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Obtaining High-Quality Monoammonium Phosphate from the Enrichment Solutions of Washed Burnt Phosconcentrate of Central Kyzylkums

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ABSTRACT: The results of researchers on the processing of solutions of enrichment of washed burnt phosphor concentrate of Central Kyzylkums with extraction phosphoric acid at their ratio of 1 : (5 and 6) for high-quality monoammonium phosphate are presented. It is shown that in order to obtain monoammonium phosphate of feed purity, it is necessary to ammonify the enrichment solutions to a pH of 4.4-5.1, separate the liquid and solid phases, evaporate and dry the liquid phase. In this case, monoammonium phosphate is obtained with a content of 57.36-58.61% P_2O_5 and 0.038-0.047% fluorine. Subsequent recrystallization makes it possible to obtain monoammonium phosphate with a content of 99.5%, no more than 0.30% sulfates and no more than 0.01% fluorine.

I. INTRODUCTION

Ammonium phosphates are used in the food and pharmaceutical industries, they are used as flame retardants for the impregnation of fabrics, wood and building materials in order to make them fire resistant. Special methods have been developed for growing large crystals of monosubstituted ammonium phosphate used in electronic engineering. Ammonium phosphates are most widely used in agriculture as complex nitrogen-phosphorus fertilizers.

II. LITERATURE SURVEY

Ammophos, diammophos, salts of phosphoric acid are obtained by neutralizing the extraction phosphoric acid with gaseous ammonia. Due to the fact that extraction phosphoric acid is highly contaminated with impurities, it is processed mainly into fertilizers and only partially into feed phosphates and technical salts of phosphoric acid [1, 2].

Phosphorus is an essential element for the human body, animals, fish, and plants. The most important mineral elements in the diet of animals, in addition to phosphorus, are calcium, sodium, nitrogen, chlorine, etc. The range of mineral supplements includes more than ten items [3, 4]. Calcium, sodium and ammonium phosphates are predominantly used. In winter, when plant foods contain a lot of calcium in case of phosphorus deficiency, ammonium phosphates containing nitrogen make up for the lack of protein in animal diets and improve the balance of phosphorus and other indicators of phosphorus metabolism.

In the Republic of Uzbekistan, the production of feed ammonium phosphates at JSC Ammofos-Maxam with a low content of toxic fluorine compounds, which is on the verge of the maximum permissible concentration and a high

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content of sulfate compounds, has been mastered. Therefore, studies aimed at reducing the fluorine content and increasing phosphoric anhydride in feed ammonium phosphates are relevant.

Uzbekistan has a powerful base for the production of phosphorus-containing fertilizers from phosphorites of Central Kyzylkums (CK). However, due to the lack of the required amount of high-quality phosphate raw materials, the capacities are not loaded enough. The Kyzylkum phosphorite Combine supplies only 716 thousand tons of washed burnt phosphor concentrate (WBPC) for the production of ammophos. After enrichment, washing, calcination, the yield of high-quality raw materials is 58%, which contains at least 26.0% P_2O_5 and has a calcium modulus ($CaO:P_2O_5$) from 1.9 to 2.15. Processing of such cheeses requires a large consumption of acid reagent compared to Karatau phosphorites and apatite. In addition, the resulting ammophos contains 46-48% P_2O_5, which is associated with the transition of accompanying impurities of phosphorite into extraction phosphoric acid (EPA) and the presence of sulfuric acid in excess, against stoichiometry during extraction. All this leads to an increase in the cost of the P_2O_5 unit in fertilizer.

One of the ways to reduce the cost of phosphorus-containing fertilizers is to reduce the calcium modulus of phosphate raw materials, or in other words, its enrichment.

The most common method of enrichment of phosphorous ore is flotation. But the Kyzylkum phosphorites, along with a high degree of carbonation, are characterized by thin germination of a phosphate mineral with calcite, and therefore flotation does not give the desired result.

Many works are devoted to the enrichment of phosphorite ore by acidic methods. However, none of the acidic enrichment methods has found application, which is explained by the significant consumption of reagents, the formation of large quantities of enrichment solutions.

To obtain enrichment solutions suitable for further use in the production of phosphoric fertilizers and phosphoric acid salts, studies have been conducted on the enrichment of WBPC with extraction phosphoric acid. In this case, enrichment solutions (ES) are formed with a low content of sulfates, fluorine, compared with the initial EPA, and containing calcium in the form of monocalcium phosphate.

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. For this purpose, the WBPC of the Central Committee of the composition (wt. %): 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.

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 [5–7].

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IV. EXPERIMENTAL RESULTS

During ammonization of ES obtained at the ratio WBPC:EPA equal to 1 : (5 and 6) to pH 4.5 content of P_2O_{5assim}. It is 48.29-49.65%, nitrogen 10.64-11.03%, CaO 11.45-11.82. The ratio of $P_2O_{5\ water}$ to $P_2O_{5\ general.}$ it is equal to 62.13-64.84% with a content of assimilable forms of P_2O_5 of more than 99.2%. Unlike ammophos from EPA, the content of P_2O_5 increases by 2-4%, nitrogen remains 9-10%, sulfates decreases to 2.31-2.71%, fluorine to 2.19-2.27%, and the content of calcium oxide is 11.45-11.82%. At the same time, the fertilizer is enriched with calcium. The direct use of ES for the production of ammophos does not allow to obtain a more concentrated P_2O_5 fertilizer. To obtain a higher quality of ammophos, the ES was ammoniated to a pH of 4.4, 4.8, 5.1, the liquid and solid phases were separated, followed by their processing into phosphorus-containing fertilizers. Table 2 shows the chemical compositions of the initial EPA and suspensions of ammophos obtained from ES at a ratio of WBPC:EPA 1:(5 and 6) depending on pH.

Table 2 The effect of the degree of ammonization on the chemical composition of the suspension of monoammonium phosphate

no	pH pulp	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	4,4	16,35	3,54	3,85	1,41	0,80	0,71	0,20	0,79
2	4,8	16,31	3,73	3,83	1,39	0,79	0,70	0,20	0,78
3	5,1	16,28	3,92	3,82	1,38	0,78	0,69	0,20	0,77
The enrichment solution obtained at S:L =1:6									
4	4,4	16,69	3,68	3,95	1,43	0,78	0,72	0,20	0,78
5	4,8	16,67	3,84	3,94	1,42	0,77	0,71	0,20	0,76
6	5,1	16,64	4,00	3,93	1,41	0,76	0,70	0,19	0,75

The table shows that during ammonification, the contents of all ES components decrease slightly, and the nitrogen content ranges from 3.54% to 4.00%.

A filtration unit was used to separate the liquid and solid phases. The effect of pH 4.4, 4.8 and 5.1, temperature 20, 40, 60 and 80°C on the filtration rate was studied. The data obtained are shown in table 3.

Table 3 Influence of the degree of ammonization and temperature on the filtration rate of neutralized solutions enrichment

no	pH	Temperature, °C	Filtration rate, $kg/m^2 \cdot h$		
			by pulp	by solid phase	by filtrate
The enrichment solution obtained at S:L =1:5					
1	4,4	20	625.67	180.19	445,48
		40	677.97	195.25	482.72
		60	702.93	202.44	500.49
		80	732.75	220.03	512.72
2	4,8	20	574.00	165.31	408.69
		40	621.99	179.13	442.86
		60	644.89	185.73	459.16
		80	671.83	193.49	478.34
3	5,1	20	545.30	157.04	388.26
		40	590.89	170.18	420.71
		60	612.65	176.45	436.20
		80	638.56	183.91	454.65

The enrichment solution obtained at S:L =1:6					
1	4,4	20	672,76	193,75	479,01
		40	729,00	209,95	519,05
		60	755,84	217,68	538,16
		80	787,90	226,91	560,99
2	4,8	20	617,21	177,76	439,45
		40	668,81	192,62	476,19
		60	693,43	199,71	493,72
		80	722,40	208,05	514,35
3	5,1	20	586,35	168,87	417,48
		40	635,37	182,99	452,38
		60	658,76	189,72	469,04
		80	686,62	197,75	488,87

The table shows that with an increase in the pH of ammoniated enrichment solutions, the filtration rate decreases. So, at a temperature of 20°C at pH 4.4, the filtration rate is 672.76 kg/m^2·h, at pH 4.8 617.21 kg/m^2·h and at pH 5.1 586.35 kg/m^2·h, which is explained by an increase in the mass of sediment falling with an increase in pH and the dispersion of the sediment

An increase in temperature increases the filtration rate of ammoniated enrichment solutions for all pH values.

The most important, from the point of view of the possibility of transporting the pulp at the stage of neutralization, granulation and drying, are the density and viscosity of the resulting solutions and pulps. In this regard, the influence of the degree of ammonization and temperature on the density and viscosity of pulps and purified solutions obtained by neutralization of enriched solutions obtained at a ratio of S:L = 1:6. The results obtained are shown in tables 6 and 7.

Table 6 Effect of pH and temperature on the density and viscosity of pulps of ammoniated enrichment solutions obtained at S:L=1:6

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								
4,4	1.218	1.216	1.215	1.214	9.49	4.25	2.69	1.68
4,8	1.223	1.222	1.220	1.218	9.67	4.74	2.92	1.77
5,1	1.227	1.225	1.224	1.222	9.93	5.76	3.24	1.92
The enrichment solution obtained at S:L =1:6								
4,4	1,223	1,221	1,220	1,219	9,53	4,27	2,71	1,69
4,8	1,228	1,227	1,225	1,223	9,71	4,76	2,93	1,78
5,1	1,232	1,230	1,229	1,227	9,97	5,78	3,26	1,93

Pulp density and viscosity increase with increasing pH and decrease with increasing temperature. Pulp density with an increase in pH from 4.4 to 5.1 will increase from 1,223 g/cm^3 to 1,232 g/cm^3 at a temperature of 20°C, and with an increase in temperature from 20°C to 80°C decreases from 1,223 g/cm^3 to 1,219 g/cm^3. Pulp viscosity at these parameters increases from 9.53 MPa·s to 9.97 MPa·s and decreases from 9.53 MPa·s to 1.69 MPa·s (table 4).

Based on the data in table 4, regression equations were constructed describing the dependence of the density (1) and viscosity (2) of monoammonium phosphate pulp based on enriched solutions from WBPC and EPA on pH and temperature:

$$\rho = 1{,}2070+0{,}0016\cdot pH+0{,}0004\cdot(pH)^2-0{,}0001\cdot t, \qquad (1)$$

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$$\mu = -3,7916+3,1686\cdot P_H+0,1200\cdot t+17,4696\cdot \log(t)-0,8106\cdot \log(pH)-$$

$$-0,2631\cdot t\cdot \log(pH)-1,9122\cdot pH\cdot \log(t)+0,0782\cdot pH\cdot t \quad (2)$$

The accuracy of the approximation was 0.9939 and 0.9918, respectively, for regression equations (1) and (2).

The nature of the effect of pH and temperature on the density and viscosity of solutions after separation of the solid phase is similar to the effect on the density and viscosity of ammoniated pulps. Densities vary in the range of 1,203 - 1,231 g/cm^3, viscosity from 1.15 to 3.68 MPa·s (table 7).

Table 7 The effect of pH and temperature on the density and viscosity of purified monoammonium phoshpate solutions, obtained from an enrichment solution at S:L=1:6

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								
4,4	1.214	1.209	1.204	1.198	3.39	2.18	1.48	1.14
4,8	1.219	1.213	1.207	1.202	3.54	2.26	1.53	1.18
5,1	1.226	1.220	1.215	1.209	3.66	2.34	1.61	1.21
The enrichment solution obtained at S:L =1:6								
4,4	1,219	1,214	1,209	1,203	3,41	2,18	1,49	1,15
4,8	1,224	1,218	1,212	1,207	3,56	2,27	1,54	1,19
5,1	1,231	1,225	1,220	1,214	3,68	2,35	1,62	1,22

Under the conditions of obtaining monoammonium phosphate - pH 4.5-5, the density of ammoniated enriched solutions with an increase in temperature from 20^{o}C to 80^{o}C decreases from 1.224 g/cm^3 to 1.207 g/cm^3, while the viscosity decreases from 3.56 MPa·s to 1.19 MPa·s.

Based on the data in table 4, regression equations were constructed describing the dependence of the density (3) and viscosity (4) of ammonium phosphate solutions formed after separation of the precipitate during ammonification based on enriched solutions from WBPC and EPA on pH and temperature:

$$\rho = 1,2164-0,0002\cdot pH+0,0005\cdot (pH)^2-0,0003\cdot t, \quad (3)$$

$$\mu = 1,7790+0,9569\cdot pH+0,0325\cdot t+2,4751\cdot \log(t)-0,7286\cdot \log(pH)-$$

$$-0,0518\cdot t\cdot \log(pH)-0,3234\cdot pH\cdot \log(t)+0,\cdot 0125\cdot pH\cdot t \quad (4)$$

The approximation confidence value was 0.9935 and 0.9944 for regression equations (7) and (8), respectively.

The liquid phase represents the sable nothing and as a solution of monoammonium phosphate purified from accompanying impurities.

The resulting solutions are very diluted (density at 20°C is 1,220 - 1,240 g/cm^3) and they must be concentrated for drying and granulation. The clarified phosphate-ammonia solutions were evaporated on a vacuum evaporation unit at a temperature of 100 - 105°C until a solution density of 1.3 - 1.4 g/cm^3 (60-80% $NH_4H_2PO_4$) was reached.

Monoammonium phosphate salts obtained on the basis of these solutions contain, after drying, 57.36 - 58.61% P_2O_5, 11.18 - 11.72% nitrogen and 0.038 - 0.047% fluorine depending on the pH of the initial solution (table 4).

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Table 4 Influence of the degree of ammonization on the chemical composition of the monoammonium phosphate solution

no	pH	Chemical composition suspension, wt. %					
		P_2O_5	N	CaO	MgO	SO_3	F
The enrichment solution obtained at S:L =1:5							
1	4,4	57,36	11,18	0,51	0,31	0,28	0,047
2	4,8	58,45	11,61	1,19	0,87	0,75	0,042
3	5,1	58,49	11,69	0,98	0,77	0,69	0,040
The enrichment solution obtained at S:L =1:6							
4	4,4	57,43	11,23	0,45	0,28	0,24	0,045
5	4,8	58,53	11,67	1,50	0,93	0,72	0,041
6	5,1	58,61	11,72	1,13	0,81	0,67	0,038

In terms of fluorine content, the product meets the requirements for feed ammonium phosphate (no more than 0.2%) and does not meet the requirements of the European Standard (no more than 0.02%). However, the resulting monoammonium phosphate meets the requirements for fertilizers for drip irrigation.

To obtaining monoammonium phosphate of higher qualification, a deeper purification of ammonium dihydrophosphate was carried out by recrystallization.

The essence of the method consists in evaporation of a monoammonium phosphate solution to a concentration of 60-80%, followed by cooling of the solution to a temperature of 20-25°C, separation of monoammonium phosphate crystals and drying.

As a result, transparent, needle-like crystals containing at least 99.5% monoammonium phosphate, no more than 0.3% sulfate ions and no more than 0.01% fluorine were obtained.

The solid phase, after separation of the ammoniated suspension, contains phosphates of ammonium, calcium, oxides and a half, fluorine, which can be used as a slow-acting fertilizer. By composition, it contains monoammonium phosphate, dicalcium phosphate, iron and aluminum phosphates (table 5).

Table 5 The effect of pH on the chemical composition of sediments isolated from ammoniated enrichment solutions after washing and drying.

no	pH pulp	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	4,4	40,69	8,97	14,99	5,51	2,95	2,67	0,73	3,19
2	4,8	41,52	10,13	15,76	5,56	3,01	2,98	0,81	3,21
3	5,1	42,93	11,08	15,97	5,64	3,04	3,01	0,83	3,23
The enrichment solution obtained at S:L =1:6									
4	4,4	40,11	9,24	15,89	5,67	2,81	2,75	0,76	3,13
5	4,8	41,39	10,39	16,07	5,61	2,92	3,02	0,85	3,24
6	5,1	42,85	11,23	16,25	5,72	2,97	3,08	0,87	3,25

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V. CONCLUSION

The process of obtaining monoammonium phosphate based on enrichment solution and ammonia with a relatively high content of water-soluble phosphorus has been studied. The effect of pH on the content of water-soluble forms of phosphorus and nitrogen was studied and their optimal parameters were established, at which (pH - 4.8-5.1) the resulting dried monoammonium phosphate has the following composition (wt.%): P_2O_5 - 57.36-58.61; N - 11.18-11.72; F - 0.038-0.047.

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