

# Physical and Chemical Properties of Phosphorus-Containing Calcium Ammonium Nitrate

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**ABSTRACT:** When obtaining samples of phosphorus and potassium-containing calcium ammonium nitrate (CAN), the mass ratios of AN : DM: PhF (ammonium nitrate : dolomite mineral : phosphate flour) varied from 100 : 0.5 : 0.5 to 100 : 25 : 25. The pelletizing method was used to granulate the nitrate-phosphate-carbonate melts. The composition and properties of the obtained fertilizers were determined. The main modification indicator is the strength of the granules. If for pure AC it is 1.32 MPa, then for fertilizer with the ratio AN : DM : PhF = 100 : 0.5 : 0.5 and 100 : 25 : 25 it is 3.58 and 12.45 MPa, respectively. Thus, it is shown that fertilizers based on AN melt with the addition of powdered DM and PhF should be packed in paper or polyethylene bags.

**KEY WORDS:** ammonium nitrate, dolomite mineral, phosphate flour, potassium chloride, phosphorus and potassium-containing ammonium nitrate, composition and properties.

## I. INTRODUCTION

AN is the most widely used and effective nitrogen fertilizer worldwide. However, it has three serious drawbacks. First, it is explosive; second, it tends to cake during storage; and third, it is physiologically acidic, which prevents its use on acidic soils. To address these shortcomings, a technology was developed for producing ammonium nitrate by introducing calcareous materials (limestone, chalk, or dolomite) into molten ammonium nitrate. Worldwide, 42 companies currently produce this ammonium nitrate, with a nitrogen content of 20-33%, 31 of which are located in Europe, where acidic soils are most prevalent [1-3].

The share of CAN capacity is estimated at approximately 7% [4]. In recent years, Russian plants: the Angarsk Fertilizer Plant, Kuibyshev Azot, Dorogobuzh OJSC, Nevinnomyssk Azot OJSC, and Novomoskovsk Azot JSC have also begun producing CAN with a nitrogen content of 32%. Uzbekistan also has several large deposits of dolomite minerals: Shursu (Fergana region), Navbahor (Navoi region), Karnab and Ingichka (Samarkand region), Ketmonchi (Navoi region), Dehkanabad (Kashkadarya region), and others. Therefore, it became possible to organize the production of magnesium-containing CAN in Uzbekistan [5, 6].

Previously [7-9] we studied the composition and properties of magnesium-containing CAN obtained on the basis of AN melt (34.5% N) and DM "Shursu" and "Navbahor" deposits in Uzbekistan. It was shown that, for the studied ranges of the ratios AN : DM = 100 : (3-35), the products with the addition of the Shursu dolomite contain 25.49-32.77% nitrogen, and with the addition of the Navbahor dolomite they contain 25.54-32.52% nitrogen. The strength and the time of complete dissolution of the granules of pure ammonium nitrate are 1.32 MPa and 44.6 sec. The introduction of dolomite into the ammonium nitrate melt increases both the strength and the time of complete dissolution of the granules. Thus, if at the ratio AN: DM = 100: 3 (Shursu dolomite) the granule strength is 2.81 MPa and the time of complete granule dissolution is 57.71 sec, then at the ratio AN: DM = 100: 35 these figures are as follows: 10.18 MPa and 67.85 sec. In the case of using Navbahor dolomite at the ratio AN: DM = 100: 3 the strength of the fertilizer granule is 3.44 MPa, and the time of complete granule dissolution is 58.82 sec, at the ratio AN: DM = 100: 35 these figures are 10.44 MPa and 71.26 sec. These data indicate that the resulting fertilizers have greater thermal stability than pure ammonium nitrate and, in comparison, they will be washed out of the soil much more slowly.

## II. OBJECTS AND METHODS OF RESEARCH

The objective of this work is to study the composition and commercial properties of products obtained by the interaction of AN melt with powdered dolomite "Ingichka" of the Samarkand region, Kyzylkum ordinary phosphorite flour (PhF  $P_2O_{5\text{total}}$  – 20.23%;  $CaO_{\text{total}}$  – 43.54%;  $MgO_{\text{total}}$  – 3.14%) and KCl ( $K_2O$  – 60%) produced by the Dehkanabad plant. To obtain samples of phosphorus-containing nitrate-carbonate phosphate, experiments were carried out as follows: a sample of AN was melted in a metal cup using electrical heating. Then, DM and PhF were added to the AN melt at mass ratios of AN : DM : PhF = 100 : (0.5-25) : (0.5-25). Next, the nitrate-carbonate-phosphate melt was maintained at 170-175°C for 10 minutes. Afterwards, it was poured into a laboratory granulator, which was a metal cup with a perforated bottom, the diameter of the holes in which was 1.2 mm. A pump at the top of the cup created pressure and the melt was sprayed from a height of 35 m onto a polyethylene film lying on the ground. The resulting granules were sieved by particle size. After that, the products were crushed and analyzed using known methods [10].

The pH of 10% aqueous suspensions of the studied samples was measured using a Mettler Toledo Five Easy F 20 laboratory ion meter. The caking properties of fertilizers were determined using a rapid method. The caking properties ( $X$  - kg/cm<sup>2</sup>) were calculated using the formula:  $X = P/S$ , where  $P$  is the breaking force, N (kgf);  $S$  is the cross-sectional area of the sample, cm<sup>2</sup>. The absorption capacity of granules in relation to liquid fuel (diesel oil) was determined using the method provided by TU 6-03-372-74 for granulated porous AN brand "P". This indicator is expressed as the number of grams that can absorb 100 g of granules (g/100 g).

The dissolution rate of the sample granules in water was determined as follows. A fertilizer granule was dropped into a beaker containing 100 ml of distilled water, where its complete dissolution was visually observed and recorded. The tests were repeated five times at room temperature. Granular  $NH_4NO_3$  (without additive) and AN (with 0.28%  $MgO$  additive) were selected as comparison samples to the test samples.

## III. RESULTS AND THEIR DISCUSSION

The results are shown in Table 1.

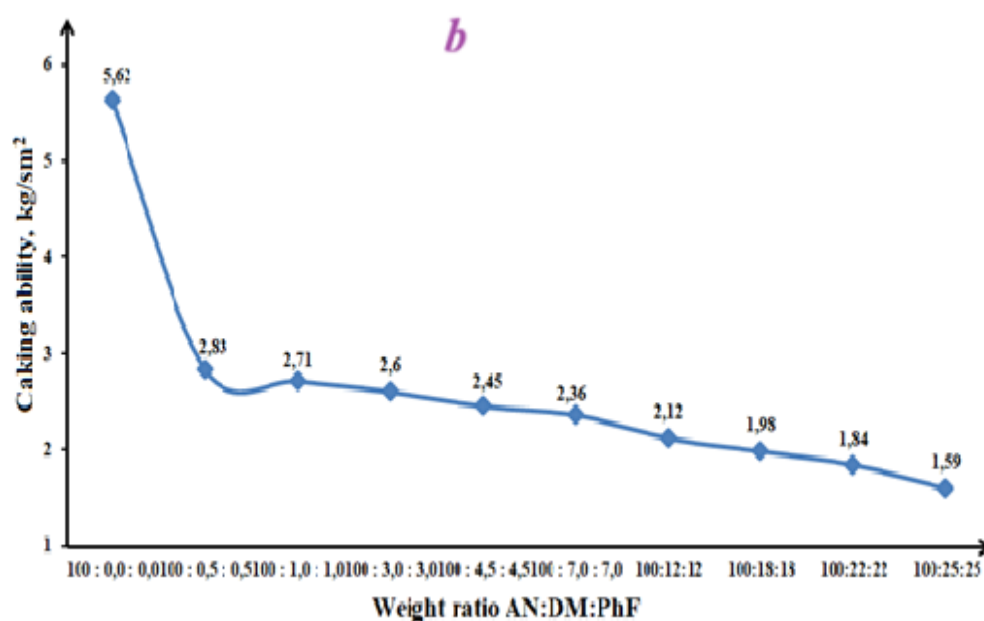
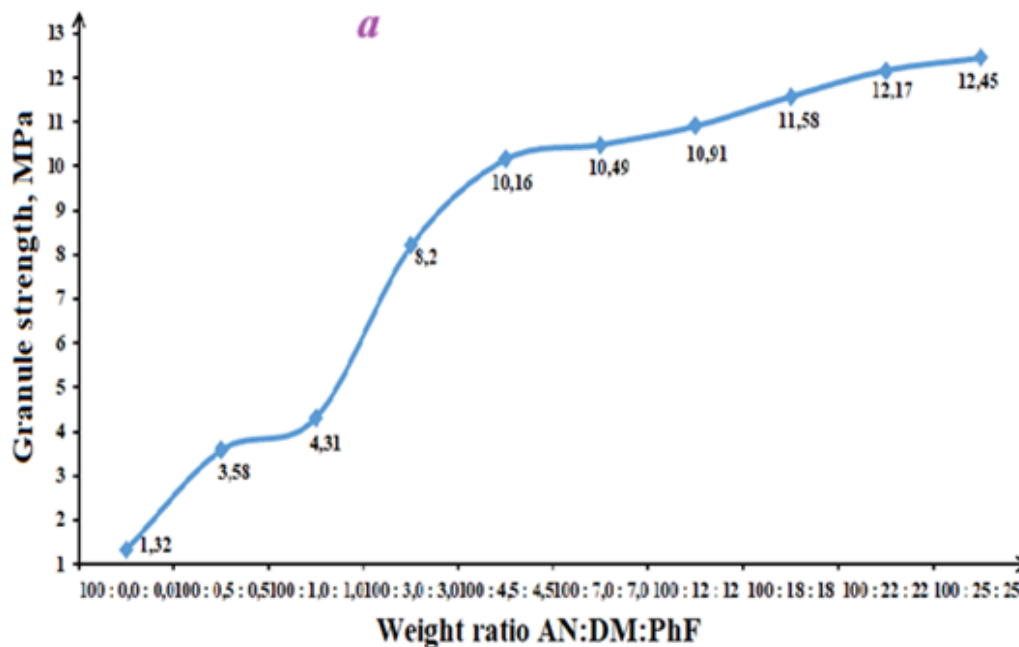
Table 1  
**Composition of phosphorus-containing calcium ammonium nitrate**

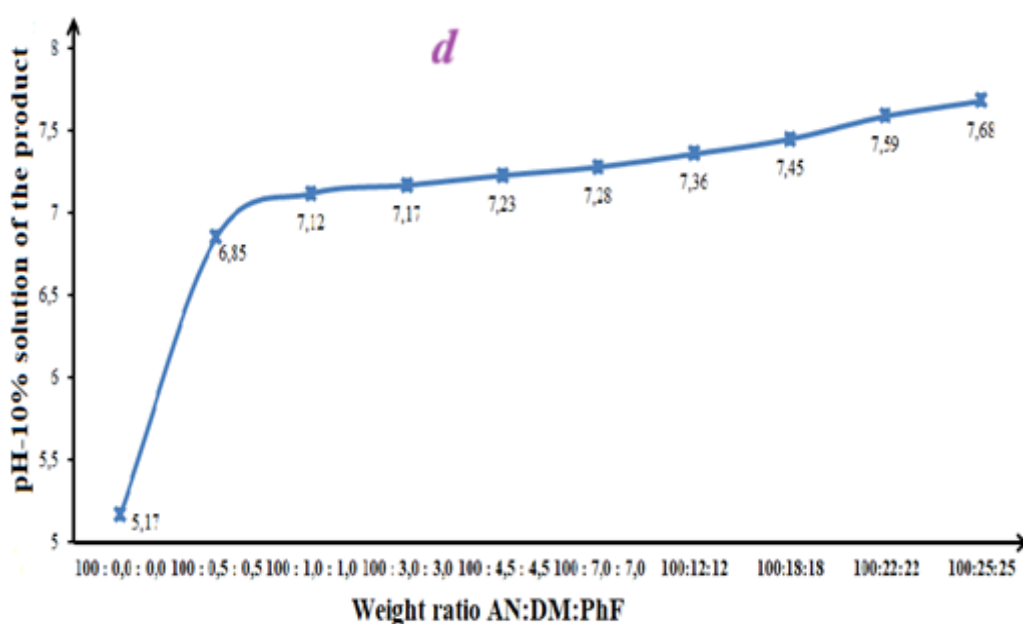
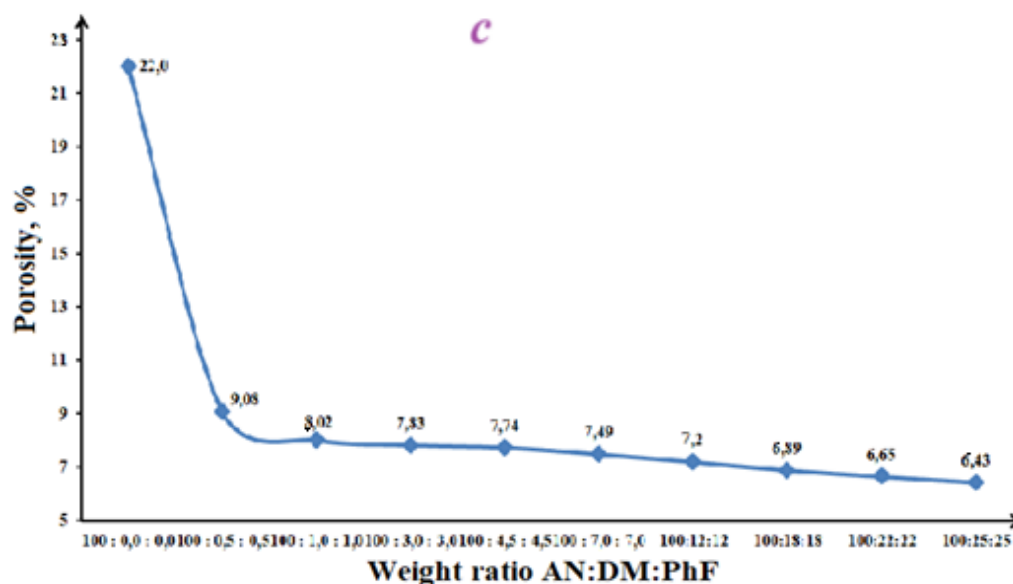
Mass ratio of the initial components AN : DM : PhF	Content of components, mass. %				
	$N_{\text{total}}$	$P_2O_{5\text{total}}$	$K_2O$	$CaO_{\text{total}}$	$MgO_{\text{total}}$
100 : 0.5 : 0.5	34.57	0.18	—	0.58	0.18
100 : 1.0 : 1.0	34.19	0.29	—	0.79	0.27
100 : 1.5 : 1.5	33.90	0.41	—	1.17	0.41
100 : 4.5 : 4.5	32.01	1.27	—	3.49	1.12
100 : 7.0 : 7.0	30.53	1.68	—	5.06	2.47
100 : 12 : 12	28.14	2.13	—	6.90	2.78
100 : 15 : 15	26.76	2.48	—	8.01	2.78
100 : 20 : 25	24.93	3.19	—	10.32	3.39
100 : 25 : 25	23.35	4.22	—	13.01	4.28

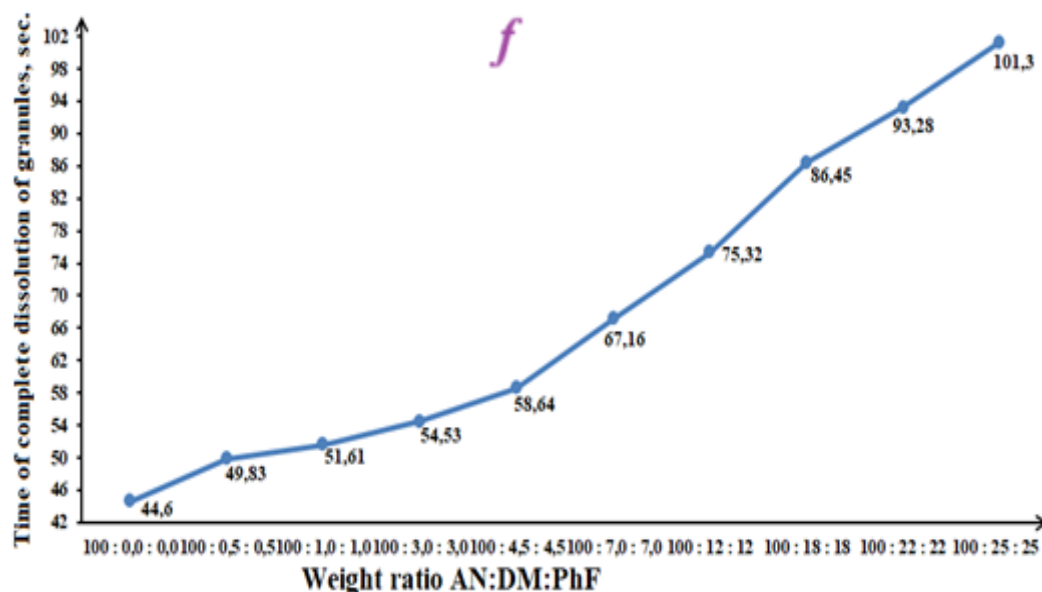
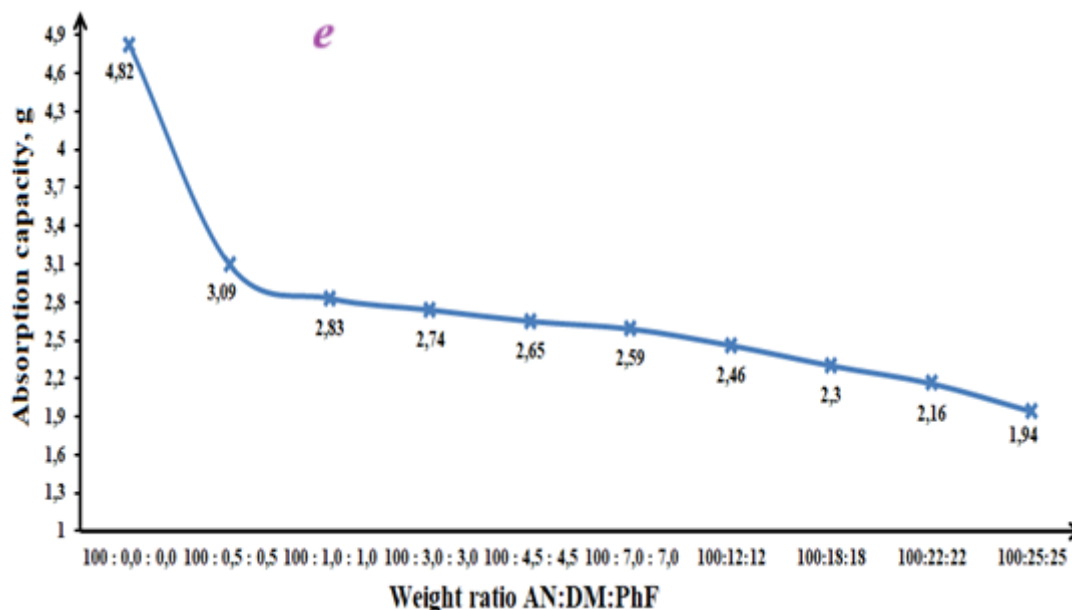
Table 1 shows that by adding DM and PhF to the AN melt at the ratios of AN : DM : PhF = 100 : (0.5-25) : (0.5-25), it is possible to obtain nitrogen-phosphorus-calcium-magnesium fertilizers of the following composition (wt.%): 23.35-34.57% N, 0.18-4.22%  $P_2O_5$ , 0.58-13.01 CaO and 0.18-4.28 MgO. Dolomite and phosphate rock are used as the starting material for the production of phosphorus-containing CAN, it contains four nutrients (NPCaMg). These four elements play a very important role in plant life. If they are added to the soil in a form assimilated by plants, it will give a significant increase in yield.

The figure shows that increasing the mass fractions of DM and PhF leads to a noticeable increase in the strength of the granules. The strength of the fertilizer granules obtained at the ratio of AN : DM : PhF = 100 : (0.5-25) : (0.5-25) is in the range of 3.58-12.45 MPa (Fig. a). At these ratios of AN : DM : PhF, the caking (Fig. b), porosity of the granules (Fig. c) and absorbency by them (Fig. d) are 2.83-1.59 kg/cm<sup>2</sup>, 8.52-6.43% and 3.04-1.94 g, respectively. And the strength, caking, porosity and absorbency of the granules of pure AC are 1.32 MPa, 5.62 kg/cm<sup>2</sup>, 22.0% and 4.82 g, respectively. This means that an increase in the strength of saltpeter granules indicates

a decrease in its porosity and internal specific energy surface, and leads to a decrease in the penetration of diesel fuel into the granule, and, consequently, a decrease in the detonation ability of the nitrate.







1- Figure. Dependence of the change in strength (a), caking (b), porosity (c), pH (d), absorbency (d) and the time of complete dissolution of granules (e) of phosphorus-containing CAN on the ratio AN: DM: PhF

It was also found that AN granules with the studied DM and PhF additives dissolve in water significantly more slowly (1.12 to 2.3 times less) than pure AN (*Fig. d*). This means that AN granules containing DM and PhF dissolve significantly more slowly in the soil solution. Consequently, the presence of DM and PhF in the nitrate facilitates the gradual release of nitrogen from the granule. Furthermore, the addition of DM and PhF to the  $\text{NH}_4\text{NO}_3$  melt increases the pH of a 10% solution of the latter from 5.17 to 6.85-7.68 (*Fig. f*), which demonstrates its greatest effectiveness in neutral and acidic soils.

In this report, we present the results of determining the hygroscopic point and sorption capacity of phosphorus-containing calcium ammonium nitrate granules. To study the hygroscopic points, several fertilizer samples were selected, which are listed in Table 2.

Table 2  
**Hygroscopic point and moisture content of granules of phosphorus-containing calcium ammonium nitrate samples**

№	AC: DM: PhF	Humidity, %	Hygroscopic point, %
1	"Pure" grade $\text{NH}_4\text{NO}_3$	0.27	62.0
2	100 : 0.5 : 0.5	0.18	50.6
3	100 : 1.0 : 1.0	0.20	51.7
4	100 : 1.5 : 1.5	0.22	51.9
5	100 : 4.5 : 4.5	0.24	52.0
6	100 : 7.0 : 7.0	0.25	52.2
7	100 : 12 : 12	0.27	52.4
8	100 : 15 : 15	0.28	52.9
9	100 : 20 : 25	0.29	53.7
10	100 : 25 : 25	0.31	54.5

The hygroscopic point of fertilizer samples with granule sizes of 2-3 mm was determined using the desiccator method [10] at a temperature of 25°C.

Table 2 shows that the initial moisture content of the first sample (AN) was 0.27%, the second – 0.18%, the third – 0.20%, the fourth – 0.22%, the fifth – 0.24%, the sixth – 0.25%, the seventh – 0.27%, the eighth – 0.28%, the ninth – 0.29%, and the tenth – 0.31%. The moisture gain or loss in the substance was determined at a constant temperature and specified relative air humidities over a period of 3 hours. The required relative air humidity was created in a closed desiccator over a layer of sulfuric acid of known concentration poured into it. The relative air humidity at which the substance neither becomes moistened nor dries out is called the hygroscopic point of the substance. If the hygroscopic point is lower than the relative air humidity, the substance absorbs moisture from the air. If it is higher than the relative humidity of the air, the substance dries out. The values of the hygroscopic points for our fertilizers were equal: for sample 1 - 62.0%, for sample 2 - 50.6%, for sample 3 - 51.7%, for sample 4 - 51.9%, for sample 5 - 52.0%, for sample 6 - 52.2%, for sample 7 - 52.4%, for sample 8 - 52.9%, for sample 9 - 53.7% and for sample 10 - 54.5%. The reason for the low value of the hygroscopic point of the products is explained by the fact that the mixture of salts is more hygroscopic than its components [11].

#### IV. CONCLUSION AND FUTURE WORK

Research was conducted to produce a phosphorus-containing nitrate-containing ammonium nitrate based on an AN melt and powdered DM and PhF. It was shown that the higher the amount of DM and PhF, the lower the caking, porosity, and absorption of the diesel oil, and the higher the strength and water solubility of the ammonium nitrate granules.

Thus, samples of phosphorus-containing CAN have improved physicochemical, agrochemical and low detonation properties and should be packaged in paper or polyethylene bags.

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