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Investigation of the Process of Obtaining Ammophos from a Solution of Enrichment of Phosphorites of Central Kyzylkums with Extraction Phosphoric Acid

Umarov Shavkat, Mirzakulov Kholtura, Arifdjanova Kamola, Nuriddinov Uktam

DSc Student, Department of Chemical Technology of Inorganic Substances, Tashkent Institute of Chemical Technology, Tashkent, Uzbekistan
Professor, Department of Chemical Technology of Inorganic Substances, Tashkent Institute of Chemical Technology, Tashkent, Uzbekistan
DSc, Department of Chemical Technology of Inorganic Substances, Tashkent Institute of Chemical Technology, Tashkent, Uzbekistan
Teacher, Department of Chemistry and its Teaching Methodology, Jizzakh State Pedagogical University, Jizzakh, Uzbekistan

ABSTRACT: The results of studies on the processing of solutions for the enrichment of washed burnt phosphoric concentrate with extraction phosphoric acid obtained at S:L =1: (5 and 6) for ammophos are presented. It is shown that with an increase in the degree of ammonification, the composition of ammophos based on enrichment solutions changes towards a decrease in all components of the fertilizer. At S:L =1:5, ammophos contains 48.29% $P_2O_{5\ assim.}$, whereas at S:L =1:6, this indicator is 49.65%. A significant decrease in the composition of ammophos is the proportion of the water-soluble form of P_2O_5, which at pH 4.5 is 62.13-64.84%, while the proportion of the digestible form of P_2O_5 exceeds 99.2%. The compositions of ammophos were determined using physico-chemical methods of analysis - X-ray phase, IR spectroscopic and scanning electron microscopic.

I. INTRODUCTION

One of the main directions of economic and social development of the national economy of the Republic of Uzbekistan is the growth in the production of phosphorus-containing mineral fertilizers, because, the food security of our country largely depends on this. To solve this problem, it is necessary to create an appropriate raw material base for the production of phosphorus-containing fertilizers through the development of an effective technology for the enrichment of refractory, phosphorus-poor ores with the production of concentrates suitable for chemical processing. The chemical industry places high demands on the quality of processed phosphorus-containing raw materials, not only in terms of a useful component, but also in terms of harmful impurities, such as iron and aluminum oxides, carbonates, etc. In this regard, when developing phosphorite ore deposits poor in phosphorus, it is necessary to create such technologies for their enrichment, which would take into account all the requirements of the production of mineral fertilizers for phosphorus-containing raw materials in the process of its processing into conditioned phosphoric acid and water-soluble, concentrated mineral fertilizers.

II. LITERATURE SURVEY

The phosphorus industry of Uzbekistan is based on the processing of local phosphorites of Central Kyzylkums (CK) [1, 2]. The enterprises receive washed burnt phosphate concentrate (WBPC) CK with a P_2O_5 content of at least 26.0% P_2O_5 [3]. The main phosphorus-containing fertilizer produced in Uzbekistan was and remains ammophos. Its distinctive feature is the high concentration of nutrients, which is achieved by binding all calcium from phosphate raw materials with sulfuric acid and removing it in the form of calcium sulfate (phosphogypsum) at the stage of obtaining extraction phosphoric acid. The consumption of sulfuric acid per 1 ton of P_2O_5 in ammophos reaches 2.5 - 2.6 tons when using

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apatite, 3.6 - 3.7 tons when using Karatau phosphorites. The consumption of sulfuric acid at JSC "Ammofos - Maxam" for 1 ton of P_2O_5 in the production of ammophos from WBPC CK is more than 4.5 tons. In the production of EPA, free calcium oxide increases the temperature of the decomposition process in the extractor to 95-100^oC and above, which activates the corrosion ability of phosphoric acid and leads to the formation of agglomerates of calcium sulfate semihydrate clogging the extractor [4].

In addition, it should be taken into account that almost all the phosphoric anhydride in ammophos is in a water-soluble form. This was also due to the fact that agriculture in previous years required from the mineral fertilizers industry exactly this form of phosphoric anhydride in phosphorus-containing fertilizers.

However, gradually the requirements of agriculture for mineral fertilizers began to be revised due to the accumulated experience in the use of fertilizers and the shortage of sulfur and calcium in phosphorus-containing fertilizers, as well as the requirement to produce part of mineral fertilizers with reduced solubility of nutrients.

Ammophos obtained from WBPC CK contains 46-48% P_2O_5 due to the high content of sulfates, oxides and a half, fluorine [5]. In addition, due to the high calcium modulus ($CaO:P_2O_5$) equal to 1.9-2.1, the consumption of sulfuric acid is greatly increased. All this makes ammophos from phosphorites of the CK economically inefficient. The conducted studies on the enrichment of WBPC with solutions of nitric and extraction phosphoric acids have shown the possibility of reducing the calcium modulus to 1.6, which reduces the consumption of sulfuric acid to 0.2 tons per ton of enriched phosphorite, compared with unenriched [6, 7]. When enriching WBPC, in addition to calcium oxide, the content of sulfate ions and fluorine in enrichment solutions decreases to 0.8% due to the formation of insoluble calcium sulfate dihydrate and calcium fluoride.

III. RESEARCH METHODS

Processing of enrichment solutions (ES) for ammophos was carried out in a glass reactor equipped with a mechanical stirrer, taps for supplying ammonia, installing a reverse refrigerator and a thermostat. To do this, we used the WBPC of the CK of the composition (mass. %): P_2O_5 - 26.20; CaO - 57.70; $CaO:P_2O_5$ - 2,202; MgO - 1,30; Fe_2O_3 - 0.43; Al_2O_3 - 0.60; SO_3 - 3.21; F - 2.84, enrichment solutions obtained at the ratio of WBPC:EPA=1 : (5-6) of the following composition (table 1). The analysis of the initial, intermediate and final products was carried out by known methods of chemical and physico-chemical analysis [8-10].

Table 1. Chemical composition of the enrichment solution

Enrichment solution, S:L	Chemical composition, mass. %						
	P_2O_5	CaO	MgO	Al_2O_3	Fe_2O_3	SO_3	F
1:5	16,93	3,98	1,45	0,73	0,21	0,82	0,84
1:6	17,32	4,10	1,48	0,75	0,21	0,81	0,83

To identify the phase composition of initial and intermediate substances, finished products, in addition to chemical [8–10] and physicochemical (X-ray phase, IR spectroscopic and scanning electron microscopic methods) analysis [11 - 13].

X-ray diffraction patterns of the samples were taken on an XRD-6100 apparatus (Shimadzu, made in Japan) with computer control [11]. In this case, CuK_α radiation was used (β-filter, Ni, 1.54178 mode of current and tube voltage 30 mA, 30 kV) and a constant detector rotation speed of 4 deg/min with a step of 0.02 deg. (ω/2θ-coupling), and the scanning angle varied from 4 to 80°.

Spectra of the samples were taken on an IRTracer-100 IR-Fourier spectrometer complete with a single ATR attachment with a diamond/ZnSe MIRacle 10 prism. It is designed for the analysis of solid, liquid, paste-like, gel-like and hard-to-

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process substances in the scanning range of 4600–600 cm^{-1}. To do this, a sample in the form of a powder was placed on a diamond window in the center of the attachment [12].

The surface morphology and the study of the microstructure of the samples were carried out using a SEM - EVO MA 10 scanning electron microscope (Carl Zeiss, Germany) with an Aztec Energy Advanced X-Act–Oxford Instruments X-ray spectrometer [13]. Experiments on a scanning electron microscope were carried out as follows. To carry out the sample preparation process, a metal alloy holder was installed on the microscope stage, on top of which an aluminum foil with a double-sided adhesive surface was glued. The test sample was applied to this foil. Next, the object stage was installed in the working chamber of the microscope, from which air was evacuated to create a vacuum. To carry out the measurement, an accelerating voltage of 12 kV was applied to the filament, while the working distance was 8.5 mm. The images were obtained on scales from 50 µm.

IV. EXPERIMENTAL RESULTS

To study the behavior of the components of enrichment solutions obtained during the treatment of WBPC EPA at S:L = 1 : (5-6), the effect of the degree of ammonization (pH) on the composition of the suspension was studied (table 2).

Table 2. Chemical composition of the suspension of ammophos obtained from enrichment solutions

no	Pulp pH	Chemical composition suspension, wt. %							
		P_2O_5	N	CaO	MgO	SO_3	Al_2O_3	Fe_2O_3	F
The enrichment solution obtained at S:L =1:5									
1	3,2	16,54	2,28	3,89	1,42	0,93	0,71	0,20	0,82
2	3,5	16,48	2,70	3,87	1,41	0,92	0,71	0,20	0,82
3	3,8	16,41	2,95	3,86	1,41	0,92	0,71	0,20	0,81
4	4,1	16,38	3,21	3,85	1,40	0,92	0,70	0,20	0,81
5	4,5	16,33	3,57	3,84	1,40	0,91	0,70	0,19	0,80
The enrichment solution obtained at S:L =1:6									
6	3,2	16,92	2,32	4,01	1,45	0,80	0,74	0,21	0,81
7	3,5	16,84	2,79	3,99	1,44	0,79	0,73	0,20	0,80
8	3,8	16,81	3,05	3,98	1,43	0,79	0,72	0,20	0,79
9	4,1	16,77	3,29	3,96	1,43	0,78	0,72	0,20	0,78
10	4,5	16,69	3,68	3,94	1,42	0,77	0,71	0,19	0,77

An increase in pH from 3.2 to 4.5 significantly affects the nitrogen content, which increases from 2.28% to 3.57% at S:L = 1:5 and practically does not affect the content of the remaining components.

When ammonizing the enrichment solution obtained at S:L = 1:6, the same patterns are observed. So, the content of P_2O_5 is 16.54-16.33% at S:L = 1:5 and 16.92-16.69% at S:L =1:6, respectively, the nitrogen content increases from 2.28-3.57% to 2.32-3.68% when the pH changes from 3.2 to 4.5. The contents of other impurities are slightly reduced.

Viscosity, density of suspensions and pulps are important characteristics for the selection of technological schemes, equipment. Therefore, rheological properties of ammophos suspensions have been studied depending on pH and temperature changes (table 3).

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Table 3. Effect of temperature on the density and viscosity of ammophos suspensions

№	pH	Density, g/cm^3				Viscosity, MPa*s			
		20°C	40°C	60°C	80°C	20°C	40°C	60°C	80°C
The enrichment solution obtained at S:L =1:5									
1	3,2	1,273	1,262	1,254	1,250	8,97	5,12	3,01	2,27
2	3,5	1,331	1,318	1,309	1,306	10,61	6,47	3,37	2,61
3	3,8	1,390	1,378	1,369	1,365	12,88	7,61	3,92	2,96
4	4,1	1,445	1,432	1,423	1,420	14,93	8,89	4,29	3,49
5	4,5	1,491	1,478	1,469	1,466	17,51	10,98	5,71	4,01
The enrichment solution obtained at S:L =1:6									
6	3,2	1,281	1,270	1,261	1,258	9,24	5,27	3,12	2,34
7	3,5	1,339	1,326	1,317	1,314	10,93	6,67	3,47	2,69
8	3,8	1,398	1,386	1,377	1,373	13,27	7,84	4,03	3,05
9	4,1	1,454	1,440	1,432	1,429	15,38	9,16	4,42	3,59
10	4,5	1,498	1,487	1,478	1,475	18,03	11,31	5,88	4,13

The data obtained indicate acceptable rheological properties of ammoniated to pH 3.2-4.5 suspensions of ammophos obtained from ES by enrichment of WBPC EPA at S:L = 1 : (5-6). Thus, with an increase in pH, the density at 20°C increases from 1.273 g/cm^3 at pH 3.2 to 1.491 g/ cm^3 at pH 4.5, and with an increase in temperature from 20°C to 80°C, the density at pH 4.5 decreases from 1.491 g/cm^3 to 1.466 g/cm^3. for a suspension obtained with a ratio WBPC:EPA=1:5. Reducing S:L to 1:6 slightly increases the density of the suspension, which is 1.281-1.498 g /cm^3 at 20°C and changes from 1.498 g /cm^3 to 1.475 g/cm^3 when the temperature rises from 20°C to 80°C.

The viscosity of ammophos suspensions increases markedly with an increase in pH and amounts to 8.97-17.51 MPa s at a pH of 3.2-4.5 and for a ratio of 1:5 when obtaining ES. An increase in temperature from 20°C to 80°C leads to a significant decrease in viscosity from 17.5 MPa s at 20°C to 4.01 MPa s at 80°C for suspensions obtained from ES at S:L =1:5.

A similar pattern of changes in the viscosity of suspensions is observed for suspensions obtained from ES at S:L = 1:6. The maximum viscosity of the suspension is noted at pH 4.5 equal to 18.03 MPa s at 20°C and the minimum at pH 4.5 equal to 4.13 MPa s at a temperature of 80°C.

The composition of ammophos obtained during the ammonization of WBPC EPA enrichment solutions at S:L = 1 : (5-6) after evaporation and drying is shown in table 4.

Table 4 - Composition of ammophos obtained from enrichment solutions

no	pH	Chemical composition of the product, wt. %										$\frac{P_2O_{5assim.}}{P_2O_{5gener.}}$ x100%	$\frac{P_2O_{5water}}{P_2O_{5gener.}}$ x100%
		$P_2O_{5\ gener.}$	$P_2O_{5\ assim.}$	$P_2O_{5\ water.}$	N	CaO	MgO	SO_3	Al_2O_3	Fe_2O_3	F		
The enrichment solution obtained at S:L =1:5													
1	3,2	51,17	50,82	45,22	7,02	12,04	4,39	2,88	2,19	0,62	2,41	99,32	88,37
2	3,5	50,39	50,04	42,35	8,25	11,83	4,31	2,81	2,17	0,61	2,38	99,30	84,05
3	3,8	49,98	49,63	40,79	8,99	11,76	4,29	2,80	2,16	0,60	2,34	99,29	81,62
4	4,1	49,61	49,24	38,69	9,72	11,66	4,24	2,79	2,12	0,59	2,32	99,26	77,98
5	4,5	48,67	48,29	30,24	10,64	11,45	4,17	2,71	2,09	0,57	2,27	99,22	62,13
The enrichment solution obtained at S:L =1:6													
6	3,2	52,56	52,21	46,84	7,20	12,45	4,50	2,48	2,30	0,65	2,39	99,34	89,12
7	3,5	51,67	51,31	44,04	8,55	12,24	4,42	2,42	2,24	0,61	2,33	99,31	85,23

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8	3,8	51,24	50,88	42,44	8,74	12,13	4,38	2,39	2,21	0,60	2,30	99,30	82,78
9	4,1	50,75	50,39	40,38	9,95	12,01	4,33	2,36	2,18	0,59	2,27	99,28	79,57
10	4,5	50,03	49,65	32,44	11,03	11,82	4,26	2,31	2,13	0,57	2,19	99,25	64,84

The table shows that with an increase in the pH of the resulting ammophos, the content of all forms of P_2O_5 decreases. Thus, the content of assimilable forms of P_2O_5 decreases from 51.7% at pH 3.2 to 48.67% at pH 4.5. However, the ratio of $P_2O_{5\ assim.}$ to $P_2O_{5\ gener.}$. It is 99.32-99.22% at S:L = 1:5 of the enrichment solution. When obtaining ES at S:L = 1:6 and subsequent ammonification, the ratio of forms is maintained, but the contents of all forms of P_2O_5 increase. The content of water forms from 45.22-30.24% at S:L = 1:5 increases to 46.84-32.44% at S:L = 1:6, and the ratio of $P_2O_{5\ water.}$ to the $P_2O_{5\ assim.}$ they are 88.37-62.13% and 89.12-64.84%, respectively. The decrease in the aqueous form of P_2O_5 is explained by the formation, with an increase in the pH of the pulp, of dicalcium phosphate and salts of oxides and a half.

The nitrogen content in ammophos increases from 7.02% to 10.64% with an increase in pH from 3.2 to 4.5. The contents of CaO, MgO, Al_2O_3, Fe_2O_3, SO_3 and F decrease slightly.

The conducted surveys show that when using ES to obtain ammophos, the contents of all forms of phosphorus increase from 46-48% to 49-50% when using ES, the finished product contains 11.45-11.85% CaO and 37.4-34.7% P_2O_5 in a slowly soluble form.

To conduct studies of physico-chemical properties, ammophos was obtained from ES with neutralization with gaseous ammonia (pH = 4.1). The X–ray image shows only diffraction maxima characteristic of monoammonium phosphate ($NH_4H_2PO_4$) with interplane distances of 5.32; 3.75 Å, ferruginous lazulite $(Mg,Fe)Al_2(PO_4)_2(OH)_2$ - 3.20 Å, dicalcium phosphate $CaHPO_4 \cdot 2H_2O$ - 3.04 Å; monocalcium phosphate $Ca(H_2PO_4)_2 \cdot H_2O$ - 2.00 Å, as well as 2.68 and 1.65 Å, attributed to $CaSO_4 \cdot 2H_2O$ and CaF_2.

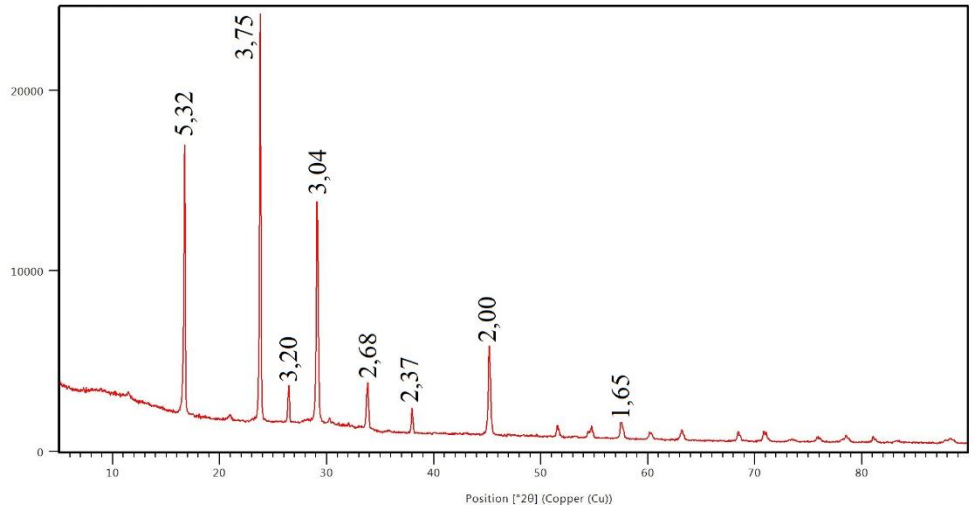

Fig. 1. X-ray of ammophos, pH = 4.1

Figure 2 shows the data of the IR spectrum of ammophos at pH = 4.1

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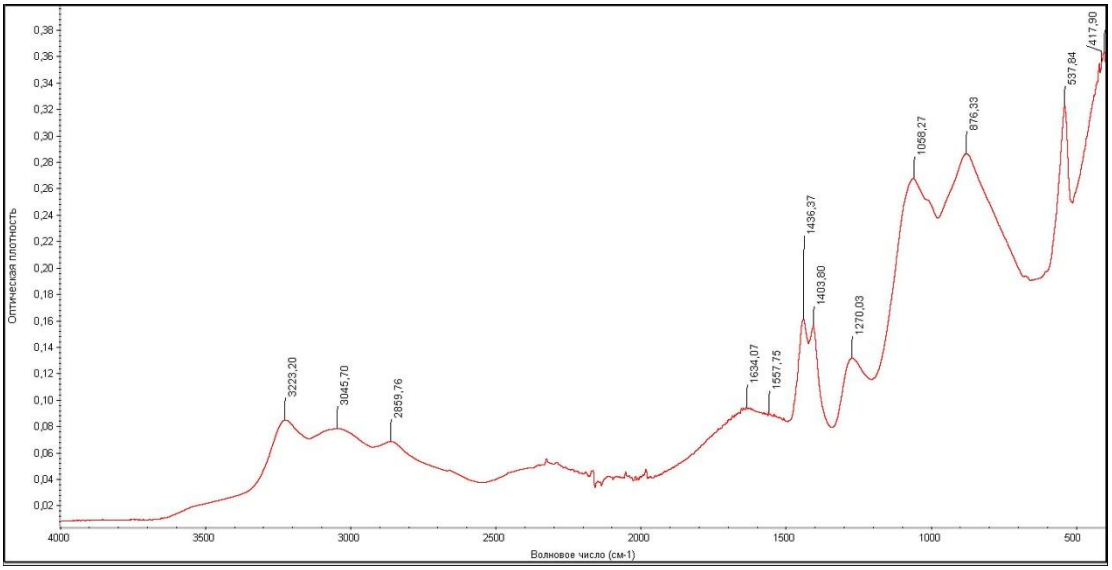
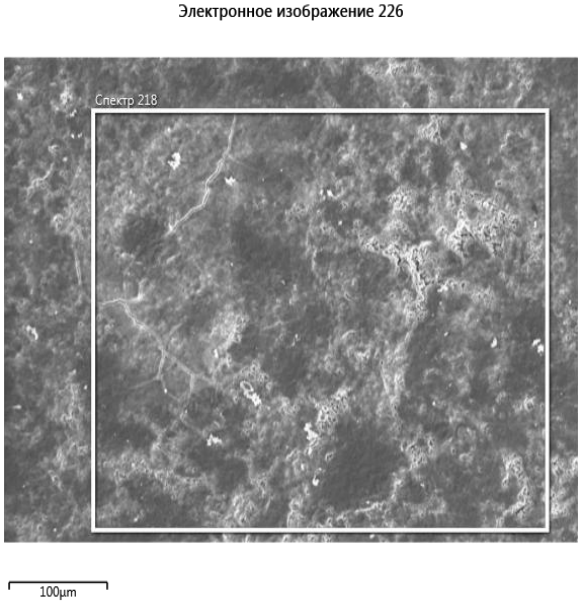


Fig. 2. IR spectrum of ammophos

The results of the IR spectroscopic studies show that the IR spectra of the main ammophos and the impurity coincide in the absorption bands of certain groups. For example, in the range of 1650-1590 cm^{-1}, plane deformation vibrations of the NH and NH_2 groups are observed, bands in the region of 1600-1400 cm^{-1} correspond to deformation vibrations of NH_3^+, NH_2^+, NH^+.

The IR spectrum of ammophos has wide bands in the region of 876.33-1058.27 cm^{-1} PO_4^{2-} and bands appear at 1634.07 cm^{-1}, related to $CaSO_4{=}2H_2O$. The absorption bands at 2859.76-3223.20 cm^{-1} correspond to crystallization water.

Electron microscopic analysis of ammophos, the results of elemental chemical analysis are shown in figure 3. Energy dispersion analysis of ammophos showed the following element content: N-9.74%; O-46.38%, F-2.49%; Na-0.08%; Mg-2.68%; Al-1.17%; Si-0.26%; P-23.13%; S-1.02%; Ca-12.54%; Fe-0.51%, which corresponds to the requirement for ammophos.



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Element	The weight.%	Sigma Wt.%
N	9.74	0.68
O	46.38	0.37
F	2.49	0.34
Na	0.08	0.08
Mg	2.68	0.17
Al	1.17	0.17
Si	0.26	0.07
P	23.13	0.26
S	1.02	0.18
Ca	12.54	0.16
Fe	0.51	0.17
Sum:	100.00	

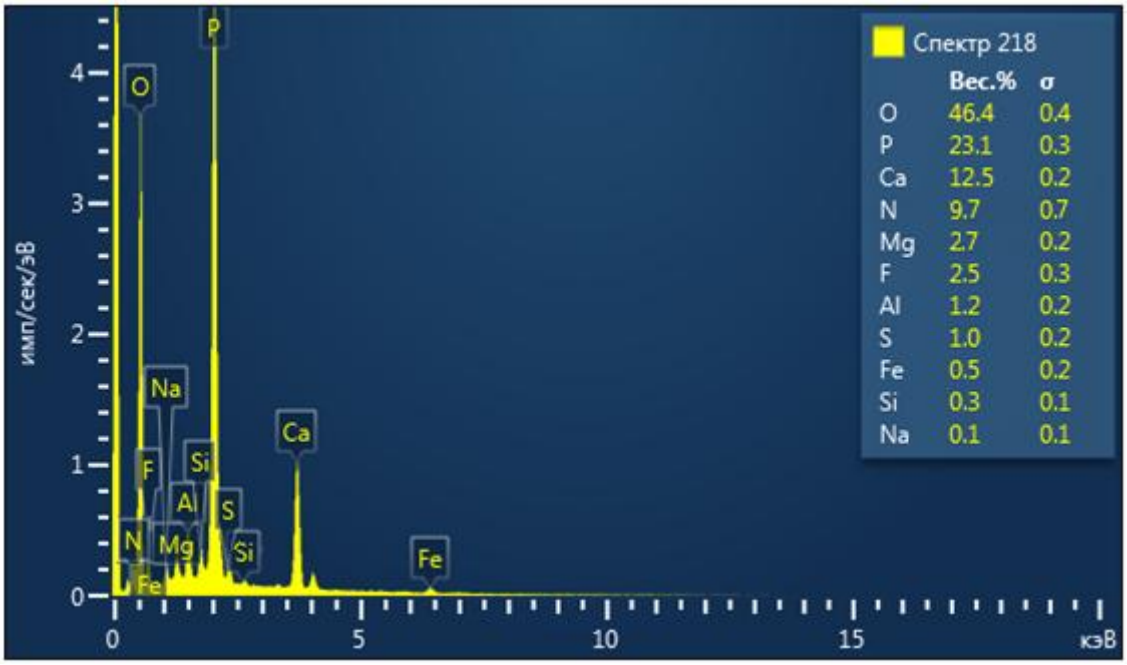

Fig. 3 - Energy dispersion analysis of ammophos, pH = 4.1

Thus, the possibility of obtaining ammophos has been experimentally established, optimal parameters of all stages of the process have been determined, and its physico-chemical properties have been clarified.

V. CONCLUSION

Thus, the conducted studies have shown the possibility of processing ES WBPC EPA into nitrogen-phosphorus fertilizer with a low content of nitrogen, sulfates and fluorine in contrast to ammophos, and, accordingly, increase the content of P_2O_5. The physico-chemical characteristics of ammophos have been studied by methods of physico-chemical analysis using radiography, IR spectroscopy and scanning electron microscopy.

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