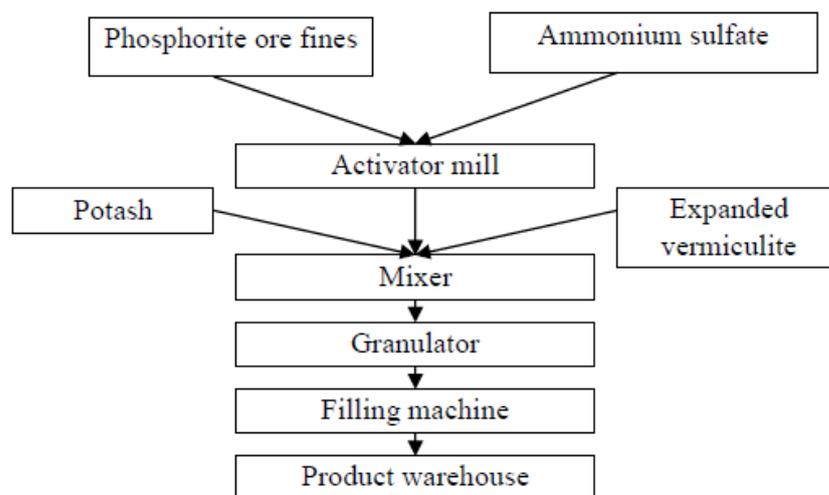


Figure 13. Technological scheme for the production of composite phosphate-containing long-acting fertilizers.

The results of the studies performed in this work are consistent with the results published by other researchers in the works [55,65–72].

The authors of [67,68] also believe that mechanochemical activation is an effective and ecological way of processing low-grade phosphorite raw materials into fertilizers. The results of their studies showed that a significant increase in the solubility of phosphorus in mechanochemically activated phosphorite ore and an increase in the available phosphorus in slightly acidic soil is due to an improvement in reactivity during mechanochemical activation.

In comparison with conventional acid methods of processing phosphate raw materials, mechanochemical activation has the advantages of the simplicity of process, ecological purity, and the increased reactivity of natural or synthetic phosphate minerals [67–70].

The authors' work [71] investigated the physical and chemical properties of Juanmailin phosphorite ore using scanning electron microscopy (SEM) and X-ray diffraction (XRD) methods before and after mechanochemical activation. These studies concluded that mechanochemical activation altered the crystal structure of apatite.

4. Conclusions

The performed studies confirm the rather high efficiency of the mechanical activation of the phosphorite ore fines and mechanochemical activation of phosphorite-containing mixtures, which make it possible to significantly increase the content of assimilable phosphorus pentoxide P_2O_5 in composite phosphorus-containing fertilizers.

In the process of mechanical activation, an amorphous layer is formed on the surface of dispersed phosphorite particles and the density of the phosphate substance decreases, which significantly increases its reactivity and solubility.

During the mechanical activation of the phosphorite ore fines in an activator mill, the relative content of the citrate-soluble form of P_2O_5 in the activated phosphorite increases more than three times from 17.63% to 53.18%.

As a result of the research, it was found that through using the mechanochemical activation of a mixture of the phosphorite ore fines and ammonium sulfate, it is possible to obtain a complex nitrogen–phosphorus fertilizer using acid-free and waste-free technology.

With the subsequent displacement of the resulting nitrogen–phosphorus fertilizer with potash and expanded vermiculite, it is possible to obtain long-acting composite phosphorus-containing mineral fertilizers.

The proposed new innovative technology has fundamental differences from existing analogues, since the mechanochemical activation of the phosphorite ore fines will allow

for direct acid-free and waste-free processing into phosphorus and composite phosphorus-containing mineral fertilizers.

The developed flexible technological scheme of composite phosphorus-containing fertilizers allows, depending on the agrochemical properties of the soil, as well as the characteristics of crops, to vary the composition of composite mineral fertilizers.

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