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Research of Physico-Chemical Characteristics of Low-Polymerized Calcium Polyphosphate Based on Central Kyzylkum Phosphorites

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ABSTRACT: The aim of the research is to obtain low-polymerized calcium polyphosphate based on phosphorites of the Central Kyzylkum and evaporated extraction phosphoric acid. Decomposition of phosphorite raw materials of the Central Kyzylkum with concentrated extraction phosphoric acid in various proportions, the resulting acidic suspension was neutralized with gaseous ammonia to pH 3.1-3.4, dehydration at a temperature of 230-250°C. The individuality of the synthesized substances was established by X-ray diffraction, IR spectroscopy and scanning electron microscopy.

I. INTRODUCTION

In our republic, a number of fundamental scientific research works are devoted to obtaining concentrated phosphorus fertilizers based on local raw materials. However, they pay little attention to condensed phosphates, which have specific properties compared to orthophosphates. The importance of condensed phosphates in plant metabolism is very great. Among them, the most widespread in the world are complex fertilizers based on ammonium polyphosphates

The phosphate raw material production industry is one of the most important, technically refined branches of heavy industry, 90% of whose output is used to produce phosphorus-containing fertilizers [1]. The share of phosphate raw material production in the mining industry is quite significant: it is comparable with other branches of solid mineral production, such as ferrous and non-ferrous metallurgy, coal and building materials.

By now, the consumption of phosphate raw materials in the world has increased to 190 million tons or 43 million tons of P_2O_5 per year. According to forecasts, the consumption of phosphate raw materials will increase by 1.3 million tons by 2020 and by 2 million tons in the period up to 2030. By 2050, annual consumption will reach 220 million tons of phosphate raw materials or about 70 million tons of P_2O_5 [2].

Condensed phosphates are highly concentrated fertilizers and have advantages over conventional low-percentage fertilizers in terms of savings in transportation, storage and application. They are less susceptible to degradation in the soil, have a long aftereffect and a higher coefficient of phosphorus use by plants [3, 4].

The low use of phosphorus fertilizers in the year of application is caused by the fact that phosphorus compounds are fixed in the soil in immobile or extremely low-mobility forms and therefore cannot be fully absorbed by plant roots. One way to increase the coefficient of use of phosphorus fertilizers is to use fertilizers with a prolonged action. One of such types of phosphorus fertilizers are polyphosphates or condensed calcium phosphates, which are also used for other purposes [5-7].

Phosphorus fertilizers containing condensed phosphates have a higher phosphorus content and can be obtained in various ways from low-grade phosphorites [7, 8]. By changing the degree of condensation and the crystalline structure, it is

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possible to regulate the solubility of calcium polyphosphates and thereby increase the degree of phosphorus use by plants [9].

When obtaining calcium polyphosphate by heat treatment of superphosphates, temperature has a significant effect on the process of condensation of P_2O_5 and the chemical composition of calcium polyphosphate. Therefore, our research was aimed at studying the effect of calcination temperature and other parameters of the process of decomposition of phosphorites of the Central Kyzylkum with extraction phosphoric acid on the chemical composition of calcium polyphosphate.

II. RESEARCH METHODS

For the studies, we used phosphorites of the Central Kyzylkum with the following composition (wt.%): P_2O_5 - 28.34; CaO - 53.20; CaO:P_2O_5 - 1.88; MgO - 0.45; Fe_2O_3 - 0.39; Al_2O_3 - 0.41; SO_3 - 3.05; F - 2.94 and EPA from the same raw material with the following composition (wt.%): P_2O_5 - 21.6; CaO - 0.21; MgO - 0.41; Fe_2O_3 - 0.37; Al_2O_3 - 0.43; SO_3 - 2.00; F - 1.30. phosphorites decomposed EPA at 80°C for 90 minutes. The mass ratio of the sum of $P_2O_{5\ EPA}$ and $P_2O_{5\ PRM}$ to the sum of calcium, magnesium, iron, aluminum oxides of phosphorite and EPA (R) varied from 1.33 to 2.04, which corresponds to the ratio $P_2O_{5\ EPA}$:$P_2O_{5\ PRM}$ = 2.15 - 4.50. The acidic pulp was neutralized with gaseous ammonia to a pH of 3.1 - 3.4 and dried at a temperature of 90-100°C.

The samples were identified based on diffraction patterns obtained on an XRD-6100 diffractometer (Shimadzu). CuKα radiation (β filter, Ni, 1.54178, tube current and voltage mode 30 mA, 30 kV) and a constant detector rotation speed of 4 deg/min with a step of 0.02 deg (ω/2θ coupling) were used, and the scanning angle varied from 4 to 80°.

The spectra of the samples were recorded using an IRTracer-100 FTIR spectrometer equipped with a single-pass ATR attachment with a diamond/ZnSe MIRacle 10 prism in the scanning range: 4600 – 600 cm^{-1}.

The microstructure of the samples was studied using a scanning electron microscope SEM-EVO MA 10 (Carl Zeiss) with an Aztec Energy Advanced X-Act–Oxford Instruments X-ray spectrometer, accelerating voltage of 12 kV.

III. EXPERIMENTAL RESULTS

The chemical compositions of the obtained fertilizers depending on the ratio of $P_2O_{5\ EPA}$:$P_2O_{5\ PRM}$ or R are shown in the table.

Table - The influence of the ratio $P_2O_{5\ EPA}$:$P_2O_{5\ PRM}$ on the chemical composition of phosphorus fertilizers before calcination

№	$\frac{P_2O_{5\ EPA}}{P_2O_{5\ PRM}}$	R	Chemical composition, mass, %				
			$P_2O_{5\ total.}$	$P_2O_{5\ assim.}$	$P_2O_{5\ water\text{-}sol.}$	$\frac{P_2O_{5\ assim}}{P_2O_{5\ total}}$	$\frac{P_2O_{5\ water}}{P_2O_{5\ total}}$
1	2,15	1,33	36,43	26,09	14,14	71,64	38,83
2	2,85	1,56	39,78	32,06	17,17	82,10	43,00
3	3,65	1,80	44,17	37,60	26,56	85,10	60,10
4	4,00	1,90	45,20	39,36	28,83	86,44	63,80
5	4,50	2,04	46,61	40,81	31,86	87,56	68,36

As can be seen from the table, with an increase in the ratio of $P_2O_{5\ EPA}$:$P_2O_{5\ PRM}$ from 2.15 to 4.5 or R from 1.33 to 2.04, the content of total P_2O_5 increases from 36.43% to 46.61%, assimilable P_2O_5 from 26.09% to 40.81% and aq P_2O_5 from 14.14% to 31.86%. At the same time, the share of the assimilable norm of P_2O_5 increases from 71.64% to 87.56%, and the water-soluble from 38.83% to 68.36%.

The effect of calcination duration on the chemical composition of ammoniated granulated phosphorus fertilizers obtained at mass ratios of $P_2O_{5\ EPA}$:$P_2O_{5\ PRM}$ = 3.65 was studied at temperatures of 200, 240 and 260 °C.

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The degrees of increase in the total assimilable P_2O_5 and polymerization were chosen as the parameter characterizing the process of dehydration of calcium ammonium phosphate, the dependences of which on the conditions of the calcination process are shown in figure 1.

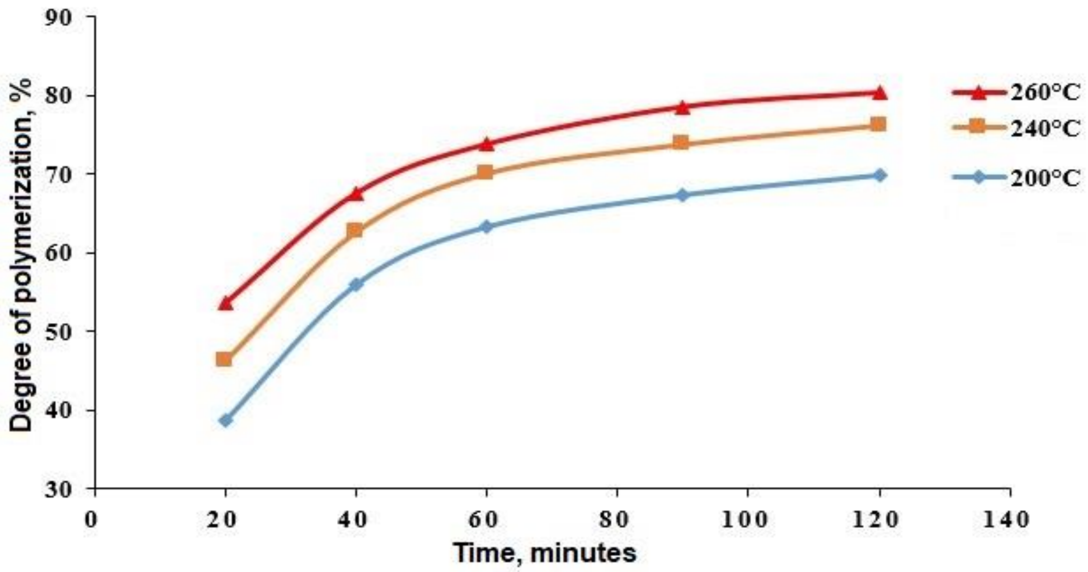

Fig. 1. Effect of calcination duration on the degree of polymerization

With increasing calcination duration, the degree of polymerization increases sharply during the first 60 minutes and then slows down. At a temperature of 200°C after 90-120 minutes of calcination, the degree of polymerization reaches 67.31-69.79%, at 240°C 74.67-78.42%, at 260°C 75.89-79.30%.

To conduct research on the physic-chemical properties, calcium polyphosphate was obtained from evaporated EPA by neutralization with gaseous ammonia to pH = 3.1-3.4.

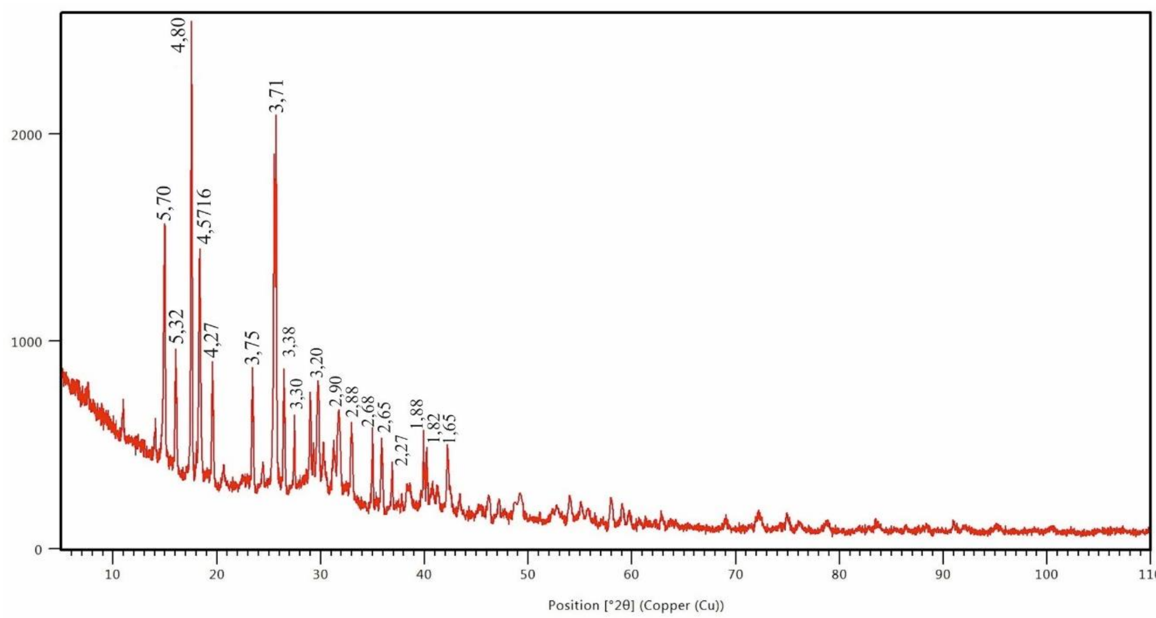

Fig. 2. – X-ray diffraction pattern of calcium polyphosphate

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The X-ray diffraction pattern (Fig. 2) contains only diffraction maxima characteristic of calcium diphosphates ($Ca(H_2PO_4)_2$) with interplanar distances of 5.70; 4.80; 3.71; 3.38; 3.30 Å and ammonium polyphosphates ($(NH_4)_3HP_2O_7$ and $(NH_4)_3HP_2O_7$) - 4.5716; 4.27 Å, monoammonium phosphate ($NH_4H_2PO_4$) - 5.32; 3.75 Å, ferrous lazulite $(Mg,Fe)Al_2(PO_4)_2(OH)_2$ - 3.20 Å. Replicas with interplanar distances of 2.90; 2.27 Å also belong to unreacted phosphorite, and 1.88; 1.82 Å - quartz, as well as 2.88, 2.68 and 1.65 Å, attributed to $CaSO_4{\cdot}2H_2O$ and CaF_2.

To study the chemical composition of the obtained product, IR spectra of the obtained product were analyzed as a result of the IR spectrum of calcium polyphosphate (Fig. 3).

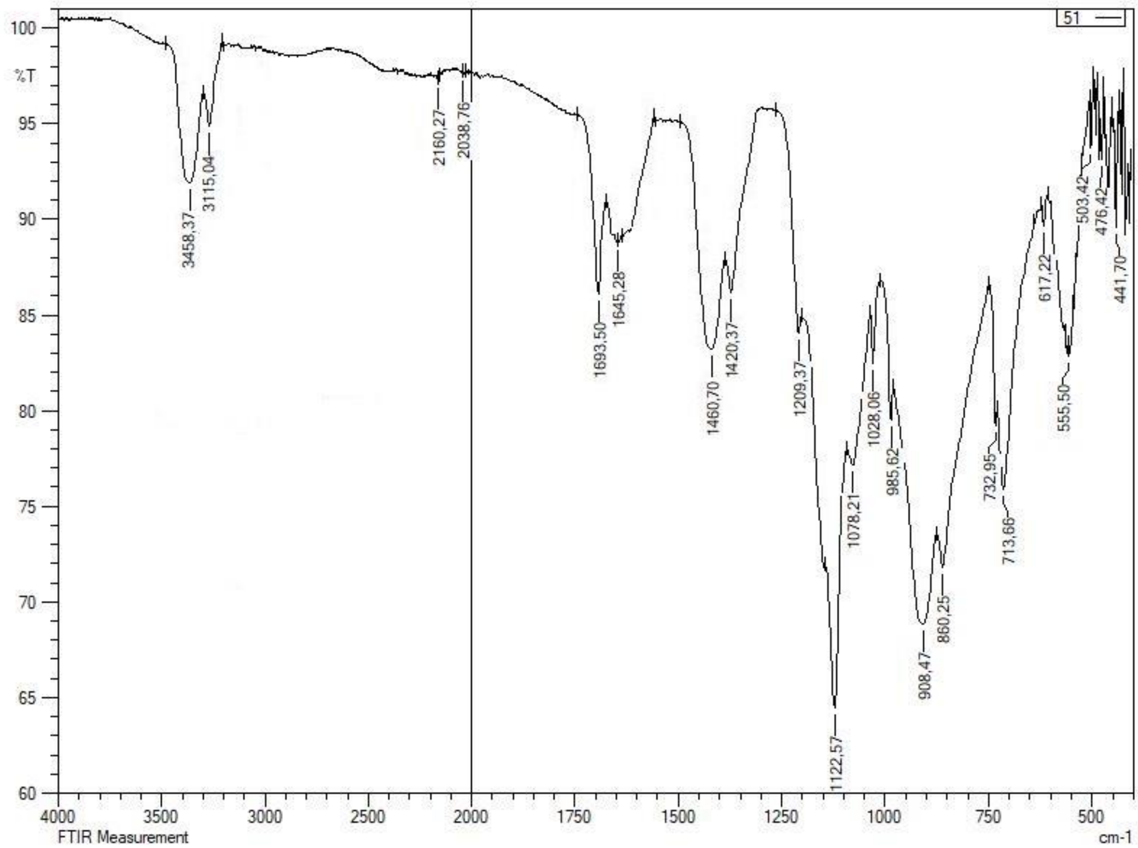

Fig. 3. IR spectrum of calcium polyphosphate (EPA:PRM = 3.65).

The results of the IR spectroscopic study show that the bands of calcium ammonium phosphate and impurity coincide with the absorption bands of certain groups. For example, in the range of 1435.10 cm^{-1}, flat deformation vibrations of the N-H and NH_2 groups are observed, the bands in the region of 1600-1400 cm^{-1} correspond to the deformation vibrations of NH_3^+, NH_2^+, NH^+. In the IR spectrum of calcium ammonium phosphate, there are wide bands in the region of 913.33-1096.58 cm^{-1} PO_4^{2-} and (550-617 cm^{-1}) in the composition of the phosphate substance, bands appear at 1661.75 cm^{-1}, related to $CaSO_4{\cdot}2H_2O$. The medium intensity absorption band at 2300-3540 cm^{-1} characterizes the main valence vibrations of water in the composition of clay minerals, crystal hydrates, and also physically adsorbed water on the surface of mineral grains.

Electron microscopic analysis of calcium polyphosphate fertilizer, the obtained results of elemental chemical analysis are shown in figure 4.

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Element	Weight.%	Sigma Weight%
N	3.02	0,57
O	51.07	0.26
F	1.58	0.24
Na	0.23	0.05
Mg	0.73	0.05
Al	0.64	0.16
Si	0.32	0.05
P	21.96	0.18
S	1.88	0.17
Ca	17.86	0.18
Fe	0.71	0.15
Sum:	100.00	

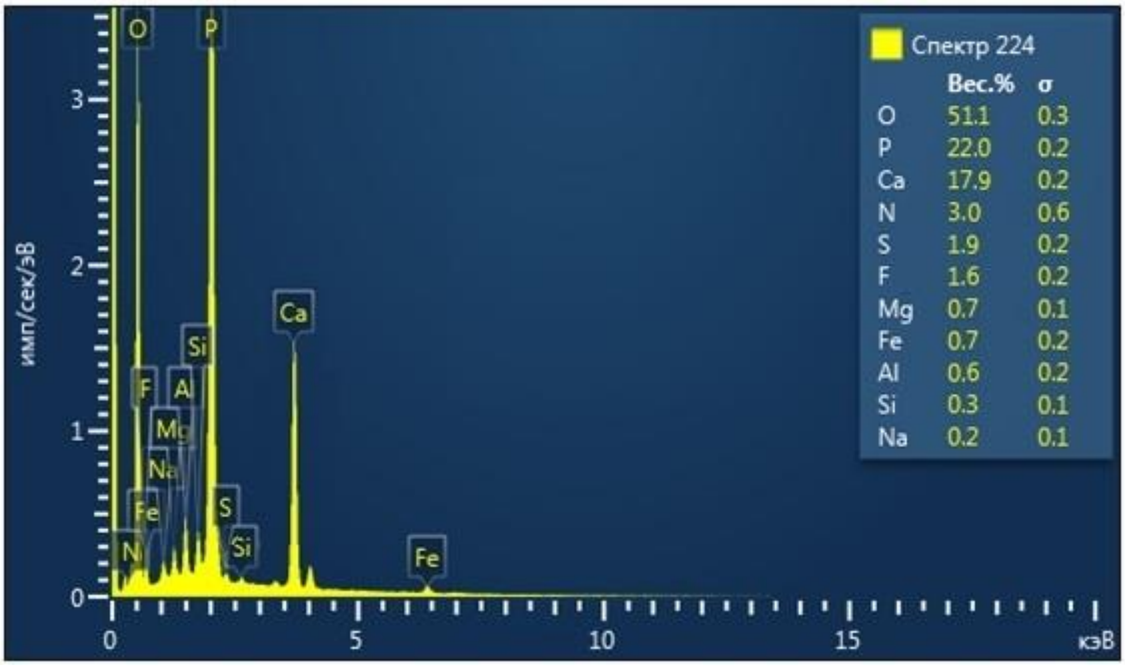

Fig. 4. - Energy dispersive analysis of calcium polyphosphate ($P_2O_{5\ EPA}$:$P_2O_{5\ PRM}$ = 3.65, R = 1.80)

Energy dispersive analysis of calcium polyphosphate showed the following content of elements: N-3.02%; O-51.07%, F-1.58%; Na-0.23%; Mg-0.73%; Al-0.64%; Si-0.32%; P-21.96%; S-1.88%; Ca-17.86%; Fe-0.71%, which corresponds to the composition of calcium polyphosphate.

IV. CONCLUSION

Thus, the conducted studies have shown the possibility of obtaining prolonged-action phosphorus fertilizers containing low-polymerized calcium polyphosphate from phosphorites of the Central Kyzylkum by decomposing them with EPA, partial ammoniation of the decomposition products with gaseous ammonia and subsequent calcination at 250-260°C for 60-90 minutes. In the form of low-polymerized calcium and ammonium monophosphates.

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