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Granulated Complex Nitrogen-Sulfur-Containing Fertilizers based on Ammonium Niter Flush and Phosphogypsum with the Additive of Ammonium Sulfate

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ABSTRACT: Samples of granulated NS-fertilizer were made by combining natural gypsum (PG) with ammonium nitrate (AN) melt at a mass ratio of 99.5: 0.5 to 60: 40, adding 1-5% of ammonium sulfate from the combined mass of AS and PG, and then prilling the resulting mixture on a granulation tower to grind it into granules. The collected samples' composition and characteristics were investigated. It was demonstrated that increasing the amount of PG from 0.5 to 40 g in relation to 99.5 to 60 g of NH_4NO_3 melt and ammonium sulfate, taken in amounts of 1 and 5% of the total mass of the mixture of AS and PG, results in a decrease in the nitrogen content in the product from 34.68 to 20.80%, but an increase in the amounts of $\text{SO}_{3\text{tot}}$ and CaO_{tot} from 0.23 to 17.96% and 0.16

KEYWORDS ammonium nitrate, natural gypsum, ammonium sulfate, nitrogen-sulfur fertilizer, composition and strength of granules.

I. INTRODUCTION

An inexpensive, highly concentrated, large-capacity nitrogen fertilizer is ammonium nitrate (AN). It is utilized in all cultural contexts and on all soil types. Numerous nations throughout the world, including AS, China, the Russian Federation, the USA, India, Indonesia, Trinidad & Tobago, Ukraine, Canada, etc., are involved in the manufacturing of nitrogen fertilizers. IFA estimates that in 2017 and 2018, global nitrogen fertilizer production capacity reached 185.10 million tons of nutrients/year and 187.0 million tons of nutrients/year, respectively. [1]. The Russian Federation, Ukraine, Uzbekistan, Belarus, and Kazakhstan are the CIS nations that produce NPPs, and they have more than 28 production facilities amongst them. The Russian Federation, whose annual output exceeds 12 million tons, holds the top spot in this group. The top producers of AS in this area are JSC UCC Uralchem, JSC Akron, JSC MCC EuroChem, JSC PhosAgro, and JSC SDS Azot [1]. They produce roughly 8.0 million tons of AS. The companies Azot, SDVO Azot, Rovnoazot, and Stirol Concern produce AS in Ukraine. [2]. There are 1.2 million tons produced year overall. Three JSCs, Maxam-Chirchik, Ferganaazot, and Navoiiazot, with a combined capacity of 1,075,000 tons, produce the AS in Uzbekistan [3]. In addition, recent years have seen a number of troubling events brought on by explosions and fires that happened during the production, storage, shipping, and usage of ammonium nitrate [4]. These incidents have affected both nuclear power plant manufacturers and customers. The AU is characterized by flammability and explosion hazard, according to usage patterns around the world. [5]. This is as a result of its propensity for heat disintegration and oxidizing characteristics. AS thermally decomposes when slowly heated, beginning at 110°C and higher. Ammonia and nitric acid are the byproducts of thermal breakdown at low temperatures, and nitrous oxides, nitrogen oxides, and oxygen are the byproducts at high temperatures [6, 7]. At the same time, the creation of the latter products is explosive at high temperatures. Consequently, a portion of the product is lost as a result of the heat degradation of AS. Numerous methods and strategies for AS stabilization are utilized in practice to either totally inhibit or sluggish the process of heat degradation [8, 9]. As a result, producers have been tasked with assuring the switch to fertilizers based on AS, which maintain their agricultural efficacy but have a substantially higher resilience to external influences and, as a result, a lower risk of explosion.

Presently, ammonium nitrate is added to the melt before spewing carbonate phosphorite flour (17-18% P_2O_5) or lime powder on the grantower to produce AFU (nitrogen-phosphorus fertilizer with a content of 22-28% N and 2-6% P_2O_5) [10] and IAS (calcic ammonium nitrate with a content of 22-28% N) [11].

The goal of this effort is to broaden the range of ballast compounds, enhance the AS's quality and thermal stability, and raise the amount of sulfur, the fourth nutrient, in the fertilizer's composition. In Uzbekistan, there are numerous sizable natural gypsum (GHG) deposits, which provides us with a wealth of chances to organize the manufacture of nitrogen-sulfur fertilizer. They selected Shursu (Fergana region), Ok Oltin, Ingichka (Samarkand region), and Okhangaron as the subject of their research, taking into account the chemical composition, development, availability, and enormous reserves (Tashkent region).

II. SIGNIFICANCE OF THE SYSTEM

Utilizing the SG Shursuisky (32.18% CaO; 46.09% SO₃) resources of Uzbekistan to produce nitrogen-sulfur fertilizer was the goal of this study. PG was first ground to a particle size of 0.25 mm in a porcelain mortar. And for comparison, granulated NH₄NO₃ was used as the sample.

III. METHODOLOGY

The experiments were conducted as follows: an electric heater was used to melt a sample of ammonium nitrate in a metal cup. In the following step, PG was added to the melt at AS in mass ratios ranging from 99.5: 0.5 to 60: 40. Additionally, ammonium sulfate was added in amounts of between 1 and 5 percent of the combined mass of the AS and PG mixture. The ingredients were well combined. The gypsum-nitrate melt AS was then held at 170°–175°C for 3 minutes before being placed into a laboratory granulator, which is a metal glass with perforations in the bottom that are 1.2 mm in diameter. The melt was shot from a height of 35 meters onto a plastic film that was resting on the ground thanks to pressure exerted by the pump in the upper portion of the glass. According to particle size, the final granules were sieved. GOST 21560.2-82 was used to measure the tensile strength of particles that were 2-3 mm in size. The items were then crushed and examined using established techniques [12].

IV. EXPERIMENTAL RESULTS

Tables 1-2 present the results. The results show that increasing the amount of PG from 0.5 to 40 g in relation to 99.5 to 60 g of NH₄NO₃ melt and adding ammonium sulfate in amounts of 1 and 5% of the total mass of the mixture of AS and PG causes the product's nitrogen content to decrease from 34.68 to 20.80% while increasing the content of SO_{3tot} from 0.23 to 17.96% and CaO from 0.16 to 12.87%.

Table 1. NS-fertilizers based on ammonium nitrate melt, natural gypsum and ammonium sulfate

Mass ratio AS: ПГ	Content in the mixture (NH ₄) ₂ SO ₄ , %	Content of components, weight. %					$\frac{CaO_{вод.}}{CaO_{общ.}}$, %	$\frac{SO_{3водн.}}{SO_{3общ.}}$, %
		N	CaO _{общ.}	CaO _{водн.}	SO _{3общ.}	SO _{3водн.}		
NH ₄ NO ₃	–	34,9	–	–	–	–	–	–
99,5 : 0,5	–	34,68	0,16	0,06	0,23	0,095	37,5	41,6
99,5 : 0,5	1	34,56	0,16	0,059	0,234	0,096	36,92	42,30
99,5 : 0,5	5	34,02	0,15	0,054	0,25	0,1	36,34	40,96
99,0 : 1,0	–	34,51	0,32	0,11	0,46	0,17	37,70	39,70
99,0 : 1,0	1	34,38	0,32	0,11	0,46	0,18	35,15	39,04
99,0 : 1,0	5	33,86	0,30	0,1	0,47	0,19	34,62	40,2
98,0 : 2,0	–	34,14	0,64	0,22	0,92	0,35	34,05	37,86
98,0 : 2,0	1	34,03	0,63	0,21	0,92	0,34	33,44	37,12
98,0 : 2,0	5	33,55	0,61	0,20	0,92	0,35	32,80	39,50
97,0 : 3,0	–	33,82	0,96	0,31	1,38	0,49	32,25	35,80
97,0 : 3,0	1	33,69	0,95	0,30	1,37	0,48	31,70	35,20



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97,0 : 3,0	5	33,23	0,92	0,28	1,34	0,50	31,15	37,52
95,0 : 5,0	–	33,12	1,70	0,52	2,30	0,78	30,54	33,90
95,0 : 5,0	1	32,98	1,59	0,47	2,28	0,76	29,90	33,25
95,0 : 5,0	5	32,55	1,53	0,45	2,22	0,79	29,35	35,62
92,0 : 8,0	–	32,04	2,73	0,78	3,68	1,17	28,82	31,95
92,0 : 8,0	1	31,97	2,55	0,72	3,65	1,14	28,25	31,36
92,0 : 8,0	5	31,53	2,45	0,67	3,54	1,19	27,60	33,70
90,0 : 10	–	31,37	3,22	0,87	4,61	1,38	27,08	30,05
90,0 : 10	1	31,58	3,18	0,84	4,57	1,34	26,50	29,40
90,0 : 10	5	30,86	3,06	0,79	4,42	1,40	25,85	31,82
88,0 : 12	–	30,64	3,86	0,98	5,53	1,55	25,35	28,10
88,0 : 12	1	30,55	3,82	0,94	5,48	1,51	24,70	27,52
88,0 : 12	5	30,21	3,67	0,88	5,30	1,58	24,20	29,80
85,0 : 15	–	29,32	4,83	1,14	6,92	1,81	23,60	25,25
85,0 : 15	1	29,53	4,77	1,10	6,85	1,76	23,04	26,63
85,0 : 15	5	29,19	4,60	1,03	6,61	1,84	22,45	27,90
82,0 : 18	–	28,57	5,79	1,26	8,29	2,01	21,85	24,32
82,0 : 18	1	28,48	5,73	1,22	8,22	1,94	21,26	24,65
82,0 : 18	5	28,23	5,51	1,14	7,93	1,98	20,70	25,04
80,0 : 20	–	27,86	6,43	1,29	9,22	2,05	20,10	22,45
80,0 : 20	1	27,81	6,43	1,25	9,13	2,10	19,55	22,70
80,0 : 20	5	27,60	6,25	1,18	9,81	2,25	18,79	23,12
75,0 : 25	–	26,14	8,04	1,48	11,52	2,36	18,40	20,48
75,0 : 25	1	26,08	7,96	1,41	11,41	2,26	17,80	19,82
75,0 : 25	5	25,87	7,66	1,32	11,00	2,33	17,21	21,21
70,0 : 30	–	24,39	9,65	1,60	13,84	2,56	16,65	18,55
70,0 : 30	1	24,36	9,56	1,53	13,7	2,43	16,04	17,80
70,0 : 30	5	24,22	9,19	1,42	13,2	2,52	15,46	19,10
60,0 : 40	–	20,89	12,87	1,92	17,43	2,91	14,90	16,72
60,0 : 40	1	20,85	12,74	1,85	17,96	2,88	14,52	16,32
60,0 : 40	5	20,80	12,25	1,73	17,59	3,14	14,13	17,90

Table 2. Strength of NS-fertilizer granules based on ammonium nitrate melt, natural gypsum and ammonium sulfate

Mass ratio AC: ПГ	Content in the mixture (NH ₄) ₂ SO ₄ , %	Granule strength		
		kg/garnoul	kg/cm ²	MPa
NH ₄ NO ₃	–	0,67	81,3	1,32
99,5 : 0,5	–	2,43	49,06	4,81
99,5 : 0,5	1	2,51	50,69	4,97
99,5 : 0,5	5	2,63	53,14	5,21
99,0 : 1,0	–	2,75	55,39	5,43
99,0 : 1,0	1	2,87	57,83	5,67
99,0 : 1,0	5	2,96	59,77	5,86



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98,0 : 2,0	–	3,05	61,50	6,03
98,0 : 2,0	1	3,16	63,75	6,25
98,0 : 2,0	5	3,24	65,38	6,41
97,0 : 3,0	–	3,36	67,73	6,64
97,0 : 3,0	1	3,46	69,87	6,85
97,0 : 3,0	5	3,53	71,19	6,98
95,0 : 5,0	–	3,63	73,13	7,17
95,0 : 5,0	1	3,70	74,66	7,32
95,0 : 5,0	5	3,81	76,90	7,54
92,0 : 8,0	–	3,94	79,36	7,78
92,0 : 8,0	1	4,00	80,68	7,91
92,0 : 8,0	5	4,08	82,31	8,07
90,0 : 10	–	4,16	83,84	8,22
90,0 : 10	1	4,27	86,19	8,45
90,0 : 10	5	4,41	88,84	8,71
88,0 : 12	–	4,51	90,98	8,92
88,0 : 12	1	4,58	92,31	9,05
88,0 : 12	5	4,66	93,94	9,21
85,0 : 15	–	4,77	96,29	9,44
85,0 : 15	1	4,87	98,12	9,62
85,0 : 15	5	4,95	99,86	9,79
82,0 : 18	–	5,03	101,49	9,95
82,0 : 18	1	5,11	103,12	10,11
82,0 : 18	5	5,19	104,75	10,27
80,0 : 20	–	5,32	107,30	10,52
80,0 : 20	1	5,44	109,65	10,74
80,0 : 20	5	5,54	111,69	10,95
75,0 : 25	–	5,67	114,34	11,21
75,0 : 25	1	5,78	116,59	11,43
75,0 : 25	5	5,91	119,14	11,68
70,0 : 30	–	6,01	121,28	11,89
70,0 : 30	1	6,14	123,80	12,14
70,0 : 30	5	6,31	127,29	12,48
60,0 : 40	–	6,53	131,68	12,91
60,0 : 40	1	6,70	135,15	13,28
60,0 : 40	5	6,88	138,72	13,67

Proteins and amino acids during crop development contain sulfur. Sulfur should come in third behind nitrogen and phosphorus in terms of its physiological importance in plant nutrition, according to one study [13]. Calcium comes in fifth place in terms of relevance for plant nutrition, behind nitrogen, phosphorus, potassium, and sulfur. A large boost in production will result if it is incorporated into the soil in a way that plants can digest it [14]. So, we can claim that the AU's composition is also enriched with two macroelements: calcium and sulfur. An increase in the water-soluble calcium (CaO_{aq}) and sulfur ($\text{SO}_{3\text{aq}}$) fertilizer samples from 36.92 to 14.13% and from 42.3 to 17.9% respectively shows that the reaction between NH_4NO_3 and $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, which results in the creation of $\text{Ca}(\text{NO}_3)_2$ and $(\text{NH}_4)_2\text{SO}_4$, has progressed.



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Table 2 demonstrates that the strength of the final granules improves as the amount of additions as sulfate raw materials increases. The strength of the granules changes when the mass ratio of AS melt to PG and ammonium sulfate varies as follows: 5.21 MPa at an AS:PG ratio of 99.5:0.5 and a 5% addition of ammonium sulfate; 10.95 MPa at an 80:20 and 5% addition of ammonium sulfate; and 13.67 MPa at a 60:40 and 5% addition of ammonium sulfate; compared to 1.32 MPa for pure AS granules alone. The higher the strength of the granules, the lower their porosity and internal specific surface, the less diesel fuel gets inside the granules, and as a result, the lower the detonation ability of ammonium nitrate.

V. CONCLUSION AND FUTURE WORK

Thus, high-quality nitrogen-sulfur fertilizers with enhanced physicochemical and decreased detonation qualities can be produced by mixing ammonium nitrate melt with powdered natural PG and ammonium sulfate, then granulating the resulting mixture in a granulation tower. In addition, the composition of saltpeter has been supplemented with macroelements like calcium and sulfur, which helps to increase crop yields.

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