

Obtaining ammophosphate and sulfoammophosphate fertilizers on base of the washed dry concentrate containing 26% P₂O₅

Azam Rasulov¹, Bakhtiyor Juraev¹, Sadokat Toshtemirova¹, Shafaoat Namazov², and Uktam Temirov^{3*}

¹Namangan State University, Namangan, Republic of Uzbekistan

²Institute General and inorganic chemistry Academy Sciences of the Republic Uzbekistan, Toshkent, Republic of Uzbekistan

³Navoi State University of Mining and Technologies, Navoi, Republic of Uzbekistan

Abstract. The process of obtaining ammophosphate by means of phosphoric acid decomposition of washed dried concentrate (WDC with 26% P₂O₅ and 10% CO₂) - raw material for the production of thermally fired concentrate, has been studied. The wet process phosphoric acid (WPA) contains (wt.%): 16.46 P₂O₅, 0.06 CaO, 1.11 MgO, 0.27 Fe₂O₃, 0.41 Al₂O₃, 2.98 SO₃ and 0.99 F. The weight ratio of WPA: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 (P₂O_{5t}) 41.48-46.44%, phosphorus acceptable by citric acid (P₂O_{5ac.c.a.}) 34.79-45.11%, phosphorus form of water soluble (P₂O_{5w.s.}) 23.49-37.73%. Weight fractions of H₂SO₄ - 5 and 7.5 were optimal and 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}, 6.03 and 7.08% nitrogen, respectively. The strength of granules of fertilizers averages 3.50 MPa and are quite suitable for bulk storage and transportation.

1 Introduction

Ammophosphate is a nitrogen-phosphorus fertilizer belonging to the class of partially decomposed phosphates. The process of its production based on the decomposition of natural phosphates with a high rate (150-200%) of phosphoric acid, followed by neutralization of the remaining acidity with ammonia, granulation and drying of the product [1-5]. Unlike ammophos, the consumption of sulfuric acid for the production of 1 ton of P₂O₅ 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 monoammonium phosphate, as impurities - dicalcium phosphate (CaHPO₄ - calcium hydrogen phosphate) and highly basic calcium phosphates, that is hydroxylfluorapatite. The latter group includes

* Corresponding author: temirov-2012@mail.ru

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 [6].

The production of ammophosphate was mastered from Karatau phosphorites at the Dzhambul 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 PhA Minfertilizers 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 [7-12].

Earlier, in [13-18], the process of obtaining ammophosphate fertilizers based on the decomposition of various types of Kyzylkum phosphorites by wet process phosphoric acid (WPA with a concentration of 21.45% P_2O_5) was studied. 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 WPA leads to a decrease in its decomposition coefficient ($C_{d.c.}$) 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 [19-22], which was subjected to chemical enrichment, that is, 52% nitric acid to dissolve and remove calcite in the form of calcium nitrate.

In [23-27] the results of phosphate fertilizer process investigation using decompose of phosphorite with mixture of phosphoric and sulphuric acids at ratios of SO_3 : P_2O_5 equal to 1.2; 1.65; 2.6, as well as at various ratios of acids mix to phosphate raw materials, have been given. The advantages of this process in comparison with ammonium sulphate-phosphate were shown. 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.

At present, at the Kyzylkum phosphorite complex, in the process of washing phosphate flour from 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 ammophosphate based on former, has not been studied.

2 Materials and methods

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 (wt.%): 26.08 P_2O_5 ; $P_2O_{5_{sacc.a.}}$: $P_2O_{5_{st.}}$ = 13.08; 51.74 CaO; 0.89 MgO; 0.31 Fe_2O_3 ; 1.02 Al_2O_3 ;

1.59 SO₃; 9.95 CO₂; 2.49 insoluble residue; CaO_{t.}:P₂O_{5t.} = 1.98. And for its decomposition, WPA was used, obtained from a thermoconcentrate by the dihydrate method at JSC "Ammofos-Maxam" and having a composition (wt%): 16.46 P₂O₅, 0.06 CaO, 1.11 MgO, 0.27 Fe₂O₃, 0, 41 Al₂O₃, 2.98 SO₃ and 0.99 F, with a density of 1.18 g / cm³.

The experiments were carried out in a thermostated cylindrical reactor equipped with a helical stirrer. The temperature in the thermostat was 65°C. The weight ratio of WPA: WDC ranged from 100: 10 to 100: 30. Phosphate raw materials were introduced into the reactor with a sample of WPA. 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. Determination of all forms of P₂O₅ (total (t.), acceptable by citric acid (ac.c.a.), water soluble (w.s.) was carried out by the differential method widely used in the analysis of phosphate ores on a KFK-3 instrument (λ = 440 nm) in the form of a phosphorus vanadium - molybdenum complex. The assimilable form of P₂O₅ was determined by its solubility both in 2% citric acid and in a 0.2 M solution of Trilon 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 by citric acid form of CaO - only 2% citric acid.

3 Results and discussion

The composition of the samples of ammophosphate fertilizers is given in Table 1. As shown that an increase in the weight 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 more free H₃PO₄ remains in it and the more NH₃ 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 WPA: WDC, concentrated nitrogen-phosphorus fertilizers were obtained and the nitrogen content in them lies in the range of 4.92-7.11%, P₂O_{5t.} 41.48-46.44%, P₂O_{5 ac.c.a.} by lim. to-those 34.79-45.11%, P₂O_{5ac.tr.b.} by trilon B 31.7-44.29%, P₂O_{5w.s.} 23.49-37.73%. Also important is the fact that in ammophosphate a significant part of calcium is in the acceptable form 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 a form assimilable for plants, it will give a significant increase in yield.

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The change in the relative contents of acceptable by citric acid, acceptable by trilon B and water soluble forms of P₂O₅ depending on the WPA: WDC ratio can be clearly seen in Figure 1. At that, ammophosphate fertilizers have P₂O_{5ac.c.a.} by citric acid: P₂O_{5t.} = 84-97%, P₂O_{5ac.tr.b.} by trilon B: P₂O_{5t.} = 76-95%, P₂O_{5w.s.}: P₂O_{5t.} = 57-81%. The high content of total and acceptable form of P₂O₅ makes them suitable for use as an effective nitrogen-phosphorus fertilizer. It should be noted that a product with a ratio of WPA: 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.

Table 1. Composition of ammophosphate samples obtained on the basis of the decomposition of the washed dried concentrate with wet process phosphoric acid.

Weight ratio of WPA: WDC	pH	Chemical composition of dried products, wt. %						
		P ₂ O _{5t}	P ₂ O _{5ac.ca.} in citric acid	P ₂ O _{5ac.tr.b.} on Trilon B	P ₂ O _{5w.s.}	CaO _t	CaO _{ac.ca.} in citric acid	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

In Figure 2 shows the strength values of granules of ammophosphate depending on the weight ratio of WPA: WDC. 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 mm - no less than 4%, and granules over 6 mm - absent.

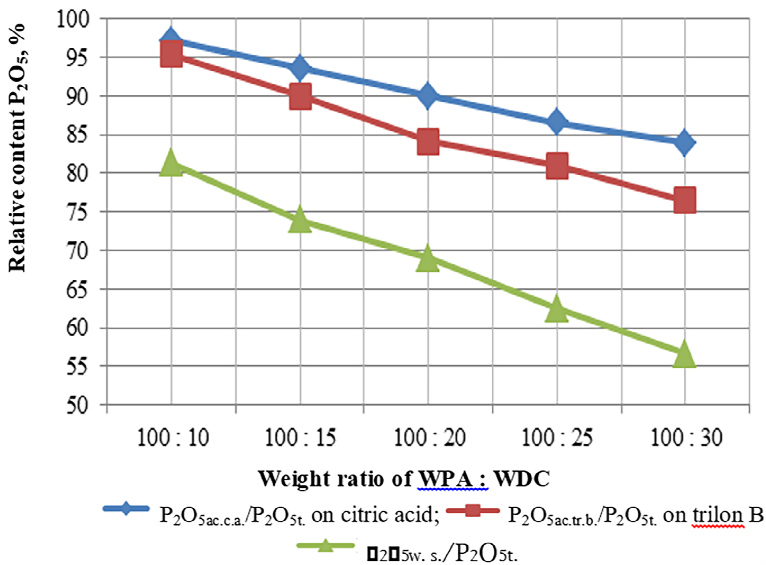


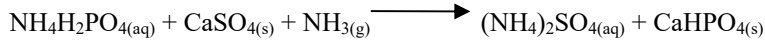
Fig. 1. Change in the relative content of acceptable by citric acid, acceptable by trilon B and water soluble forms of P₂O₅ (%) depending on the weight ratio of WPA: WDC.

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.

From Figure 2 shown that with an increase in the weight fraction of WDC's from 10 to 30 g in relation to 100 g of WPA, 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 WPA: 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 WPA) and from 3.2 to 2.5 MPa (with the addition 7.5 g H₂SO₄ relative to 100 g WPA) (Figure 2-b). 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 dicalcium phosphate are formed. In this case, instead of calcium sulfate, ammonium sulfate acts as a structurant.

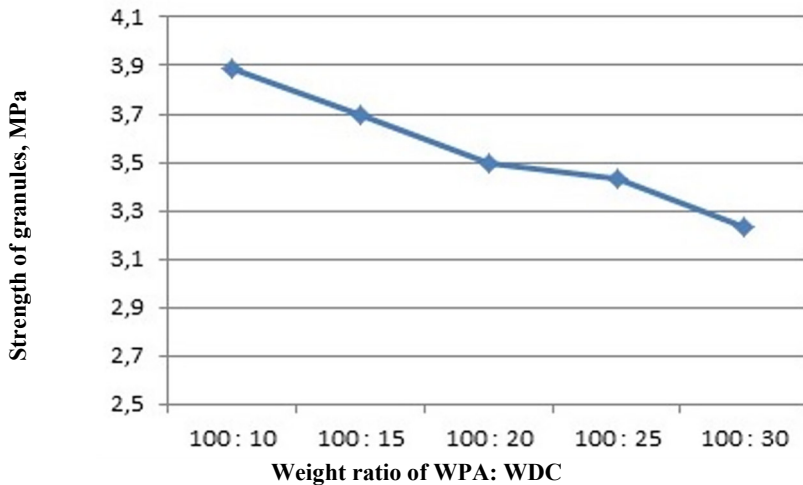


Fig. 2. Strength of granules of ammophosphate samples depending on the weight ratio of WPA: WDC.

At the next stage, to intensify the process of phosphoric acid decomposition of phosphate raw materials, 92.5% sulfuric acid were used as additives. The amount of H₂SO₄ 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 WPA (Table 2).

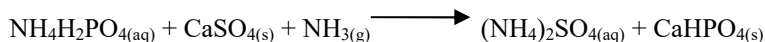
Table 2 demonstrates that with the same ratio of WPA: WDC with an increase in the weight fraction of H₂SO₄, the content of the total forms of P₂O₅ and CaO in the products decreases. However, at the same time, there is an increase in the relative content of their acceptable and water solubility forms, as well as nitrogen. So, with a weight fraction of WDC - 30 and weight 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}, 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 weight fraction of H₂SO₄ - 5 with an increase in the weight 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 weight fraction of H₂SO₄ - 7.5. They differ only in the absolute values of the components in the products.

Table 2. 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.

Weight ratio of nutrients, wt. %	Weight ratio of WPA: 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.} by citric acid	39.20	38.11	33.37	36.02	35.18	31.85
P ₂ O _{5ac.tr.b.} by trilon 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	14.72	19.85	8.64	13.14	14.35
SO _{3t.}	14.10	12.86	10.35	17.66	15.12	13.57
$\frac{P_2O_{5ac.c.a.}}{P_2O_{5t.}} \times 100$ by citric acid	99.98	97.34	88.75	100.00	98.69	92.40
$\frac{P_2O_{5ac.tr.b.}}{P_2O_{5t.}} \times 100$ by trilon B	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	78.51	82.33	87.80	77.11	65.05

Figure 2 shows the strength values of granules of sulfoammophosphate fertilizers depending on the weight ratio of WPA: WDC. With a decrease in the amount of WDC's, in the WPA: 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 WPA).

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 dicalcium phosphate are formed. In this case, instead of calcium sulfate, ammonium sulfate acts as a structurant.

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

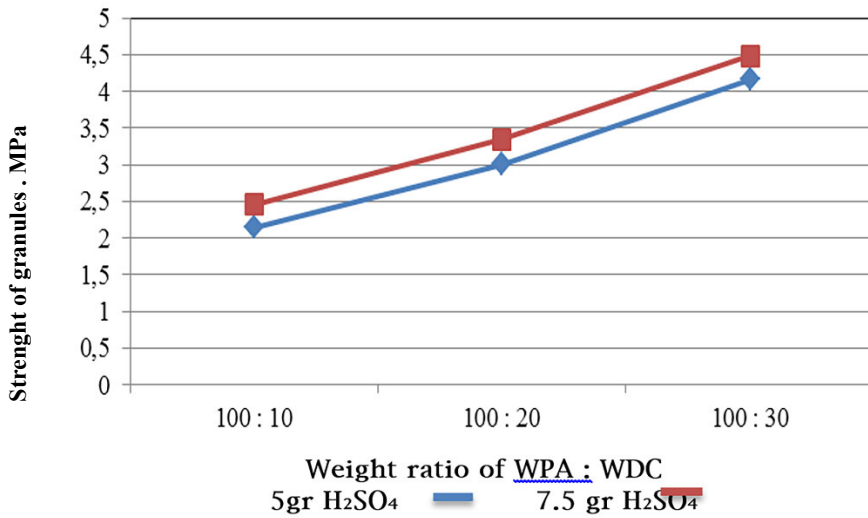


Fig. 3. Strength of granules of ammophosphate samples depending on the weight ratio of WPA: WDC.

Thus, with all the studied options, the strength of granules of ammophosphate and sulfoammophosphate fertilizers are at not 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.

4 Conclusion

The process of obtaining ammophosphate by means of phosphoric acid decomposition of a washed dried concentrate containing 26% P₂O₅ 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% H₂SO₄. As a result concentrated nitrogen-phosphorus fertilizers with a high content of nitrogen, total, acceptable by citric acid and by trilon B and water-soluble P₂O₅ were produced. In addition, the products contain calcium in the acceptable form for plants. It was revealed that the strength of granules of all grades of ammophosphate and sulfoammophosphate fertilizers meets the requirements of agriculture (at least 2 MPa) and is quite suitable for bulk storage and transportation.

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