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TECHNOLOGY OF ORGANIC AND INORGANIC CHEMISTRY

Nitrogen-Phosphoric Fertilizers Obtained by Interaction of the Concentrated Solutions of Ammonium Nitrate with the Mineralized Mass of the Phosphorites of Central Kyzylkum

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Abstract—The results of determination of composition and strength of the granules of nitrogen-phosphoric fertilizers containing 1.5 to 5.0% of P_2O_5, obtained by interaction of the mineralized mass of the phosphorites of Central Kyzylkum with the 70–90% solutions of ammonium nitrate at 110°C, are presented.

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The purpose of this work is double. First, to convert multitonnage production waste of phosphorite powder at the Kyzylkum phosphorite plant, namely, mineralized mass, containing 12–14% of P_2O_5, into the effective phosphoric fertilizer. This would be successful when not assimilable form of P_2O_5 in the raw material is transformed into the form assimilable by plants. Second, to obtain the stabilized ammonium nitrate. Achieving the first goal will make it possible to increase the gross release of the phosphorus-containing fertilizers from the poor phosphate raw material. Reaching of the second goal will considerably improve the quality of the most important multitonnage nitric fertilizer, such as is ammonium nitrate.

Reality of the stated problems follows from the works [1–7] showed that working up of rich by carbonate but poor by phosphate raw material by solution or molten ammonium nitrate leads to the sharp increase in the content of the assimilable by plants form of P_2O_5. In [8] was indicated the perspective of adding the phosphorus-containing additive to the ammonium nitrate, which would not only remove a tendency to cake, but also to a considerable degree increase its explosion-proof properties.

In our work we used the mineralized mass of the phosphorites of Central Kyzylkum of the following composition (wt %): P_2O_5 total 14.68; CaO 40.80; Al_2O_3 1.17; Fe_2O_3 1.37; MgO 0.53; F 1.85; CO_2 12.84; P_2O_5 assimilable : P_2O_5 total = 16.41%, and ammonium nitrate, produced by joint stock company "Maksam-Chirchik". The particle size distribution (disperseion composition) of the mineralized mass appeared as follows: 2–0.5 mm 4.4%; 0.5–0.315 mm, 10.2%; 0.315–0.16 mm, 34.1%; 0.16–0.1 mm, 14.5%; 0.1–0.063 mm, 16.3%; 0.063–0.05 mm, 4.7%, and >0.05 mm, 15.8%.

The experiments were carried out in the thermostatically controlled cylindrical reactor of a volume of 200 ml, equipped with a paddle mixer. Thermostat was filled with glycerol. The solutions of 70, 75, 80, 85 and 90% concentration were prepared. To the reactor with the solution of ammonium nitrate was gradually dosed the mineralized mass in the amount to provide 5% content of P_2O_5 in the final composition. The process of interaction duration was 30 min, at 110°C. After that the obtained pulp was dried at 100–105°C and then analyzed on the content of various forms of phosphorus, calcium, nitrogen and CO_2 by standard methods [9]. The assimilable forms of phosphorus and calcium were determined by measuring solubility in the 2% citric acid.

The granulation of product was performed as follows. After the end of interaction the content of reactor was poured into the china cup and intensively mixed by glass rod. The round solid particles formed upon cooling. The mass of these particles was dried, cooled, and then was sown according to the sizes. The particles with the size of 2–3 mm there analyzed on the strength of granules according to GOST 21560.2-82.

The results of studies are given in Tables 1 and 2.

Table 1. Chemical composition of the fertilizers, obtained by introduction into the solution of ammonium nitrate of the mineralized mass of the phosphorites of central Kyzylkum

Mass of solution of ammonium nitrate, g	Mass of mineralized mass, g	pH of 10% solution of product	N,%	P_2O_5 total, %	P_2O_5 assimilable, %	CaO total	CaO assimilable	CaO water soluble	CO_2, %	P_2O_5 assimilable/ total	CaO assimilable/ total	CaO water soluble/ total	Degree of decarbonization, %
1	2	3	4	5	6	7	8	9	10	11	12	13	14
Amminium nitrate concentration 70%													
71.4	6.0	6.794	30.71	1.51	1.08	4.51	2.98	1.09	1.07	71.52	66.07	24.16	22.42
	8.0	6.816	29.69	2.02	1.39	5.77	3.73	1.13	1.39	68.81	64.64	19.58	21.79
	10.0	6.829	28.76	2.44	1.62	6.92	4.35	1.14	1.72	66.39	62.86	16.47	19.97
	13.0	6.836	27.77	3.03	1.93	8.41	5.13	1.18	2.16	63.69	60.99	14.03	18.86
	15.0	6.845	26.67	3.49	2.12	9.39	5.49	1.19	2.49	60.74	58.46	12.67	16.37
	18.0	6.852	25.58	4.01	2.29	10.95	6.13	1.24	2.93	57.10	55.98	11.32	14.20
	21.0	6.859	24.66	4.45	2.41	12.14	6.49	1.25	3.37	54.15	53.46	10.29	11.64
	24.0	6.871	23.82	4.94	2.56	13.46	6.87	1.26	3.79	51.82	51.04	9.36	9.32
Amminium nitrate concentration 75%													
66.6	6.0	6.791	30.74	1.49	1.08	4.54	2.98	1.09	1.10	72.48	65.63	24.01	20.25
	8.0	6.819	29.57	2.04	1.39	5.74	3.72	1.11	1.45	68.13	64.80	19.33	18.37
	10.0	6.828	28.81	2.41	1.59	6.89	4.32	1.13	1.77	65.97	62.69	16.40	17.59
	13.0	6.839	27.75	3.01	1.90	8.35	5.09	1.18	2.24	63.12	60.95	14.13	15.79
	15.0	6.847	26.71	3.51	2.12	9.39	5.47	1.18	2.55	60.39	58.25	12.56	14.30
	18.0	6.852	25.57	4.02	2.29	10.91	6.11	1.21	2.98	56.96	56.01	11.09	12.69
	21.0	6.866	24.66	4.47	2.42	12.12	6.47	1.21	3.40	54.14	53.38	9.98	10.82
	24.0	6.879	23.91	4.91	2.54	13.41	6.85	1.24	3.82	51.73	51.08	9.24	8.58

Table 1 (Contd.)

1	2	3	4	5	6	7	8	9	10	11	12	13	14
Amminium nitrate concentration 80%													
62.5	6.0	6.796	30.69	1.49	1.05	4.49	2.97	1.07	1.11	70.46	66.44	23.83	19.49
	8.0	6.826	29.63	2.01	1.36	5.70	3.71	1.09	1.45	67.66	65.08	19.12	18.37
	10.0	6.834	28.74	2.42	1.59	6.89	4.30	1.10	1.77	65.70	62.41	15.96	17.59
	13.0	6.844	27.75	2.98	1.89	8.38	5.09	1.14	2.24	63.42	60.74	13.60	15.79
	15.0	6.849	26.64	3.47	2.09	9.36	5.41	1.15	2.56	60.23	57.79	12.28	13.96
	18.0	6.857	25.57	3.97	2.27	10.89	6.08	1.19	2.99	57.17	55.83	10.92	12.38
	21.0	6.866	24.58	4.44	2.39	12.08	6.47	1.21	3.42	53.82	53.56	10.01	10.28
	24.0	6.889	23.74	4.91	2.52	13.44	6.85	1.24	3.83	51.32	50.96	9.23	8.33
Amminium nitrate concentration 85%													
58.8	6.0	6.795	30.67	1.46	1.06	4.44	2.95	1.06	1.13	72.60	66.14	23.87	18.02
	8.0	6.825	29.64	2.01	1.34	5.70	3.68	1.06	1.47	66.67	64.56	18.59	17.07
	10.0	6.839	28.74	2.39	1.56	6.84	4.29	1.07	1.80	65.27	62.72	15.64	16.08
	13.0	6.844	27.68	2.96	1.88	8.29	5.06	1.11	2.29	63.51	61.03	13.39	13.89
	15.0	6.854	26.59	3.45	2.09	9.25	5.39	1.13	2.59	60.58	58.27	12.21	12.93
	18.0	6.857	25.53	3.95	2.24	10.89	6.07	1.16	3.03	56.70	55.74	10.65	11.18
	21.0	6.861	24.57	4.44	2.39	12.08	6.44	1.19	3.47	53.82	53.31	9.85	8.92
	24.0	6.885	23.76	4.89	2.53	13.38	6.83	1.21	3.85	51.73	51.05	9.04	7.83
Amminium nitrate concentration 90%													
55.5	6.0	6.801	30.59	1.47	1.05	4.45	2.94	0.99	1.18	71.43	66.06	22.24	14.35
	8.0	6.827	29.45	1.98	1.35	5.66	3.65	0.99	1.53	68.18	64.48	17.49	13.80
	10.0	6.841	28.61	2.37	1.56	6.84	4.29	1.02	1.87	65.82	62.72	14.91	12.85
	13.0	6.857	27.64	2.91	1.84	8.25	5.02	1.05	2.35	63.23	60.84	12.72	11.56
	15.0	6.869	26.47	3.41	2.07	9.21	5.37	1.07	2.66	60.70	58.30	11.61	10.50
	18.0	6.874	25.41	3.95	2.23	10.84	6.05	1.07	3.10	56.45	55.81	9.87	9.06
	21.0	6.881	24.44	4.41	2.37	12.01	6.41	1.09	3.51	53.74	53.37	9.07	7.83
	24.0	6.889	23.66	4.85	2.48	13.38	6.83	1.11	3.90	51.13	51.05	8.29	6.58

Table 2. Strength of the granules of fertilizers, obtained by introduction into the solution of ammonium nitrate of the mineralized mass of the phosphorites of central Kyzylkum

No.	Mass of solution of ammonium nitrate, g	Mass of mineralized mass, g	N, %	P_2O_5, %	Strength of granules		
					kg per granule	kg cm^{-1}	MPa
			Amminium nitrate concentration 70%				
1	71.4	6.0	30.71	1.51	1.75	35.28	3.46
2		8.0	29.69	2.02	2.26	45.56	4.47
3		10.0	28.76	2.44	2.67	53.83	5.28
4		13.0	27.77	3.03	3.03	61.08	5.99
5		15.0	26.67	3.49	3.36	67.73	6.64
6		18.0	25.58	4.01	3.57	71.97	7.05
7		21.0	24.66	4.45	3.71	74.79	7.33
8		24.0	23.82	4.94	3.79	76.41	7.49
			Amminium nitrate concentration 75%				
9	66.6	6.0	30.74	1.49	1.72	34.67	3.40
10		8.0	29.57	2.04	2.21	44.55	4.37
11		10.0	28.81	2.41	2.61	52.61	5.16
12		13.0	27.75	3.01	3.01	60.68	5.95
13		15.0	26.71	3.51	3.38	68.14	6.68
14		18.0	25.57	4.02	3.58	72.17	7.07
15		21.0	24.66	4.47	3.69	74.39	7.29
16		24.0	23.91	4.91	3.80	76.60	7.51
			Amminium nitrate concentration 80%				
17	62.5	6.0	30.69	1.49	1.73	34.87	3.42
18		8.0	29.63	2.01	2.19	44.15	4.33
19		10.0	28.74	2.42	2.62	52.82	5.18
20		13.0	27.75	2.98	2.97	59.87	5.87
21		15.0	26.64	3.47	3.26	65.72	6.44
22		18.0	25.57	3.97	3.51	70.76	6.93
23		21.0	24.58	4.44	3.69	74.39	7.29
24		24.0	23.74	4.91	3.75	75.60	7.41
			Amminium nitrate concentration 85%				
25	58.8	6.0	30.67	1.46	1.69	34.07	3.34
26		8.0	29.64	2.01	2.19	44.15	4.33
27		10.0	28.74	2.39	2.57	51.81	5.08
28		13.0	27.68	2.96	2.97	59.87	5.87
29		15.0	26.59	3.45	3.26	65.72	6.44
30		18.0	25.53	3.95	3.49	70.35	6.89
31		21.0	24.57	4.44	3.64	73.38	7.19
32		24.0	23.76	4.89	3.73	75.19	7.37

Table 2 (Contd.)

No.	Mass of solution of ammonium nitrate, g	Mass of mineralized mass, g	N, %	P_2O_5, %	Strength of granules		
					kg per granule	kg cm^{-1}	MPa
Amminium nitrate concentration 90%							
33	55.5	6.0	30.59	1.47	1.57	31.65	3.10
34		8.0	29.45	1.98	2.14	43.14	4.23
35		10.0	28.61	2.37	2.53	51.00	5.00
36		13.0	27.64	2.91	2.89	58.26	5.71
37		15.0	26.47	3.41	3.19	64.31	6.31
38		18.0	25.41	3.95	3.42	68.94	6.76
39		21.0	24.44	4.41	3.60	72.57	7.11
40		24.0	23.66	4.85	3.73	75.19	7.37

From the data in Table 1 it is evident that at any concentration of the ammonium nitrate solution in the range from 70 to 90% occurs high degree of the activation of the phosphate raw material. If in the initial mineralized mass the ratio of the assimilable form of P_2O_5 to its total content was 16.41% only, then in the products after interaction with the solution of ammonium nitrate this ratio increases to the range of 51–72%. Concentration of the solution of ammonium nitrate in this case does not affect the ratio of P_2O_5(assimilable) : P_2O_5(total). All probably depends on the temperature and duration of the interaction. The more the mineralized mass is taken for the interaction with the solution of ammonium nitrate, the less the degree of activation of the phosphate raw material. But even at adding 5% of P_2O_5 we obtain in the products high (51%) ratio of the assimilable form of P_2O_5 to it total content. Due to such high ratio, the phosphate component in the complex nitrophosphoric fertilizer can be considered as effective phosphoric fertilizer.

The essence of the activation of the mineralized mass of the phosphorites of central Kyzylkum by the solution of ammonium nitrate consists in the destruction of the structure of the phosphorus-containing mineral, that is, in deformation of its crystal lattice without decomposition, that leads to an increase in the relative content of assimilable P_2O_5 in the fertilizer by the several times. From Table 1 it is evident that in the reaction products of the mineralized mass with the solutions of ammonium nitrate appears the water-soluble form of CaO in amount a bit more than 1% only. Obviously at 110°C occurs the reaction between ammonium nitrate and calcium carbonate in the mineralized mass with the formation of calcium nitrate:

$$2NH_4NO_3 + CaCO_3 \rightarrow Ca(NO_3)_2 + 2NH_3 + CO_2 + H_2O$$

In the phosphorites of central Kyzylkum is observed a very close mutual germination of phosphate mineral with calcium carbonate. The partial decomposition of the calcium carbonate (degree of the decarbonization of the mineralized mass is in the range of 6.58–22.42%) also contributes to the deformation of crystal lattice of phosphate mineral.

Table 2 lists the values of the strength of the fertilizer granules obtained by the method described above. The greatest strength of granules 7.37–7.51 MPa has ammonium nitrate containing 4.85- 4.94% of P_2O_5 additive. This strength of granules testifies about the decrease in the granules porosity and in the area of internal specific surface of ammonium nitrate. Hence the possible penetration of diesel fuel inside the granule falls, which leads to decrease in the detonation ability of ammonium nitrate.

Therefore we suggest that the optimum additive to the ammonium nitrate is precisely 5% of P_2O_5 in the form of the mineralized mass. Nitrophosphoric fertilizer in this case contains 23.7–23.9% of N and 5% of P_2O_5, and the ratio P_2O_5(assimilable) to P_2O_5 (total) is equal to 51%. But at the practical realization of this process it is necessary to provide absorption of the ammonia liberating to the gas phase.