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Research of the Process of Obtaining Purified Ammonium Phosphates from Phosphorites of Central Kyzylkums

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ABSTRACT: The aim of the study is to develop a technology for processing phosphorites of the Central Kyzylkum for fodder monoammonium phosphate and higher qualification. The results of studies on the deep purification of ammonium phosphates from commercially produced phosphorus-containing products based on phosphorites of the Central Kyzylkum are presented. The influence of the recrystallization process on the purity of the obtained monoammonium phosphate from ammophos, fertilizer monoammonium phosphate and feed ammonium phosphate was studied. It has been shown that to obtain monoammonium phosphates of fodder and higher qualification, it is sufficient to recrystallize fodder ammonium phosphate once, and fertilizer monoammonium phosphate at least twice.

I. INTRODUCTION

Ammonium phosphates are used in the food and pharmaceutical industries, they are used as flame retardants for impregnation of fabrics, wood and building materials in order to make them fire resistant [1]. Special methods have been developed for growing large crystals of monosubstituted ammonium phosphate used in electronic engineering [2]. Ammonium phosphates are most widely used in agriculture as complex nitrogen-phosphorus fertilizers [3–5].

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 [6–8].

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 [9–11]. 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. The Republic has mastered the production of feed ammonium phosphates at JSC "Ammophos-Maxam" with a low content of toxic fluorine compounds, which is on the verge of the maximum permissible concentration and a high content of sulfate compounds. Therefore, studies aimed at reducing the fluorine content and increasing phosphoric anhydride in feed ammonium phosphates are relevant.

In the system of complex assessment of the nutritional value of feed, a special role belongs to protein. The word "protein" comes from the Greek - the first. It really is of paramount importance in the life of animals. The very body of animals, along with other substances, consists of protein. Nitrogen is a building material for the synthesis of proteins, which are the main component of every living organism, as well as animal products: milk, meat, eggs, wool. In addition, many biologically active substances (BAS): enzymes that determine the rate of synthesis and decay processes occurring at the cellular level; hormones involved in the regulation of vital processes are represented by proteins. They are part of the

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Vol. 10, Issue 5, May 2023

immune bodies that determine the protective functions of the body, in the composition of antibiotics. The energy function of the protein is not the main one, since the main source of energy for animals are carbohydrates and fats [12].

In feed and livestock production, all nitrogen-containing substances in the feed, calculated by multiplying the total nitrogen by a factor of 6.25, are called crude protein. The average nitrogen content in crude protein, regardless of the type of feed, is considered to be 16%. Therefore, to determine the content of crude protein in feed, the total nitrogen is multiplied by 6.25, although in other cases this factor may be different. For example, to recalculate nitrogen for protein of fodder wheat grain, a coefficient of 6.25 is used, for food wheat grain - 5.70 [12].

The production of high purity ammonium phosphates is based on the neutralization of phosphoric acid of reactive grades with ammonia [6]. The high cost of purified grades of orthophosphoric acid determines the high final cost of the obtained ammonium phosphates. The use of relatively cheap raw materials, such as products manufactured at JSC "Ammophos-Maxam" from extractive phosphoric acid based on phosphorites of the Central Kyzylkum, will reduce the cost of high-purity ammonium phosphates by several times.

The aim of the work is to study the possibility of deep purification of ammonium phosphates, produced on an industrial scale from phosphorites of the Central Kyzylkum, by the method of successive recrystallization.

III. RESEARCH METHODS

The studies were carried out in a thermostated glass reactor equipped with a mechanical stirrer. The initial 30% solution was prepared from ammophos, fertilizer monoammonium phosphate (MAP-F) and feed ammonium phosphate (FAP) by dissolving in hot distilled water. The resulting pulp was filtered on a Buechner funnel at a residual pressure of 0.08 MPa. The clarified solution was evaporated to a concentration of 40-65% ammonium phosphate with constant stirring and a temperature of 90°C. Further stripped off the solution was cooled to a temperature of 25°C for 1-5 hours with stirring. To obtain transparent, acicular crystals, the filtrate was seeded with ammonium dihydrogen phosphate in an amount of 0.05% of the initial reaction mass to start mass crystallization. After the specified time, the solid phase was separated by filtration and analyzed by known methods [13–15].

IV. EXPERIMENTAL RESULTS

Ammophos, three samples of MAP-F and FAP were used for research. The chemical composition of the ammonium phosphates used is shown in Table 1.

Ammophos contains 46.30% $P_2O_{5tot.}$ and 11.85% nitrogen. The sum of impurities is 17.20%. MAP-F samples contain 51.11 and 53.96% P_2O_{5tot} and 12.05-12.22% nitrogen. The amount of undesirable components is 9.03-12.93%. Feed ammonium phosphate contains 55.81% P_2O_{5tot} and 12.12% nitrogen. The amount of impurities is 2.01%. As can be seen from the above data, only feed ammonium phosphates meet the requirements for fluorine content, the values of which are at the limit of permissible concentration. Secondly, a very low concentration of phosphoric anhydride, due to the high content of sulfates, sesquioxides and fluorine. Therefore, in order to obtain ammonium phosphates corresponding in purity to feed phosphates and of higher qualification, additional purification from impurities, and especially from fluorine, is necessary.

Table 1. Chemical composition of used industrial products

Ammonium phosphate	Chemical composition, wt. %							
	$P_2O_{5tot.}$	N	SO_3	CaO	MgO	Al_2O_3	Fe_2O_3	F
Ammophos	46,30	11,85	7,54	2,15	0,85	1,51	0,95	4,20
MAP-F, sample 1	51,11	12,22	5,95	2,82	0,81	0,67	0,87	1,81
MAP-F, sample 2	52,75	12,15	4,82	2,58	0,63	0,65	0,74	1,64
MAP-F, sample 3	53,90	12,04	3,68	2,17	0,47	0,63	0,88	1,21
FPA	55,81	12,12	1,16	0,08	0,59	-	-	0,18

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To identify the effect of the degree of evaporation of solutions on the yield of the product, a 30% solution of MAP-F, sample 2 was evaporated to a concentration of 40-65% and the yield of crystalline monoammonium phosphate was determined (table 2). Crystallization time 1 hour.

Studies of the effect of the duration of crystallization of stripped off solutions with a ratio of S:L = 1:1 for 1, 2, 3 and 5 hours showed that the duration of crystallization significantly affects the yield of the product. The studies were carried out with MAP-F samples 2 and 3. The data obtained are shown in table 3.

With an increase in the duration of crystallization, the yield of the product increases from 40.75-42.15 to 73.46-76.42%. An increase in the duration of the crystallization process leads to a decrease in the content of P_2O_5 and an increase in the content of fluorine.

Table 2. Influence of the concentration of stripped off solutions on the composition and yield of the product

no	$NH_4H_2PO_4$ concentration, %	Product yield taking into account moisture, %	P_2O_{5tot}, %	F, %
1	40	40,75	59,73	0,062
2	45	47,32	59,78	0,063
3	50	67,91	59,97	0,064
4	55	69,90	59,96	0,064
5	60	72,12	59,12	0,086
6	65	72,53	59,09	0,095

Table 3. Effects of crystallization time on product composition and yield

no	Time, hour.	Wet product yield, %	P_2O_{5tot}, %	F, %
MAP-F, sample 2				
1	1	40,75	59,73	0,062
2	2	57,91	59,57	0,064
3	3	71,53	59,09	0,110
4	5	76,42	59,11	0,160
MAP-F, sample 3				
5	1	42,15	59,52	0,068
6	2	58,20	59,33	0,062
7	3	69,16	59,22	0,080
8	5	73,46	59,22	0,092

The optimal technological parameters for the recrystallization of ammonium phosphates are evaporation of solutions to a concentration of 60%, the duration of crystallization of monoammonium phosphate is at least 3 hours at a cooling temperature of 25°C. In this case, the product yield will be 69.16-71.53%, and the fluorine content will be 0.080-0.110%.

Table 4 shows the results of recrystallization of ammophos, samples of fertilizer MAP-F and FPA, produced at «Ammophos-Maxam» JSC.

During the recrystallization of feed ammonium phosphate, already after one stage of recrystallization, it was possible to obtain a product containing $P_2O_{5tot.}$ - 61.84% and 0.0075% fluorine.

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Vol. 10, Issue 5, May 2023

Table 4 Influence of the recrystallization process on the chemical composition of industrial ammonium phosphates

no	Name of product	Chemical composition, wt. %								Exit, %
		$P_2O_{5total.}$	N	CaO	MgO	Fe_2O_3	SO_3	F	H_2O	
1	Ammophos *	58,00	11,76	0,36	0,41	0,320	4,22	0,510	5,78	45,73
2	Ammophos **	58,71	11,65	0,26	0,40	0,120	2,45	0,340	6,121	38,02
3	Ammophos ***	59,45	11,60	0,21	0,26	0,060	1,26	0,220	5,60	29,15
4	MAP-F, sample 1	59,21	11,63	0,54	0,40	0,041	1,45	0,090	6,99	72,84
5	MAP-F, sample 2	59,72	11,83	0,47	0,71	0,025	0,95	0,085	9,31	71,76
6	MAP-F, sample 3	59,30	11,99	0,46	0,21	0,013	1,18	0,055	7,11	68,21
7	FPA	61,84	12,02	0,024	0,23	0,009	0,21	0,0075	7,08	755,20

* - one recrystallization, ** - two recrystallizations, *** - three recrystallizations

Table 5 Chemical composition of ammonium phosphates after the second stage of MAP-F recrystallization

№	Name of product	Chemical composition, wt. %		
		$P_2O_{5total.}$	N	F
1	MAP-F, sample 1	60,90	11,12	0,020
2	MAP-F, sample 2	61,21	11,64	0,018
3	MAP-F, sample 3	60,83	11,80	0,012

After the first stage of recrystallization from fertilizer MAP, ammonium phosphates were obtained with a content of $P_2O_{5tot.}$ - 59.2-59.7% and less than 0.1% fluorine.

After one stage of recrystallization of ammophos, the content of $P_2O_{5tot.}$ is 58%, and the fluorine content is 0.51%, which does not meet the requirements for feed phosphates. Therefore, ammophos was recrystallized. After three repeated recrystallizations of ammophos, it was not possible to achieve fodder purity. The fluorine content is 0.22%.

The yield of the product during purification of the fertilizer MAP-F is 68.21-72.84%, and the yield of the fodder-grade product after three stages of ammophos recrystallization is 29.15%.

To improve the quality of ammonium phosphates from fertilizer MAP-F, ammonium phosphates after the first recrystallization were re-recrystallized. The results of the second stage of purification of MAP-F are presented in table 5.

As can be seen from the table, the content of phosphorus in terms of $P_2O_{5tot.}$ is 60.83-61.21%, and the fluorine content was reduced to 0.012-0.020%. As a result, after two stages of MAP-F recrystallization, it is possible to obtain a product that is not inferior in quality to foreign samples.

Monoammonium phosphate was obtained to conduct studies of the physicochemical properties. To check the obtained monoammonium phosphate, an X-ray diffraction pattern was taken (Fig. 1). On the X-ray pattern there are only diffraction maxima characteristic of monoammonium phosphate with interplanar distances of 5,32; 3,75; 3,075; 2,651; 2,373 Å $NH_4H_2PO_4$, 2,00 Å $Ca(H_2PO_4)_2 \cdot H_2O$.

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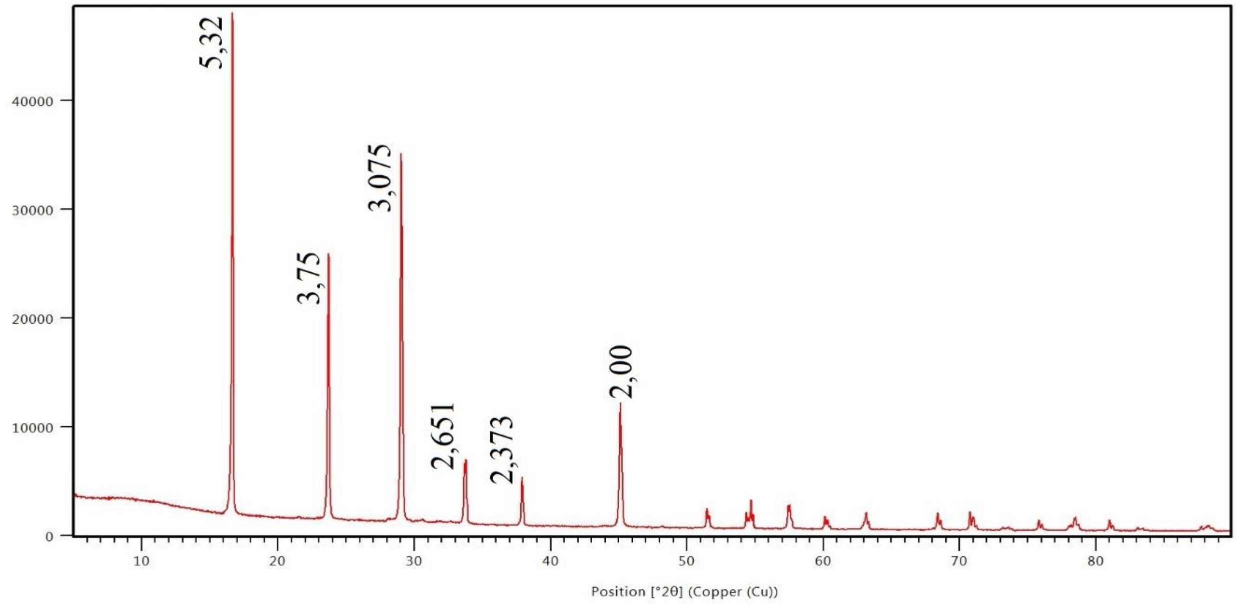

Figure 1 - X-ray of monoammonium phosphate

Figure 2 shows the data of the IR spectrum of monoammonium phosphate at pH=4.1. The results of the conducted IR spectroscopic studies show that the IR spectra of monoammonium phosphate and impurities coincide in the absorption bands of certain groups. So, for example, in the range of 1651.71-1402.65 cm^{-1}, plane 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^+.

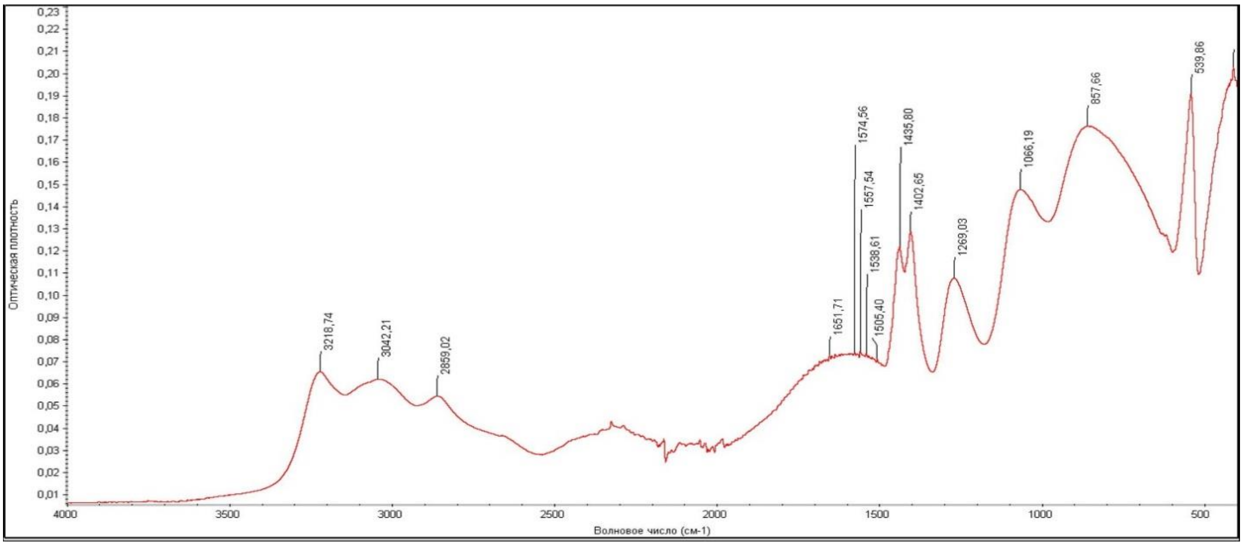

Figure 2 - IR spectrum of monoammonium phosphate

The IR spectrum of monoammonium phosphate contains broad bands in the region 857.66-1066.19 cm^{-1} PO_4^{2-}. The absorption bands at 2859.02-3218.74 cm^{-1} correspond to water of crystallization.

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Vol. 10, Issue 5, May 2023

V. CONCLUSION

Thus, the studies on the production of high-purity monoammonium phosphate from industrially produced phosphorus-containing products showed that by recrystallization of FPA it is possible to obtain monoammonium phosphate with a content of 61.84% P_2O_5 and 0.0075% fluorine, and from fertilizer MAP-F, monoammonium phosphate with a content of 60 .83-61.21% P_2O_5 and 0.012-0.020% fluorine. To do this, FPA must be recrystallized once, and fertilizer MAP-F twice. The obtained monoammonium phosphate from ammophos after the third stage of recrystallization contains 59.45% P_2O_5 and 0.22% fluorine. The yield of the product is 29.15%, while in the purification of FPA the yield is 75.20%, and from MAP-F it is 60.65%.

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