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Non-Caking Ammonium Nitrate with Additive Serpentinite from the Arvaten Deposit

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ABSTRACT: The process of obtaining non-caking ammonium nitrate (AN) based on its melt and the addition of serpentinite (SP) from the Arvatin deposit (Jizzakh region, Uzbekistan) was studied. The prilling method was used to granulate the serpentinite-nitrate melt. The composition and properties of the obtained fertilizers were determined. It was shown that the AN melt activates SP, i.e. it converts the indigestible form of MgO into a form assimilable for plants.

KEYWORDS: ammonium nitrate, melt, serpentinite, non-caking ammonium nitrate, composition, strength and caking of granules.

I.INTRODUCTION

The most important nitrogen fertilizer after urea is ammonium nitrate (AN). However, AN surpasses urea in its fast action, i.e. due to its absorption by plants. Currently, Uzbekistan produces about 2 million tons of it per year for domestic needs (agricultural crops) and for export [1, 2].

The volume of AN production is constantly increasing. The main disadvantages of the fertilizer are its high caking, due to hygroscopicity, solubility, modification transitions, thermal instability [3, 4].

Currently, an important task is to improve the commercial and consumer properties of AN. For this purpose, research is being conducted to select highly effective additives that improve the strength of granules and increase the thermal stability of the fertilizer [5]. The issue of caking of AN is of great importance for transportation, which is why new conditioning additives are being actively sought. In the world, the problem of eliminating the caking of AN is solved by using various additives: dolomite, limestone, bentonite, caustic magnesite, phosphate-sulfate and phosphate-sulfate-borate additives, which are a mixture of orthoboric acid, diammonium phosphate, ammonium sulfate and others [6]. One of the best additives to AN that eliminates its caking is a magnesite additive. The raw material for its preparation is caustic magnesite obtained by roasting a natural mineral - magnesite of the Satka deposit, mined in the Urals (Russia). Caustic magnesite, produced as a commercial product, is a fine, dry, free-flowing powder of a grayish or yellowish color. According to GOST 1216-75, it is produced in several grades, the composition of some of them (in %) is given in Table 1.

For its decomposition, 35% nitric acid is used, obtaining approximately 40% magnesium nitrate solution **Table 1.**

Composition of quality additives of magnesite of various grades

Brand	MgO	CaO	CO_2	R_2O_3	PPP	H_2O
PMK-75	73	4,5	3,5	Not standardized	18	1,5
PMK-83	83	2,5	2,5		8	1,3
PMK-87	87	1,8	1,8	2,2	6	1,0

In the AN production cycle, magnesium solution can be introduced either into neutralizing devices, in which nitric acid is neutralized with ammonia, or into solutions fed for evaporation. With a residual moisture content in the

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finished product of 0.3-0.4%, the magnesium nitrate content in the product (in terms of MgO) should be 0.36-0.48%. Magnesium nitrate is an additive that binds water in the AN melt. Magnesium nitrate is introduced into the technological process of saltpeter production in the form of a solution, which is dehydrated as it evaporates and a highly concentrated saltpeter melt is obtained. When in saltpeter granules, anhydrous magnesium nitrate binds the free water remaining in the melt into the chemical compound $Mg(NO_3)_2\ 6H_2O$ (magnesium nitrate crystal hydrate), resulting in an anhydrous product with good physicochemical properties [7].

Our plants use caustic magnesite – MgO and brucite – $Mg(OH)_2$ as an additive to AN, which are purchased from abroad, which leads to an increase in the cost of the product. Given the large-tonnage of AN, in order to save foreign currency, it is necessary to replace both magnesite and brucite with local raw material sources.

In this regard, the most promising additive may be serpentinite, the reserves of which in Uzbekistan are quite large.

Serpentinite from the Arvatin deposit also contains from 33 to 42% magnesium oxide (Table 2).

Table 2. Chemical composition of serpentinite from the Arvatene deposit

Content of components, wt. %	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	NiO	SO_3	H_2O
	42,9-43,5	2,16-2,20	7,03-8,41	1,6-4,76	33-41,78	0,3-1,38	0,05-0,1	2-5

In addition to $Mg(NO_3)_2$, water-removing additives include soluble inorganic salts capable of producing crystal hydrates, such as $Ca(NO_3)_2$, $Al(NO_3)_3$, $Fe(NO_3)_2$, $Cu(NO_3)_2$, $Zn(NO_3)_2$ and inorganic salts with other anions and cations capable of adding significant amounts of crystallization water. If powdered serpentinite is added to the nitrate melt to obtain modified AS with the addition of serpentinite, then in addition to magnesium nitrate it contains $Ca(NO_3)_2$, $Al(NO_3)_3$ and $Fe(NO_3)_2$, which improves the commercial properties of the nitrate granules than the magnesite additive AN.

II. SIGNIFICANCE OF THE SYSTEM

The article shows the production of non-caking AN by adding Arvatinsky serpentinite to the AN melt in the ratio AN: SP = from 100 : 0.5 to 100 : 2.5. The study of methodology is explained in section III, section IV covers the experimental results of the study, and section V discusses the future study and conclusion.

The aim of this work was to determine the component composition and properties of non-caking AN with the addition of serpentinite, obtained by the interaction of NH4NO3 melt of the “pure” grade with powdered serpentinite (SP) from the Arvatin deposit in the Jizzakh region.

III. METHODOLOGY

The experiments were conducted as follows. The AN sample was melted in a metal cup by electric heating. Serpentinite was added to the saltpeter in such an amount that the mass ratio of AN : SP in the mixture varied from 100 : 0.5 to 100 : 2.5. The mixture was thoroughly mixed. The melts were maintained at a temperature of 170-175ºC. The total interaction time of the components was 3 minutes. After that, 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 in the upper part 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 dispersed by particle size. Particles of 2-3 mm in size were tested for strength according to GOST 21560.2-82 on the GSM-1 (granule strength meter) device. After that, the products were crushed and analyzed using known methods [8, 9]. The caking of fertilizers was determined using the express method [10]. The caking (X - kg/cm^2) was 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^2.

The results of the experiments are presented in Tables 3 and 4.

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IV. EXPERIMENTAL RESULTS

Table 3. Composition, strength and caking of granules of non-caking AN with the addition of serpentinite

Mass ratio AC : SP	Content of components, mass %			
	N	$MgO_{total.}$	MgOass. MgOtotal by lim. k-te, %	Mghyd., Mgtotal %
Pure NH_4NO_3	34.96	–	–	–
100 : 0.5	34.62	0.20	90	65
100 : 1.0	34.45	0.41	88	53
100 : 1.5	34.31	0.62	85	42
100 : 2.0	34.20	0.65	77	38
100 : 2.5	34.06	1.09	68	24

It is evident from them that, at the studied ranges of ratios AN : SP = 100 : (0.5-2.5), the products contain 34.06-34.62% N and 0.20-1.09% MgO. With an increase in the mass fraction of serpentinite in the mixture, the relative content of the assimilable and water-soluble forms of magnesium oxide changes from 90 to 68% and from 65 to 24, respectively. The main advantages of non-caking AN with the addition of serpentinite over traditional AN are that in addition to nitrogen, it has one additional component – magnesium. We believe that the optimal samples of non-caking AN are those whose compositions are given in Table 3. The reason is that the nitrogen content in all samples is not less than 34%. Therefore, the strength and caking of the granules of these selected samples were determined.

From Table 4. Strength and caking properties of non-caking AN granules with the addition of serpentinite

Mass ratio AC:SP	Granule strength			Granule caking, kg/cm2
	kg/granules	kg/cm^2	MПa	
Granulated "clean" NH_4NO_3	0,67	13,50	1,32	5.62
Granulated AS with 0.28% MgO	0,80	16,12	1,58	4.67
100 : 0,5	1,892	38,14	3,74	3.20
100 : 1,0	1,938	39,07	3,83	3.15
100 : 1,5	2,09	42,13	4,13	3.00
100 : 2,0	2,181	43,96	4,31	2.93
100 : 2,5	2,388	48,14	4,72	2.85

To obtain non-caking AN granules (containing at least 34% N) with sufficiently high strength (3.74-4.72 MPa), the SP is no more than 2.5 g per 100 g of NH_4NO_3. For comparison, the strength of pure NH_4NO_3 granules without any additives is 1.32 MPa, and that of nitrate with a magnesium additive is 1.58 MPa. The caking of AN with the addition of SP at the ratio of AN : SP = 100 : 2.5 is 2.85 kg/cm^2, which is 1.6 times less than the caking of industrial AN with the addition of 0.28% MgO (the caking of which is 4.67 kg/cm^2).

V. CONCLUSION AND FUTURE WORK

Thus, based on the results of laboratory studies, the possibility of obtaining a process for non-caking AN based on a melt of saltpeter with serpentinite from the Arvatena deposit in the Jizzakh region has been shown. Serpentinite allows eliminating a number of AN disadvantages, improves the physicochemical and consumer properties of the fertilizer: increases the strength of granules, reduces caking and explosiveness.

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