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Research of the Process of Obtaining Ammophosphate on the Basis of Enrichment Solution from Central Kyzylkum Phosphorites with Extraction Phosphoric Acid

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ABSTRACT: Development of a technology for the production of ammophosphate based on enrichment solutions obtained from phosphorites of the Central Kyzylkum with solutions of extraction phosphoric acid with a high content of nutrients in a water-soluble form. The optimal conditions for the process of enrichment of the washed burnt phosphate concentrate of the Central Kyzylkum with solutions of extraction phosphoric acid were found and the mutual influence of the process parameters was established: S:L = 1:6, temperature - 25°C and mixing time - 30-40 minutes, at which there is no transition of washed burnt phosphate concentrate into enrichment solutions, a decrease in the calcium module from 2.2 to 1.56 is noted. This makes it possible to obtain ammophosphate from solutions of phosphoric acid enrichment of the washed burnt phosphate concentrate.

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 the Central Kyzylkum (CK) [1, 2]. The enterprises receive washed burnt phosphate concentrate (WBPC) of CK with a P_2O_5 content of at least 26.0% P_2O_5 [3]. A distinctive feature of WBPC from other types of phosphate raw materials is a high calcium module of 1.9-2.3 and the presence of up to 17% free calcium oxide in its composition. The main one is the high consumption (4.5 tons per 1 ton of P_2O_5) of sulfuric acid in the production of extraction phosphoric acid (EPA). In the production of EPA, free calcium oxide contributes to an increase in the temperature of the decomposition process in the extractor to 95–100°C

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and higher, which activates the corrosivity of phosphoric acid and leads to the formation of calcium sulfate hemihydrate agglomerates that clog the extractor [4].

Numerous publications are devoted to studies of the processes of enrichment of phosphorites with CK [5–10]. All work was mainly carried out with phosphate ore, the use of mineral and organic acids, the formation of large-tonnage enrichment solutions and did not find application in industrial conditions. Therefore, our research is aimed at enrichment of WBPC, the supplied volumes of which are several times less than the mined ore.

III. RESEARCH METHODS

For experimental work, EPA, unenriched phosphate raw materials (UPRM), WBPC, gaseous ammonia, enrichment solution (ES) were used. The chemical composition of the raw materials used is shown in table 1.

Table 1 - The chemical composition of the raw materials used in the work

Reagent	Chemical composition, wt. %						
	P_2O_5	CaO	MgO	Al_2O_3	Fe_2O_3	SO_3	F
EPA	17,98	0,31	1,12	1,12	0,93	2,32	1,0
ES	17,32	4,10	1,48	0,75	0,21	0,81	0,83
UPRM	17,65	47,48	1,75	1,21	2,47	2,65	1,81
WBPC	26,20	57,70	0,60	0,60	0,43	3,78	2,84

The beneficiation process was carried out at S:L = 1:6, the duration of pulp mixing for 30-40 minutes and a temperature of 25°C, followed by the separation of the beneficiation pulp into a thickened sediment of a large WBPC fraction and a suspension of EPA and fine particles by decantation. The enriched solid and liquid phases were analyzed for the content of P_2O_5 by photocolorimetric, CaO by complexometric methods.

To identify the phase composition of initial and intermediate substances, finished products, in addition to chemical [11–13] and physicochemical (X-ray phase, IR spectroscopic and scanning electron microscopic methods) analysis [14–16].

X-ray diffraction patterns of the samples were taken on an XRD-6100 apparatus (Shimadzu, made in Japan) with computer control [14]. 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-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 [15].

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 [16]. 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.

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IV. EXPERIMENTAL RESULTS

In the study, the influence of the mass ratio of ES : PRM and pH of the pulp on water-soluble ammophosphate was studied. The effect at different mass ratios of ES : PRM and pH on the basis of an enrichment solution obtained from phosphorites of CK on the chemical composition and properties of ammophosphate was also studied. The experiments were carried out as follows: phosphorites were introduced at 70°C into the reactor with a sample of enrichment solution, neutralization with gaseous ammonia. Two parameters were varied: the mass ratio of ES : PRM (in g) from 100 : 5 to 100 : 25 and the pH of the ammophosphate pulp.

In the production of ammophosphate, the neutralization of phosphoric acid is carried out stepwise with solid and gaseous (liquid) components.

At the first stage, EPA is partially neutralized with phosphorite, and at the second stage, with ammonia. The composition of ammophosphate will depend on the proportion of phosphoric acid that is neutralized by phosphate. Therefore, the less acid is neutralized by phosphate, the more ammonia is required for its final neutralization. With an increase in the amount of phosphorite in the first stage, the nitrogen content in the finished product decreases and the proportion of calcium and magnesium phosphates increases.

The main component of the solid phases of ammoniated pulps is ammonium dihydrogen phosphate. The pulp also contains magnesium dihydro- and hydrophosphate. The sesquioxides of iron and aluminum are bound into complex complex compounds.

An important advantage of the ammophosphate technology is the possibility of its production on the basis of existing equipment for the production of ammophos. In this regard, experiments were carried out to obtain ammophosphate from phosphate solutions of enrichment (ES). To do this, enrichment solutions, as well as enrichment solutions into which UPRM and WBPC were additionally introduced to a total ratio of ES:PRM equal to 100 : (5 ÷ 25), were ammoniated to pH 3.5-4.5. Then the chemical composition of the suspension was determined by known methods (table 2).

Table 2 - Chemical composition of ammophosphate suspension obtained from enrichment solutions

№	Mass ratio of ES : PRM	pulp pH after ammonization.	Chemical composition of the suspension, wt. %							
			P_2O_5	N	CaO	MgO	SO_3	Al_2O_3	Fe_2O_3	F
UPRM										
1	100 : 5	4,37	17,58	3,58	6,06	1,47	0,89	0,77	0,23	0,90
2	100 : 10	4,10	17,82	2,95	7,88	1,46	0,96	0,80	0,26	0,97
3	100 : 15	3,92	18,02	2,54	9,56	1,44	1,06	0,81	0,28	1,04
4	100 : 20	3,79	18,28	2,34	11,13	1,42	1,11	0,83	0,30	1,09
5	100 : 25	3,54	18,44	1,83	12,60	1,40	1,16	0,84	0,32	1,15
WBPC										
6	100 : 5	4,28	17,75	3,31	6,65	1,44	0,95	0,71	0,24	0,91
7	100 : 10	4,05	17,96	2,87	8,89	1,39	1,07	0,72	0,27	0,99
8	100 : 15	3,87	18,24	2,45	10,95	1,35	1,18	0,73	0,30	1,07
9	100 : 20	3,74	18,41	2,30	12,77	1,31	1,28	0,74	0,31	1,12
10	100 : 25	3,51	18,59	1,81	14,22	1,28	1,34	0,74	0,33	1,18

The manufacturability and efficiency of the implementation of individual stages of the process of obtaining a suspension of ammophosphate is largely determined by the rheological characteristics of the intermediate suspensions.

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The most important, from the point of view of the possibility of transporting the suspension to the stage of decomposition and neutralization, are the density and viscosity of the resulting suspension. In this regard, the influence of the mass ratio of ES : PRM, the degree of ammoniation and temperature on the density and viscosity of the suspension was studied.

The mass ratio of ES : PRM was varied from 100 : 5 to 100 : 25, and the temperature from 20 to 80°C. Experimental data is presented in tables 3.

Table 3 shows the rheological properties of the ammophosphate slurry.

Table 3 - Influence of ES : PRM mass ratio and temperature on the density and viscosity of ammophosphate suspension

№	Mass ratio ES : PRM	Density, g/cm^3				Viscosity, mPa·s			
		20°C	40°C	60°C	80°C	20°C	40°C	60°C	80°C
UPRM									
1	100 : 5	1,267	1,256	1,248	1,244	3,243	2,265	1,491	1,260
2	100 : 10	1,324	1,312	1,303	1,300	3,603	2,516	1,657	1,399
3	100 : 15	1,383	1,371	1,362	1,359	6,332	4,256	2,913	2,365
4	100 : 20	1,438	1,425	1,416	1,413	9,062	5,995	4,168	3,332
5	100 : 25	1,484	1,471	1,462	1,459	12,091	7,999	5,562	4,445
WBPC									
6	100 : 5	1,272	1,315	1,307	1,309	3,238	2,259	1,482	1,255
7	100 : 10	1,330	1,376	1,366	1,367	3,597	2,510	1,646	1,386
8	100 : 15	1,390	1,433	1,420	1,422	6,326	4,249	2,901	2,349
9	100 : 20	1,446	1,482	1,470	1,468	9,055	5,982	4,152	3,305
10	100 : 25	1,494	1,531	1,519	1,470	12,079	7,985	5,539	4,404

With a decrease in the mass ratio of ES : UPRM from 100 : 5 to 100 : 25 of the suspension, the density and viscosity increase slightly and at a temperature of 20 °C are 1.267-1.484 g/cm^3 and 3.243-12.091 mPa•s, respectively.

Increasing the temperature of the suspension leads to a decrease in the density and viscosity of the suspension. At a mass ratio of ES : UPRM of 100 : 5, an increase in temperature from 20 to 80 °C reduces the density from 1.267 g/cm^3 to 1.244 g/cm^3, and the viscosity under these conditions - from 3.243 mPa•s to 1.260 mPa•s. This indicates acceptable rheological properties of the ammophosphate slurry.

The results of the analysis of the chemical compositions of the products are shown in table 4.

Table 4 - Composition of ammophosphate obtained from enrichment solutions

№	Mass ratio ES : PRM	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		
UPRM													
1	100 : 5	47,53	47,01	41,15	9,44	16,38	3,98	2,42	1,99	0,62	2,43	98,91	86,58
2	100 : 10	45,51	44,57	35,28	7,12	20,13	3,74	2,46	2,02	0,66	2,48	97,94	77,52
3	100 : 15	44,93	43,62	33,16	6,05	23,83	3,61	2,58	2,05	0,69	2,54	97,08	73,80
4	100 : 20	43,97	41,60	31,22	5,40	26,81	3,47	2,66	2,08	0,71	2,60	94,61	71,00
5	100 : 25	43,54	40,88	30,18	4,29	29,75	3,38	2,73	2,10	0,75	2,63	93,89	69,32
WBPC													
6	100 : 5	48,89	48,34	42,25	8,38	18,35	3,96	2,63	2,05	0,58	2,54	98,87	86,42
7	100 : 10	47,15	46,18	36,55	6,89	23,36	3,65	2,82	2,08	0,59	2,64	97,94	77,52

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8	100 : 15	46,84	45,47	34,57	5,82	28,13	3,46	3,04	2,11	0,60	2,75	97,07	73,81
9	100 : 20	46,21	43,72	31,76	5,31	32,04	3,28	3,22	2,15	0,61	2,86	94,61	68,73
10	100 : 25	45,80	43,21	30,83	4,12	34,15	3,19	3,29	2,19	0,62	2,97	94,34	67,32

It can be seen from the table that a decrease in the ES:PRM ratio from 25:1 to 5:1 leads to a decrease in the content of all forms of P_2O_5. If the values of total and assimilable P_2O_5 are close, then the content of the aqueous form decreases sharply with a decrease in the ratio. This suggests that monocalcium phosphate and sesquioxides formed as a result of decomposition in solution form sparingly soluble compounds.

So monocalcium phosphate partially turns into dicalcium phosphate.

The conducted studies on the processing of enrichment solutions for ammophosphate show the possibility of utilizing solutions of phosphoric acid enrichment of WBPC with obtaining a phosphate fertilizer of prolonged action.

Thus, the conducted studies have shown the fundamental possibility of processing phosphoric acid enrichment solutions into concentrated phosphate fertilizers.

To conduct research on the physicochemical properties, ammophosphate was obtained from ES : WBPC and by neutralization with ammonia (mass ratio of ES : WBPC from 100:5 to 100:25 and pH = 3.5-4.5).

To check the resulting ammophosphate, an X-ray diffraction pattern was taken (fig. 1). On the X-ray pattern there are only diffraction maxima characteristic of ammophosphate with interplanar distances of 5.32; 3.75; 2.37 Å $NH_4H_2PO_4$, 3.16 Å $FeAlF_5$, 3.01; 2.95; 2.00 Å $Ca(H_2PO_4)_2\ H_2O$, 2.65 Å $MgNH_4PO_4\ 6H_2O$ and 1.60 Å $CaHPO_4$.

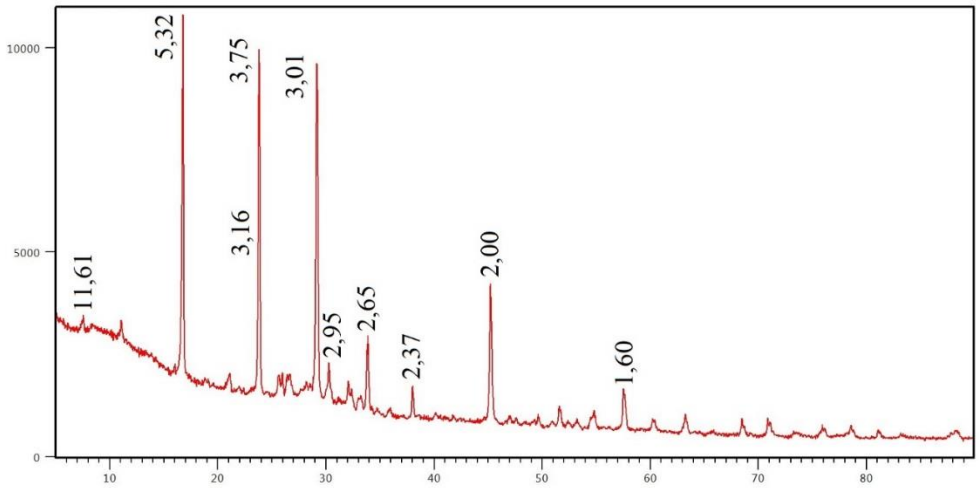

Fig. 1. X-ray pattern of ammophosphate (mass ratio ES : WBPC = 100 : 5, pH = 4.3).

Figure 2 shows the data of the IR spectrum of ammophosphate at a mass ratio of ES : WBPC = 100 : 5, pH = 4.3.

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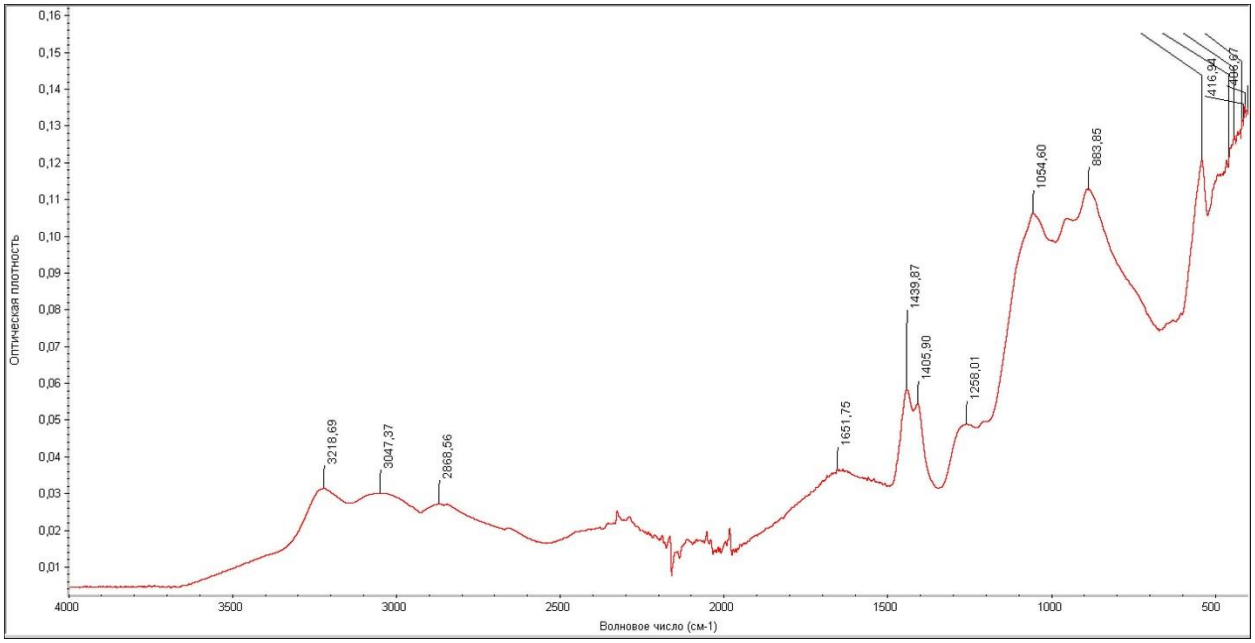
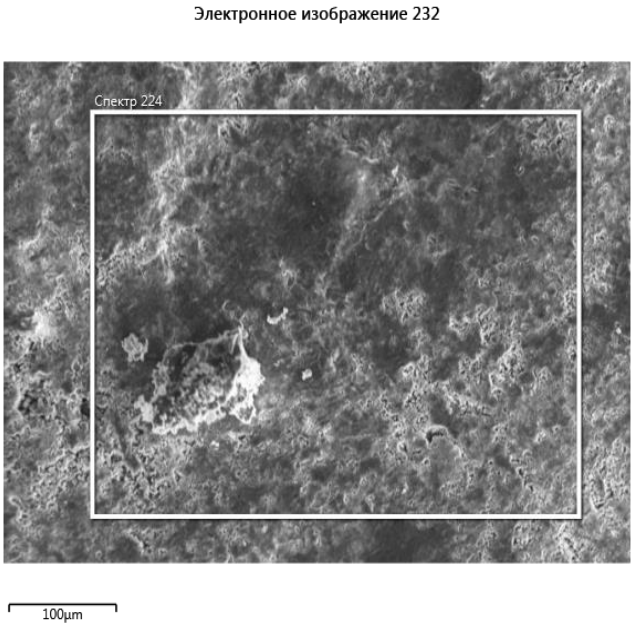


Fig. 2. IR spectrum of ammophosphate

The IR spectrum of ammophosphate contains broad bands in the region of 883.85-1054.60 cm^{-1} $PO4^{2-}$, the band at 1405.90-1439.87 cm^{-1}, characteristic of nitrogen compounds, remains, and bands appear at 1651.75 cm^{-1} related to $CaSO_4 \cdot 2H_2O$.

Electron microscopic analysis of fertilizer ammophosphate, the results of elemental chemical analysis are shown in figure 3. Energy dispersive analysis of ammophosphate showed the following element content: N-11.02%; O-46.28%, F-2.58%; Na-0.09%; Mg-2.48%; Al-1.19%; Si-0.06%; P-22.21%; S-1.03%; Ca-12.54%; Fe-0.52%, which meets the requirement for ammophosphate.



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Element	The weight.%	Sigma Wt.%
N	11.02	0,72
O	46.28	0.25
F	2.58	0.24
Na	0.09	0.05
Mg	2.48	0.05
Al	1.19	0.05
Si	0.06	0.05
P	22.21	0.18
S	1.03	0.05
Ca	12.54	0.12
Fe	0.52	0.12
Sum:	100.00	

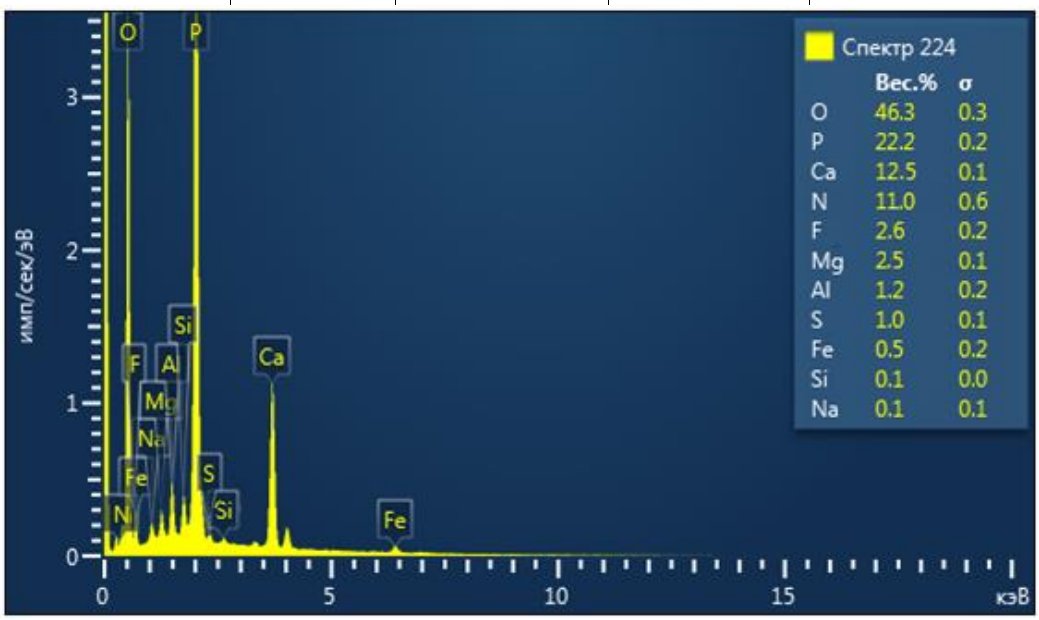

Fig. 3 - Energy dispersive analysis of ammophosphate (mass ratio ES : WBPC = 100 : 5, pH = 4.3).

Thus, the possibility of obtaining ammophosphate was established experimentally, the optimal parameters of all stages of the process were determined, and its physicochemical properties were clarified.

V. CONCLUSION

The process of obtaining ammophosphate based on enrichment solution, phosphate and ammonia with a relatively high content of water-soluble phosphorus has been studied. The effects of pH and the mass ratios of the components ES : PRM the content of water-soluble forms of calcium, phosphorus, nitrogen were studied and their optimal parameters were established, at which (mass ratios ES : PRM = 100 : (5 ÷ 25), pH - 3.5 - 4.5 , temperature - 70°C and stirring time - 30 minutes) the resulting dried ammophosphate has the following composition (wt.%): $P_2O_{5gener.}$ - 43.54-48.89; $P_2O_{5assim.}$ - 40.88-48.34; P_2O_{5water} - 30.18-42.25; N - 4.12-9.44; CaO - 16.38-34.15; MgO - 3.19-3.98; Al_2O_3 - 1.99-2.19; Fe_2O_3 - 0.58-0.75; SO_3 - 2.42-3.29; F - 2.43-2.97.

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