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Nitrogen-phosphorous fertilizers on the base of concentrated ammonium nitrate solution and Central Kyzylkum phosphate raw material

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This article presents obtaining of nitrogen-phosphate fertilizers by reacting ordinary phosphate powder from Central Kyzylkum (Uzbekistan) with 70–90% ammonium nitrate solution at 100ºC. Chemical composition of the fertilizers was determined fully. Relevant consistence of acceptable forms of P_2O_5 and CaO in the product extremely decreased by the increase of amount of phosphate raw material (PRM) in reaction mixture. The addition of phosphate additive into ammonium nitrate solution significantly increases toughness of ammonium nitrate granules and their growth velocity proportionally by phosphate powder added. Herewith, initial concentration of ammonium nitrate did not effect practically on the granule's toughness. It is described that, phosphate additive decreases the speed of solubility of ammonium nitrate granules almost up to 1.83 times. On our opinion, decrease of fertilizer solubility is the result of growing phosphorite share in the products. The more is the phosphorite share, the more slowly dissolution process of the fertilizer granule does occur.

Keywords: ammonium nitrate solution, phosphate raw material, activation, nitrogen phosphorous fertilizer, toughness of granules, velocity of granules dissolution.

INTRODUCTION

Ammonium nitrate is one of the most effective and widespread nitrogen fertilizers. In Uzbekistan, ammonium nitrate is produced for agricultural aims by the following three giant industrial enterprises: Open Joint Stock Companies "Maxam Chirchik", "Navoiazot", and "Ferganaazot". Their total capacity is over one million tonnes a year. However, this fertilizer has two disadvantages – caking while keeping in repository and its explosiveness risk[1, 2, 3]. While the caking can be diminished by introducing to the ammonium nitrate of some additives (calcium, magnesium etc), the problem of explosion hazard in world's practice is not solved yet totally.

It is known that ammonium nitrate (AN) is an oxidant, able to support combustion[4]. At normal conditions of environment AN is a stable substance. It's heating in closed space leads to a blast, and products of thermal decomposition are not able to move freely. It can also be detonated by the influence of strong shock load or initialization of explosive materials.

Accordingly, there is a great demand for fertilizers on the base of AN around the world, with maximum agro-chemical effectiveness and the outer influence resistance to an explosive risk. Inorganic substances containing special additives give a hope to solving the problem of explosiveness of the ammonium nitrate[5]. On a complex of target criteria of positive influence on properties of AN and commercial value a potential number of fertilizers on the basis of AN can be presented as follows:

– Nitrogen-phosphorus (NP)-fertilizers with water-soluble phosphorus > 5.0% P_2O_5;

– Nitrogen-potassium (NK)-fertilizers with potassium additive 30–60%;

– Calcium ammonium nitrate (CAN), calcium magnesium ammonium nitrate;

– Other mixtures with ammonium nitrate (ammonium sulfate, etc.).

Basis of reception of calcium-ammoniac saltpeter is a mixture of fines of a calcium carbonate (limestone, swept etc.) with fusion cake of AN and the subsequent granulation of a product. CAN is issued with various ratio NH_4NO_3 : $CaCO_3$ characteristic for the various countries so in Germany it is accepted at a level of 65:35; in England – 53–57:43–47; in Poland – 58.5–60:40–41.5; in the USA – 60:40; in France - 78-80:20-224. Proceeding from safety of a product, it is considered to be the maximum permissible content of nitrogen in CAN equal to 29%. Nowadays the mixture of ammoniac saltpeter and ammonium sulfate (Lane saltpeter) is produced at Germany by «Uhde GmbH» company.

The Russian plants "Azot" (Kemerovo city), JSC "Kirovo-Chepetskii Khimkombinat" JSC "Minudobreniya" (Rossosh city) and Novgorod's JSC "Akron" came up to production of stabilized ammonium nitrate by adding of phosphorus-containing materials. The were the first known enterprises approaching by 2001 the industrial production of NP-fertilizers based on AN used as the phosphorus-containing raw material by extraction of phosphoric acid or ammonium di-hydrogen phosphate solution produced from this acid[6, 7, 8]. The problem they faced to were the following: (1) strong metal equipment's corrosion due to fluorine containing in the phosphoric acid, (2) sedimintation of Fe, Al, Mg and Ca salts on the equipment's walls leading even to sealing. The system productivity felt down twice in compare with pure ammonium nitrate's scheme.

By 2003 year the industrial production of NP-fertilizers (32% N and 6% P_2O_5) started with the preliminary purified nitric and phosphoric acid extract from "azofoska"[9, 10]. This led to the problems similar to those based on extractive phosphoric acid derivatives.

Therefore searching for appropriate phosphorus-containing material for stabilization of AN is continued. At Kirovo-Chepetsk chemical mill (Russia) it was proposed to load mixed extractive phosphoric and sulfuric acids into the nitric acid prior to ammonization[11]. But at evaporation

of the solution formed and granulation the equipment stoppage is also at big risk. So in order to avoid the above disadvantages we decided to carry out obtaining of stabilized ammonium nitrate by introduction of thoroughly powdered phosphate from Central Kyzylkum to their solution.

MATERIAL AND METHODS

The materials were applied the following; Central Kyzylkum's phosphate raw material of composition (weight %): $P_2O_{5total(tot.)}$ 17.20; CaO 46.22; Al_2O_3 1.24; Fe_2O_3 1.05; MgO 1.75; F 2.00; CO_2 16.00; $P_2O_{5acceptable.}$: P_2O_{5total} = 18.49%.

In a composition of phosphorite's flours the aqua soluble form of phosphorus was not found out. Proceeding from the scanty maintenance of organic carbon in phosphorite of the Central Kyzyl Kum (0.1–0.3%), it's content was neglected in calculations so we have defined only inorganic carbon there. Dispersed composition of phosphate raw material was the following: (–0.5 + 0.315 mm) – 1,5%; (–0.315 + 0.16 mm) – 6.3%; (–0.16 + 0.1 mm) – 20.3%; (–0.1 + 0.063 mm) – 38.3%; (–0.063+ 0.05 mm) – 17.2%; (–0.05 mm) – 16.4%. As the secondary initial component the ammonium nitrate produced at OJSC "Maxam-Chirchik" with 34.5% nitrogen in its composition was applied.

X-ray analysis of initial untreated phosphorous powder was carried out at difractometer DRON-3 (Russia) characterized with filtration of cobalt radiation at 20 kV voltage on counter, amperage 20 mA, velocities of the rotation of the disk counter 2 grad/min, difractometer band 600 mm/h, limit of the measurement $1´10^3$, area of recording was $2\theta=3–72^o$ CuK_a. Encoding of X-ray diagram carried out by American card file and Mikheev's X-ray finder of minerals[12, 13].

X-ray diagram of phosphorite flour is presented in Figure 1. It is visible, that diffraction strips 1.72; 1.83; 1.88; 1.93; 2.24; 2.63; 2.70; 2.80; 3.17; 3.45 Å belong to fluorine-carbonate-apatite, while interplane distances 1.90; 2.09; 2.29; 2.49; 3.04; 3.87 Å concern to calcite. Strips 3.34 Å belong to quartz. The basic minerals of phosphorite flour are fluorine-carbonate-apatite and a calcium carbonate.

The experiments carried out in thermostatic cylindrical reactor (200 ml), supported with paddle mixer and filled with glycerine. Afterwards, ammonium nitrate solutions with 70, 80, and 90% concentrations were prepared and phosphate raw material gradually dozed where final concentration of the product (P_2O_5) was from 1.5 to 5%. The process of interaction was carried out for 30 minutes at 100°C. The gained pulps were dried up at 100–105°C and analysed to define amount of different forms of phosphor, calcium, nitrogen and CO_2 composition by standard methods. Investigation of all forms [total and acceptable] of P_2O_5 was conducted by differential photometric method which is widespread method in the analysis of phosphorous ore using KPK-3 device[14]. This method is based on measurement of optical density of yellow colored solution which is formed by phosphor--vanadium-molibdenium complex at l = 440 nm wave length. A solution with established P_2O_5 concentration was used as a control sample. Acceptable form of P_2O_5 was investigated by the dissolution in 2% citric acid.

Definition of CaO content was performed by complexonometric method where titration of 0.05 N solution of Trilon-B in the presence of fluorexon and navy-blue chrome indicators[15]. Acceptable form of CaO was defined using 2% citric acid solution.

Definition of nitrogen content was carried out by Keldale in which process involve removing of ammonia in alkaline condition with alloying Devard and titration process[15].

Investigation of carbon dioxide content in samples was conducted by the decomposition of carbonates in chloride acid[15]. In this case changing of CO_2 content was counted by the decarbonization of phosphorous raw material. Laboratory ion measurement device I-130 M was used for the definition of pH value of reaction media with 0.05 accuracy.

Granulation of product in laboratory conditions which practically did not differ from industrial conditions was performed. A technique of definition of durability of the received granules carried out at a device MIP-10-1 in conformity in State standard. The activities were the following. After completion of interaction process the mass in the reactor was poured into porcelain cup and intensively mixed with glass stick. As the cooling the solid particles of round shape were formed. The mass of these particles were dried up, cooled and dissipated by size. The particles with 2–3 mm size were analysed for granule resistance on the MIP-10-1 device of State standard[16]. At the scale of the device the force rank was measured for granules destruction. The statistical resistance for granules was calculated by the following formula:

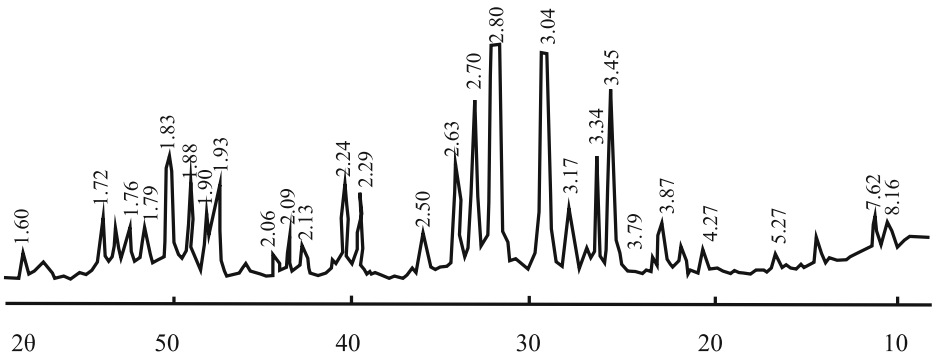


Figure 1. XRD spectra of phosphate raw material

$$X = \frac{P_1 + P_2 + P_3 + ... + P_{20}}{20}$$

where P_1, P_2, P_3,.....P_{20} – the force required for destruction of granules (kg).

Statistical resistance for granules Y [kgf/cm^2] by the following formula:

$$Y = \frac{\sum_{i=1}^{i20} P_i}{20 \cdot S} = \frac{\sum_{i=1}^{i20} P_i}{20\ \frac{\pi d_{av}^2}{4}} = 0.063\ \frac{\sum_{i=1}^{i20} P_i}{d_{av}^2}$$

where:

Pi – the force required for destruction of one granule [kgf];

S – cross sectional area of granule [cm^2];

d_{av} – average diameter of granule [cm].

For results submission on experiments an MPa according to latter dimension formula were divided to 10.2.

Determination of the dissolution rate of nitrogen phosphorus fertilizer's granules was conducted according to State Standard[16]; the method consisted of visual observation and dissolution time recording for fertilizer pellets lowered into distilled water at 25°C, bathed into a chemical glass of 100 ml volume.

RESULTS AND DISCUSSION

On the base of interaction of Central Kyzylkum (Uzbekistan) phosphate raw material with 70–90% ammonium nitrate solution the different grade of nitrogen phosphorous fertilizers (NPF) grades were obtained (Table 1). From Table 1 it is seen that at all ammonium nitrate solution compositions taken together from 70–90%, there is high level phosphate raw material activation. If we compare the ratio towards the acceptable (acc.) form of P_2O_5 of the initial phosphate raw material total level ($P_2O_{5acc.}$: $P_2O_{5tot.}$) is 18.49%, then that ratio towards to products with interaction of ammonium nitrate solution achieves within 76.23–95.57% (Figs. 2–4). However, the water soluble form of phosphorous in the composition of nitrogen-phosphorous fertilizers was not found out.

From the data adduced in Figure 2 it is visible, that according to an increase in quantity of the phosphatic raw material added to 70% solution of ammoniac saltpeter, that is with reduction of a mass ratio - a solution of ammoniac saltpeter AN: phosphatic raw material, the relative contents of assimilated forms of P_2O_5 and CaO gradually decrease from 95.57 down to 76.63 and from 91.34 down to 71.26% accordingly. At application of 80% solution of ammoniac saltpeter for interaction with phosphatic raw material, these parameters locate within the intervals: 95.42–76.63 and 91.18–71.12% accordingly (Fig. 3). And at application of 90% solution of ammoniac saltpeter the relative contents of assimilated forms of P_2O_5 and CaO in fertilizers decrease from 95.33 down to 76.21 and from 90.59 down to 70.89% accordingly (Fig. 4).

The reduction of the relative content of assimilated forms of P_2O_5 and CaO in N-P fertilizer, in our opinion, occurs as a result of increase in concentration of phosphorite.

In this case ammonium nitrate concentration has no influence on $P_2O_{5acc.}$: $P_2O_{5tot.}$

The maximal adding (20.0 g) of the PRM allow to obtain high rate of acceptable P_2O_5 form (76.21–76.63%) and CaO (70.89–71.26%) to total form. Products with acceptable form of P_2O_5 and CaO can be considered as highly effective nitrogen phosphorus fertilizer. On contents of nourishing component, obtained fertilizers fully correspond to with standard specifications of "Nitrogen-

Table 1. Chemical composition of fertilizers obtained by the addition of PRM to ammonium nitrate solution

Mass solution NH_4NO_3 [g]	Mass PRM [g]	pH 10% – solution of product	N [%]	P_2O_{5total} [%]	P_2O_5 acceptable [%]	CaO_{total} [%]	$CaO_{acceptable}$ [%]	CaO water soluble [%]	CO_2 [%]	Degree of decarbonization [%]
Concentration of ammonium nitrate solution 70%										
71.4	5.0	6.942	31.21	1.58	1.51	4.39	4.01	1.13	1.05	24.26
	6.5	6.951	30.88	2.04	1.91	5.63	5.08	1.16	1.35	23.09
	9.0	6.963	29.48	2.66	2.45	7.29	6.46	1.24	1.82	21.89
	10.0	6.975	29.30	3.00	2.70	8.21	7.07	1.25	2.02	20.66
	12.0	6.998	28.19	3.51	3.08	9.58	8.01	1.29	2.42	18.16
	15.0	7.026	27.10	4.12	3.51	11.12	8.90	1.33	2.98	15.48
	16.7	7.054	26.09	4.55	3.70	12.37	9.41	1.38	3.33	12.89
	20.0	7.080	25.19	5.05	3.87	13.57	9.67	1.41	3.90	10.59
Concentration of ammonium nitrate solution 80%										
62.5	5.0	6.946	31.15	1.53	1.46	4.31	3.93	1.08	1.10	20.62
	6.5	6.958	30.83	2.01	1.87	5.59	5.02	1.14	1.41	19.63
	9.0	6.966	29.41	2.61	2.40	7.19	6.34	1.22	1.89	18.84
	10.0	6.988	29.23	2.94	2.64	8.09	6.96	1.22	2.11	17.07
	12.0	7.014	28.12	3.47	3.04	9.53	7.96	1.28	2.49	15.74
	15.0	7.037	27.05	4.07	3.46	11.13	8.86	1.29	3.03	14.03
	16.7	7.060	26.07	4.50	3.66	12.28	9.30	1.34	3.38	11.55
	20.0	7.086	25.16	5.01	3.82	13.47	9.58	1.37	3.97	8.92
Concentration of ammonium nitrate solution 90%										
55.5	5.0	6.951	31.10	1.50	1.43	4.19	3.80	1.01	1.14	18.43
	6.5	6.962	30.76	1.94	1.80	5.41	4.82	1.07	1.45	17.32
	9.0	6.975	29.35	2.58	2.37	7.13	6.28	1.19	1.94	16.65
	10.0	6.996	29.18	2.89	2.58	7.98	6.81	1.20	2.15	15.45
	12.0	7.023	28.04	3.44	3.01	9.45	7.87	1.23	2.53	14.36
	15.0	7.048	26.98	4.03	3.42	11.02	8.77	1.26	3.08	12.57
	16.7	7.071	26.02	4.47	3.62	12.18	9.17	1.31	3.43	10.19
	20.0	7.098	25.09	4.96	3.78	13.33	9.45	1.32	3.99	8.45

phosphorous fertilizers TSh 6.1-00203849-111:2007", in which fertilizers must content 22–30% of nitrogen and 1–6% of P_2O_5.

The essence of activation phosphate powder with ammonium nitrate solution is destruction of internal structure of phosphor or – crystal structure deformation of phosphor contained mineral without its decomposition, which results in tangible ratio composition increase of phosphor and calcium acceptable forms.

Table 1 shows that products reacted with phosphate powder and ammonium nitrate solution acquire water soluble form of CaO – more than 1%. It proves that at 100°C the reaction occurs between ammonium nitrate and calcium carbonate in the phosphate raw material leading to formation of calcium nitrate, NH_3 and CO_2: $2NH_4NO_3 + CaCO_3 = Ca(NO_3)_2 + 2NH_3 + CO_2 + H_2O$.

During laboratory researches it has been established, that at interaction of a phosphoritic flour with a solution of ammoniac saltpeter, at 100°C there is an activation of natural phosphate, i.e. transformation of a quantity of inaccessible P_2O_5 form to the form accessible to plants, and it means, that at activation of phosphorite with a solution of AN the reaction proceeds:

$Ca_3(PO_4)_2 + 2NH_4NO_3 = 2CaHPO_4 + Ca(NO_3)_2 + 2NH_3$

$Ca_3(PO_4)_2$ is a basic component included into phosphorite composition. Thus reactions between AN and calcium carbonate included into phosphorite with formation of calcium nitrate, ammonia and carbonic gas also proceed.

In these conditions the level of phosphate powder decorbonation depending on the amount of additives ranges within 10.59–24.26; 8.92–20.62 and 8.45–18.43%, and at the concentration of ammonium nitrate solution 70, 80, and 90% respectively (Table 1).

The more is phosphate raw material is added in the melt, the fewer grades of phosphate raw material decarbonisation in the obtained products. The partial calcium carbonate decomposition also assists crystal lattice deformation of phosphate mineral.

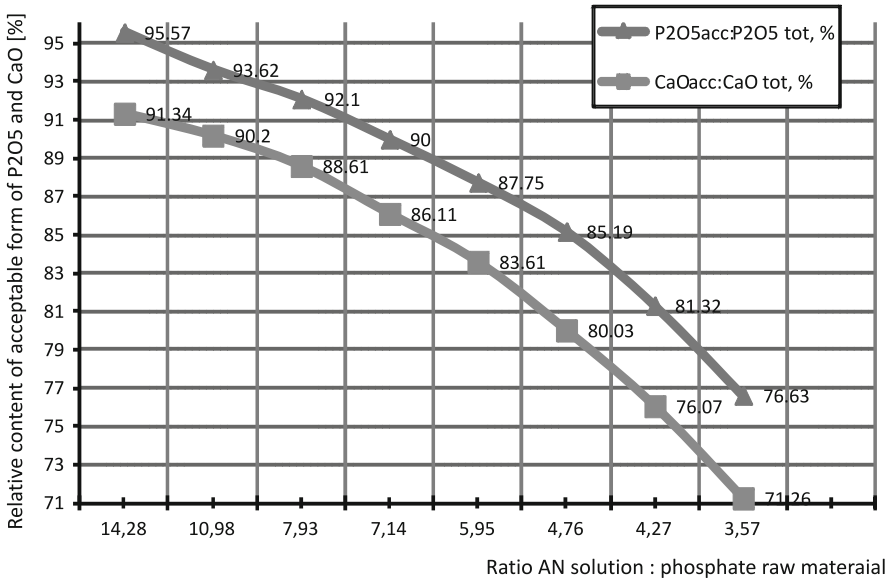


Figure 2. The dependence of the relative content of acceptable form of P_2O_5 and CaO NPF fertilizers on the amount of additive. The concentration of ammonium nitrate solution – 70%

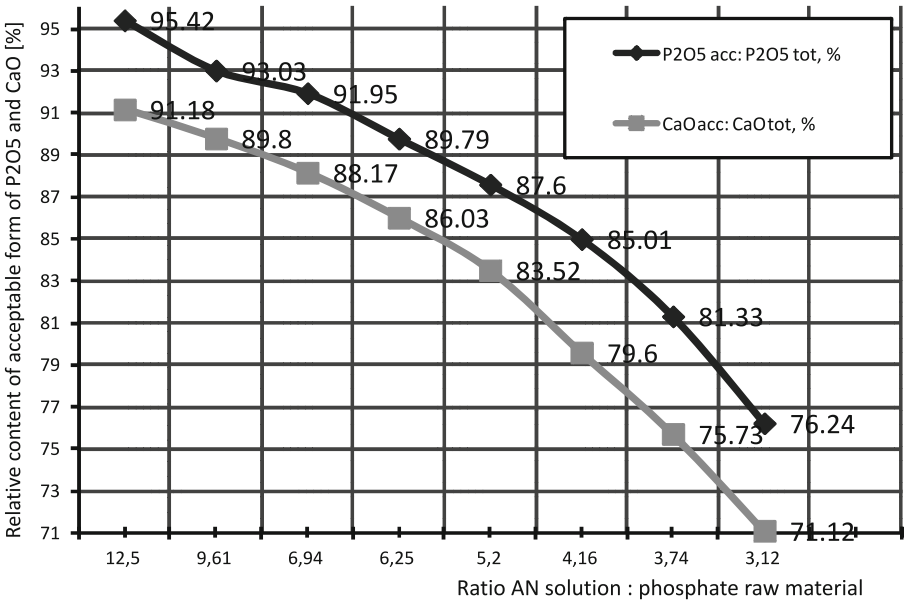


Figure 3. The dependence of the relative content of acceptable form of P_2O_5 and CaO NPF fertilizers on the amount of additive. The concentration of ammonium nitrate solution – 80%

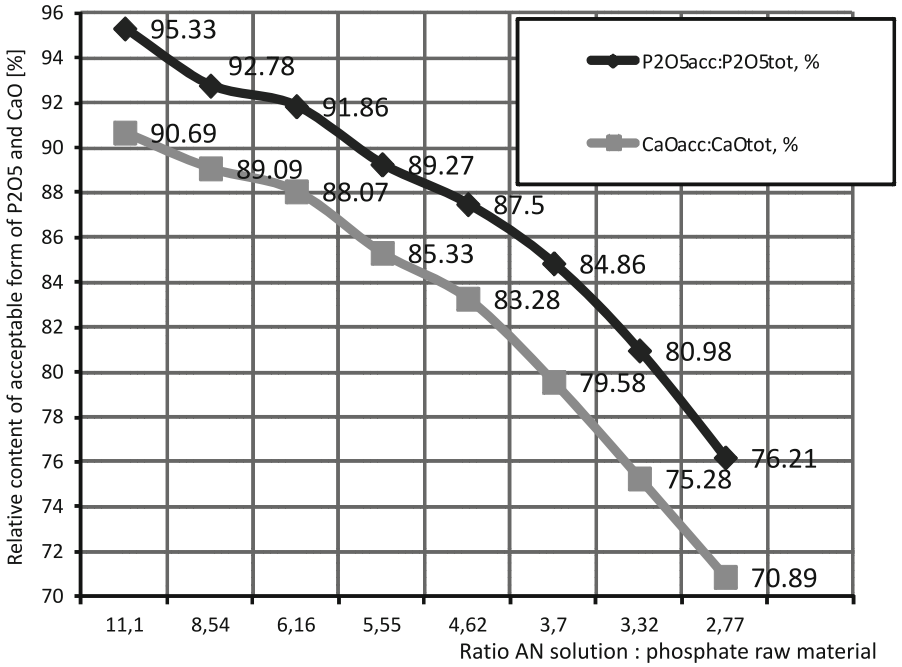


Figure 4. The dependence of the relative content of acceptable form of P_2O_5 and CaO NPF fertilizers on the amount of additive. The concentration of ammonium nitrate solution – 90%

In Table 2 shown significance of granule resistance for fertilizers, obtained by above mentioned methods. It is seen from Table 2, addition of phosphate powder into ammonium nitrate concentrate solution at the amount from 5.0 to 20 g increases granule resistance from 2.60 to 6.97; from 2.53 to 6.85 and from 2.43 to 6.74 MPa respectively, at 70, 80 and 90 concentration of ammonium nitrate solution. In this case the ammonium nitrate solution's concentration practically does not render any effect on durability of granules of obtained NP fertilizers.

The high granule resistance with 6.74–6.97 MPa was observed ammonium nitrate with 20 g phosphate powder additive. Such density of granules testifies not only on porosity decrease and inner specific surface of nitrate but also on diminution of access risk of diesel fuel inside granule, which leads to reduction of nitrate detonation aptitude.

The influence of phosphate additive on granule's dissolution of nitrogen phosphorus fertilizers was also investigated. The results are given at Table 3. The data indicates that addition of phosphate additive into ammonium nitrate decreases speed of granule dissolution of nitrogen phosphorous fertilizers in comparison with pure ammonium nitrate. The increase of mass fraction

Table 2. Toughness of fertilizer's granules obtained by ammonium nitrate solution of Central Kyzylkum phosphate powder

№	Mass solution NH_4NO_3 [g]	Mass PP [g]	N [g]	P_2O_5 [g]	Granule strength		
					[kg/granule]	[kg/cm^2]	[MPa]
1	2	3	4	5	6	7	8
Concentration of ammonium nitrate solution – 70%							
1	71.4	5.0	31.21	1.58	1.32	26.61	2.60
2		6.5	30.88	2.04	1.88	37.90	3.71
3		9.0	29.48	2.66	2.30	46.37	4.55
4		10.0	29.30	3.00	2.64	53.22	5.21
5		12.0	28.19	3.51	2.96	59.67	5.85
6		15.0	27.10	4.12	3.19	64.31	6.30
7		16.7	26.09	4.55	3.38	68.14	6.68
8		20.0	25.19	5.05	3.53	71.16	6.97
Concentration of ammonium nitrate solution – 80%							
9	62.5	5.0	31.15	1.53	1.28	25.80	2.53
10		6.5	30.83	2.01	1.82	36.69	3.59
11		9.0	29.41	2.61	2.25	45.36	4.44
12		10.0	29.23	2.94	2.58	52.01	5.09
13		12.0	28.12	3.47	2.89	58.26	5.71
14		15.0	27.05	4.07	3.12	62.89	6.16
15		16.7	26.07	4.50	3.31	66.72	6.54
16		20.0	25.16	5.01	3.47	69.95	6.85
Concentration of ammonium nitrate solution – 90%							
17	55.5	5.0	31.10	1.50	1.23	24.79	2.43
18		6.5	30.76	1.94	1.77	35.68	3.49
19		9.0	29.35	2.58	2.19	44.15	4.32
20		10.0	29.18	2.89	2.51	50.60	4.96
21		12.0	28.04	3.44	2.82	56.85	5.57
22		15.0	26.98	4.03	3.05	61.48	6.02
23		16.7	26.02	4.47	3.24	65.31	6.40
24		20.0	25.09	4.96	3.41	68.74	6.74

Table 3. The rate of granule's dissolution of nitrogen phosphorus fertilizers obtained by addition of phosphate raw material into 80% ammonium nitrate solution in water

№	Ratio solution AN:PRM	N [%]	P_2O_5 [%]	Time of granules dissolving [sec]					
				1	2	3	4	5	average
1	Ammonium nitrate			51	51	42	47	43	46.8
2	62.5:6.5	30.83	2.01	65	71	63	69	72	68.0
4	62.5:10.0	29.23	2.94	72	71	77	79	76	75.0
6	62.5:15.0	27.05	4.07	76	84	82	79	84	81.0
8	62.5:20.0	25.16	5.01	85	88	82	84	91	86.0

of phosphate powder from 6.5 to 20 g in the obtained NPF samples leads to the time increase of granules total solution from 68.0 to 86.0 sec against the time of total pure nitrate solution 46.8 sec. that is increases to 1.83 times.

According to our opinion, the decrease of fertilizer's solubility is the result of phosphorite share growing in the products. The more is the phosphorite's share, the more slowly the fertilizer's granules do dissolve.

CONCLUSIONS

The study showed the possibility of obtaining of nitrogen phosphorous fertilizers by addition of concentrated solution of AN (70–90%) with Central Kyzylkum phosphate powder with high relative composition of acceptable forms of P_2O_5 (76.21–76.63%) and CaO (70.89–71.26%). Concentration of initial AN solution practically has no influence on relative composition of P_2O_5 and CaO.

Addition of low grade phosphate powder in the concentrated ammonium nitrate solution in the amount from 5.0 to 20.0 g increases resistance of nitrate granule from 2.60 to 6.97; from 2.53 to 6.85 and from 2.43 to 6.74 MPa, accordingly to solution concentration of 70, 80 and 90 AN. Phosphate additives introduced into ammonium nitrate composition form fine inclusions in the structure of crystalline blocks and reduces crystal sizes. Reducing the sizes of separate crystal salts and raising their packaging density essentially increases nitrogen phosphorous granules resistance.

Addition of phosphate powder to ammonium nitrate decreases the speed of dissolution of granules up to 1.83 times. According to our opinion, the decrease of fertilizer's solubility is the result of phosphorite share growing in the products. The more is the phosphorite's share, the more slowly the fertilizer's granules do dissolve.

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