Ammonium nitrate with improved properties for agricultural crops

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Abstract. This article presents the results of research aimed at developing enhanced mineral fertilizers based on ammonium nitrate. The main objective was to improve the quality and strength of fertilizer granules by adding local unconventional natural minerals and technogenic wastes to ammonium nitrate. During the research, bentonite and glauconite powders, along with lime-quenching residues, were introduced into the ammonium nitrate solution to identify optimal formulations and proportions. The experiments demonstrated that granules produced with the new additives significantly surpassed conventional ammonium nitrate granules in strength and were enriched with microelements. Field trials confirmed that the application of these newly developed fertilizers considerably increased the productivity of agricultural crops. The technology developed through this research effectively expands the variety of mineral fertilizers available and has practical significance in enhancing agricultural efficiency.

1 Introduction

Ammonium nitrate (AN) - NH4NO3 - is used both as a fertilizer in agriculture and as an ingredient for industrial explosives (for quarries, mine tunnels, etc.). It is an oxidizing agent that has good resistance to detonation, but when heated to high temperatures in closed rooms can lead to violent reactions and explosions, especially if it is contaminated or mixed with various materials such as combustibles, acids, alkalis, chlorides, etc.[1]. Ammonium nitrate is an inorganic product of industrial synthesis, produced from gaseous ammonia and nitric acid. It was first obtained by Glauber in 1659. In its production form, it is a colorless crystalline substance with a content of 35% of total nitrogen in ammonia and nitrate forms. For fertilizing purposes, it is produced in granular form The physico-chemical properties of ammonium nitrate are regulated by the regulatory requirements of ISC 2-2013 [2].

Even more promising is the use of local unconventional natural minerals – bentonite and glauconite flour, available on the territory of the Republic of Uzbekistan. Therefore, the development of scientific foundations and technology of AN with improved properties is an urgent task.

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All research work on the production of mineral fertilizers with improved composition and properties by adding additives to ammonium nitrate was carried out at the Ferghana Polytechnic Institute.

2 Materials and research methods

In accordance with state standard 2-2013, examples of AN with improved properties are ammonium nitrate grade B, which became non-standard during storage and transportation (<1 mm, >4 mm), AN liquid, incompleteness (sludge) after lime quenching - waste of man-made and local production non-traditional natural minerals (bentonite and glauconite powder).

Surface treatment of granular ammonium nitrate with a solution of ammonium sulfate binder (40-45%), followed by separate powder treatment of selected additives based on mixing of a half-finished (suspension) after quenching lime with AN liquid and local non-traditional natural minerals (bentonite and glauconite powder), depending on the weight ratios of the property, is a study of the process of obtaining improved AN, as well as physical, mechanical and commodity properties of products.

The results of quantitative analysis, physico-mechanical, IR spectral, XRD analysis, electron microscopic analysis were confirmed by tests in agricultural experimental fields during this research work.

3 Method of research

Introduction of crushed waste (CaCO3) from technogenic production and local non-traditional natural minerals (bentonite and glauconite powder) into the NH4NO3 alloy, followed by granulation of nitrate-carbonate melts by prilling, as well as determination of the composition and properties of the product according to state standard 2-2013. A 40-45% solution of (NH4)2SO4 was used as a binder. Consumption rates of 25-30 kg (2,5-3,0%) per 1 ton of finished products have been adopted. Below is information about the partial formation of complex salts with a binder [3].

Obtaining experimental samples and their study.

The experiments were carried out as follows: granular ammonium nitrate produced JSC Ferganaazot (grades B, AN with a content of 34.4% N according to ISC 2-2013) was liquefied in a metal container on an electric stove. At a temperature of 170-175°C, waste from man-made production was added to the liquid after lime quenching, mixing evenly in a ratio of 100: (5-40), without temperature change. Preliminary results showed that the addition of industrial waste to the liquid after lime quenching significantly reduces the crystallization temperature of the liquid (up to 150-155°C). Liquid stir for 10-15 minutes and bring to a homogeneous state, after which they are poured into a container (glass) made of stainless (ligated) steel for the purpose of granulation, as a result of which drops falling from a height of 8-12 meters are formed through holes with a diameter of 1.2 mm at the bottom of the container. In this case, ammonium nitrate fertilizer with improved properties was obtained, resembling standard AN grains in appearance.

The mass was cooled and then dispersed by particle size. Particles of 2-3 mm in size were tested for strength according to ISC 2-2013. After that, the products were crushed and analyzed according to known methods [2]. According to the change in the CO_2 content, the degree of decarbonization of carbonate raw materials was calculated. The experiment was carried out on a pH meter of 10% solution of (experimental) samples equipped with a stationary pH meter F20-Standard Five Easy, including a universal plastic pH electrode 3-in-1 le438 and an integrated thermal sensor. To determine the rate of dissolution of the

granules of the studied fertilizers, the product granule was lowered into a glass with 100 ml of distilled water, in which its complete dissolution was visually observed and recorded. Room temperature, five-fold tests. The pH measurement result was calculated based on the results of two parallel measurements of pH1 and pH2, the discrepancy between which, with a probability of reliability of P = 0.95, did not exceed the criterion of the standard (P) % control of practical (operational) repeatability [2,4,5].

The relative error of detection did not exceed 1.5%.

During the experiments, it was found that when NH_4NO_3 melt interacts with limestone at the above temperatures, the formation of a rapidly destructible fine-meshed foam is observed in the reaction mass. This suggests that the carbonates included in the limestone undergo partial decomposition, i.e. decarbonization, which indicates the reaction between NH_4NO_3 and $CaCO_3$. In this case, $Ca(NO_3)_2$, NH_3, CO_2 and water vapor are formed. In this regard, we have determined the degree of decarbonization of limestone depending on its amount added to the saltpeter melt.

4 Research results and discussion

The article proposes a technological process and scheme for the production of ammonium nitrate with improved properties by adding technogenic waste generated by softening process water as an additive to ammonium nitrate.

The optimal ratio of AN:(NH4)2SO4 solution[6]:

- additives = 82:3:15 was found, at which AN has low caking, high strength and improved properties compared to conventional AN;
- a method has been developed for producing ammonium nitrate with improved qualities, enriched with microelements, by treating the surface of ammonium nitrate granules with a solution of ammonium sulfate binder (concentration 40-45%), followed by separate treatment with powders of selected additives;
- it has been proven that granules of mineral fertilizers, obtained taking into account the optimal rates of selected additives, have greater strength compared to existing AN granules, are more effective in terms of chemical composition, and ensure the stability of the round shape of the granules during storage and transportation.

PDF#47-0867: QM=Star(S); d=Diffractometer; I=Diffractometer — **PDF Card**

Nitrammite, syn [NR]
N H4 N O3

Radiation=CuKa1 Lambda=1.54056 Filter=
Calibration=Internal(Si) 2T=17.9815-74.5392 I/Ic(RIR)=
Ref: Heyding, R., Queen's Univ., Kingston, Ontario, Canada.
Private Communication (1995) CAS#:6484-52-2

Orthorhombic - (Unknown), Pnmm (59) Z=2 mp=
CELL: 4.9288 x 5.4408 x 5.7529 <90.0 x 90.0 x 90.0> P.S=oP18 (?)
Density(c)=1.723 Density(m)=1.64A Mwt=80.04 Vol=154.27 F(30)=52.6(.0108,53/0)
Ref: Wyckoff, R.
The Structure of Crystals, 2nd ed., v2 p371

NOTE: Pattern taken at 25 C. Ammonium nitrate 99.999% supplied by Aldrich Chemical Co., Lot No. 14012TW. Analysis (wt.%): N O3 75.8 (with Nitron); Si 6.0 ppm, Mg 4.0 ppm, Fe 2.0 ppm, Na 2.0 ppm, Ti 0.5 ppm. Form IV.

Color: White

Strong Lines: 3.09/X 2.72/6 3.95/5 2.26/4 2.25/3 4.93/3 2.88/1 2.48/1 2.38/1 1.79/1

30 Lines, Wavelength to Compute Theta = 1.54056Å(Cu), I%-Type = (Unknown)

#	d(nm)	I(f)	(h k l)	2-Theta	Theta	1/(2d)	#	d(nm)	I(f)	(h k l)	2-Theta	Theta	1/(2d)
1	0.49290	31.0	(1 0 0)	17.9815	8.9908	0.01014	16	0.17700	1.0	(2 1 2)	51.5943	25.7972	0.02825
2	0.39530	46.0	(0 1 1)	22.4730	11.2365	0.01265	17	0.17300	3.0	(0 3 1)	52.8785	26.4392	0.02890
3	0.36540	3.0	(1 1 0)	24.3390	12.1695	0.01368	18	0.16320	5.0	(1 3 1)	56.3265	28.1632	0.03064
4	0.30850	100.0	(1 1 1)	28.9178	14.4589	0.01621	19	0.15800	4.0	(3 0 1)	58.3553	29.1776	0.03165
5	0.28770	11.0	(0 0 2)	31.0593	15.5297	0.01738	20	0.15730	2.0	(3 1 0)	58.6402	29.3201	0.03179
6	0.27200	64.0	(0 2 0)	32.9015	16.4508	0.01838	21	0.15130	4.0	(2 0 3)	61.2088	30.6044	0.03305
7	0.24840	9.0	(1 0 2)	36.1301	18.0651	0.02013	22	0.14930	4.0	(1 2 3)	62.1190	31.0595	0.03349
8	0.23820	8.0	(1 2 0)	37.7343	18.8672	0.02099	23	0.14650	3.0	(1 3 2)	63.4427	31.7213	0.03413
9	0.22600	43.0	(1 1 2)	39.8551	19.9276	0.02212	24	0.14610	3.0	(2 3 0)	63.6367	31.8183	0.03422
10	0.22450	32.0	(2 1 0)	40.1328	20.0664	0.02227	25	0.14380	2.0	(0 0 4)	64.7775	32.3887	0.03477
11	0.20910	4.0	(2 1 1)	43.2313	21.6157	0.02391	26	0.13660	3.0	(3 2 1)	68.6511	34.3256	0.03660
12	0.19760	4.0	(0 2 2)	45.8863	22.9432	0.02530	27	0.13600	2.0	(0 4 0)	68.9967	34.4983	0.03676
13	0.18350	4.0	(1 2 2)	49.6403	24.8201	0.02725	28	0.13380	2.0	(1 1 4)	70.2966	35.1483	0.03737
14	0.18090	1.0	(0 1 3)	50.4032	25.2016	0.02764	29	0.13220	2.0	(2 2 3)	71.2761	35.6380	0.03782
15	0.17870	6.0	(1 0 3)	51.0680	25.5340	0.02798	30	0.12720	1.0	(0 2 4)	74.5392	37.2696	0.03931

Fig. 1. Results of XRD analysis of ammonium nitrate according to GOST 2-2013.

To obtain samples of ammonium nitrate with improved properties, the mass ratio NH_4NO_3:$CaCO_3$ ranged from 100:5 to 100:40. The prilling method was used to granulate the nitrate-carbonate melt. The composition and properties of new types of fertilizers have been studied. It is shown that with the ratio NH_4NO_3:$CaCO_3$ = 100:20 the product contains 28.67% N, 11.2% CaO and has a granule strength of 4.07 MPa, which is 2.56 times higher than the strength of pure AC granules (1.59 MPa). The time of complete dissolution of granules of pure AC in water is 44.1 seconds. With an increase in the proportion of limestone to NH_4NO_3:$CaCO_3$ = 100:40 waste from man-made production, the time of complete dissolution of ammonium nitrate granules with improved properties is steadily increasing and reaches 93.4 seconds.

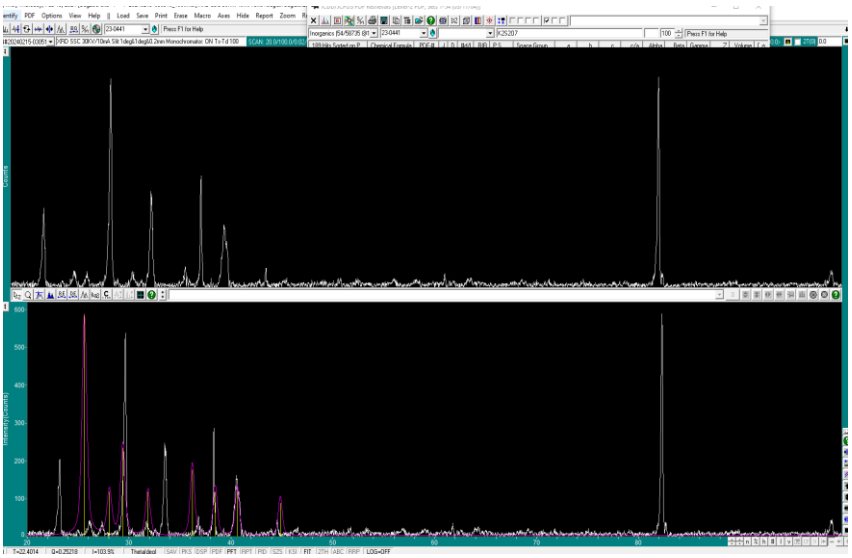


Fig. 2. Results of XRD analysis of ammonium nitrate treated with man-made waste (binder of 40-45% ammonium sulfate solution)

A 40-45% solution of $(NH_4)_2SO_4$ was used as a binder. Consumption rates of 25-30 kg (2.5-3.0%) per 1 ton of finished products have been adopted. Below is information on the partial formation of complex salts with a binder [1].

The results show that the more bentonite (BT) is introduced into the fertilizer with ammonium nitrate (AS), the stronger the grains of the product, in the case of glauconite (Gl) this indicator is slightly different.

[Begzod aka#1##2#20230215-023248_100.mdi] XRD SSC 30KV/10mA Slit:1deg&1deg&0.2m...								Peak Search Report
SCAN: 20.0/100.0/0.02/5(sec), Cu, I(max)=866, 02/15/24 02:32								
PEAK: 21-pts/Parabolic Filter, Threshold=3.0, Cutoff=1.0%, BG=3/2.0, Peak-Top=Summit								
NOTE: Intensity = Counts, 2T(0)=0.0(deg), Wavelength to Compute d-Spacing = 1.54056Å (Cu/K-alpha1)								
#	2-Theta	d(nm)	BG	Height	Height%	Area	Area%	FWHM
1	23.0611	0.38535	25	466	55.6	6366	47.8	0.232
2	27.2173	0.32738	26	76	9.1	1271	9.5	0.284
3	29.4809	0.30273	28	838	100.0	13323	100.0	0.270
4	31.5998	0.28290	29	62	7.4	1262	9.5	0.346
5	33.4796	0.26743	30	508	60.6	6813	51.1	0.228
6	36.7202	0.24454	29	63	7.5	1320	9.9	0.356
7	38.2422	0.23515	28	131	15.6	1648	12.4	0.214
8	40.4394	0.22287	27	307	36.6	10184	76.4	0.564
9	40.6400	0.22181	27	421	50.2	9372	70.3	0.378
10	43.6988	0.20697	24	46	5.5	787	5.9	0.291
11	46.3569	0.19570	21	25	3.0	419	3.1	0.285
12	51.6582	0.17680	21	44	5.3	595	4.5	0.230
13	56.9199	0.16164	17	40	4.8	966	7.3	0.411
14	62.6340	0.14820	19	24	2.9	1053	7.9	0.746
15	82.2599	0.11710	16	361	43.1	6445	48.4	0.304

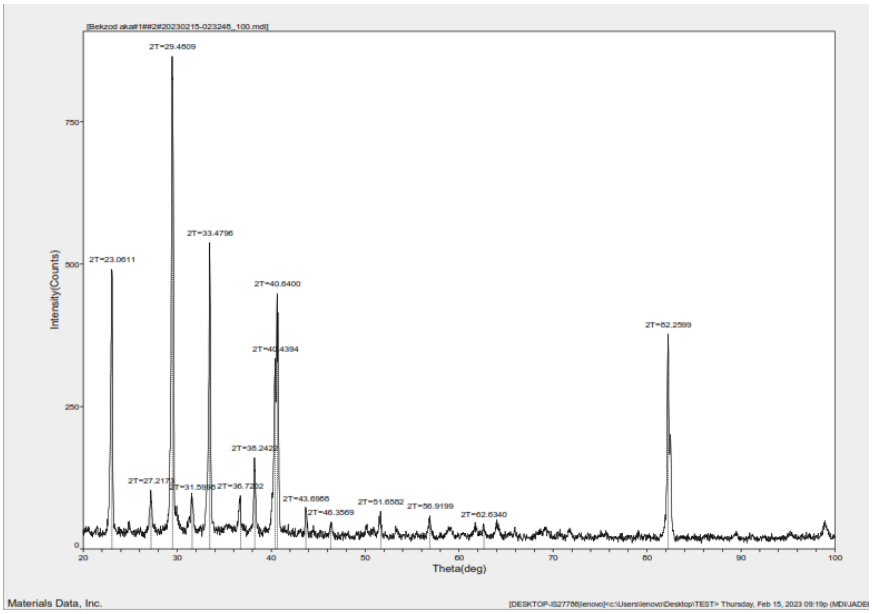
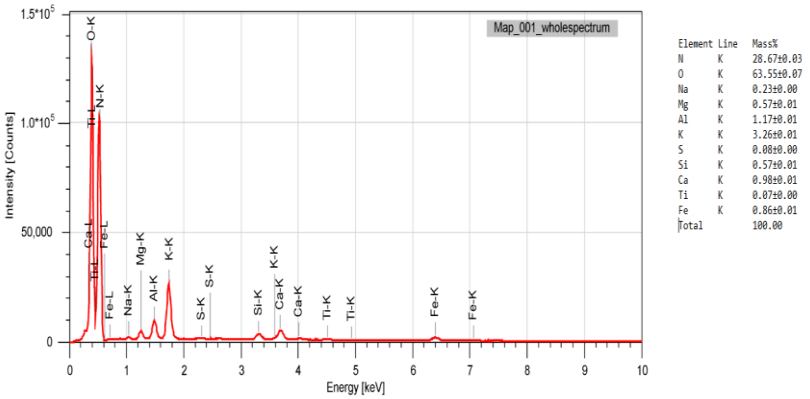


Fig. 3. The results of the XRD analysis are samples of ammonium nitrate with improved properties with local non-traditional additives such as bentonite and glauconite flour.

Table 1. The chemical composition of the AN modified by a local unconventional natural mineral - bentonite (Log‘on)

AN: BT weight ratio	pH value	N, %	K_2O, %	CaO, %	MgO, %	Fe_2O_3, %	Al_2O_3, %	SiO_2, %	SO_3, %	Granule strength, MPa
100:5	6,80	32,76	1,61	0,16	0,18	0,21	0,55	0,35	0,08	3,45
100:10	7,10	31,27	2,37	0,28	0,22	0,32	0,98	0,42	0,15	4,52
100:15	7,23	29,91	3,26	0,39	0,37	0,47	1,17	0,57	0,23	5,27
100:20	7,31	28,67	3,98	0,47	0,46	0,56	1,65	0,95	0,31	6,27
100:25	7,43	27,52	4,64	0,62	0,54	0,67	2,14	1,48	0,42	6,96
100:30	7,50	26,46	5,08	0,78	0,67	0,75	2,76	1,91	0,50	7,47
100:35	7,68	25,48	5,71	0,91	0,83	0,93	3,33	2,54	0,57	7,71
100:40	7,70	24,57	6,36	1,14	0,97	1,01	3,74	2,91	0,63	8,16



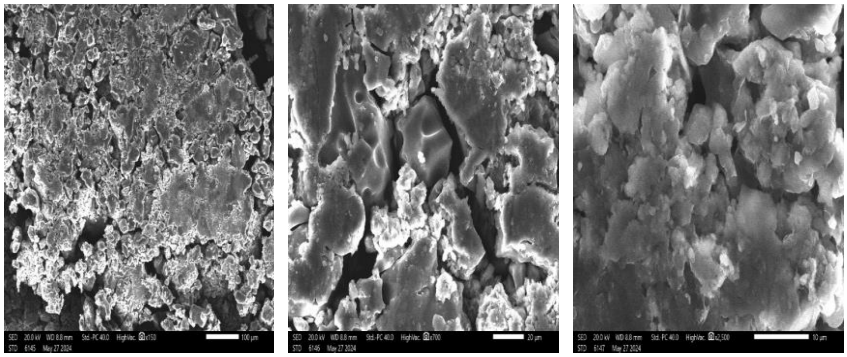


Fig. 4. SEM analysis of the composition of (AN: $(NH_4)_2SO_4$ solution:bentonite) with a ratio of 82: 3:15.

From the above Table 1 and Figure 4, it can be seen that if the density of AN granules meeting the requirements of GOST 2-2013 is 1.6 MPa, then the density of samples obtained by adding in the ratio: AN:BT = 100:5, the density of the samples is 3.45 MPa; AN:BT= 100:10, sample density is 4.52 MPa; AN:BT=100:15, sample density is 5.27 MPa; AN:BT = 100:20, the density of the samples is 5.27 MPa; AN:BT = 100:25, the density of the samples is 6.27 MPa; AN:BT = 100:30, sample density is 6.96 MPa; AN:BT=100:35, sample density is 7.71 MPa; AN:BT = 100:40, the density of the samples is 8.16 MPa. The solution of the samples taken has a pH of up to 6.8-7.7. A sample of an AN solution with a concentration of 10% has a pH of up to 6.8-7.7 [7-10].

Table 2. The chemical composition of the AN modified by a local unconventional natural mineral - glauconite (Changi)

AN: Gl weight ratio	pH value	N, %	K_2O, %	CaO, %	MgO, %	Fe_2O_3, %	Al_2O_3, %	SiO_2, %	SO_3, %	Granule strength, MPa
100:5	6,46	32,76	0,17	0,032	0,06	0,323	0,61	0,561	0,29	2,76
100:10	6,49	31,27	0,54	0,064	0,12	0,646	1,22	1,122	0,47	3,86
100:15	6,53	29,91	1,07	0,096	0,28	0,969	1,84	1,683	0,63	4,97
100:20	6,58	28,67	1,39	0,128	0,38	1,292	2,45	2,244	0,86	5,37
100:25	6,62	27,52	1,86	0,161	0,51	1,615	3,06	2,805	1,03	5,96
100:30	6,67	26,46	2,23	0,193	0,69	1,938	3,67	3,366	1,19	7,19
100:35	6,72	25,48	2,71	0,225	0,77	2,261	4,28	3,927	1,27	7,47
100:40	6,78	24,57	3,18	0,257	0,88	2,584	4,89	4,488	1,42	7,95

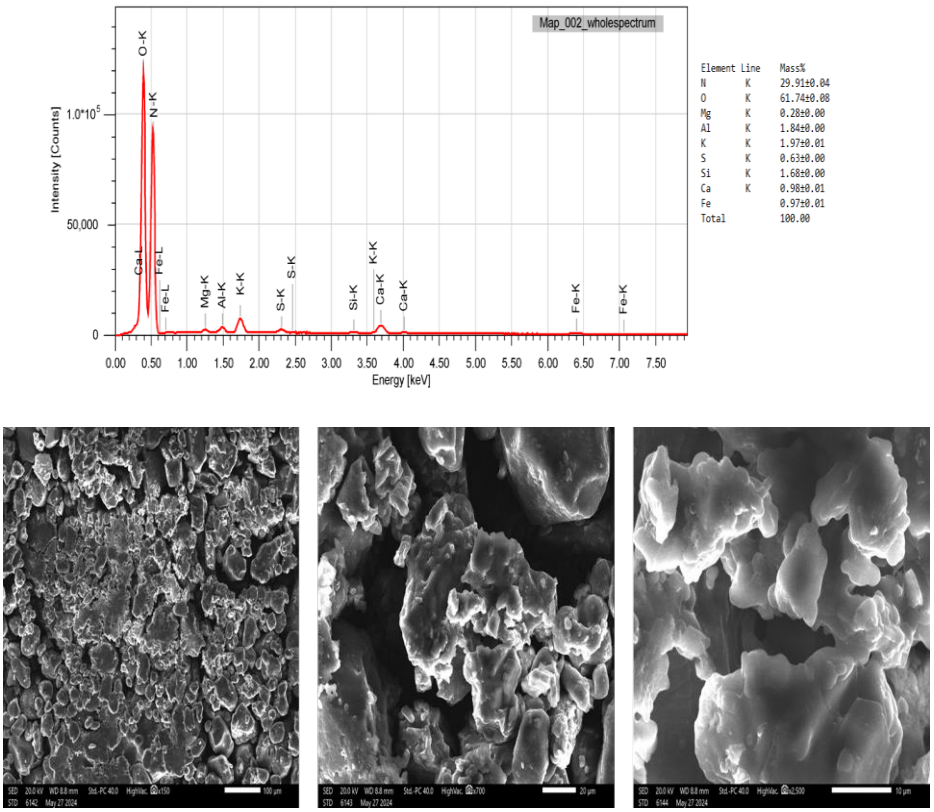


Fig. 5. SEM analysis of the composition of (AN: $(NH_4)_2SO_4$ solution: glauconite) with a ratio of 82: 3:15

From the presented Table 2 and Figure 5, it can be seen that if the strength of the AN granules meeting the requirements of GOST 2-2013 is 1.6 MPa, then the density of the samples obtained by adding in the ratio: AN:Gl = 100:5, the density of the samples is 2.76 MPa; AN:Gl = 100:10, the density of the samples is 3.86 MPa; AN:Gl = 100:15, the density of the samples is 4.97 MPa; AN:Gl = 100:20, sample density is 5.37 MPa; AN: Gl= 100:25, sample density is 5.96 MPa; AN:Gl = 100:30, the density of the samples is 7.19 MPa; AN:Gl = 100:35, the density of the samples is 7.47 MPa; AN:Gl = 100:40, the density of the samples is 7.95 MPa. The solution of the samples taken has a pH of up to 6.8-7.7. A sample of an AN solution with a concentration of 10% has a pH of up to 6.46÷6.78.

5 Conclusions

The scientific significance of the research results lies in the fact that currently, at enterprises producing nitrogen mineral fertilizers produced in accordance with GOCT 2-2013, the introduction of non-standard (<1 mm, > 4 mm) fractions of ammonium nitrate into the powder, which have lost their marketable properties as a result of untimely use of AS and prolonged storage in warehouses, treatment with a solution binder (ammonium sulfate 40-45%) using local non-traditional natural additives (bentonite and glauconite powder) and treatment containing Ca^{2+}, Rheological properties and commercial properties of fertilizers containing K^+ and trace elements have been studied. A technological system for the

production of these fertilizers by granulation in a drum granulation plant has been developed.

When spraying the surface of the AN granules with a solution of $(NH_4)_2SO_4$ (concentration 40-45%) with further application of additive powders to the moistened surface of the AN granules, the optimal ratio, in masses, NH_4NO_3:$(NH_4)_2SO_4$:additive powder = 82:3:15 was established.

The high strength of the AN granules with the addition of man-made waste-incompleteness (sludge) after lime quenching, indicates an increase in the thermal stability of the AN with improved qualities. The strength of the obtained AN granules is in the range of 3.27-4.43 MPa. This indicator is 2.06-2.78 times higher than that of a conventional speaker.

For each type of samples obtained and the technological production system, economic calculations were developed in a separate order.

As a result of the production of samples of ammonium nitrate fertilizers with improved properties in the amount of 50 kg each and the use of samples in the fields of the Andijan and Ferghana scientific experimental stations of the Scientific Research Institute of Breeding, Seed Production and Agrotechnologies of cotton cultivation of the Academy of Sciences of the Republic of Uzbekistan allowed to increase to 1.9-3.7% and 2.1-3.9% samples of cotton crops compared to with a standard fertilizer option ($N_{200}P_{140}K_{60}$).

Thanks to these laboratory and experimental studies, the resulting ammonium nitrate with improved properties makes it possible to expand the available types (assortment)mineral fertilizers.

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