

PROCESSING OF A WASHED DRY CONCENTRATE CONTAINING 26% P_2O_5 INTO AMMOPHOSPHATE, SULPHO- AND NITROAMMOPHOSPHATE FERTILIZERS

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ABSTRACT

The process of obtaining ammophosphate by means of phosphoric acid decomposition of washed dried concentrate (WDC) with 26 % P_2O_5 and 10 % CO) - raw material for the production of thermally fired concentrate, has been studied. The extraction phosphoric acid contains (mass. %): 16.46 P_2O_5 , 0.06 CaO, 1.11 MgO, 0.27 Fe_2O_3 , 0.41 Al_2O_3 , 2.98 SO_3 and 0.99 F. The mass ratio of WPPA: WDC ranged from 100: 10 to 100: 30. Then acidic phosphate pulps (at 65°C) after 45 minutes were ammoniated to pH = 3.8, granulated and dried at 85 - 90°C. It has been shown that the nitrogen content in the finished product ranges from 4.92 - 7.11 %, total phosphorus (P_2O_{5t}) 41.48 - 46.44 %, phosphorus assimilated by plants ($P_2O_{5acceptable}$) 34.79 - 45.11 %, water-soluble phosphorus (P_2O_{5ws}) 23.49 - 37.73 %. The addition of 5 - 7.5 % H_2SO_4 or HNO_3 in the form of a monohydrate makes it possible to intensify the process of phosphoric acid decomposition of phosphate raw materials and to obtain sulfo- and nitroammophosphate with significantly high contents of $P_2O_{5acceptable}$ and P_2O_{5ws} . So, with a weight fraction of WDC equals to 30 and weight fractions of H_2SO_4 - 5 and 7.5, there have been 37.6 and 34.47 % P_2O_{5total} in sulfoammophosphate; 24.11 and 22.06 % CaO, 88.75 and 96.4 % $P_2O_{5acceptable}$: P_2O_{5t} , 77.39 and 79.54 % P_2O_{5ws} : P_2O_{5t} , 6.03 and 7.08 % nitrogen, respectively. In the case of using HNO_3 , nitroammophosphate contains the largest amount of nitrogen due to additionally introduced nitric acid, but the phosphate raw material has a relatively low decomposition coefficient. The strength of granules of all brands of fertilizers averages 3.50 MPa and are quite suitable for bulk storage and transportation. Material balances for the production of ammophosphate, sulfoammophosphate and nitroammophosphate have been calculated.

Keywords: washed dried concentrate, phosphoric acid, decomposition, ammophosphate, sulfuric and nitric acids, intensification, sulfo- and nitroammophosphates.

INTRODUCTION

Ammophosphate is a nitrogen-phosphorus fertilizer belonging to the class of partially decomposed phosphates. The process of its production is took place dissolution of natural phosphates using a high consumption of 150 - 200 % from stoichiometric norm of phosphoric acid, followed by neutralization of the remaining acidity with ammonia, granulation and drying of the product [1]. Unlike ammophos, the consumption of sulfuric acid for the production of 1 ton of P_2O_5 in

the form of ammophosphate is 10 - 15 % lower, and the degree of utilization of phosphate raw materials is 1.0 - 1.5 % higher. The phosphate component of ammophosphate is ammonium dihydrogen phosphate, as impurities - calcium hydrogen phosphate ($CaHPO_4$) and highly basic calcium phosphates, which is hydroxyapatite ($Ca_5(PO_4)_3OH$) [2]. The latter group includes variously substituted calcium phosphates, formed during the ammonization of the pulp, and unreacted phosphorite. The latter is significantly different in structure from the original. Its grains are acid-etched, have a porous

structure and are 15 - 30 times smaller than the original. Therefore, although it is water insoluble, but its P_2O_5 is available to plants.

Extensive agrochemical tests of ammophosphate have shown that in terms of efficiency it is not inferior to ammophos and double superphosphate and can be used in various soil and climatic zones for all agricultural crops [3].

The production of ammophosphate was mastered from Karatau phosphorites at the Dzhabbul superphosphate plant in Kazakhstan, at the Chardzhov chemical plant in Turkmenistan, at the Almalyk OJSC Ammophos (now "Ammofos-Maxam" JSC) in Uzbekistan, from apatite concentrate at the Balakovo PA Minudobreniya in Russia. An important advantage of ammophosphate is the possibility of using practically any kind of phosphate raw material in its production. It was necessary to check the process using the example of Kyzylkum phosphorites (Uzbekistan). Currently, the Kyzylkum phosphorite complex provides phosphate raw materials for the factories of Uzbekistan that produce phosphorus-containing fertilizers.

Earlier, the process of obtaining of ammophosphate fertilizers based on the decomposition of various types of Kyzylkum phosphorites by extraction phosphoric acid (EPA) with a concentration of 21.45 % P_2O_5 was studied [4-6]. It has been established that an increase in the weight fraction of phosphate raw materials from 5 to 30 g in relation to 100 g of EPA leads to a decrease in its decomposition coefficient (C_{dec}) from 72.32 to 26.90; from 89.14 to 47.06; from 69.07 to 25.47 %, from 84.26 to 28.57 and from 18.84 to 51.33 %, respectively, for phosphorite powder (17.65 % P_2O_5 ; 15.2 % CO_2 ; $CaO : P_2O_5 = 2.69$), chemical concentrate (26.76 % P_2O_5 ; 4.51 % CO_2 ; $CaO : P_2O_5 = 1.73$); thermoconcentrate (27.26 % P_2O_5 ; 2.41 % CO_2 ; $CaO : P_2O_5 = 1.96$), dust fraction (18.54 % P_2O_5 ; 14.8 % CO_2 ; $CaO : P_2O_5 = 2.4$) and mineralized mass (14.33 % P_2O_5 ; 14.7 % CO_2 ; $CaO : P_2O_5 = 3.0$). The first raw material is processed into nitrocalcium phosphate fertilizer (NCPF - 6 % N; 16 % P_2O_5) at JSC "Samarqandkimyo", the second was obtained according to the method described in [7], which was subjected to chemical enrichment, that is, 52 % nitric acid to dissolve and remove calcite in the form of calcium nitrate.

The third is the main raw material for sulfuric acid extraction to produce ammophos (10 % N; 46 % P_2O_5)

at Ammofos-Maxam JSC. And the last two types of material are wastes from the thermal enrichment process of the Kyzylkum phosphorite ore (with a content of 16 - 18 % P_2O_5). The pulverized fraction is formed in the process of fine grinding of raw materials, and the mineralized mass - during the primary dry sorting of ore.

Whereas in another version, it was checked whether the activation of carbonate phosphorites of Kyzylkum occurs in the case of their treatment with partially ammonized EPA [8].

In the works under consideration, it is noted that purely phosphoric acid leaching of phosphate raw materials does not lead to its complete decomposition [4 - 6]. However, there is a way out of this situation. It is possible to intensify the process of decomposition of phosphates by phosphoric acid, which means to increase the coefficient of decomposition of raw materials, by adding a small amount of sulfuric acid [9, 10]. This method is already widely used in the production of double superphosphate. So, if for phosphorite powder (PP) with EPA : PP = 100 : 20 without the use of sulfuric acid $K_{decom.}$ is 47.48 %, then this value was achieved already with EPA : $H_2SO_{4monohydrate}$: PP = 93 : 7 : 25 [10]. The intensification of the process of phosphoric acid decomposition of natural phosphates is facilitated by the use of a small amount of nitric acid as an additive [11]. So, with the ratio of EPA : PP = 100 : 30, an increase in the rate of added HNO_3 from 10 to 50 % leads to an increase in the decomposition coefficient of raw materials from 26.90 (without additive) from 33.68 to 64.49 %, respectively. Table 1 shows the optimal compositions of products obtained from phosphate powder with EPA : PP = 100 : 30 and 100 : 40 and with the addition of 25 % HNO_3 .

But the products obtained from thermoconcentrate are better in composition than from phosphorite powder.

The products obtained belong to the so-called partially decomposed phosphates, which, in terms of their agrochemical efficiency, are not inferior to water-soluble forms of phosphorus fertilizers [12]. In several works, the preparation of NP fertilizers on base of different phosphorites of Central Kyzyl Kum and a mixture of phosphoric and sulfuric acid is given [13 - 15]. These samples of fertilizers fully meet the requirements of agriculture for content of nutrients.

At present, at the Kyzylkum phosphorite complex, in the process of washing phosphate powder from

Table 1. Optimal compositions of products [11].

Mass ratio of EPA : PP	N, %	P_2O_{5t} , %	Mass ratio of N : P_2O_{5t}	$P_2O_{5ac.c.a.} / P_2O_{5t} \cdot 100$, %	$P_2O_{5w.s.} / P_2O_{5t} \cdot 100$, %	Mass ratio of $P_2O_{5w.s.} : P_2O_{5ac.c.a.}$
100 : 30	10.04	36.84	1 : 3.6	81.89	42.10	0.52 : 1
100 : 40	9.33	33.25	1 : 3.54	78.02	36.24	0.46 : 1

chlorine, another raw material is obtained - washed dried concentrate (WDC). This phosphate rock is used for the production of washed roasted concentrate by roasting at 950 - 1000°C.

Concerning WDC, the process of obtaining both ammophosphate and sulfur- and nitrophosphate based on former, has not been studied.

EXPERIMENTAL

At the initial stage, we studied the process of obtaining ammophosphate based on the phosphoric acid decomposition of WDC. For research WDC was used with composition (mass %): 26.08 P_2O_5 ; $P_2O_{5ac.c.a.} : P_2O_{5t} = 13.08$; 51.74 CaO; 0.89 MgO; 0.31 Fe_2O_3 ; 1.02 Al_2O_3 ; 1.59 SO_3 ; 9.95 CO_2 ; 2.49 insoluble residue; $CaO_t : P_2O_{5t} = 1.98$. And for its decomposition, EPA was used, obtained from a thermoconcentrate by the dihydrate method at JSC "Ammofos-Maxam" and having a composition (mass %): 16.46 P_2O_5 , 0.06 CaO, 1.11 MgO, 0.27 Fe_2O_3 , 0.41 Al_2O_3 , 2.98 SO_3 and 0.99 F, with a density of 1.18 g cm^{-3} .

The experiments were carried out in a thermostated cylindrical reactor equipped with a screw stirrer. The temperature in the thermostat was 65°C. The weight ratio of EPA : WDC ranged from 100 : 10 to 100 : 30. Phosphate raw materials were introduced into the reactor with a sample of EPA. The duration of the decomposition process from the moment the feedstock is loaded is 45 minutes. After the end of the decomposition process, the pulp was ammoniated to pH = 3.8. The granulation of ammonized slurries was carried out during drying at 85 - 90°C by the balling method. Then the product was cooled and analyzed for the content of nitrogen, various forms of phosphorus and calcium [16]. Determination of all forms of P_2O_5 (total (t.), acceptable, water-soluble(w.s.)) was carried out by the differential method widely used in the analysis of phosphate ores on a KFK-3 instrument ($\lambda = 440$ nm) in the form of a phosphorus vanadium - molybdenum complex. The acceptable form of P_2O_5

was determined by its solubility both in 2 % citric acid (ac.c.a.) and in a 0.2 M solution of Trilon B (ac. tr.B.) The determination of CaO content was carried out by a volumetric complexometric method: titration with 0.05 N Trilon B solution in the presence of the fluorexon indicator. The acceptable form of CaO - only 2 % citric acid (ac.c.a.).

RESULTS AND DISCUSSION

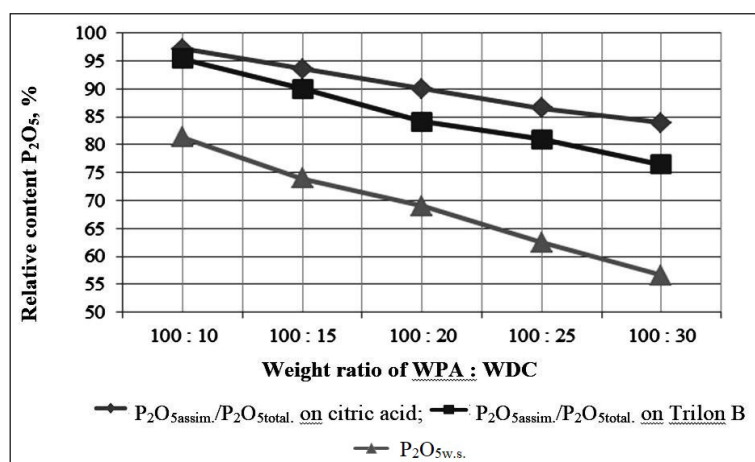
The composition of the samples of ammophosphate fertilizers is given in Table 2. As shown that an increase in the mass fraction of phosphate raw materials leads to a decrease in the total, assimilable and water-soluble forms of phosphorus in products. The less phosphate is introduced into the system, the freer H_3PO_4 remains in it and the more NH_3 is required to neutralize it, therefore, the higher the N content in the products. In this case, the finished product is dominated by ammonium phosphate over calcium phosphate. In any case, with the studied ratios of EPA:WDC, concentrated nitrogen-phosphorus fertilizers were obtained and the nitrogen content in them lies in the range of 4.92 - 7.11 %, P_2O_{5t} 41.48 - 46.44 %, $P_2O_{5ac.c.a.}$ by citric acid to those 34.79 - 45.11 %, $P_2O_{5ac.c.a.}$ by Trilon B 31.7 - 44.29 %, $P_2O_{5w.s.}$ 23.49 - 37.73 %. Also important is the fact that in ammophosphate a significant part of calcium is in the form assimilable for plants (9.66 - 14.55 %). Ca is the fifth most important nutrient after N, P, K and S. If it introduced into the soil in an acceptable form for plants, it will give a significant increase in yield [17].

The change in the relative contents of assimilable and water-soluble forms of P_2O_5 depending on the EPA: WDC ratio can be clearly seen in Fig. 1.

At that, ammophosphate fertilizers have $P_2O_{5ac.c.a.}$ by citric acid: $P_2O_{5t} = 84 - 97$ %, $P_2O_{5ac.c.a.}$ by Trilon B: $P_2O_{5t} = 76 - 95$ %, $P_2O_{5w.s.} : P_2O_{5t} = 57 - 81$ %. The high content of total and assimilable P_2O_5 makes them suitable for use as an effective nitrogen-phosphorus fertilizer. It should be noted that a product with a ratio of EPA : WDC =

Table 2. Composition of ammophosphate samples obtained on the basis of the decomposition of the washed dried concentrate with wet process phosphoric acid.

Mass ratio of EPA : WDC	pH	Chemical composition of dried products, mass %						
		P ₂ O _{5t.}	P ₂ O _{5ac.c.a.}	P ₂ O _{5ac.tr. B.}	P ₂ O _{5w.s.}	CaO _{t.}	CaO _{ac.c.a.}	N
100 : 10	3.70	46.44	45.11	44.29	37.73	11.81	9.66	7.11
100 : 15	3.78	45.39	42.46	40.86	33.54	15.93	11.61	6.93
100 : 20	3.88	44.00	39.60	36.99	30.38	19.40	12.45	6.53
100 : 25	3.97	42.55	36.84	34.46	26.57	22.03	13.28	5.53
100 : 30	4.06	41.48	34.79	31.70	23.49	24.50	14.55	4.92

Fig. 1. Change in the relative content of acceptable and water-soluble forms of P₂O₅ (%) depending on the weight ratio of EPA: WDC.

100 : 30 and having a minimum nitrogen content (less than 5 % N) can be applied under autumn fall plowing as a one-sided phosphorus fertilizer. The fact is that complex nitrogen-phosphorus fertilizers should not be applied for autumn fall plowing. Since in the winter period before sowing there will be large losses of nitrogen because of washing out by atmospheric precipitation and melt water. Nitrogen must be applied before sowing, with sowing and in top dressing. And phosphate fertilizers are most effective when they are applied under fall plowing.

At the next stage, to intensify the process of phosphoric acid decomposition of phosphate raw materials, 92.5 % sulfuric and 55 % nitric acids were used as additives. The amount of H₂SO₄ and HNO₃ was 5 - 7.5 g in the form of monohydrate (the calculation was made for a pure substance without water), and WDC - 10; 20 and 30 g in relation to 100 g of EPA.

From Tables 3 and 4 it can be seen that with the same ratio of EPA : WDC with an increase in the mass fraction of both H₂SO₄ and HNO₃, the content of the

total forms of P₂O₅ and CaO in the products decreases. However, at the same time, there is an increase in the relative content of their assimilable and aqueous forms, as well as nitrogen. So, with a mass fraction of WDC - 30 and mass fractions of H₂SO₄ - 5 and 7.5, the product contains 37.6 and 34.47 % of P₂O_{5t.}; 24.11 and 22.06 % CaO_{t.}, 88.75 and 92.40 % P₂O_{5ac.c.a.} by citric acid: P₂O_{5t.}, 84.21 and 89.7 % P₂O_{5ac.tr. B.} by Trilon B: P₂O_{5t.}, 77.39 and 79.54 % P₂O_{5w.s.}; P₂O_{5t.}:P₂O_{5t.}, 6.03 and 7.08 % nitrogen, respectively (Table 2). The higher the proportion of WDC in the mixture, the lower the content of P₂O_{5t.} in the products and N, the higher the CaO_{t.} content and the lower is the decomposition rate of phosphate raw materials. So, with a mass fraction of H₂SO₄ - 5 with an increase in the mass fraction of WDC from 10 to 30, the content in the product of P₂O_{5t.}, N, CaO_{t.}, P₂O_{5ac.c.a.} by citric acid: P₂O_{5t.} and P₂O_{5w.s.}:P₂O_{5t.} is ranged from 39.21 to 37.6 %, from 12.43 to 6.03 %, from 10.73 to 24.11 %, from 99.98 to 88.75 % and from 92.88 to 77.39 %, respectively. A similar picture is observed for the mass

Table 3. Composition of sulfoammophosphate samples obtained on the basis of the decomposition of the washed dried concentrate with a mixture of wet process phosphoric and sulfuric acids.

Mass ratio of nutrients, mass %	Mass ratio of EPA : H ₂ SO ₄ ^{monohydrate} : WDC					
	100: 5 : 10	100: 5 : 20	100: 5 : 30	100:7,5:10	100:7,5:20	100:7,5:30
pH	3.78	3.78	3.80	3.79	3.81	3.80
P ₂ O _{5t.}	39.21	39.15	37.60	36.02	35.65	34.47
N	12.43	7.55	6.03	14.28	8.79	7.08
P ₂ O _{5ac.c.a.}	39.20	38.11	33.37	36.02	35.18	31.85
P ₂ O _{5ac.tr.B.}	38.88	37.22	31.66	35.96	34.30	30.92
P ₂ O _{5w.s.}	36.42	33.05	29.10	35.03	33.65	27.42
CaO _{t.}	10.73	18.75	24.11	9.84	17.04	22.06
CaO _{ac.c.a.}	8.31	12.72	14.18	8.64	13.14	14.35
SO _{3t.}	14.1	12.86	10.35	17.66	15.12	13.57
$\frac{P_2O_{5ac.c.a.}}{P_2O_{5t.}} \times 100$	99.98	97.34	88.75	100.00	98.69	92.40
$\frac{P_2O_{5ac.tr.B.}}{P_2O_{5t.}} \times 100$	99.17	95.07	84.21	99.84	96.21	89.70
$\frac{P_2O_{5w.s.}}{P_2O_{5t.}} \times 100$	92.88	84.41	77.39	97.25	94.38	79.54
$\frac{CaO_{ac.c.a.}}{CaO_t.} \times 100$	77.45	67.84	58.81	87.80	77.11	65.05

Table 4. Composition of nitroammophosphate samples obtained on the basis of the decomposition of a washed dried concentrate with a mixture of extraction phosphoric and nitric acids.

Mass ratio of nutrients, mass %	Mass ratio of EPA : : HNO ₃ ^{monohydrate} : WDC					
	100 : 5 : 10	100 : 5 : 20	100 : 5 : 30	100 : 7,5 : 10	100 : 7,5 : 20	100 : 7,5 : 30
pH	3.81	3.81	3.82	3.79	3.80	3.80
P ₂ O _{5t.}	39.71	39.09	38.06	37.10	36.91	36.81
N	13.37	10.43	7.98	14.43	11.05	9.26
P ₂ O _{5ac.c.a.}	39.21	36.50	33.10	37.01	35.13	33.10
P ₂ O _{5ac.tr.B.}	38.94	34.92	29.40	36.57	33.86	29.09
P ₂ O _{5w.s.}	35.82	28.60	23.42	34.70	30.52	26.94
CaO _{t.}	10.84	18.56	24.13	10.14	17.69	23.58
CaO _{ac.c.a.}	8.39	11.93	13.43	7.16	11.79	13.49
$\frac{P_2O_{5ac.c.a.}}{P_2O_{5t.}} \times 100$	98.73	93.37	86.94	99.76	95.19	89.92
$\frac{P_2O_{5ac.tr.B.}}{P_2O_{5t.}} \times 100$	98.05	89.33	77.24	98.57	91.75	79.02
$\frac{P_2O_{5w.s.}}{P_2O_{5t.}} \times 100$	90.20	73.16	61.54	93.54	82.68	73.18
$\frac{CaO_{ac.c.a.}}{CaO_t.} \times 100$	77.40	64.28	55.66	70.61	66.65	57.21

fraction of H_2SO_4 - 7.5. They differ only in the absolute values. of the components in the products.

The same pattern is retained when using nitric acid as an additive (Table 3). In this case, nitroammophosphate contains the greatest amount of nitrogen, which is explained by the additionally introduced amount of nitric acid, but the phosphate raw material decomposes with

a relatively low coefficient.

The strength values of granules of ammophosphate, sulfoammophosphate and nitroammophosphate depending on the mass ratio of EPA : WDC, are shown in Fig. 2 - 4. It should be noted that the granulometric composition of the products is as follows: for granules less than 1 mm - no more than 3 %, 1 - 3 mm - no less than 90 %, 4 - 6

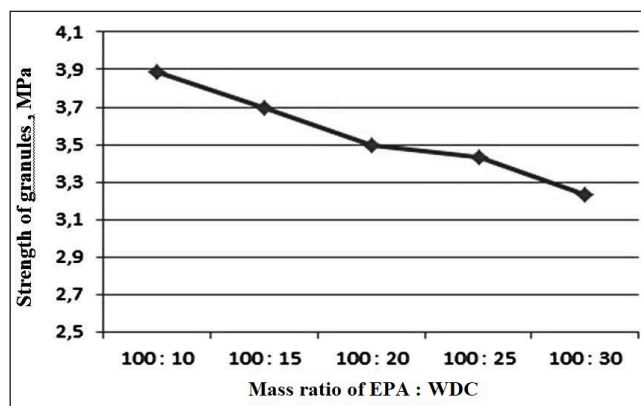


Fig. 2. Strength of granules of ammophosphate samples depending on the mass ratio of EPA : WDC.

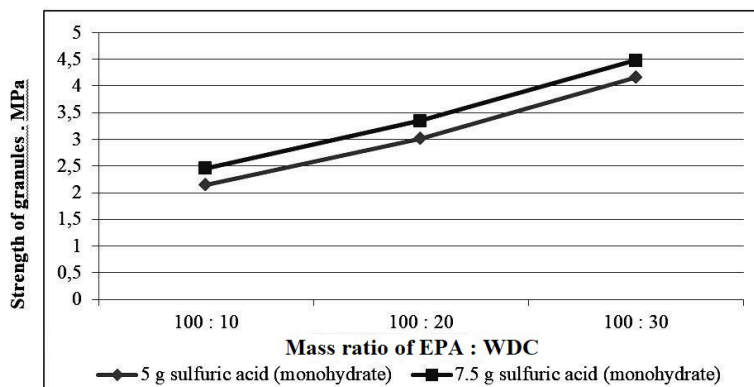


Fig. 3. Strength of granules of sulfoammophosphate samples depending on the mass ratio of EPA : WDC (note: Mng - monohydrate, g - gram).

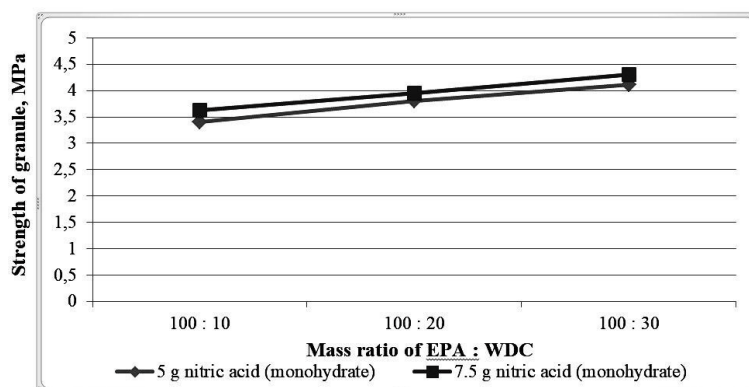
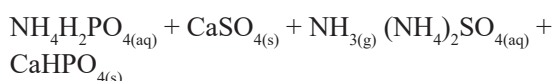


Fig. 4. Strength of granules of nitroammophosphate samples depending on the mass ratio of EPA : WDC (note: Mng - monohydrate, g - gram).

mm - no less than 4 %, and granules over 6 mm - absent.

Fig. 2 shown that with an increase in the mass fraction of WDC's from 10 to 30 g in relation to 100 g of EPA, the strength of ammophosphate granules decreases from 3.9 to 3.2 MPa, which is explained by a decrease in the proportion of ammonium phosphates in the product, instead of an increase in the weight of less strong phosphates calcium.

With a decrease in the amount of WDC's, in the EPA: WDC ratios from 30 to 10 g, a decrease in the strength of sulfoammophosphate granules is observed from 4.2 to 2.2 (with the addition of 5 g H₂SO₄ in relation to 100 g of EPA) and from 3.2 to 2.5 MPa (with the addition 7.5 g H₂SO₄ relative to 100 g EPA) (Fig. 3). This is because in the process of ammonization of phosphoric acid gypsum pulp, the gypsum conversion reaction occurs:



as a result of which the least strong salts of their ammonium sulfate and calcium hydrogen phosphate are formed. In this case, instead of calcium sulfate, ammonium

sulfate acts as a structurant. In nitroammophosphate, this property is given by ammonium nitrate (Fig. 4). However, an increase in its mass fraction in the product leads to a slight decrease in the strength of the granules from 4.12 to 3.40 (at 5 g HNO₃) and from 4.31 to 3.63 MPa (at 7.5 g HNO₃).

Thus, with all the studied options, the strength of granules of both ammophosphate (Fig. 2) and sulfo- (Fig. 3) and nitroammophosphate (Fig. 4) is at least 2 MPa, and on average 3.50 MPa. That is, the products meet the requirements of agriculture and are quite suitable for bulk storage and transportation.

Based on the results of experimental work, we calculated the material balance of nitrogen-phosphorus fertilizers. In Fig. 5 schematically shows the material flows of production of ammophosphate (Fig. 5a), sulfoammophosphate (Fig. 5b) and nitroammophosphate (Fig. 5c).

In Fig. 5. Scheme of material flows for the production of ammophosphate (at ratios (v.p.): a - EPA: WDC = 100: 30), sulfoammophosphate (b - EPA : H₂SO_{4mng} : WDC = 100 : 5 : 30) and nitroammophosphate (c - EPA: HNO_{3mng} : WDC = 100 : 5 : 30).

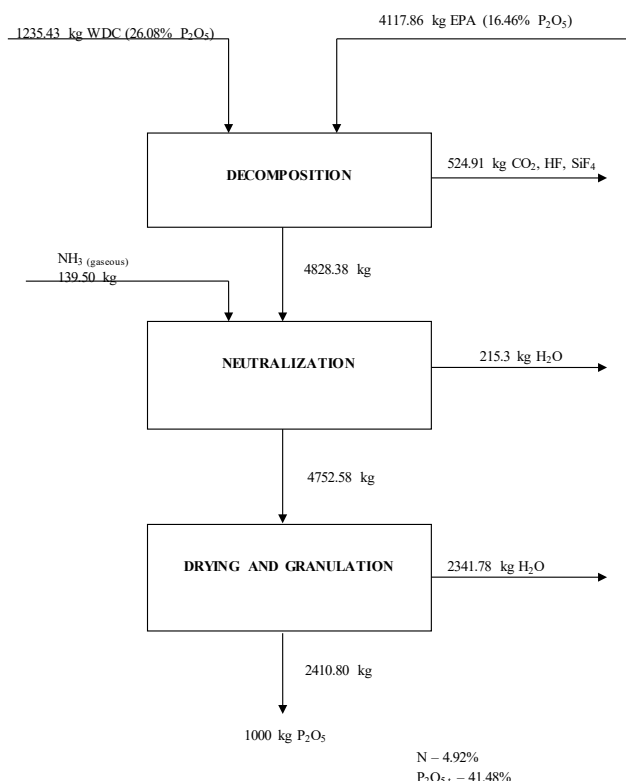


Fig. 5. Scheme of material flows for the production of ammophosphate (at ratios a EPA : WDC = 100 : 30), sulfoammophosphate (b - EPA : H₂SO_{4mng} : WDC = 100 : 5 : 30) and nitroammophosphate (c - EPA : HNO_{3mng} : WDC = 100 : 5 : 30).

CONCLUSIONS

The process of obtaining ammophosphate by means of phosphoric acid decomposition of a washed dried concentrate containing 26 % P_2O_5 with subsequent neutralization of acidic phosphate pulp with ammonia and drying of the product has been studied.

It was shown that it is possible to intensify the process of decomposition of the concentrate with phosphoric acid and increase the decomposition coefficient of the phosphate mineral by adding sulfuric or nitric acids with concentrations of 92.5 % H_2SO_4 and 55 % HNO_3 . The more the additive is introduced, the more intensive is the process of decomposition of phosphate raw materials. As a result concentrated nitrogen-phosphorus fertilizers with a high content of nitrogen, total, assimilable and water-soluble P_2O_5 were produced. In addition, the products contain calcium in a form assimilable for plants.

It was revealed that the strength of granules of all grades of ammophosphate fertilizers meets the requirements of agriculture (at least 2 MPa) and is quite suitable for bulk storage and transportation. Material balances of production of ammophosphate, sulfo- and nitroammophosphates have been calculated.

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