STUDY ON THE COMPOSITION OF PHOSPHORUS FERTILIZERS OBTAINED ON THE BASIS OF KIZILKUM PHOSPHORITES AND NITRIC ACID

Abduaziz L.Giyasidinov[1], Bokhodir E.Sultonov[2], Oleg Dormeshkin[3]

[1]Institute of Technology-Engineering of Namangan
7 Kasansay st., Namangan, Uzbekistan
[2]Namangan State University, 316 st. Uychi, 160136
Namangan, Uzbekistan
[3]Belarusian State Technological University, Belarus
E-mail:bse-chemist-68@mail.ru

Received 23 June 2022
Accepted 30 October 2022

ABSTRACT

The composition of a sample of phosphorus fertilizer obtained on the basis of mineralized mass (MM) was studied by a modern physical and chemical analyzer. The quantitative values of the mineral-salt composition of MM and fertilizers obtained on its basis were determined. It is shown that MM can participate in the production of phosphate fertilizers.

Keywords: phosphorus fertilizer, mineralized mass, nitric acid, quantitative value, salt content, physical and chemical analysis.

INTRODUCTION

Currently, the food problem is aggravating in the world due to the reduction of arable land and population growth. One of the main tasks of the food industry and agriculture is to provide the population with food. In this regard, it is necessary to effectively use chemicals, including mineral fertilizers, which are one of the main factors in obtaining a high-quality crop. An important factor in solving these problems is to obtain greater crop yields. The role of fertilizers in obtaining a rich harvest is invaluable. Currently, the main macronutrients for crop nutrition are nitrogen, phosphorus, potassium, calcium and sulfur. Phosphorus plays an important role in these nutrients. The main raw materials for the production of simple and complex phosphorus-containing fertilizers are phosphorites and apatites [1, 2]. Phosphorites are used with a moderate, low and very low amount of mobile phosphorus in the soil (the amount of P_2O_5 in 100 g of soil is 0 - 10 mg); acidic (pH = 4.5), slightly acidic (pH = 5.1 - 5.5) and close to neutral environment (pH = 5.6 - 6.0) [3]. It is also important to obtain a mixed type fertilizer by mechanochemical activation of phosphate raw materials, in which the activity of phosphorus in phosphate raw materials is high, and the resulting fertilizers contain other nutritional components. Several studies have shown that with the mechanical activation of phosphorites of the Karatag basin (Kazakhstan), using organo-mineral activators, it is possible to obtain multicomponent mineral fertilizers [4, 5].

The most common method for processing phosphorites into double superphosphate is the reverse method (Dorr-Oliver processes), in which phosphoric acid with a concentration of 37 - 39 % P_2O_5 is used [6]. It is also important to obtain simple long-acting phosphorus fertilizers (precipitates) from phosphorus-containing raw materials. On the basis of phosphorite sludge isolated from wastewater, a fertilizer containing 41.21 % - 41.23 % P_2O_5 was produced [7, 8]. The work was carried out to increase the components of phosphate fertilizers by washing them with calcium nitrate. On the basis of MM , phosphate fertilizers containing 21.64 % - 22.65 % P_2O_5 was obtained [9].

Liquid and solid complex fertilizers based on the incomplete decomposition of Kyzylkum phosphorites with nitric acid have been obtained. The process of obtaining nitrogen-phosphorus-calcium-containing fertilizers (NPCa) by partial isolation of calcium nitrate from the decomposition products of Kyzylkum phosphate rock at reduced rates of nitric acid is carried out by various methods [10, 11]. Phosphorus fertilizers and precipitates were obtained by Giyasidinov et al. by decomposition of Central Kyzylkum phosphorites with nitric acid [12]. The essence of the above works is based on the determination of the rate of acid required to obtain dicalcium phosphate. However, in most of the above studies, the composition of raw materials and products of their processing was not studied by modern physical and chemical methods and no conclusions were drawn about the extent to which these phosphorites can be used in production.

In this research work, the mineralized mass, which is the primary phosphorite raw material, and the products based on it were analyzed by physicochemical methods (scanning electron microscope, elemental and X-ray phase analyzes) and showed that this phosphate raw material can be involved in processing.

EXPERIMENTAL

Materials

For laboratory experiments, MM of the following composition (mass, %) was used: 14.60 - P_2O_5; 3.07 - $P_2O_{5\text{ acceptable by citric acid}}$; 43.99 - CaO; 14.11 - CO_2; 1.01 - MgO; 1.04 - Al_2O_3; 0.89 - Fe_2O_3; 1.58 - SO_3; 1.30 - F; 1.02 - H_2O and 10.82 - insoluble residue; CaO:P_2O_5 = 3. For the decomposition of phosphorites, nitric acid with a concentration of 55 % was used. Nitric acid is introduced 110 % according to the stoichiometric quantity for the formation of $CaHPO_4$.

Experimental procedure

The procedure for conducting experiments for obtaining simple phosphorus fertilizers from a mineralized mass by treatment with nitric acid is described in detail by Giyasidinov et al. [13].

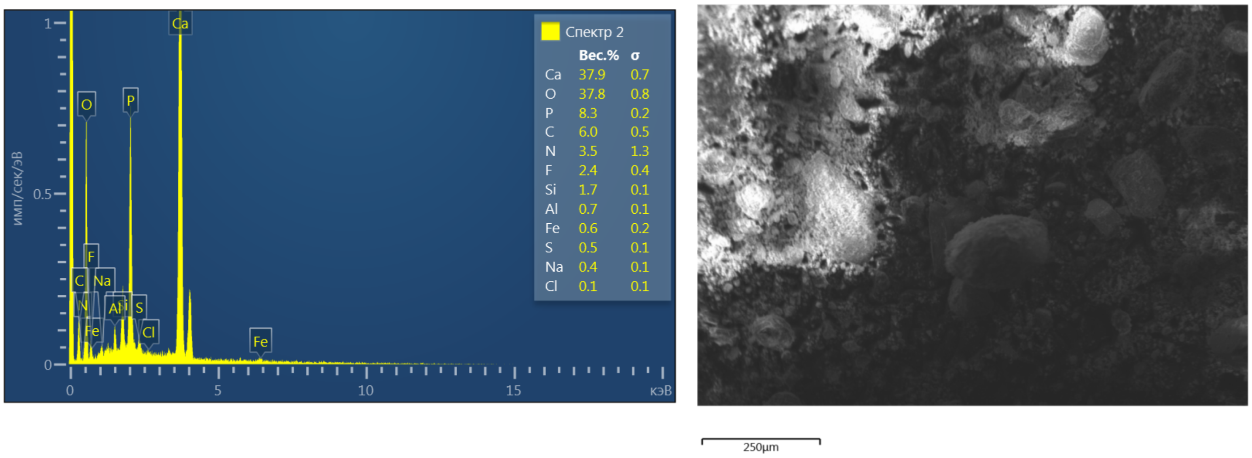
Analytical methods

The methodology for conducting experiments to obtain simple phosphate fertilizers by technological methods is based on the analysis of the main chemical composition of fertilizers by mineralized mass and nitric acid [14].

The surface microstructure of the obtained fertilizer samples was studied using a SEM-EVO MA 10 scanning electron microscope (Zeiss, Germany). Experiments with scanning electron microscope were carried out as follows: sample preparing - the surface of the test sample is rubbed on a round pressure surface consisting of a metal alloy glued to the surface with aluminum foil double-sided adhesive or a piece separated from the sample is glued. For fine powders, tablets of different diameters 7 mm and thicknesses 2 mm are prepared. Further, they are subjected to pressing, and then a round clamp is installed on the microscope table. The microscope table is mounted in the vacuum working chamber of the microscope. During the measurement, the voltage is set to 15.00 kV (EHT - Extra High Tension) and the working distance (WD - working distance) is 8,5 mm. Images of different scales are obtained using the SmartSEM software. Images of individual microparticles are also recorded. The elemental composition of the samples was determined on an energy dispersive X-ray spectrometer - equipment for energy dispersive analysis type (EDS - Oxford Instrument), Aztec Energy Advanced X-act SDD. For elemental composition of the samples, electronic images, tables of compositions and their graphical spectra are presented. X-ray images of the samples were obtained on a powder diffractometer "Panalytical Empyrean" (Netherlands) with computer control. CuK_a was carried out under the influence radiation ($K\alpha_1$ = 1.5406 Å , current and voltage in the X-ray tube 30 mA, 30 kV). In this case, the constant rotation speed of the detector is 4 deg min $^{-1}$, with a step of 0.02° (ω /2θ -bond), and the scanning angle is drawn from 5° up to 90°. The samples were analyzed in a rotating chamber with a rotation speed of 30 rpm. The obtained X-ray diffraction patterns were analyzed in comparison with XTM mineral X-ray tables compiled according to the American ASTM file cabinet, Mikheev and Giller [15, 16].

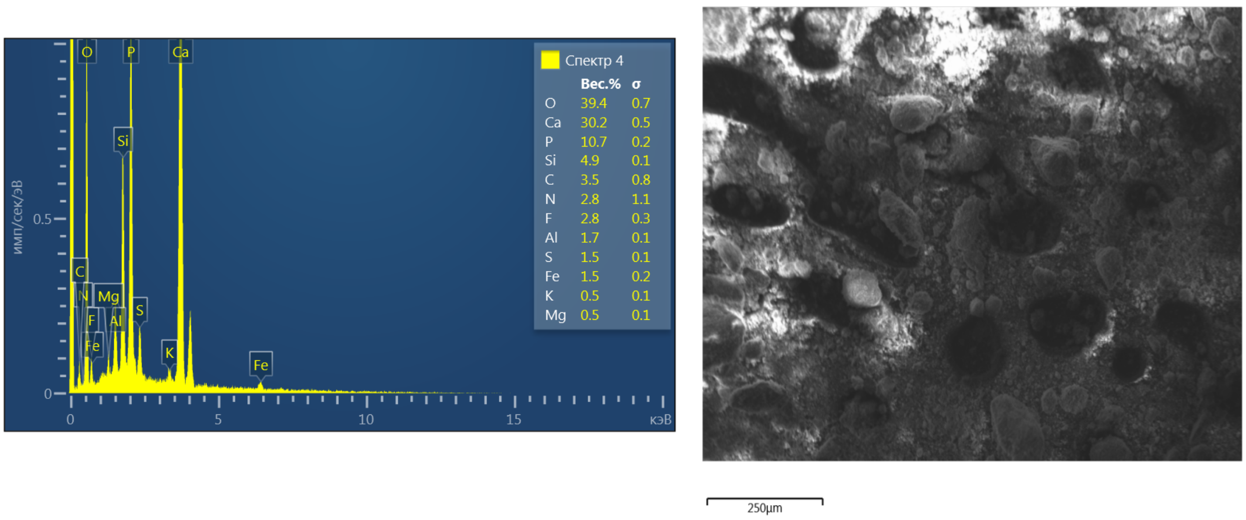
RESULTS AND DISCUSSION

The results obtained are presented in Fig. 1(a), (b) (for MM) and Fig. 2(a), (b) (for fertilizer based on MM) and in Table 1. The electron microscope shows 250 times magnified images of the inside of the raw material MM (Fig.1(a)) and phosphate fertilizer (Fig. 2(a)). The figures show that the samples are easily distinguished from each other and change in composition after the decomposition



a) b)

Fig. 1. Electron microscopic view of MM and elemental analysis structure.



a) b)

Fig. 2. Electron microscopic view of the fertilizer obtained based on MM and elemental analysis of the composition.

of phosphorite with nitric acid.

In addition, the results of elemental analysis reveal that the composition of MM (Fig. 1(b) and fertilizers obtained on its basis (Fig. 2(b)) differ significantly. For example, the carbon content in MM decreased from 6.04 % to 3.07 % and the amount of calcium from 40.01 % to 30.61 %, while the amount of phosphorus and nitrogen increase from 6.37 % to 9.99 % and from 1.95 % to 2.41 %, respectively.

This suggests that when nitric acid acts on MM, calcium carbonate decomposes, and by neutralizing the mass with $Ca(OH)_2$, phosphorus remains in the resulting fertilizer. A part of the nitrogen, being bound by the composition of the fertilizer, can become the basis for increasing the macroelements necessary for the plant. These results and the quantitative data in the Table 1 indicate that this phosphate raw material is suitable for the production of phosphate fertilizers.

Fig. 3 and Fig. 4 show X-ray patterns of MM and phosphorus fertilizers based on it, also presented in Table 1, and their mineral and salt composition (Tables 2 and 3).

As can be seen from the X-ray graphs, mineral and salt content of the phosphorous fertilizers, the mineral and

Table 1. Elemental composition of MM and fertilizers based on it.

MM raw												
Element	C	N	O	F	Na	Al	Si	P	S	Cl	Ca	Fe	others
Weight, %	6.04	1.95	37.02	1,31	0.33	0.97	2.41	6.37	0.71	0.06	40.01	0.83	1.99
Phosphorus fertilizer based on MM													
Element	C	N	O	F	Na	Al	Si	P	S	K	Ca	Fe	others
Weight, %	3.07	2.41	39.22	1.90	0.50	1.52	4.74	9.99	1.51	0.52	30.61	1.46	2.55

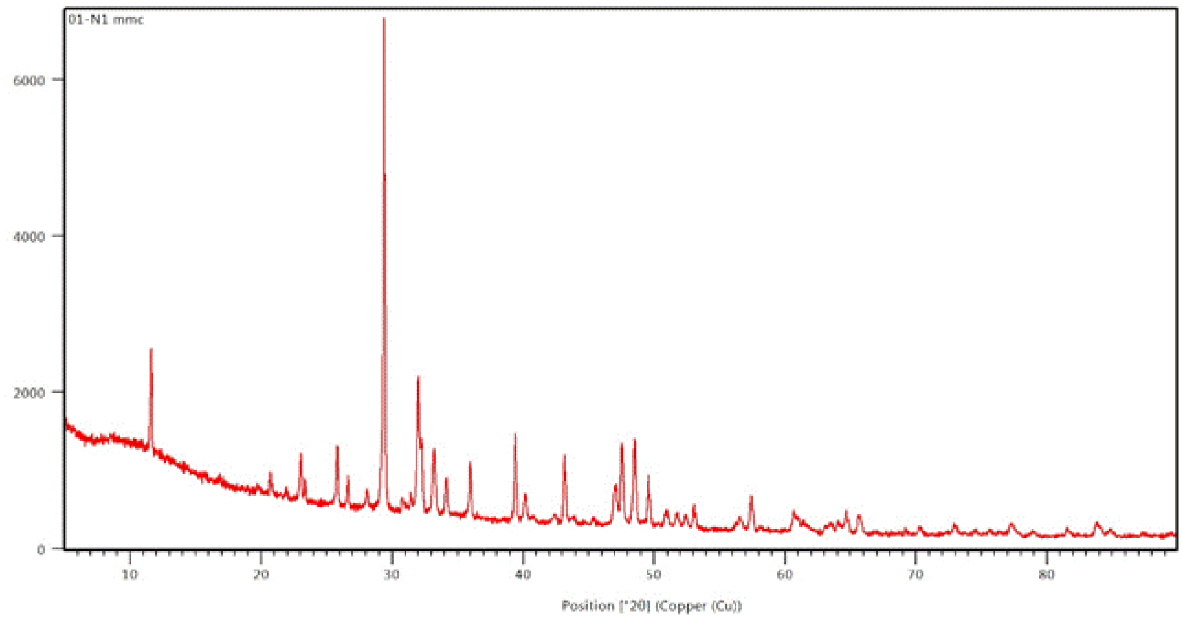


Fig. 3. X-ray MM of phosphate raw material.

Table 2. Mineral composition of phosphate raw materials MM.

Mineral content MM	Mass fraction, %	Mineral content MM	Mass fraction, %
Francolite ($Ca_{10}P_{5.2}C_{0.8}O_{23.2}F_{1.8}OH$)	39.24	Calcium ortosilicate (Ca_2SiO_4)	7.16
Calcite ($CaCO_3$)	28.07	Fluorite (CaF_2)	2.77
Dolomite ($CaMg(CO_3)_2$)	4.74	Aluminum oxide (Al_2O_3)	1.83
Gypsum ($CaSO_4 \cdot 2H_2O$)	3.81	Iron oxide (Fe_2O_3)	1.43
Quartz (SiO_2)	0.45	Insoluble residue	10.50

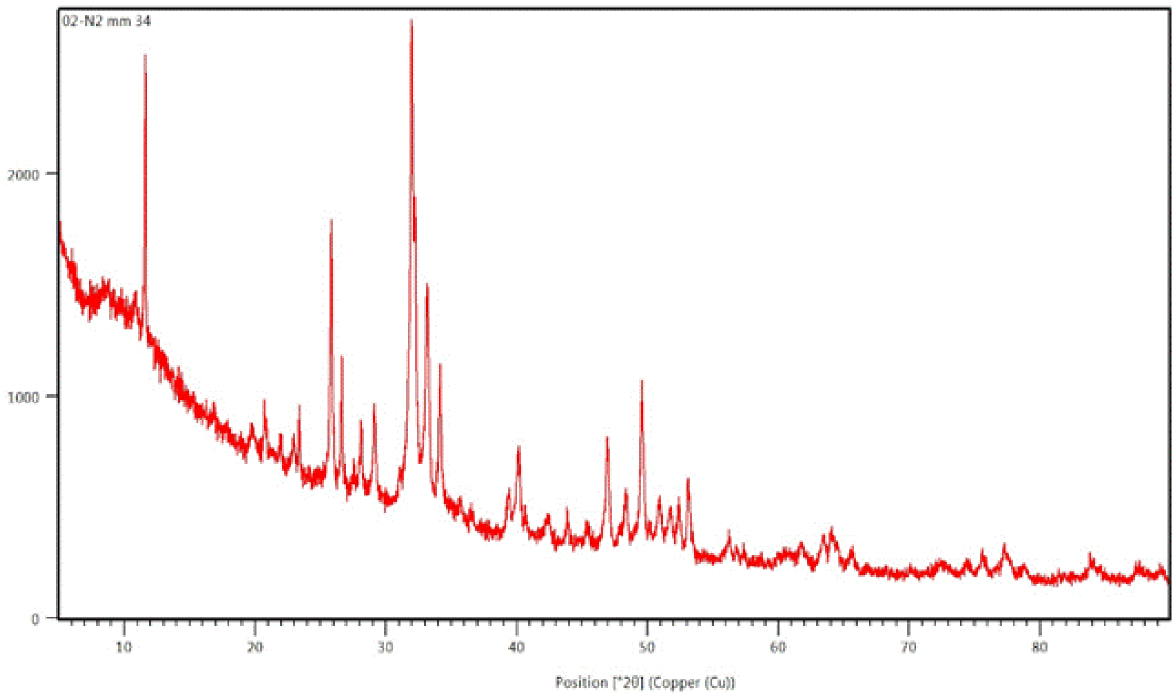


Fig. 4. X-ray pattern of phosphate fertilizers based on MM.

Table 3. Mineral and salt content of phosphorus fertilizer based on MM.

Phosphorus fertilizer obtained from MM mineral content	Mass fraction, %	Phosphorus fertilizer obtained from MM mineral content	Mass fraction, %
Frankolite ($Ca_{10}P_{5.2}C_{0.8}O_{23.2}F_{1.8}OH$)	28.46	Calcium ortosilicate (Ca_2SiO_4)	8.50
Calcium hydrogen phosphate ($CaHPO_4{\cdot}2H_2O$)	29.78	Fluorite (CaF_2)	3.03
Calcite ($CaCO_3$)	10.54	Aluminum oxide (Al_2O_3)	3.15
Dolomite ($CaMg(CO_3)_2$)	3.63	Iron oxide (Fe_2O_3)	2.08
Gypsum ($CaSO_4{\cdot}2H_2O$)	8.11	Insoluble residue	2.1
Quartz (SiO_2)	0.62		

salt content of MM and phosphorous fertilizers based on it are significantly different. The mineral and salt content of phosphorous fertilizer samples are mainly francolite ($Ca_{10}P_{5.2}C_{0.8}O_{23.2}F_{1.8}OH$), $CaHPO_4{\cdot}2H_2O$, $Ca(H_2PO_4)_2$, $CaSO_4{\cdot}2H_2O$, $MgHPO_4$, CaF_2, $Ca(NO_3)_2$, iron, aluminum phosphates, and it forms Ca_2SiO_4 and insoluble residue.

CONCLUSIONS

In conclusion, to confirm the results of laboratory analysis of MM raw materials and phosphate fertilizers obtained on its basis, the results of microstructural patterns and elemental analysis of fertilizer samples were obtained using modern equipment. The consistent of the results of elemental analysis and laboratory one proves the reliability of the obtained results. In addition, the waste of phosphate raw materials resulting from the thermal enrichment of phosphorites is a MM suitable for the production of phosphate fertilizers and can be fully utilized in the processing of the MM. A new type of phosphate fertilizer is a cheap and high-quality fertilizer, and can play an important role in agriculture.

REFERENCES

1. B.M. Beglov, Sh.S. Namazov, Phosphorites of the Central Kyzylkum and their processing, 2013.
2. Phosphates in the XXI century, Almaty, 2006.
3. B.A. Sushenisa, V.N. Kapranov, Sh.A. Aliev, V.N. Dyshko, Technology of production and application of local phosphorites in agriculture, Journal of Fertility, 1, 2005, 20-21, (in Russian).
4. K.T. Zhanatasov, Sh. Moldabekov, M.K. Zhanatasov, K.S. Baibolov, M.I. Nalibayev, D.M. Zhantasova, K.N. Bazirova, Zh.M. Altybayev, T.A. Kadynceva, O.B. Dormeshkin, A. Minakovsky, V. Shatilo, G.F. Pinayev, Mechanical Activation of the Phosphorites (Karatau basin) by using Organic-Mineral Co-Activators for Multicomponent Mineral Fertilizers, Eurasian Chemico-Technological Journal, 17, 2015, 317-326.
5. A.F. Minakovsky, V.I. Shatilo, Acid free method for processing phosphorites (Karatau basin) into complex fertilizers, Proceedings of the National academy of sciences of Belarus, Chemical series, 54, 3, 2018, 376-384.
6. Emission Estimation Technique Manual for Phosphate Manufacturing, Version 2.0, 2004, 29.
7. K. Gorazda, Z. Kowalski, Z. Wrozek, From sewage sludge ash to calcium phosphate fertilizers, Polish Journal of Chemical Technology, 14, 3, 2012, 54-58.
8. K. Gorazda, B. Tarko, Z. Wrozek, A. Nowak, J. Kulczycka, A. Henclik, Characteistic of wet method phosphorus recovery from polish sewage sludge ash with nitric acid, Open Chemistry, 14, 2016, 37-45 .
9. A.L. Giyasidinov, B.E. Sultonov, Sh.S. Namazov, J.E. Kholmurodov, Investigation of the influence of washed water quantity on the main indicators of fertilizer precipitation, J. Chem. Technol. Metall. 56, 4, 2021, 738-743.
10. A.M. Reimov, A.U. Erkaev, Sh.S. Namazov, B.M. Beglov, Nitric acid processing of ordinary phosphate flour of the Central Kyzylkum deposit, Vestnik KKO AN Ruz, 5, 2001, 37-39.
11. A.M. Reimov, Sh.S. Namazov, Kh.Ch. Mirzakulov, B.M. Beglov, Nitrogen-phosphorus-calcium fertilizers based on the decomposition of ordinary phosphate flour of the Central Kyzyl Kum with an incomplete norm of nitric acid, Reports of the Academy of Sciences of the Republic of Uzbekistan, 5, 2002, 50-52.
12. A.L. Giyasidinov, B.E. Sultonov, Sh.S. Namazov, Investigation of the Influence of Temperature of Washed Water on the Main Indicators of Fertilizer Precipitate, Curr. J. Appl. Sci. Technol., 40, 7, 2021, 73-81.
13. A.L. Giyasidinov, B.E. Sultonov, Sh.S. Namazov, G.U. Pulatova, Studying the processes of nitric acid processing mineralized mass from phosphorites of the Central Kyzylkum into single fertilizers, Namangan Engineering - Technological Institute, Scientific and Technical Journal, 2, 2020, 144 -151, (in Russian).
14. B.E. Sultonov, Sh.S. Namazov, B.S. Zakirov, Investigation of nitric acid beneficiation of low grade phosphorites from Central Kyzylkum, J. Chem. Technol. Metall. 50, 1, 2015, 26-34.
15. V.I. Mikheev, X-ray determinant of minerals, 1, 1957, 868.
16. Y.L. Giller, Tables of interplanar distances, 1,2, 1966, 330.