

Theoretical Basis of the Process of Obtaining Granular Magnesium Lime-Ammonium Nitrate with the Addition of Dolomites of Uzbekistan

Nabiev A.A. Tashkent Institute of Chemical Technology. Head of the Department of Inorganic, Analytical, Physical and Colloid Chemistry, PhD, Associate Professor. nabievximik@mail.ru (+99890-948-91-58)

Alikhonova Z. S. Tashkent Institute of Chemical Technology. Department of Inorganic, Analytical, Physical and Colloid Chemistry. Associate professor

Rizaev Sh.N. Tashkent Institute of Chemical Technology, Ph.D. associate professor

Talipova H. S. Tashkent Institute of Chemical Technology. Department of Inorganic, Analytical, Physical and Colloid Chemistry, Ph.D. Associate professor

Annotation: The degree of carbonation of lime-ammonium nitrate samples obtained after the addition of dolomite flour to ammonium nitrate solution, chemical composition, porosity of fertilizer grains, melting times, viscosity, grain strength, grain diesel oil absorption, modification changes, crystalline grains. The initial decomposition temperature and the activity energy of the samples obtained were determined by heating in the range of 25 to 300 °C. The thermal stability of magnesium lime-ammonium nitrate grains to heating-cooling cycles of 20 ↔ 60 °C was studied. Radiographs of primary products and magnesium-lime ammonium nitrate were studied.

Keywords: dolomite, magnesium lime - ammonium nitrate, adsorption, X-ray, interactive peaks, viscosity, grain strength, thermal stability.

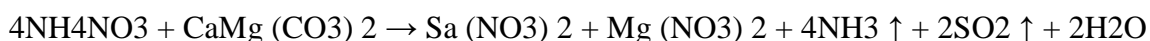
Introduction. Research in ammonium nitrate (AN) producing countries around the world today selects high-performance additives that improve the consumer properties of ammonium nitrate and substantiate the following scientific and technical recommendations for the production of non-adhesive, thermally stable ammonium nitrate, including: filling the pores and microcracks of ammonium nitrate grains by adding weight ratios, resulting in the creation of multiple crystallization centers based on the formation of a much improved inner surface and structure of nitrate grains; to determine the effect of additives on reducing the viscosity and explosive properties of the finished product, while increasing the strength of ammonium nitrate grains; it is necessary to develop a thermally stabilized ammonium nitrate extraction technology with good physicochemical and agrochemical properties.

Experimental part: In our research work, the composition and properties of non-viscous and thermally stabilized ammonium nitrates obtained by adding dolomite in weight ratios of ammonium nitrate: DU = 100: 0.5 to 100:45 to NH₄NO₃ liquid were studied. Dolomite was ground to a size of 0.25 mm before being added to the NH₄NO₃ liquid. For the preparation of the experimental samples, the specified amount of pure NH₄NO₃ was liquefied at 170-175 °C, then the measured DU was added to the liquid [1]. It was found that as the amount of DU increases, the crystallization temperature of the dolomite-nitrate liquid decreases [2]. For example, in the ratio ammonium nitrate: DU = 100: 0.5 to 100:45 (34.78 to 24.10% N; 0.15 from

9.32% CaO ; from 0.12 to 6.05% MgO) the crystallization temperature of NH_4NO_3 (crystal.) decreases from the initial 165.0 in the product to 152.1 (°C). sharply lowers the temperature, which is explained by the fact that the insoluble components in dolomite form central crystals in the pores and microcracks of ammonium nitrate and accelerate the solidification of the liquid.

The main properties of modified ammonium nitrate by adding DU (grain viscosity, strength, 20–60°C thermal resistance to repetitive cycles on heating-cooling, porosity and adsorption of liquid fuel adsorption) were studied. The strength of the fertilizer grains is high enough (1.88–13.02 MPa) and can withstand 50 and more cycles on heating and cooling [1,3]. and the viscosity is 1.88–2.61 MPa and 4.17–3.38 kg / cm², respectively). The amount of DU per 100g of NH_4NO_3 should be up to 2g. 1.32 MPa, and the strength of magnesite-added nitrate is 1.58 MPa [3].

It should be noted that the mixing of NH_4NO_3 with DU results in a decomposition reaction to one degree or another:



The degree of carbonation of DU in dolomite-nitrate liquid was investigated. The results are shown in Figure 1.

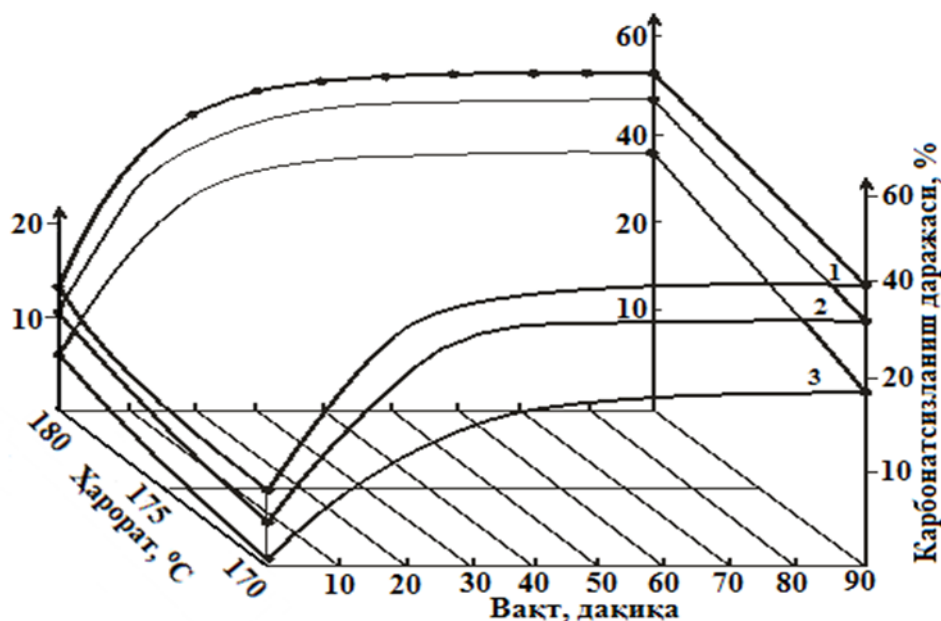


Figure 1. The dependence of the degree of carbonation of dolomite on it depends on the temperature and the time of exposure. Weight ratios AS: DU: 1 = 100: 5; 2 = 100: 15; 3 = 100: 25.

It is clear from the curves that at all ammonium nitrate: DM ratios and temperatures, the process of interaction of the ammonium nitrate liquid with the carbonated DU is sufficiently rapid in the first 30 minutes. The higher the amount of DU in the mixture or the lower the mass fraction of NH_4NO_3 , the lower the degree of carbonation of DU. For example, if the degree of carbonation of DU increases from 41.52 to 44.85% after 15 minutes of exposure in the ratio ammonium

nitrate: DU = 100: 5 and the temperature rises from 170 to 180 ° C, in the ratio ammonium nitrate: DU = 100: 25 this figure is 28, Increases from 68 to 33.30%, i.e. decreases by an average of 1.5 times. It has been found that 10 minutes or more of exposure time of the starting materials is sufficient for fertilizer grains to achieve high strength [4,5].

Tables 1 and 2 show the composition and properties of thermally stabilized AS samples added to Navbahor DU.

Table 1
Composition of samples of magnesium lime-ammonium nitrate

Ammonium nitrate : DU weight ratio	Amount of components, weight. %						
	N	CaO	MgO	CaO _{self.} : CaO _{general.}	MgO _{self.} : MgO _{general.}	CaO _{wat.solut.} : CaO _{general}	MgO _{wat.sol.} : MgO _{general}
NH ₄ NO ₃ “ro3a”	35,0	-	-	-	-	-	-
0,28% MgO additional ammonium nitrate	34,5	-	0,28	-	-	-	-
100 : 3,0	32,52	0,82	0,60	44,28	37,51	14,09	11,20
100 : 5,0	32,84	1,35	0,97	41,07	33,79	12,57	10,45
100 : 10	31,33	2,58	1,83	37,12	30,65	11,65	9,04
100 : 15	29,95	3,66	2,64	32,65	28,48	10,40	8,38
100 : 20	28,72	4,70	3,35	29,74	24,37	9,28	7,13
100 : 25	28,0	5,61	3,89	24,89	20,92	8,34	6,21
100 : 30	26,48	6,47	4,62	21,41	18,16	6,81	5,0
100 : 35	25,54	7,29	5,16	17,83	15,04	5,70	4,18
100 : 45	24,10	9,32	6,05	16,53	13,66	4,45	3,06

Table 2
Properties of samples of magnesium lime and ammonium nitrate

Ammonium nitrate : DU Weight ratio	Strength, МПа	Viscosity, кг/см ²	Porosity, %	Inflation of diesel oil, гр.	Melting time in water, second
NH ₄ NO ₃ “clear”	1,32	5,62	22,0	4,82	44,60
0,28% MgO Additional ammonium nitrate	1,58	4,67	9,10	4,33	46,80
100 : 3	3,44	3,29	8,43	3,17	57,71
100 : 5	4,13	3,10	8,09	2,96	59,56
100 : 10	4,86	2,93	7,78	2,81	60,83
100 : 15	5,28	2,75	7,50	2,60	61,16
100 : 20	6,60	2,58	7,16	2,44	63,17

100 : 25	7,98	2,37	6,87	2,25	65,38
100 : 30	8,89	2,16	6,61	2,08	66,56
100 : 35	10,44	2,0	6,25	1,89	67,85
100 : 45	13,02	1,81	5,90	1,67	71,08

It can be seen that an increase in the amount of DU additive in NH_4NO_3 dilution reduces the amount of N in the products on the one hand and increases the amount of CaO and MgO on the other hand. For example, in the weight ratio Ammonium nitrate: DU = 100: 3, the amount of N in the product decreases from 32.52% to 28% at Ammonium nitrate: DU = 100: 25, and 24.1% at Ammonium nitrate: DU = 100: 45. At the same time, the amounts of CaO and MgO increase from 0.82 and 0.60% to 5.61 and 3.89%, respectively, to 9.32 and 6.05%.

Most importantly, at 170-175 (C), the nitrate solution activates DU, that is, it converts the insoluble form of CaO and MgO into an absorbable form.) 2 and $\text{Mg}(\text{NO}_3)_2$ salts, resulting in an increase in the amount of absorbable form of CaO and MgO . For example, depending on the amount of additive introduced (Ammonium nitrate: DU = 100: 3-45) in products 2% lemon of CaO and MgO the relative amounts of assimilated forms of acid vary between 44.28-16.53% and 37.51-13.66 %.The values of the absorbable form of CaO and MgO allow to consider the dolomite component in AS as an effective calcium-magnesium fertilizer.

An increase in the proportion of DU increases from 3.44 to 13.02 MPa, which has a positive effect on the grain strength of the product (Table 2). The viscosity of AS grains with DU additive is 3.29-1.81 kg / cm^2 , which is almost 2-3 times lower than that of nitrate without additive (5.62 kg / cm^2).

One of the indicators characterizing the explosive properties of ammonium nitrate is the porosity of the grains and the ability to adsorb liquid fuel. The porosity of AS grains with pure NH_4NO_3 and magnesite added is 22.0 and 9.10%, respectively. Adding 3.0 to 45g of DU relative to 100g of NH_4NO_3 helps to reduce the porosity of the grains from 8.43 to 5.90%, respectively.

The lower the porosity of the grains, the lower their fuel swelling rate should be. This situation is really interconnected. Depending on the amount of DU additive (Ammonium nitrate: DU = 100: 3-45), the fuel absorption of magnesium lime-ammonium nitrate grains varies from 3.17 to 1.67g per 100g of product. It is equivalent to 4.82 and 4.33g, respectively, in Ammonium nitrate with the addition of NH_4NO_3 and magnesite without additives (Table 5).

Thus, the higher the strength of the grains, the lower their porosity and internal specific surface area, the less diesel fuel falls into the grains, and as a result the lower the detonation ability of the nitrate.

The radiographic results of the samples of magnesium lime-ammonium nitrate were studied, with Figures 2-4 showing the radiographs of the raw materials and finished products. 2.26 belonging to NH_4NO_3 ; 2.73; 3.08; 3.96; 4.95Å intensive peaks (Fig. 2) and their corresponding values 100; 76; 67; 45 and 44%, while the peak peaks for $\text{CaMg}(\text{CO}_3)_2$ in Navbahor DU were

2.89; 2.19; 1.80; 2.02; 2.40; 1.55 Å (Fig. 3) and their corresponding values are 100; 40; 20; 13; Were found to be equal to 10% [10,11].

Figure 4 shows pure NH_4NO_3 (2.26; 2.73; 3.08; 3.96; 4.95 Å) and $\text{CaMg}(\text{CO}_3)_2$ 2 intensive peaks in Navbahor DU (2.89; 2.19; 1, 80; 2,02; 2,40; 1,55 Å) in the interaction of NH_4NO_3 liquefaction and DU.

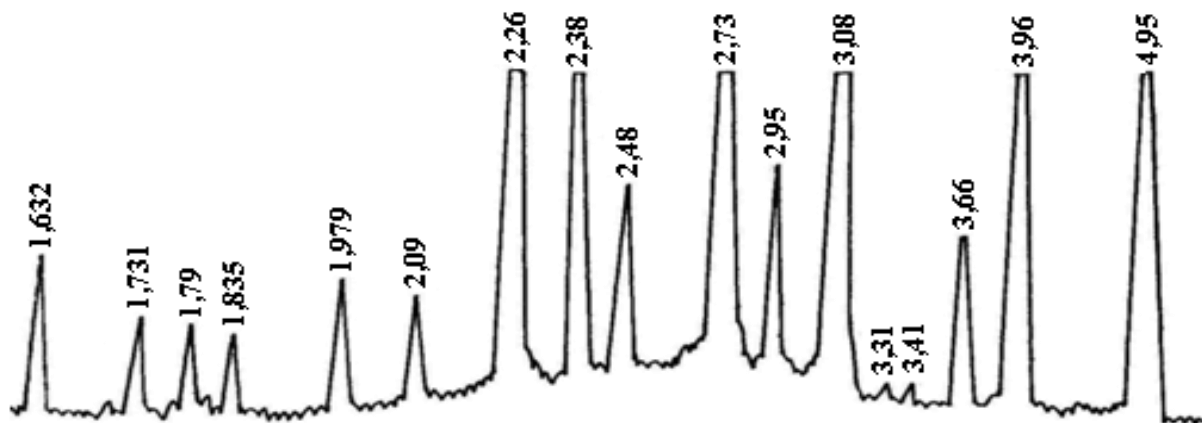


Figure 2. Radiograph of pure brand NH_4NO_3 .

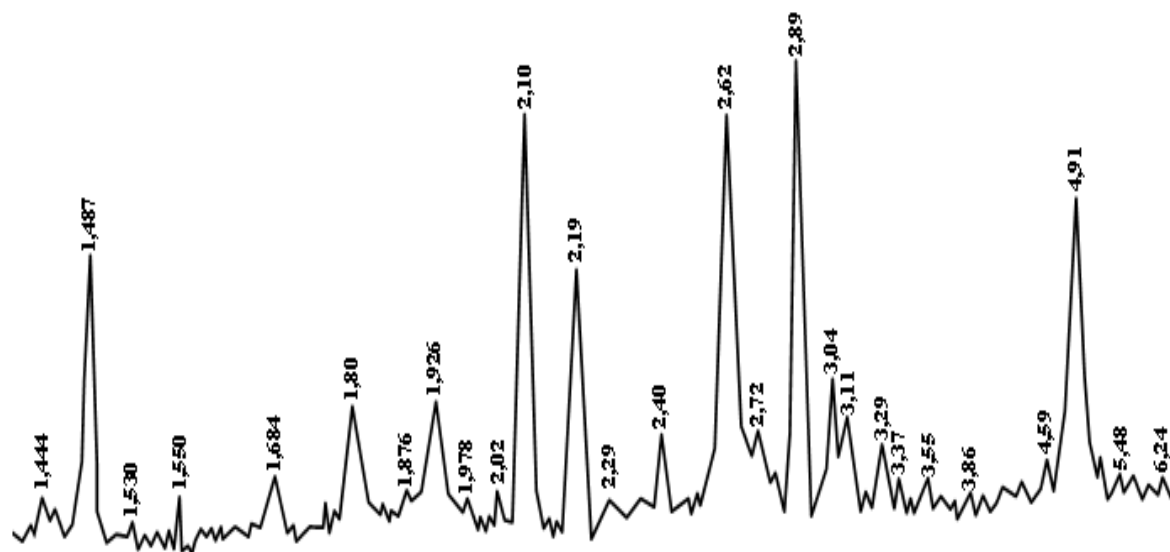
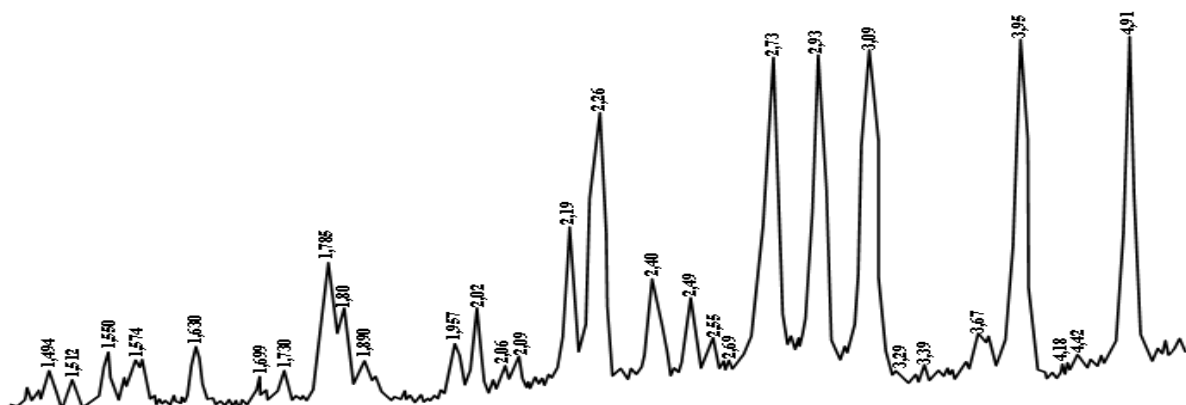
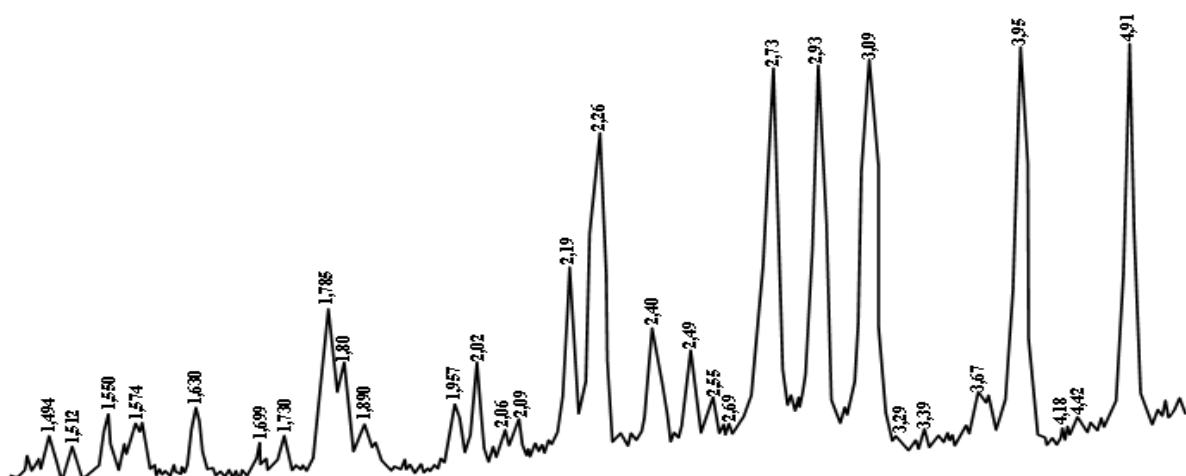


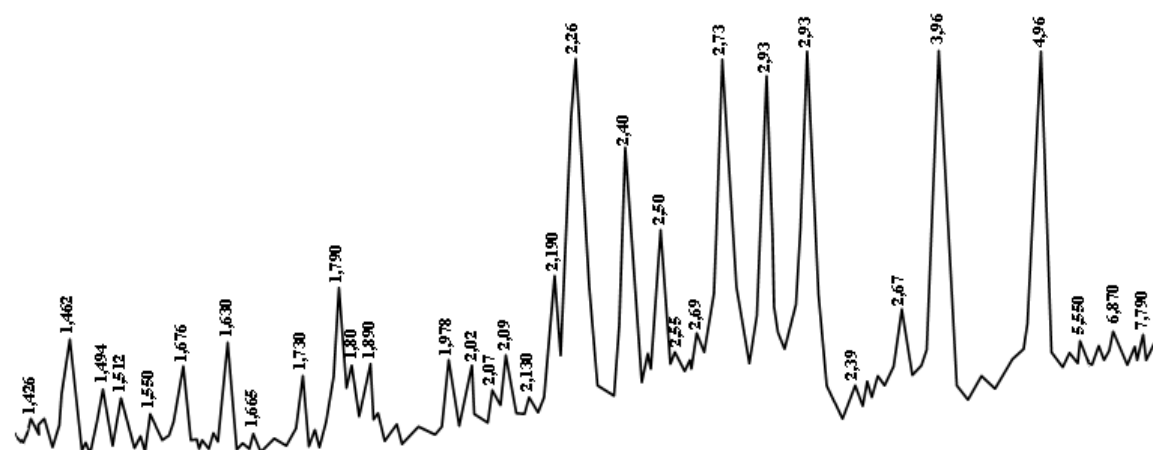
Figure 3. Radiograph of dolomite of Navbahor mine.



Weight ratio ammonium nitrate: DU = 100: 10



Weight ratio ammonium nitrate: DU = 100:25



Weight ratio ammonium nitrate:DU = 100:45

Figure 4. Radiographs of samples of magnesium-lime-ammonium nitrate based on NH_4NO_3 liquefaction and dolomite of Navbahor mine. 1.73 1.89, respectively, confirming the presence of salts of calcium and magnesium nitrates formed; 2.29; 3.09; 3.39 Å and 2.69; 2.93; 3.29; 4.18; 4.42 Å diffraction peaks are observed [8,9,12]. The increase in the absorbable forms of CaO and MgO in the composition of magnesium lime-ammonium nitrate confirms the formation of the salts $\text{Ca}(\text{NO}_3)_2$ and $\text{Mg}(\text{NO}_3)_2$ [13].

In the NETSCH STA 409 PC / PG equipment, the initial decomposition temperature and activation energy of magnesium lime-ammonium nitrate samples were determined in the temperature range of 25 to 300°C.

Table 3 shows that the initial decomposition temperature and activation energy of pure NH_4NO_3 (without additives) is 211 (S and -915 Dj / g, while in samples of magnesium lime-ammonium nitrate these values are 247.3-259 (S and -840), respectively. \div -906.6 Dj / g. It is clear that the thermal decomposition of magnesium-lime-ammonium nitrate requires higher temperatures and more energy than pure NH_4NO_3 . [5,6,7,8].

Table 3
The initial temperature of thermal decomposition of magnesium lime ammonium nitrate and the value of the activation energy

Ammonium nitrate : DU Weight ratio	Studied temperature ranges	Initial decomposition temperature, °C	Activation energy, J/gr.
«pure» NH_4NO_3	200–300	211,0	-915,1
100 : 5		247,3	-840,6
100 : 15		251,9	-856,4
100 : 25		258,6	-889,5
100 : 45		259,0	-906,6

When we study the thermal stability of magnesium lime-ammonium nitrate grains to heating-cooling cycles of 20↔60 ° C, pure NH_4NO_3 grains decompose by 5% after 10 thermocycles and completely decompose after 80 thermocycles. Magnesium lime-ammonium nitrate grains containing 5% DU decompose by 5% after 30 thermocycles.

Ammonium nitrate: DU = 100: 25 magnesium lime-ammonium nitrate in an acceptable ratio maintains the integrity of the grains up to 25% complete, and after 100 thermocycles up to 71% integrity compared to 29% broken. The higher the DU in the NH_4NO_3 dilution, the higher the thermal tolerance of the grains (Table 4).

Table 4
Thermal resistance of magnesium lime-ammonium nitrate grains to heating and cooling cycles of 20-60 ° C

Weight ratio Ammonium nitrate: DU	The amount of refraction during formation IV→ III of thermally stabilized ammonium nitrate grains				
	10 cycle	25 cycle	50 cycle	90 cycle	100 cycle
«pure» brand NH_4NO_3	5	21	36	100	—
0,28% MgO Ammonium nitrate additive	—	13	27	82	100
100 : 3,0	-	9	21	59	72
100 : 5,0	-	7	18	47	65

100 : 10	-	-	12	30	44
100 : 15	-	-	10	25	38
100 : 20	-	-	9	23	35
100 : 25	-	-	7	20	29
100 : 30	-	-	-	13	25
100 : 35	-	-	-	9	21

Analysis of the results and part of the conclusion: Based on the results, we can conclude that the addition of 3 to 45 g of DU to 100 g of NH_4NO_3 solution increases the strength of fertilizer grains from 3.44 to 13.02 MPa, respectively. Grain viscosity, porosity, and diesel oil absorption decreased from 3.29 to 1.81 kg / cm², 8.43 to 5.90%, and 3.17 to 1.67 g, respectively. These figures were 5.62 and 4.67 kg / cm², respectively, for pure NH_4NO_3 and magnesium-added ammonium nitrate obtained for comparison; 22.0 and 9.10%; 4.82 and 4.33g, respectively, which can be explained by the fact that the microcracks of ammonium nitrate are filled with dolomite flours.

The study of polymorphic changes in the heating-cooling cycle showed that the modification changes in the cooling of thermally stabilized ammonium nitrate with DU addition go through the liquid (I; I (II; II (IV. Phase III is not formed. while maintaining its integrity up to 71% compared to 29% broken. At this time, pure NH_4NO_3 grains are broken down by 5% after 10 thermocycles and completely broken down after 80 thermocycles.

Used literature

1. Таубкин И.С., Саклантй А.Р., Самойленко Н.Г., Соловьёв И.В. О взрывоопасности установок для получения аммиачной селитры и удобрений на её основе // Химическая промышленность. – 2010. – т. 87. – № 3. – С. 148-160.
2. Реймов А.М. Разработка технологии получения фосфорных и сложных азотнофосфорных удобрений на основе фосфоритов Центральных Кызылкумов; Автореферат диссертации доктора техн. наук, ИОНХА АН РУз, Ташкент. – 2014. – 81 с.
3. Резниченко О.А., Москаленко Л.В. Оценка влияния состава фосфогипса на прочность аммиачной селитры // Материалы VIII региональной науч.-техн. конф. «Вузовская наука – Северо-Кавказскому региону» – Ставрополь: Сев.Кав. ГТУ. – 2004. – С. 40-41.
4. Колесников В.П., Москаленко Л.В. Изучение влияния добавки фосфополугидрата на прочность гранул аммиачной селитры // Химическая промышленность сегодня. – 2006. – № 6. – С. 8-9.
5. Колесников В.П., Москаленко Л.В. Термографические исследования модификационных превращений удобрения, полученного на основе аммиачной селитры // Химическая промышленность сегодня. – 2006. – № 7. – С. 18-21.
6. Патент № 2281274 РФ. Кл. С 05 G 1/08, С 05 С 1/02. Способ получения гранулированного известково-аммиачного удобрения / В.Г.Казак, Н.М.Бризицкая, И.Г.Гришаев, В.В.Долгов, А.С.Малявин, В.А.Бирюкова. – Б.И. 2006. – № 22.

7. Патент № 2362757 РФ. Кл. С 05 G 1/08. Способ получения известково-аммиачной селитры / П.В.Киселевич, В.М.Хохлов, С.В.Бойков, А.Н.Шевелёв, О.Б.Абрамов, О.М.Захарова, Т.Е.Мухачева, Д.Г.Медянцева. – от 27.07.2009.
8. Набиев А.А., Намазов Ш.С., Сейтназаров А.Р., Реймов А.М., Айымбетов А.Ж. Известково-аммиачная селитра и её применение в сельскохозяйственном производстве. // Universum: Технические науки: электрон. научн. журн. – Новосибирск. – 2017. – №6 (39) – С. 25-39.
9. Набиев А.А., Реймов А.М., Намазов Ш.С., Беглов Б.М. Изучение процесса получения магнийсодержащей известковой аммиачной селитры // Химическая технология. Контроль и управление. – Ташкент. – 2018. – № 1/2. – С. 13-17.
10. Лавров В.В., Шведов К.К. О взрывоопасности аммиачной селитры и удобрений на её основе // Научно–технические новости: «ИНФОХИМ» - Спецвыпуск, 2004, № 2, с. 44-49.
11. Левин Б.В., Соколов А.Н. Проблемы и технические решения в производстве комплексных удобрений на основе аммиачной селитры // Мир серы, N, P и K. – 2004, № 2, с. 13-21.
12. Постников А.В. Производство и применение известково-аммиачной селитры // Химизация сельского хозяйства. – 1990. - № 9, с. 68-73.
13. Ильин В.А. Разработка технологии сложного азотно-фосфатного удобрения на основе сплава аммиачной селитры: Автореф. дис... канд. техн. наук, Ивановский Гос. химико-технол. ун-т, г. Иваново, 2006. - 17 с.
14. Аммиачная селитра: свойства, производство, применение / А.К.Чернышев, Б.В.Левин, А.В.Тугоуков, А.А.Огарков, В.А.Ильин. – М.: ЗАО «ИНФОХИМ», 2009, 544 с.