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PURIFICATION OF WET PROCESS PHOSPHORIC ACID BY DESULFURIZATION AND AMMONIZATION

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We studied the processes of desulfurization of phosphoric acid obtained by wet process from washed and roasted concentrate and subsequent purification of acid from bivalent and trivalent metals and fluorine via partial ammonization (at pH of 2 to 4). Purified ammoniated slurry containing 16.96% P_2O_5, 8.06% N, 0.09% CaO, 0.58% MgO, 0.004% Fe_2O_3, 0.031% Al_2O_3, 0.78% SO_3 and 0.52% F was fabricated by the removal of precipitates at the stages of desulfurization and partial ammonization. The rheological properties of ammoniated slurry with 40% moisture were studied. When the temperature is increased from 40 to 80⁰C, both the density and viscosity decrease from 1.395 to 1.365 g cm^{-3} and from 80.8 to 48.7 cP, respectively. Ammoniated suspension with pH of 5.5 and 8.5 was applied to prepare mono- and diammonium phosphates with the ratio P_2O_5:N of 52:14 and 48:18, respectively. The sludge obtained after desulfurization and ammonization processes can be used as a slow-release fertilizer.

Introduction

It is known that salts of phosphoric acid are main sources of phosphoric ions for plant nutrition. Phosphoric acid is produced in two ways: by thermal and wet processes. In the first case, a high-purity acid is produced from elemental phosphorus (thermal phosphoric acid, TPA) [1], which is preferably used in pharmaceuticals food industries. Wet process phosphoric acid (WPA) is usually fabricated by sulfuric acid decomposition of natural phosphates and ores [2]. Moreover, WPA can be prepared using nitric and hydrochloric acids to decompose phosphate ores [3]. Taking into account the existing world production of mineral fertilizers, we can state the complete superiority of the sulfuric acid method over nitric acid [4]. WPA contains up to 8−10% or more of impurities. Therefore, the acid is used mainly for production of phosphate and complex fertilizers. Despite the high purity of TPA, the process of its fabrication seems to be very energy-intensive and costly. The production of TPA requires the energy consumption that is 13 times higher than in production of WPA, besides it is environmentally dangerous [4].

Hence, the above facts can determine both the scientific and practical interest in the study of the process of WPA preparation. The basic method of production of WPA, both in Uzbekistan and abroad, is dihydrate, rather simple and reliable in operation [5]. The most common technological system in the CIS countries has a design capacity of 110 thousand tons of P_2O_5 per year (330−360 tons day^{-1}). It includes a double vessel extractor (two connected upper cross-flow cylindrical reactor) with a total volume of 900 m³, and a flume rotary vacuum filter with active (under vacuum) filtering surface of 80 m². Phosphogypsum is washed from phosphoric acid by a triple counter flow scheme.

In Uzbekistan, JSC «Ammofos-Maxam» produces wet process phosphoric acid by the sulfuric acid extraction of washed and calcinated concentrate (WCC-26), with the following composition (wt.%)

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25.77 P_2O_5; 52.70 CaO (CaO:P_2O_5=2.05); 1.20 MgO; 0.63 Fe_2O_3; 1.15 Al_2O_3; 2.67 SO_3; 0.04Cl; 3.60 CO_2; and 6.88 insoluble residue. The optimal parameters of the WPA fabrication are as follows: the extraction temperature of 85−90^{0}C, the extraction time of 4−6 hours, the concentration of sulfuric acid of 92−93%, the rate of sulfuric acid of 105% in terms of stoichiometry, the ratio of liquid to solid (L:S) of 2.9−3.1; the content of SO_3 in the liquid phase of the pulp of 2.5−3.0 g 100 cm^{-3}, and the P_2O_5 concentration of 19−20%. Meanwhile, the average composition of the produced WPA is as follows (wt.%): P_2O_5 17.0−21.5; CaO 0.4−0.6; MgO 0.8−1.2; Fe_2O_3 0.4−0.6%; Al_2O_3 0.02−0.04%; F 1.0−1.3%; Cl 0.01−0.015%; SiO_2 1.5; SO_3 1.9−3.5%.

At the present time, JSC «Ammofos-Maxam» operates in the following way. WPA is mainly used to produce concentrated nitrogen-phosphorus fertilizers [6]. Then at JSC «Ammofos-Maxam», there are other products such as suprefos-NS (8−15% N; 20−24% P_2O_5; 20−25% SO_3, obtained by deep ammonization of gypsum slurry), ammonium sulfate phosphate (15-19% N; 4-23% P_2O_5; 12-21% SO_3, it is a mixture of phosphoric and sulfuric acids), and feed phosphates ammonium (FPA, 12% N; 53−55% P_2O_5, obtained on the basis of purification of ammophos slurry) [6]. In addition, the following products have been prepared under laboratory conditions: phosphoric fertilizer analogously to PS-agro fertilizer (3.23% N; 25.45% P_2O_5; and 18.55% SO_3) [7] and enriched superphosphate (22−23% P_2O_5), obtained by treatment of phosphorite powder (17−18% P_2O_5) with phosphoric and sulfuric acid [8].

It should be noted that mono- (MAP) and diammonium phosphate (DAP) are the most valuable for Uzbekistan. They are highly concentrated, 100% water-soluble fertilizers, which are necessary for growing plants with a short growing season and on poor soils with low sorption capacity.

The production of MAP and DAP is based on WPA from the Khibin apatite concentrate (39.4% P_2O_5, Russia) and similar foreign materials Khurigba 80−82 TPL (Morocco), 84 BPL Nauru (Nauru Island) and BuuKraa 80 TPL (Morocco).

Based on these raw materials, it is possible to prepare any types of phosphoric fertilizers with acceptable technical and economic indicators. WPA derived from phosphate materials with low content of Mg, Fe, Al, Ca and other impurities is easy evaporated to reach 40−55% P_2O_5. For example, WPA produced from the Khibin concentrate, before evaporation, contains (%): P_2O_5 29−30; SO_3 1.8−2.5; F 1.5−1.8; R_2O_3 1.3−2.0; CaO 0.2−0.4; and

MgO is absent. After evaporating, the content is as follows: P_2O_5 50−54; SO_3 3.6−5.0; F 0.5−0.8; R_2O_3 1.6−1.9; CaO 0.2−0.6; and MgO is absent.

WPA based on phosphorites of Karatau (Kazakhstan) contains (%): P_2O_5 22.0; MgO 3.0; SO_3 2.5; F 1.6; R_2O_3 2.2; CaO 0.3; Fe_2O_3 1.0; and Al_2O_3 1.2. However, it cannot be subjected to evaporation due to the high content of magnesium in it.

WPA was made from WCC-26, although low-concentrated (>20% P_2O_5), but contains only 0.4−0.5% MgO and is suitable for concentration by evaporation.

Therefore, ammophos (MAP) from the Khibin apatite concentrate contains not less than 52% P_2O_5 (assimilated), not less than 48% P_2O_5 (water-soluble), and 12±1% N (prime grade) or 50±1% P_2O_5 (assimilated), not less than 46% P_2O_5 (water-soluble), and 12±1% N (medium grade.

Meanwhile, MAP of Karatau phosphorite powder refers to the grade B and contains (wt.%): 47−48 P_2O_5 (total), 43−46 P_2O_5 (assimilated), 37−38 P_2O_5 (water-soluble), 10−11 N, and 6−7 MgO.

MAP based on the WCC-26 contains (wt.%): 47−48 P_2O_5 (total), 44−46 P_2O_5 (assimilated), 37−38 P_2O_5 (assimilated), 10−11 N, 1.0−1.5 MgO, and 1.0−1.5 F.

At the same time, Chinese manufacturers produce ammophos with P_2O_5 content of ≥43%, (≥10% N). DAP produced in Canada, the United States and Europe commonly contains 47.1% P_2O_5, and 17.89% N [9].

However, the product based on WCC-26 is completely insoluble in water (the ratio of P_2O_5 (water-soluble): P_2O_5 (assimilated) is less than 80%), which is attributed to the contamination of WPA by various impurities. Naturally, the less the contents of P_2O_5 (assimilated), P_2O_5 (water-soluble) and N, the lower is its grade, i.e. the lower its cost.

In this regard, it is of practical interest to obtain MAP and DAP, the quality of which corresponds to the world standard. Generally, WPA prepared after filtration and separation of gypsum cake contains many impurities, both anionic (sulfate and fluorine-containing compounds) and cationic (iron, aluminum and magnesium). In addition, it includes some organic impurities. Therefore, to fabricate MAP and DAP of the best brand, WPA is required to be purified. There is a need for precleaning of WPA from various impurities. There are various methods for cleaning phosphoric acid solutions: the method of evaporation, precipitation with various alkaline reagents, cleaning with organic solvents, ion exchange, sorption cleaning with adsorbents and

recrystallization [4].

Recently researchers have focused on solvent extraction using various alcohols ketones [10−13]. Kijkowska et al. [10] carried out a study on preliminary purification of phosphoric acid concentrated up to 80 wt.%, obtained from apatite of the Kola deposit. First purification was carried out by precipitation of sulfate using $Ca(H_2PO_4)_2 \cdot H_2O$, $CaHPO_4 \cdot 2H_2O$ and $Ca_3(PO_4)_2$ (reactive grade) and technical calcium oxide at a molar ratio $Ca^{2+}:SO_2^{4-}$ of 0.8−1.5, temperature of 343−363 K and deposition time of 1800−7200 s. Then, sorption of volatile components (SiF_4 and HF) and liquid extraction using 4-methyl-2-pentanone (MIBK) were conducted. It has been found that $CaHPO_4 \cdot 2H_2O$ is the most effective precipitant. The removal of metals was carried out at room temperature with a weight ratio of phosphoric acid to MIBK of 1:1.22. As a result, purified phosphoric acid was fabricated with a concentration of about 50 wt.% and 1.5 wt.% MIBK containing Fe and Al at a level of 0.01−0.005 wt.%.

However, this method is multistage and requires a long agitation time for desulfurization and, moreover, the consumption of high-purity reagents is irreversible.

Amin et al. [11] reported the preparation of high-grade phosphoric acid by liquid-liquid extraction using n-butanol, n-hexanol, and n-octanol. The acid was extracted from contaminated 9.2 M H_3PO_4 at 25^0C with aqueous/organic phase ratios of 1:1, 1:3 and 1:5 in case of butanol, hexanol and octanol, respectively. The results showed 86%, 94% and 87% acid extraction in 3 steps using butanol, hexanol and octanol, respectively. The process is multistage and power-consuming, which leads to an increase in the cost of the final product.

Hannachi et al. [12] investigated WPA purification with mixtures of methyl isobutyl ketone (MIBK) and tributyl phosphate (TBP). Solvent mixtures were found which produced the highest purified acid with the highest possible P_2O_5 recovery for a typical three-step purification process. The purification process consisted of extraction, washing and desorption operations. P_2O_5 recovery increased at higher MIBK content in the solvent, while the impurity content was lower for nearly equal weight fractions of TBP and MIBK in the solvent mixture. The best cleaning performance was obtained for a solvent mixture with an optimal MIBK content of 55%, at which the impurity content was reduced. The P_2O_5 yield in the process of WPA purification at optimal conditions was about 43%. The disadvantage of this method is a relatively low degree of P_2O_5 recovery.

Earlier [13], we offered the solvent extraction to purify WPA, which can be easily regenerated and used repeatedly. Initially, desulfurization of WPA containing (wt.%) 16.46 P_2O_5, 0.052 CaO, 1.11 MgO, 2.98 SO_3, 0.28 Fe_2O_3, 0.42 Al_2O_3 and 0.99 F was performed by means of calcium carbonate. In that case, WPA desulfurization rate was 85.65%. Afterwards, more deep purification process of the desulfurized WPA was applied with using organic solvents (propanol, isopropanol, isobutanol, ethyl alcohols and acetone). Among these solvents, isopropyl alcohol turned out to be the most effective in terms of removing impurities, but significant loss of phosphorus occurs with it. Acetone can be used as an effective precipitant. After regeneration of the acetone and alcohol by distillation, WPA with concentration more than 45% P_2O_5 was produced.

To increase the content of total and water-soluble phosphorus in ammophos or diammophos of WCC-26, Namazov et al. [14] suggested to remove the solid suspensions, compounds of magnesium and iron-aluminum oxides from the slurry of ammonium phosphate (at pH 4.4) by means of separating the liquid and solid phase. The composition of the precipitate was as follows: 42.9% P_2O_5 (total), 8.33% N, P_2O_5 (assimilated):P_2O_5 (total)=97%, and P_2O_5 (water-soluble):P_2O_5 (total)=70%. The sediment contained up to 10% MgO, which makes it possible to offer it as a slow releasing NPMg-fertilizer. Then the liquid was evaporated to reach a moisture content of 40% and ammonization was carried out to pH 5.5 and 8.5. This allowed preparing the samples of ammophos (N:P_2O_5=49:13) and diammophos (N:P_2O_5=46:19) with improved quality. However, due to a high content of free sulfuric acid in initial WPA (2.61% SO_3 or 3.20% H_2SO_4), the content of nitrogen in the products was increased as a result of the formation of $(NH_4)_2SO_4$ (at least 10%), with a decrease in the total content of P_2O_5.

Taking account to the above, the goal of this research was to improve the grade of MAP and DAP based on the purification of WPA from various impurities by desulfurization and ammonization.

Materials and methods

Industrial method of removing sulfates from WPA implies the treatment with natural calcium containing material or a calcium phosphate mineral. Therefore, at the first stage of the study, we investigated the desulfurization of WPA produced by JSC «Ammofos-Maxam» with the following composition (wt.%): P_2O_5 16.46; CaO 0.052; MgO 1.11; SO_3 2.98; Fe_2O_3 0.28; Al_2O_3 0.42; and F 0.99. WCC-26, the composition of which is given above,

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as well as $Ca(OH)_2$ (64.5% CaO and 24.98% CO_2) and $CaCO_3$ (55.72% CaO and 43.78% CO_2) were used as precipitators of sulfate ions in the initial acid. It should be noted that calcium carbonate is decomposed during the thermal enrichment of phosphorite powder washed from the chlorine, the CO_2 is released, but resulting free calcium oxide (up to ~20%) remains in the WCC 26, thereby increasing calcium content in this module to 2.05% (whereas it should be no more than 1.5−1.6%). All types of raw materials were sieved and had a dispersed composition of 0.25 mm. This particle size is quite acceptable for acid decomposition. In addition, the selected particle size does not cause curtains or build-up in hoppers in industrial environment. In order to determine optimal conditions for purification of WPA from sulfate ions, laboratory experiments were conducted in a wide range of standards precipitators (100−150% of the stoichiometry for the binding of H_2SO_4 to $CaSO_4$). To this end, the initial WPA was loaded into a reactor with a screw stirrer and heated in a water thermostat to 80^0C. Then the calculated amount of precipitant was gradually dosed to it at a rate of 1.5−2 g/min. The stirrer speed was 220−250 rpm. Afterwards, estimated quantity of precipitator was gradually added into the reactor. The duration of desulfurization was 15 min. After the time, the contents of the reactor were kept for 30 min at 60−65^0C. Further, the desulfurized WPA was separated from the sediments by filtration using the Buchner funnel and a Bunsen flask at a discharge of 0.65 mm mercury through one layer of filter paper «white» type, and the precipitate was washed with water and then with acetone. After that, the precipitate was dried at 80^0C.

The degree of desulfurization was calculated according to the following equation:

$$\omega(SO_3) = \frac{m_{prec}(SO_3)}{m_{WPA}(SO_3)} \cdot 100\%,$$

where $\omega(SO_3)$ is the percentage of SO_3 in desulfurized WPA after purification (%); $m_{prec}(SO_3)$ is the content of SO_3 in precipitate (g); and $m_{WPA}(SO_3)$ is the content of SO_3 in the original WPA (g).

Next, we performed a thorough cleaning of desulfurized WPA from other impurities by partial neutralization at pH 2 to 4 with gaseous ammonia (100% NH_3) and a subsequent separation of the ammoniated pulp on liquid and solid phase by the above procedure. The solid phase was dried at a temperature not higher than 75^0C. Further, the liquid phase was evaporated at a temperature of 85−95^0C and atmospheric pressure to residual moisture of 40%. Rheological properties (density and viscosity) of evaporated ammonium suspension (at pH 4) were determined.

The final stage of the study was ammonization of evaporated ammophos suspension to reach pH 5.5 and 8.5 with preparation of the MAP and DAP, respectively. To avoid a loss of ammonia, saturation was carried out at a temperature below 70^0C. The granulation of ammoniated prepared slurries was carried out in the drying process by the method of intense mixing and balling. Drying of diammophos and ammophos was carried out at temperatures above 60^0C and less than 75^0C, respectively.

The compositions of the samples of the initial, desulfurized and ammoniated WPA, its sediments as well as fertilizers were determined by the method described elsewhere [15]. Contents of CaO and MgO were determined by volumetric chelatometric method. P_2O_5 was determined by UV-spectrometric method (UV-radiation, λ=440 nm) using phosphor-vanadium-molybdenum complex. The nitrogen content was determined by Kjeldahl-distillation of ammonia in an alkaline medium with Devard alloy followed by titration. The content of SO_3^{2-} ion was determined by via precipitation in the form of barium sulfate (gravimetric method). The contents of Al_2O_3 and Fe_2O_3 were analyzed by means of complexometric method, and K_2O and Na_2O were determined by gravimetric method with tetraphenylborate. Fluorine was determined by potentiometric method using a fluoride selecting electrode. The density of the evaporated ammophos suspension was evaluated using picnometric measurements with an accuracy of 0.05%, kinematic viscosity was determined by means of a glass capillary viscometer VPJ-2 with an uncertainty of 0.2%.

Measurements of pH of ammophos pulp and 10% aqueous suspensions of the samples were carried out using ionomer-130M (Russia) equipped with the electrodes ESL 63-07, EVL-1M3.1 and TKA-7 (an accuracy of 0.05 pH units). The strength of the granules in finished fertilizer with the sizes of granules of 2−3 mm was determined by using a device MIP-10-1 (Russia).

Results and discussion

Table 1 presents the composition of dried sludge obtained by desulfurization of WPA with WCC-26, $Ca(OH)_2$ and $CaCO_3$. The deposition coefficients of components were calculated from their content in the sediment relative to the content in the acid as a percentage (Table 2). The composition of the samples of the desulfurized WPA is given in Table 3.

It follows from Table 2 that with increasing norms of $Ca(OH)_2$, the deposition coefficient of SO_3 in WPA steadily increases from 75.15% (at a rate of 100%) to 86.74% (at the rate of 150%) and the deposition coefficient of CaO falls from 79.77% to 66%, respectively. Therefore, 125% of stoichiometry can be considered as an optimal norm of $Ca(OH)_2$ for sulfate ion deposition from WPA.

The coefficient of deposition of SO_3, CaO, MgO, Fe_2O_3, Al_2O_3 and F reaches 83.43%, 69.37%, 38.79%, 5.06%, 6.45% and 5.48%, respectively. An increase in the norm of the precipitator naturally leads to a significant increase in the deposition coefficient. However, a high rate results in an increase in the content of CaO in acid up to 1.33% (Table 3), which requires its decalciumination. The choice of 125% norm is also due to the fact that the deposition rate of SO_3 can be reduced. Thus, depending on the rate of $Ca(OH)_2$, the deposition rates of MgO, Fe_2O_3, Al_2O_3 and F are in the following ranges: 31.26–38.79%, 5.06–8.60%, 6.45–9.42% and 1.24–7.38%, respectively (Table 2). The loss of P_2O_5 with sediment is 6.64–7.16%. The greater the norm of the precipitant, the higher is the deposition coefficient of fluorine.

The composition of sediment samples is as follows (wt.%): P_2O_5 15.23–18.95, CaO 27.41–28.97, MgO 5.58–6.43, Fe_2O_3 0.21–0.38, Al_2O_3 0.39–0.52, SO_3 34.67–36.85 and F 0.20–0.98 (Table 1). They are presented mainly in the form of sulfate dihydrate and calcium phosphate, magnesium phosphate, phosphates of oxides and calcium fluoride. These sediments may be used as a phosphorus fertilizer with slow-releasing action, because the content of phosphorus is equal to that of simple superphosphate. If optimal norm is 125% and $CaCO_3$ is used, then the deposition rate of SO_3, P_2O_5, CaO, MgO, Fe_2O_3, Al_2O_3 and F reaches 85.65%, 10.72%, 73.54%, 33.66%, 7.77%, 9.67% and 4.27%, respectively.

Therefore, $CaCO_3$ ensures the greatest effect in terms of desulfurization of phosphoric acid.

In the case of use of WCC-26, an increase in the rates of precipitator results in an increase in the ratio of WPA desulfurization. However, the use of WCC-26 does not provide a sufficient level of deposition of MgO (only from 1.11 to 4.87%), which is explained by its presence in WCC-26 (Table 2).

Table 2 shows that with increasing norms of WCC-26 from 100 to 150%, the degree of deposition of P_2O_5, Al_2O_3 and F monotonically increases from 4.63% to 6.33%, from 7.10% to 9.96% and from 2.35% to 3.21%, respectively, whereas the deposition

Table 1

Sediments composition obtained by desulfurization of WPA

Rate of precipitator, %	Content in dried mass, wt.%						
	P_2O_5	CaO	MgO	Fe_2O_3	Al_2O_3	SO_3	F
Use of $Ca(OH)_2$							
100	18.95	27.42	5.58	0.38	0.43	36.02	0.20
120	18.22	28.97	5.89	0.30	0.43	36.68	0.51
125	16.78	27.54	6.43	0.21	0.40	36.85	0.81
130	16.02	27.41	6.12	0.22	0.39	36.65	0.80
140	15.79	27.78	5.76	0.24	0.43	35.83	0.82
150	15.23	28.15	5.48	0.29	0.52	34.67	0.98
Use of $CaCO_3$							
100	23.89	23.87	3.52	0.31	0.60	32.21	0.17
120	23.78	25.32	3.92	0.30	0.54	32.12	0.23
125	22.12	24.51	4.69	0.27	0.50	32.01	0.53
130	21.87	24.35	4.75	0.26	0.48	31.58	0.62
140	21.01	24.67	4.80	0.24	0.44	30.76	0.65
150	20.67	24.69	4.83	0.22	0.42	30.01	0.71
Use of WCC-26							
100	14.11	31.01	0.22	0.79	0.55	40.10	0.45
120	14.31	31.45	0.24	0.55	0.59	37.84	0.47
125	14.29	31.37	0.51	0.43	0.59	38.08	0.48
130	14.28	31.12	0.72	0.34	0.58	38.62	0.49
140	14.33	31.02	0.71	0.32	0.59	37.08	0.48
150	15.23	30.62	0.75	0.317	0.615	36.85	0.49

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Table 2

Effect of rate of precipitator on deposition coefficient from initial WPA

Rate of precipitator, %	Deposition coefficient, wt.%						
	P_2O_5	CaO	MgO	Fe_2O_3	Al_2O_3	SO_3	F
Use of Ca(OH)$_2$							
100	7.16	79.77	31.26	8.60	6.50	75.15	1.24
120	7.15	72.31	34.26	7.12	6.71	81.65	3.33
125	6.82	69.37	38.79	5.06	6.45	83.43	5.48
130	6.71	68.48	38.05	5.49	6.53	84.83	5.57
140	6.64	66.50	37.24	6.26	7.49	86.28	5.94
150	7.15	66.00	36.83	7.86	9.42	86.74	7.38
Use of CaCO$_3$							
100	10.68	82.17	23.33	8.32	10.69	79.52	1.26
120	11.12	76.30	27.18	8.43	10.06	82.94	1.79
125	10.72	73.54	33.66	7.77	9.67	85.65	4.27
130	10.92	72.13	35.16	7.71	9.55	87.08	5.15
140	10.92	71.05	36.99	7.46	9.11	88.30	5.62
150	11.17	69.08	38.70	7.14	9.05	89.57	6.38
Use of WCC-26							
100	4.63	82.93	1.11	15.42	7.10	74.46	2.35
120	5.36	81.20	1.39	12.12	8.69	80.54	2.77
125	5.41	78.31	3.19	10.09	8.68	81.87	2.84
130	5.45	76.10	4.26	7.60	8.67	83.94	2.96
140	5.82	75.53	4.49	7.70	9.28	86.01	3.06
150	6.33	71.58	4.87	7.77	9.96	87.57	3.21

Table 3

Composition of desulfurized WPA

Rate of precipitator, %	Content, wt.%						
	P_2O_5	CaO	MgO	Fe_2O_3	Al_2O_3	SO_3	F
Use of Ca(OH)$_2$							
100	18.47	0.52	0.93	0.31	0.47	0.87	1.19
120	18.43	0.82	0.88	0.31	0.47	0.71	1.16
125	18.48	0.96	0.81	0.31	0.47	0.60	1.13
130	18.53	1.04	0.82	0.31	0.46	0.53	1.13
140	18.52	1.17	0.83	0.31	0.46	0.49	1.12
150	18.96	1.33	0.87	0.31	0.47	0.47	1.14
Use of CaCO$_3$							
100	18.21	0.47	1.06	0.32	0.46	0.76	1.22
120	18.19	0.74	1.01	0.32	0.47	0.62	1.21
125	18.42	0.87	0.93	0.32	0.47	0.53	1.20
130	18.23	0.94	0.90	0.32	0.46	0.47	1.19
140	18.20	1.06	0.88	0.32	0.46	0.43	1.18
150	18.16	1.21	0.87	0.32	0.47	0.41	1.17
Use of WCC-26							
100	18.65	0.42	1.24	0.28	0.47	0.88	1.19
120	19.15	0.55	1.29	0.30	0.47	0.69	1.23
125	19.01	0.63	1.27	0.31	0.47	0.61	1.22
130	18.79	0.72	1.25	0.31	0.47	0.54	1.21
140	18.89	0.81	1.24	0.32	0.47	0.51	1.22
150	18.99	0.99	1.22	0.32	0.47	0.41	1.22

coefficient of Fe_2O_3 on the contrary reduces from 15.42% to 7.77%. Apparently, this is due to an increase in the solubility of $FePO_4$ in WCC-26.

To obtain high-quality ammonium phosphates (MAP and DAP), the acid was partially neutralized with gaseous ammonia from pH 2.0 to pH 4.0 at 80^0C. Then the contents of the reactor were filtered out. The liquid part and the dried sediment from the ammoniated pulp were subjected to chemical analysis. Table 4 presents the composition of precipitates obtained when ammonization of desulfurized WPA. The deposition coefficients of components were calculated from their contents in the sediment relative to the content in the desulfurized acid as a percentage (Table 5). The

composition of the desulfurized WPA is given in Table 6.

Since the sediments of ammoniated pulps were not washed with water or organic solvents, it is obvious that nitrogen and water-soluble form of P_2O_5 can exist as ammonium sulfate and phosphates (Table 4). The presence of nitrogen can be explained by the presence of complex salts of iron and aluminium. An increase of N in precipitates with increasing pH occurs as a result of the crystallization of monoammonium phosphate. Calcium is presented in precipitates as dicalcium phosphate. However, the main result is that 56−80% of phosphorus is in water-soluble form with respect to its total content in the precipitate. Due to a high concentration of

Table 4

Sediments composition obtained from desulfurized WPA at various pH

Slurry pH	Content, wt.%								
	P_2O_5 (total)	P_2O_5 (water)	N	CaO	MgO	Fe_2O_3	Al_2O_3	SO_3	F
2.01	54.45	30.48	4.98	7.56	1.03	4.25	2.54	3.69	3.82
2.23	53.23	31.24	5.23	5.53	1.01	5.98	5.28	2.28	4.68
2.52	48.26	29.51	5.83	3.76	1.44	4.31	5.39	1.45	4.96
2.85	46.56	29.78	5.91	3.42	1.54	3.72	4.74	1.18	4.93
3.01	45.45	30.05	6.18	3.43	1.89	3.38	4.39	1.12	5.08
3.54	40.56	30.61	6.85	3.24	2.09	2.66	3.68	0.86	4.86
4.01	37.63	29.94	7.18	3.88	3.27	2.38	3.37	1.11	5.87

Table 5

Effect of pH of ammoniated WPA on deposition coefficient of components

Slurry pH	Deposition coefficient, wt.%						
	P_2O_5	CaO	MgO	Fe_2O_3	Al_2O_3	SO_3	F
2.01	3.68	16.10	1.44	16.59	6.71	6.03	3.99
2.23	8.60	28.12	3.37	55.72	33.30	8.90	11.68
2.52	14.79	36.27	9.12	76.17	64.47	10.73	23.49
2.85	20.57	47.56	14.06	94.78	81.74	12.59	33.66
3.01	22.51	53.48	19.35	96.56	84.89	13.40	38.89
3.54	25.67	64.55	27.34	97.09	90.92	13.15	47.53
4.01	27.02	87.69	48.53	98.56	94.46	19.26	65.13

Table 6

Composition of ammoniated suspension at different pH

Slurry pH	Content, wt.%							
	P_2O_5	N	CaO	MgO	Fe_2O_3	Al_2O_3	SO_3	F
2.01	17.25	5.01	0.48	0.86	0.260	0.430	0.70	1.120
2.23	16.88	5.38	0.43	0.88	0.144	0.321	0.71	1.076
2.52	16.84	6.46	0.40	0.87	0.081	0.180	0.73	0.981
2.85	16.98	7.76	0.36	0.89	0.019	0.100	0.77	0.916
3.01	16.82	7.78	0.32	0.85	0.011	0.082	0.78	0.862
3.54	16.69	7.92	0.25	0.79	0.010	0.052	0.81	0.764
4.01	16.96	8.06	0.09	0.58	0.004	0.031	0.78	0.521

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phosphorus (37.63−54.45% P_2O_5 (total)) and nitrogen (4.98−7.18% N), the precipitate can serve as an independent fertilizer, ammophos.

According to data of Table 5 and Fig. 1, calcium and iron-aluminum oxides at pH of about 4.0 are almost completely recovered from ammonium phosphate solutions. In this case, the content of magnesium is reduces almost by half, the contents of sulfate and fluorine ions decrease by ~20% and ~65%, and the loss of P_2O_5 with sediment reaches 27%.
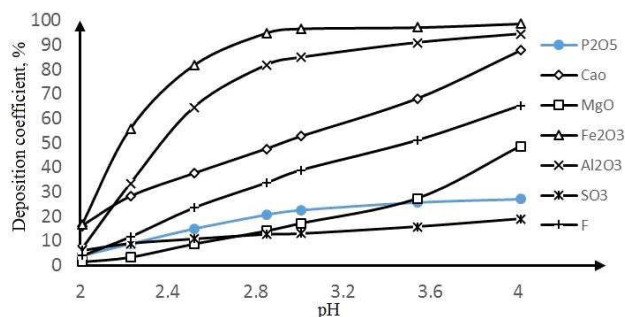

Fig. 1. Deposition coefficient from desulfurized WPA as a function of pH of ammoniated slurry

Here it is appropriate to give the results of studying the solid phases formed during the ammonization of WPA from Karatau phosphorites, which contains (wt.%): P_2O_5 20.3; CaO 0.24, SO_3 2.1; Al_2O_3 1.04; Fe_2O_3 1.02; MgO 1.78, and F 2.72. WPA under consideration is similar to this acid. So, when ammonization of WPA from Karatau phosphorite is performed to reach pH of about 2.5, the following compounds are formed that are soluble in water: $NH_4H_2PO_4$, $NH_4HSO_4 \cdot NH_4H_2PO_4$, $(NH_4)_2SiF_6$, and citric soluble complex phosphates of iron and aluminium $(Fe, Al)_3NH_4H_8(PO_4)_6 \cdot 6H_2O$, $(Fe, Al)NH_4HPO_4F_2$ and $Mg(Fe, Al)NH_4(HPO_4)_2F_2$. The first complex is well crystallized, easily filtered and separated. The second one is amorphous, it forms colloid that is hardly precipitated and poorly filterable. The soluble compound $Mg(Fe, Al)NH_4(HPO_4)_2F_2$ is formed in magnesium-containing acids and crystallizes well. When ammonization is conducted to reach pH of about 2.5, almost all iron ions and only a part of aluminum, magnesium and fluorine are released into the precipitate.

In the pH range of 2.5−5.5, the following compounds are formed: $NH_4H_2PO_4$; $(NH_4)_2SO_4$; $MgHPO_4$; $Mg(Fe, Al)(NH_4)_2(HPO_4)_2F_3$; $Mg_3(NH_4)_2(HPO_4)_4 \cdot 8H_2O$; $MgNH_4PO_4 \cdot H_2O$; $MgNH_4HFPO_4$; $(Fe, Al)NH_4(HPO_4)_2 \cdot 0.5H_2O$; $(Fe, Al)NH_4HPO_4F_2$; SiO_2; $CaHPO_4$; and $Ca_5(PO_4)_3OH$.

All phosphates contained in ammonium phosphate, except hydroxyapatite, are citric-soluble.

Particular attention was paid to the composition of the liquid phase of the ammoniated pulp at pH 4.01. The composition of this suspension can be seen in Table 6. This purified suspension served as the initial component for the production of high-quality ammonium phosphates (MAP and DAP).

According to the current production technology of ammophos, the ammoniated pulp with a moisture content of about 60% is evaporated in a surface-type apparatus with forced circulation to reach a moisture content of 30−35% and then fed to a pelletizing drum granulator-dryer. At the same time, the pulp should retain fluidity and be easily pumped by pumps.

Therefore, evaporation of the ammoniated suspension was carried out at a temperature of 85−95⁰C at atmospheric pressure to a residual moisture of 40%. The density and viscosity of the evaporated liquid phase of ammophos pulp at pH 4.01 are shown in Fig. 2.
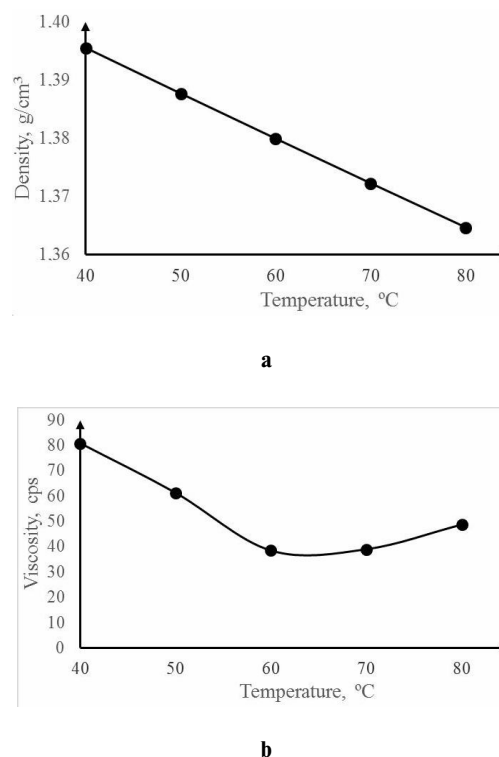

a

b

Fig. 2. Temperature dependences of density (a) and viscosity (b) of evaporated ammophos suspension

At 40% humidity, when the temperature rises from 40 to 80⁰C, the pulp density decreases from 1.395 to 1.365 g/cm^3, while viscosity decreases from 80.8 to 48.7 centipoise. With increasing temperature,

the pulp density decreases rectilinearly, but the viscosity steadily increases, which, apparently, can be explained by the transition of complex salts from the crystalline to the gel-like amorphous state.

Thus, under industrial conditions, it is advisable to evaporate the ammophos pulp originated from the WCC-26 to a humidity of 35%. At lower humidity and temperatures $80-90^0C$, monoammonium phosphate begins to crystallize and the viscosity of the pulp increases dramatically inducing hardly to pump by pumps.

At the final stage, ammonization of evaporated ammonization of the pulp was performed to reach pH 5.5 and pH 8.5 and produce ammophos and diammophos, respectively. The procedure of preparation of the finished products is described above.

According to the requirement of State standard 18918-85, MAP must contain at least 12% N and 52% P_2O_5 (assimilated), whereas according to the technical conditions 113-08-537-83, DAP should contain 18% N and 48% P_2O_5 (assimilated).

The results show that the granular MAP has the following composition (wt.%): P_2O_5 51.6; N 14; SO_3 0.98; CaO 0.5; MgO 1.74; Fe_2O_3 0.04; Al_2O_3 0.14; F not more than 1.0; the granule strength being 3.25 MPa. Ammophos possessing these characteristics is in great demand. DAP contains 48% P_2O_5 and 18.7% N, the hardness of granules being at least 2 MPa. It contains 0.44% CaO; 1.7% MgO; 0.04% Fe_2O_3; 0.13% Al_2O_3; 1% SO_3 and not more than 1.0% F.

It should be noted that phosphorus in these products is exclusively in water-soluble form. The MAP consists of $NH_4H_2PO_4$ with some $(NH_4)_2HPO_4$. DAP contains $(NH_4)_2HPO_4$ and partially $(NH_4)_3PO_4$.

Conclusions

To produce concentrated grades of ammonium phosphates that meet the requirements of the world standard towards a phosphorus component, it is necessary to use WPA desulfurized and purified from impurities. It is desirable to use $CaCO_3$ as a precipitator at the rate of 125% of stoichiometry for desulfurization of WPA of WCC-26, the rate of desulfurization reaches 85.65%. Other impurities (CaO, MgO, Fe_2O_3, Al_2O_3 and F) are further removed with gypsum. Gypsum sediment with a content of $15-19\%$ P_2O_5 can be used as a phosphorus fertilizer of slow-releasing action.

For maximum removal of the above impurities from the composition of desulfurized WPA, the latter was partially ammoniated to reach pH of 2 to 4.

Almost complete recovery of calcium was observed at pH about 4.0. The resulting sediments contain from 4.98 to 7.18% N, $37.63-54.45\%$ P_2O_5 (total); $56-80\%$ of them being in water-soluble form. Thus, they can be recycled to ammophos production.

Purified suspension of ammonium phosphate (pH 4) served as a starting component for high-quality phosphate fertilizers. Ammonization of evaporated ammophos pulp to pH 5.5 and 8.5 was the basis for the production of MAP and DAP, respectively. MAP with the ratio P_2O_5:N=52:14 and DAP with the ratio P_2O_5:N=48:18 were produced. Phosphorus in these products is exclusively in water-soluble form.

REFERENCES

1. *Babrauskas V.* Phosphorus explosions // Process Saf. Environ. Prot. − 2017. − Vol.107. − P.87-93.

2. *Behaviour* and fluxes of natural radionuclides in the production process of a phosphoric acid plant / Bolivar J.P., Martin J.E., Garcia-Tenorio R., Perez-Moreno J.P., Mas J.L. // Appl. Radiat. Isot. − 2009. − Vol. 67. − P. 345-356.

3. *The physicochemical* data of extraction with the mixed solvent of NOA and MIBK from hydrochloric acid route phosphoric acid / Li W., Peng R., Ye P., Iv X., Zhu T., Cao Z., et al. // J. Chem. Thermodyn. − 2019. − Vol.131. − P.404-409.

4. *Comparative* analysis of industrial processes for cadmium removal from phosphoric acid: a review / Kouzbour S., Gourich B., Gros F., Vial C., Allam F., Stiriba Y. // Hydrometallurgy. − 2019. − Vol.188. − P.222-247.

5. *Gobbitt J.M.* Yara hemihydrate (HH) and hemidihydrate (HDH) processes for phosphoric acid production // Procedia Eng. − 2012. − Vol.46. − P.143-153.

6. *Technology* for manufacturing fertilizer «Superfos» containing nitrogen, phosphorus, sulfur and calcium / Sadykov B.B., Volynskova N.N., Namazov S.S., Beglov B.M. // Russ. J. Appl. Chem. − 2008. − Vol.81. − P.1667-1672.

7. *Production* of NP fertilizers based on the decomposition of poor phosphates using a mixture of phosphoric and sulphuric acids / Rasulov A.A., Alimov U.K., Seytnazarov A.R., Namazov S.S., Sultonov B.E. // J. Chem. Technol. Metall. − 2019. − Vol.54. − No. 6. − P.1263-1270.

8. *Balanced* NP-and NPK-fertilizers based on purified ammophos suspension, nitrogen fertilizers and potassium chloride / Nomozov S.Y., Namazov S.S., Seytnazarov A.R., Beglov B.M., Alimov U.K. // Int. J. Sci. Technol. Res. − 2020. − Vol.9. − No. 2. − P.1572-1578.

9. *Siminovich C., Joao S.* Dynamic operator training simulators for sulphuric acid, phosphoric acid, and DAP production units // Procedia Eng. − 2014. − Vol.83. − P.215-224.

Bekhzod Karshiev, Atanazar Seytnazarov, Umarbek Alimov, Shafoat Namazov, Akhmed Reymov, A'zamjon Rasulov

10. *Wet-process* phosphoric acid obtained from Kola apatite. Purification from sulphates, fluorine, and metals / Kijkowska R., Pawlowska-Kozinska D., Kowalski Z., Jodko M., Wzorek Z. // Sep. Purif. Technol. − 2002. − Vol.28. − P.197-205.

11. *Recovery* of high grade phosphoric acid from wet process acid by solvent extraction with aliphatic alcohols / Amin M.I., Ali M.M., Kamal H.M., Youssef A.M., Akl M.A. // Hydrometallurgy. − 2010. − Vol.105. − P.115-119.

12. *Purification* of wet process phosphoric acid by solvent extraction with TBP and MIBK mixtures / Hannachi A., Habaili D., Chtara C., Ratel A. // Sep. Purif. Technol. − 2007. − Vol.55. − P.212-216.

13. *Purification* of wet process phosphoric acid using organics solvents / Karshiev B., Seytnazarov A., Namazov S., Radzhabov R., Reymov A., Alimov U. // J. Crit. Rev. − 2020. − Vol.7. − No. 17. − P.2913-2918.

14. *Processing* new concentrate from phosphorites of Central Kyzylkum, containing 26% P_2O_5, on wet-process phosphoric acid, monoammonium phosphate and diammophos / Namazov S.S., Seytnazarov A.R., Beglov B.M., Volynskova V.N., Sadykov B.S., Myrzakulov H.C. // Chem. J. Kazakhstan. − 2014. − Vol.3. − P.158-167.

15. *Vinnik M.M., Erbanova L.N., Zaytsev P.M.* Methods of analysis of phosphate raw material, phosphorus and complex fertilizers, feed phosphates. − M.: Khimiya, 1975. − 218 p.

ОЧИЩЕННЯ ЕКСТРАКЦІЙНОЇ ФОСФОРНОЇ КИСЛОТИ МЕТОДОМ ДЕСУЛЬФУРИЗАЦІЇ ТА АМОНІЗАЦІЇ

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Досліджено процес десульфуризації екстракційної фосфорної кислоти, одержаної з митого відпаленого концентрату з наступним очищенням кислоти від двох і тривалентних металів та фтору шляхом часткової амонізації (при рН від 2 до 4). Амонізована пульпа, що містить 16,96% P_2O_5; 8,06% N, 0,09% CaO, 0,58% MgO; 0,004% Fe_2O_3; 0,031% Al_2O_3; 0,78% SO_3 і 0,52% F, була одержана за допомогою видалення осадів на стадії десульфуризації і амонізації. Вивчені реологічні властивості амонізованої пульпи із вмістом 40% вологи. При зростанні температури від 40 до 80⁰C як густина, так і в'язкість знижується з 1,395 до 1,.365 г/см³ і від 80,8 до 48,7 сПз, відповідно. Амонізована суспензія з рН 5,5 і 8,5 була застосована для одержання моно- і діамонійфосфатів зі співвідношенням P_2O_5:N, рівним 52:14 і 48:18, відповідно. Шламові осади, отримані у процесі десульфуризації і амонізації, можуть бути використані як повільно діючі добрива.

Ключові слова: екстракційна фосфорна кислота, кальцієвмісні матеріали, десульфуризация, амонізація, шламовий осад, моно- і діамонійфосфати, склад.

PURIFICATION OF WET PROCESS PHOSPHORIC ACID BY DESULFURIZATION AND AMMONIZATION

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We studied the processes of desulfurization of phosphoric acid obtained by wet process from washed and roasted concentrate and subsequent purification of acid from bivalent and trivalent metals and fluorine via partial ammonization (at pH of 2 to 4). Purified ammoniated slurry containing 16.96% P_2O_5, 8.06% N, 0.09% CaO, 0.58% MgO, 0.004% Fe_2O_3, 0.031% Al_2O_3, 0.78% SO_3 and 0.52% F was fabricated by the removal of precipitates at the stages of desulfurization and partial ammonization. The rheological properties of ammoniated slurry with 40% moisture were studied. When the temperature is increased from 40 to 80⁰C, both the density and viscosity decrease from 1.395 to 1.365 g cm^{-3} and from 80.8 to 48.7 cP, respectively. Ammoniated suspension with pH of 5.5 and 8.5 was applied to prepare mono- and diammonium phosphates with the ratio P_2O_5:N of 52:14 and 48:18, respectively. The sludge obtained after desulfurization and ammonization processes can be used as a slow-release fertilizer.

Keywords: wet process phosphoric acid; calcium-containing material; desulfurization; ammonization; sludge; mono- and diammonium phosphates; composition.

REFERENCES

1. Babrauskas V. Phosphorus explosions. *Process Saf Environ Prot.* 2017; 107: 87-93. doi: 10.1016/j.psep.2017.01.026.

2. Bolivar JP, Martin JE, Garcia-Tenorio R, Perez-Moreno JP, Mas JL. Behaviour and fluxes of natural radionuclides in the production process of a phosphoric acid plant. *Appl Radiat Isot.* 2009; 67: 345-356. doi: 10.1016/j.apradiso.2008.10.012.

3. Li W, Peng R, Ye P, Iv X, Zhu T, Cao Z, et al. The physicochemical data of extraction with the mixed solvent of NOA and MIBK from hydrochloric acid route phosphoric acid. *J Chem Thermodyn.* 2019; 131: 404-409. doi: 10.1016/j.jct.2018.11.012.

4. Kouzbour S, Gourich B, Gros F, Vial C, Allam F, Stiriba Y. Comparative analysis of industrial processes for cadmium removal from phosphoric acid: a review. *Hydrometallurgy.* 2019; 188: 222-247. doi: 10.1016/j.hydromet.2019.06.014.

5. Gobbitt JM. Yara hemihydrate (HH) and hemidihydrate (HDH) processes for phosphoric acid production. *Procedia Eng.* 2012; 46: 143-153. doi: 10.1016/j.proeng.2012.09.457.

6. Sadykov BB, Volynskova NN, Namazov SS, Beglov BM. Technology for manufacturing fertilizer «Superfos» containing nitrogen, phosphorus, sulfur and calcium. *Russ J Appl Chem.* 2008; 81: 1667-1672. doi: 10.1134/S1070427208090371.

7. Rasulov AA, Alimov UK, Seytnazarov AR, Namazov SS, Sultonov BE. Production of NP fertilizers based on the decomposition of poor phosphates using a mixture of phosphoric and sulphuric acids. *J Chem Technol Metall.* 2019; 54(6): 1263-1270.

8. Nomozov SY, Namazov SS, Seytnazarov AR, Beglov BM, Alimov UK. Balanced NP-and NPK-fertilizers based on purified ammophos suspension, nitrogen fertilizers and potassium chloride. *Int J Sci Technol Res.* 2020; 9(2): 1572-1578.

9. Siminovich C, Joao S. Dynamic operator training simulators for sulphuric acid, phosphoric acid, and DAP production units. *Procedia Eng.* 2014; 83: 215-224. doi: 10.1016/j.proeng.2014.09.041.

10. Kijkowska R, Pawlowska-Kozinska D, Kowalski Z, Jodko M, Wzorek Z. Wet-process phosphoric acid obtained from Kola apatite. Purification from sulphates, fluorine, and metals. *Sep Purif Technol.* 2002; 28: 197-205. doi: 10.1016/S1383-5866(02)00048-5.

11. Amin MI, Ali MM, Kamal HM, Youssef AM, Akl MA. Recovery of high grade phosphoric acid from wet process acid by solvent extraction with aliphatic alcohols. *Hydrometallurgy.* 2010; 105: 115-119. doi: 10.1016/j.hydromet.2010.08.007.

12. Hannachi A, Habaili D, Chtara C, Ratel A. Purification of wet process phosphoric acid by solvent extraction with TBP and MIBK mixtures. *Sep Purif Technol.* 2007; 55: 212-216. doi: 10.1016/j.seppur.2006.12.014.

13. Karshiev B, Seytnazarov A, Namazov S, Radzhabov R, Reymov A, Alimov U. Purification of wet process phosphoric acid using organics solvents. *J Crit Rev.* 2020; 7(17): 2913-2918. doi: 10.31838/jcr.07.17.367.

14. Namazov SS, Seytnazarov AR, Beglov BM, Volynskova VN, Sadykov BS, Myrzakulov HC. Processing new concentrate from phosphorites of Central Kyzylkum, containing 26% P_2O_5, on wet-process phosphoric acid, monoammonium phosphate and diammophos. *Chem J Kazakhstan.* 2014; 3: 158-167. (*in Russian*).

15. Vinnik MM, Erbanova LN, Zaytsev PM. *Methods of analysis of phosphate raw material, phosphorus and complex fertilizers, feed phosphates.* Moscow: Khimiya; 1975. 218 p. (*in Russian*).

Bekhzod Karshiev, Atanazar Seytnazarov, Umarbek Alimov, Shafoat Namazov, Akhmed Reymov, A'zamjon Rasulov