Physico-chemical properties lime-ammonium nitrate based on chalk, nitrate and ammonium sulphate

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Abstract. For the granulation of nitrate-sulfate-carbonate melt, the prilling method is applied using a granulation tower. The composition and properties of new types of fertilizers were studied. It is shown that with the ratio \(\text{NH}_4\text{NO}_3: \text{CaCO}_3: (\text{NH}_4)_2\text{SO}_4 = 100: 24: 1\) the product contains 28.03% - N, 0.50% - SO₃, 10% - CaO and has a granule strength of 6.03 MPa, which is much higher than the strength of pure \(\text{NH}_4\text{NO}_3\) granules (1.32 MPa). The absorption of pure AN granules is 4.82 g. With an increase in the proportion of chalk and ammonium sulfate to the \(\text{NH}_4\text{NO}_3: \text{CaCO}_3: (\text{NH}_4)_2\text{SO}_4 = 100: 24: 1\) ratio, the absorbency of the LAN granules is 2.57g.

1 Introduction

Ammonium nitrate is the world's most widespread and effective nitrogen fertilizer. In 2007, its global production capacity amounted to 43 million tons per year [1].

In Uzbekistan, the aggregate capacities of three plants producing ammonium nitrate (JSC "Maksam-Chirchik", "Navoiazot", and "Ferganaazot") exceeded 1 million 750 thousand tons per year [2].

It is used in agriculture for all types of crops and on all types of soil. But it has one very serious drawback – explosiveness [3].

The explosion of ammonium nitrate at a warehouse of a chemical enterprise in Toulouse (France) in 2001, a series of terrorist attacks in Southeast Asia, Russia, Uzbekistan, and other countries using ammonium nitrate as explosive put consumers and producers of fertilizers in a difficult position. Several countries - China, the Philippines, Colombia, Ireland, and Algeria, have banned the use of ammonium nitrate in agriculture. In this regard, the requirements for the quality of ammonium nitrate and its storage conditions were tightened. And the manufacturers have been tasked with ensuring the transition to the production of fertilizers based on ammonium nitrate, which retains agrochemical

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efficiency, with significantly greater resistance to external influences and, accordingly, less
explo­siveness.

Currently, Uzbeki­stan has es­tablished the produc­tion of NPF (nitro­gen-phosphorus
fertilizer with a con­tent of 22-28% N and 2-6% P₂O₅) [4-7] and LAN (lime-ammonium
nitrate with a con­tent of 22-28% N) [8, 9] by in­tro­ducing ammonium nitrate into the melt
before prilling car­bonate phospho­rite flour (17-18% P₂O₅) or lime flour on the gra­nite
tower.

The fol­low­ing sub­stances are used as ad­di­tives that re­duce the level of the po­ten­tial
hazard of ammonium nitrate: car­bonate-con­tain­ing com­pounds of na­tural and tech­no­genic
ori­gin (chalk, cal­cium carbonate, dolomite); potas­sium-con­tain­ing sub­stances (cli­o­ride and
potas­sium sul­fate); sub­stances con­tain­ing the cation of the same name - ammonium
(am­monium sul­fate, ortho-, and am­monium polyphos­phates); other ballast sub­stances that
do not carry a pay­load, but de­termine only the me­chan­i­cal dilu­tion of ammonium nitrate
(gypsum, phos­phogypsum, etc.) [10].

The most­wide­spread are the ad­di­tives of the first group in pro­duc­ing the so-called lime-
ammonium nitrate [11-13].

In Eu­ro­pe, it is pro­duced by 31 firms, in Rus­sia - by five in­dus­trial en­ter­pris­ing.

Early­er [14-16], we stu­died the com­pos­i­tion and prop­er­ties of LAN ob­tained based on
am­monium nitrate (NH₄NO₃) (34.96% N) and lime­stone flour (CaCO₃), "Karmana," "Zhamansay," "Ovkhona," "Forish" and "Karnab" de­pos­its of Uzbeki­stan. It is shown that
depending on the mass ratio NH₄NO₃: CaCO₃ = 100: (5-80), the nitro­gen con­tent in the
products ob­tained varies with­in the range of 33.3-18.8%. When the Karmaninskaya
limestone flour is added to the AN melt at the ratio NH₄NO₃: CaCO₃ = 100: (5-80), the
strength of the gra­nules is 3.52-8.45 MPa, and for Zhamansai, Ovkhoninskaya,
Forishskaya, and Karnabskaya flours 2.32-6.41, 2.76-9.57, 3.02-7.77 and 2.83-7.31 MPa,
respective­ly. With the stu­died NH₄NO₃: CaCO₃ ra­tios, the caking of fin­ished pro­ducts
based on Karmaninsky limestone is in the range of 2.34-3.58 kg / sm², which is 1.3-2 times
less than the caking of stand­ard nitrate with the ad­di­tion of 0.28% MgO (4.67 kg/sm²). The
pro­posed me­cha­nism of ac­tion of lime­stone ad­di­tives, which in­crease the strength of AN
gra­nules and at the same time re­duce its caking, is based on the cre­ation of many
crystall­iza­tion cen­ters, which ac­celer­ates the crys­tall­iza­tion pro­cess and ca­uses the
for­ma­tion of small crys­tals that make the gra­nules denser and stronger.

This work aims to ex­pand the field of ap­pli­ca­tion of car­bonate com­pounds and im­pro­ve
the qual­ity, in­crease the ther­mal sta­bil­ity of the LAN and in­crease the con­tent of the fourth
nu­tri­ent, sul­fur, in the fer­tilizer.

## 2 Materials and methods

In lab­o­ratory con­di­tions, we used NH₄NO₃ grade "pure" (34.96% N) as start­ing raw
ma­ter­i­als, as well as pow­dered chalk with the com­pos­i­tion (wt%): CaO 52.23; MgO 1.11;
CO₂ 41.5. To ob­tain sam­ples of chalk-con­tain­ing LAN, the ex­per­i­ments were car­ried out as
fol­lows: a weigh­ed por­tion of NH₄NO₃ was melted in a met­al cup by el­ect­ric heat­ing. Then
(NH₄)₂SO₄ and chalk were in­tro­duced into the melt at the mass ra­tios NH₄NO₃: CaCO₃:
(NH₄)₂SO₄ = 100 : (2-58): (0.5-2.0). Then, the nitrate-car­bonate-sul­fate melt was kept at
175-180°C for 1-1.5 min­utes. Then it was poured into a lab­o­ratory gran­ulator, which is a
met­al beaker with a per­for­ated bot­tom, the di­ameter of the hol­es in which was 1.2 mm. The
pump cre­ated pres­sure in the up­per part of the glass, and the melt was sprayed from a
height of 35 m onto a plas­tic film ly­ing on the ground. The re­sult­ing gra­nules were sieved
by par­ticle size. Par­ticles 2-3 mm in size were tested for strength ac­cord­ing to GOST
21560.2-82. Then the prod­ucts were cru­shed and an­alyzed ac­cord­ing to known meth­ods
[17].
The pH value of 10% aqueous suspensions of the studied samples was measured on an I-130M laboratory ionometer with an electrode system of ESL 63-07, EVL-1M3.1, and TKA-7 electrodes with an accuracy of 0.05 pH units.

The accumulation of fertilizers was determined using the express method [18]. Sagging (X - kg/cm²) was calculated using formula: X = P / S where, P - breaking force, H (kgf); S is the cross-sectional area of the sample, sm².

The absorbency of the granules about liquid fuel (diesel oil) was determined according to the procedure provided by TU 6-03-372-74 for granular porous AN grade "P." This indicator is expressed in the number of grams that 100 g of granules (g/100g) can absorb.

The temperature of the onset of decomposition of the obtained fertilizers was determined using a NETSCH STA 409 PC / PG device (Germany) in aluminum crucibles at a sample heating rate of 2 deg/min, a sample weight of 10-16 mg. The thermal stability of granules to repeated heating-cooling cycles in the range of 20-60°C was determined according to the method described in [19].

The rate of dissolution of sample granules in water was determined as follows. The fertilizer granule was dipped into a glass with 100 ml of distilled water, in which its complete dissolution was visually observed and recorded. Room temperature tests five times. Granular samples of NH₄NO₃ (without additive) and AN (with the addition of 0.28% MgO) were selected as samples for comparison with the studied samples. The results are shown in the table and figure.

It can be seen from Table 1 that in the studied ranges of the NH₄NO₃ : CaCO₃ : (NH₄)₂SO₄ = 100 : (2-58) : (0.5-2.0) ratios, the products contain 22.04-34.19% nitrogen, 1.02-18.90% CaO and 0.3-0.8% SO₃. Sulfur is a part of proteins and amino acids during the formation of the crop.

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<tr>
<th>Mass ratio</th>
<th>Content in products, %</th>
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<tbody>
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<td>NH₄NO₃ : CaCO₃ : (NH₄)₂SO₄</td>
<td>N_total.</td>
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<tr>
<td>100 : 5.0 : 0.5</td>
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3 Results and Discussions

In terms of its physiological role in plant nutrition, sulfur should be ranked fourth after nitrogen, phosphorus, and potassium [20]. And the calcium in importance for plant nutrition is in fifth place after nitrogen, phosphorus, potassium, and sulfur. If it is introduced into the soil in a form assimilable for plants, it will significantly increase yield [21]. Thus, we can say that the composition of the AN is additionally enriched with two macroelements - sulfur and calcium. This suggests that when the NO₃ – anion is bound by alkaline cations (Ca +) of chalk, the pH value rises to a value that approaches the aqueous suspensions of chalk. It can be assumed that the carbonate raw material neutralizes the acidity of the AN.
The discovered property of the samples can provide a decrease in soil "acidification" after application of the AN.

The main properties (strength, temperature of the onset of decomposition, dissolution rate, caking, porosity, and adsorption absorption of liquid fuel granules) of ammonium sulfate LAN are studied in the figure. It was found that the addition of any amount of \((\text{NH}_4)_2\text{SO}_4\) and chalk sharply reduces caking, porosity, absorbency, increases the strength and temperature of the onset of decomposition of nitrate granules. If the strength of the granules of the industrial AN is 1.58 MPa, then at \(\text{NH}_4\text{NO}_3 : \text{CaCO}_3 : (\text{NH}_4)_2\text{SO}_4 = 100 : 2.0 : 0.5\), this indicator increases to 2.69 MPa, at 100 : 9.0 : 0.5 to 4.76 MPa, at 100 : 24 : 1.0 to 6.03 MPa, at 100 : 34 : 1 up to 7.0 MPa, and at 100 : 45 : 2 up to 7.0 MPa. The greatest effect of granule strength - 8.93 MPa is achieved at \(\text{NH}_4\text{NO}_3 : \text{CaCO}_3 : (\text{NH}_4)_2\text{SO}_4 = 100 : 58 : 2\) (Fig., a). All this indicates a decrease in the tendency of the fertilizer to detonate, which is explained by a decrease in the size of the crystals, providing them with a denser packing and the presence of chalk and ammonium sulfate in the mixture, which interrupt the homogeneity of the properties of the AN and the zone of propagation of the detonation wave.

It follows from Fig., b that the addition of any amount of \((\text{NH}_4)_2\text{SO}_4\) significantly reduces the caking of the AN (from 2.41 to 0.33 kg/sm\(^2\)), which is 2-14 times less than the caking of standard nitrate with the addition of 0.28% MgO (4.67 kg/sm\(^2\)).

Another indicator characterizing the quality of a thermostable speaker is the adsorption capacity of granules for liquid fuel. The lower the porosity of the granules, the lower their absorbency should be. As the data in Fig. c., such a provision is indeed linked. Depending on the weight ratio of the initial components, the absorbency of granules of ammonium sulfate LAN ranges from 1.75-3.24 g of fuel to 100 g of the product. It is 4.82 g for granular \(\text{NH}_4\text{NO}_3\).

With an increase in the mass fraction of chalk and ammonium sulfate in the \(\text{NH}_4\text{NO}_3\) melt from 100 : 2 : 0.5 to 100 : 58 : 2, the decomposition start temperature increases from 210\(^\circ\)C for pure \(\text{NH}_4\text{NO}_3\) to 232.9-266.2\(^\circ\)C in the finished product (Fig. d). This means that the higher the strength and temperature of the beginning of the decomposition of the granules, the less diesel fuel gets inside the granules. As a result, the less the detonation ability of nitrate ammonium.
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Fig. 1. The influence of the weight ratio of \(\text{NH}_4\text{NO}_3 : \text{CaCO}_3 : (\text{NH}_4)_2\text{SO}_4\) on strength (a), caking (b), absorbency (c), temperature onset of decomposition (d), time of complete dissolution of granules of ammonium nitrate (e) and pH of a 10% solution of the product (f).

As the data in Fig., e, the presence of chalk and ammonium sulfate in the composition of nitrate affects the dissolution rate of the latter's granules. With an increase in the amount of \(\text{CaCO}_3\) and \((\text{NH}_4)_2\text{SO}_4\) in the \(\text{NH}_4\text{NO}_3\) melt, the time for the complete dissolution of the finished product granules in water increases. The complete dissolution of granules of pure \(\text{NH}_4\text{NO}_3\) and AN with a magnesian additive (0.28% MgO) in water is 44.6 sec on average and 46.8 sec, accordingly, and with the addition of chalk and ammonium sulfate in an amount from 2 and 0.5 to 58 and 2g, slows down the dissolution rate of product granules from 83 to 116.2 sec. This means that AN granules containing chalk and ammonium sulfate dissolve much more slowly in the soil solution. Therefore, the presence of chalk and ammonium sulfate in the nitrate promotes the gradual release of nitrogen from the granule.

In addition, the addition of chalk and ammonium sulfate to the \(\text{NH}_4\text{NO}_3\) melt increases the pH of a 10% solution of the latter from 5.17 to 7.05-7.33 (Fig. f), and this is most effective in neutral and acidic soils.

4 Conclusion

Research has been carried out to obtain sulfur-containing lime-ammonium nitrate based on ammonium nitrate and powdered chalk, and ammonium sulfate. It was found that the more powdered ammonium sulfate and chalk are introduced into the ammonium nitrate melt, the
lower the N content and the higher the S and CaO content in the product. It was also shown that the greater the amount of ammonium sulfate and chalk, the lower the caking and absorbency of diesel oil, and the higher the strength, thermal stability, water solubility, and decomposition temperature of nitrate granules. Thus, the samples of sulfur-containing lime-ammonium nitrate have improved physicochemical, agrochemical, and lower detonation properties.

References