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The use of glauconite for stabilization and improvement of ammonium nitrate agrochemical properties

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The development of new forms of nitrogen-containing mineral fertilizers comporting with world safety standards is currently quite a relevant problem. Existing forms of combined fertilizers including ammonium nitrate and carbonates have a number of disadvantages (hygroscopicity, caking, partial ammonium nitrogen decline). Therefore active search of new components with certain advantages is conducted. At the same time, their inclusion into the fertilizers' composition should ensure a high level of plants' nitrogen assimilation, exclude environmental pollution and comport with Green Chemistry principles; low cost and the possibility of large-tonnage output in Russian Federation is also of great importance.

The quartz-glauconitic sandstone from Beloozero deposit (Lysogorsky district, Saratov region) is considered as such a component. Its chemical composition is determined by the mass-spectroscopy with inductively coupled plasma and atomic emission spectroscopy with inductively coupled plasma. The technique of glauconite introduction into the combined mineral fertilizer with ammonium nitrate was tested. The ammonium nitrate and glauconite ratios are selected to ensure the fertilizer thermostability and meet the European Union standards. The evaluation was carried out by thermogravimetry and differential-thermal analysis. The properties of the obtained fertilizer were tested by bioassay. It was definitely proved that the obtained fertilizer has a favorable effect on the seeds germination and seedlings development.

Thus, granulated composition containing 80% of AN and 20% of glauconite allows to decrease the nitrogen content in the fertilizer finished form to 27–28%, which provides the fire-safety and explosion-safety required level, eliminates the risk of pellets caking during storage, promotes an increase in fertilizer's agrochemical efficiency and allows to decrease the fertilizer's application rates and, consequently, to reduce the environmental burden.

Keywords: ammonium nitrate, glauconite, explosion-safety, phytotoxicity, bioassay.

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Применение глауконита для стабилизации и улучшения агрохимических свойств аммиачной селитры

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Разработка новых форм азотсодержащих минеральных удобрений, соответствующих мировым нормам безопасности, является на данный момент достаточно актуальной задачей. Существующие формы комбинированных удобрений, включающие аммиачную селитру и карбонаты, обладают рядом недостатков (гигроскопичность, слёживаемость, потеря части аммонийного азота), поэтому ведётся активный поиск новых компонентов, обладающих определёнными преимуществами. При этом их введение в состав удобрений должно обеспечивать высокий уровень усвоения азота растениями, исключать загрязнение окружающей среды и соответствовать принципам Зелёной химии, важным фактором так же является невысокая стоимость и возможность получения в крупнотоннажных объёмах на территории Российской Федерации.

В качестве такого компонента рассматривается глауконитовый песок Белоозёрского месторождения Лысогорского района Саратовской области. Установлен его химический состав масс-спектральным с индуктивно-связанной плазмой и атомно-эмиссионным с индуктивно-связанной плазмой методами. Отработана методика введения данного компонента в состав комбинированного минерального удобрения с аммиачной селитрой. Подобраны процентные соотношения аммиачной селитры и глауконита, обеспечивающие термостабильность удобрения и отвечающие критериям Европейского Союза. Оценка проводилась методом термогравиметрии и дифференциально-термического анализа. Исследованы свойства полученного удобрения в эксперименте методом биотестирования. Достоверно доказано, что полученное удобрение оказывает благоприятное влияние на прорастание семян и развитие проростков редиса и озимой ржи.

Таким образом, получение гранулированной композиции, содержащей 80% аммиачной селитры и 20% глауконита позволяет снизить содержание азота в готовой форме удобрения до 27–28%, что обеспечивает требуемый уровень пожаро- и взрывобезопасности, устраняет опасность слёживаемости гранул при хранении, способствует повышению агрохимической эффективности удобрения, позволяет снизить нормы внесения удобрения в почвы и уменьшить таким образом экологическую нагрузку на окружающую среду.

Ключевые слова: аммиачная селитра, глауконит, взрывобезопасность, фитотоксичность, биотестирование.

The orientation towards the introduction of environmental technologies and the output of products comporting with environmental standards is the most important trend in the development of modern chemical industry. Modernization of existing and development of new chemical processes and materials comporting with Green Chemistry principles [1] contributes preventing environmental pollution as well as improving the economic efficiency and competitiveness of industrial enterprises. The ecologization problem of large-tonnage chemical enterprises (e. g. the ammonium nitrate (AN) output) is of particular importance. In accordance with Merchant Research & Consulting [2], ammonium nitrate accounts for more than 15% of the world nitrogen fertilizer market, the world total demand for which will be about 120 million tons (in terms of the active matter) in 2018 [3]. Currently 13 enterprises in the Russian Federation produce AN, 8.75 million tons AN were produced there in 2017. More than 60% of the AN produced in Russia is used for domestic consumption, including for agriculture consumes 70% (3.8 million tons), and for industry – 30% (1.56 million tons) [4].

Ammonium nitrate is a highly efficient nitrogen fertilizer, suitable for use on all soils' types [5]. This fertilizer is water-soluble, contains no ballast substances and combines with other non-alkaline mineral and organic fertilizers. Ammonium nitrate can be used as a preplant (basic) fertilizer or a nitrogen top dressing during vegetation, or it can be applied in rows or holes while sowing. Despite its obvious advantages, this fertilizer has a number of significant drawbacks, including explosibility, toxicity, nitrate component leachability from the root-inhabited soil horizon, increased hygroscopicity and storage caking [6]. Due to the denitrification and leaching processes, and also microbiological nitrates soil fixing, the nitrogen mineral forms utilization by the majority of agricultural crops does not exceed 40–50% of the applied dose [7]. These drawbacks significantly decrease the AN competitiveness in the mineral fertilizer market. Moreover, nitrates' high mobility in soils is associated with the emergence of environmental problems caused by nitrate environmental pollution.

The inclusion in the AN composition of components which will increase material's thermostability and will contribute to the improvement of its technological, commodity, agrochemical and ecological characteristics is the main direction in AN drawbacks' correcting as a mineral fertilizer. At present, cheap and available calcium and magnesium carbonates (limestone, chalk, dolomite) are frequently used as such ingredients [8]. Due to the above-mentioned carbonates' inclusion in the AN composition, the obtaining an explosion-proof fertilizer that does not significantly acidify soils becomes possible. Calcium-ammonium nitrate (CAN) is widely used in the European Union countries as fertilizer [9], its output has also been mastered in Russia. Despite carbonate components obvious advantages as AN stabilizers, their inclusion in the fertilizer composition has also very significant drawbacks, such as possibility of ammonium nitrate chemical interaction with the following carbonates:

$2NH_4NO_3 + CaCO_3 = Ca(NO_3)_2 + CO_2 + 2NH_3 + H_2O$

$2NH_4NO_3 + MgCO_3 = Mg(NO_3)_2 + CO_2 + 2NH_3 + H_2O$

The carbonates chemical interaction with ammonium nitrate leads to the ammonia liberation and calcium and magnesium nitrates formation. This process's speed increases while heating (mixing of AN fusion cake with carbonates). Calcium and magnesium nitrates are highly hygroscopic, that decreases the CAN granules stability during storage. Significant problems arise when granulating a mixture of AN with lime ingredients in granulation towers, as well as in centrifugal or screw granulators. The risk of granulators holes clogging with solid particles or sticking on the apparatus parts granulated mixture inhibits or excludes the typical equipment's using in traditional AN production [10]. In addition, in order to obtain a suitable fusion cake granulation mixture or a concentrated AN solution with calcareous components, careful grinding of the appropriate ingredients and calcium nitrate formation inhibitors applying are required. Ammonium phosphate and sulfate are suitable inhibitors as they stimulate the gypsum-phosphate shell formation on carbonate particles.

It should be noted that the calcareous components applied into the moist soil simultaneously with the AN increase the soil pH, that leads to the partial ammonium nitrogen decline due to the ammonium nitrate decomposition.

The glauconite choice for inclusion in the AN was determined by the following factors [11–17]:

– glauconite is a thermostable natural mineral that has no negative environmental effect;

– rich glauconite deposits are widely distributed in Russian Federation;

– this mineral is characterized by favorable granulometric composition for inclusion in the AN composition, low cost and availability;

– high sorption and cation exchange capacity is typical for glauconite;

– glauconite includes a number of valuable for crops macro- and micronutrients (K, Ca, Mg, Mn, Cr, Co, Cu, Zn, etc.), capable of passing into the soil solution due to the ion exchange processes;

– due to ion-exchange processes glauconites are able to bind ammonium cations, that reduce nitrogen declines while nitrification and leaching;

– the applying glauconites improve soils structural and mechanical properties and provides a meliorative effect.

Thus, the calcareous components inclusion in the AN composition can not be considered as an optimal problem solution of the fertilizer's thermostability. Research to find new promising materials for the AN stabilization is of great relevance and practical value.

Analyses of the possibility and expediency of glauconite inclusion in the AN composition for ensuring thermostability and improving the agrochemical efficiency of the fertilizer ingredient, is the aim of the work.

The research problems are:

– obtaining granular composition experimental samples with 80% of AN and 20% of glauconite;

– analyses of glauconite effect on the AN thermal stability;

– evaluating the effect of glauconite supplement on the AN phytotoxic properties.

Objects and methods

Ammonium nitrate grade B (GOST 2-2013) and glauconite, isolated by magnetic separation from quartz-glauconitic sandstone (GS) from Beloozero deposit (Lysogorsky district, Saratov region), were used for the experimental studies implementation. The GS glauconite content is an average of 50%. The pit-run GS was screened for separating coarse mechanical impurities (more than 10 mm) and dried at a temperature of 70–100 °C to a residual moisture not more than 3%. The after-drying GS was fractioned:

– mechanical impurities of more than 1.5 mm;

– grits from 0.63 to 1.50 mm;

– GS used for magnetic separation (less than 0.63 mm).

GS fractioning was carried out using two shaker screens with cells of 1.5 mm and 0.63 mm.

A magnetic highly inductive separator CMVi was used to separate the glauconite (magnetic fraction) from the quartz sand ballast fraction (non-magnetic fraction). The glauconite content in purified GS was 95 to 98%. The product was a fine, loose, non-hygroscopic powder of gray-green color. The glauconite grains size was in the range from 5 to 60 μm.

The glauconite chemical composition analysis was carried out by mass spectroscopy with inductively coupled plasma (MS) and atomic emission spectroscopy with inductively coupled plasma (AE). An inductively coupled plasma mass spectrometer Elan-6100 ("Perkin-

Elmer", USA) and an atomic emission plasma-inductively coupled spectrometer Optima-4300DV ("Perkin-Elme", USA) were used for chemical analysis.

The triturated AN was mixed with purified glauconite to obtain a fertilizer granular form. The mixture was heated to 135 °C and rubbed through a stainless steel sieve with a mesh size of 2 x 2 mm. The derived grits were pelletized and dried at a temperature of 50 °C to a residual moisture not more than 3.0%. The glauconite content in the finished granules of glauconitic-ammonium nitrate (GAN) was 20±1%, the nitrogen content was 27.0–27.5%. This components ratio provided the thermostability desired level of the finished fertilizer form [18, 19]. The GAN granules sustained a load of up to 1.5 kg per granule and showed no caking signs when unclosed stored in an enclosed space at a temperature of 20–25 °C for 12 months.

The GAN thermostability was evaluated with thermogravimetry and differential thermal analysis using a differential thermal analyzer DTG-60 ("Shimadzu", Japan). The samples heating was carried out in open-type platinum crucibles (diameter 5.8 mm, height 2.5 mm, weight 136 mg, heat resistance up to 1500 °C). Aluminium oxide was used as the reference. Air was supplied at a 150 ml/min flow rate, heating rate was 10 °C/min. The device was calibrated on indium, tin, and lead.

The AN and GAN phytotoxic properties comparative assessment was carried out by biotesting (seedling method). Artificial soil prepared according to GOST R ISO 22030-2009, was used. The artificial soil (substrate) pH was 6.5±0.2. Calibrated seeds of *Raphanus sativus* var. radicula Pers. (Saxa variety) and *Secale cereale* L. (Falenskaya-4 variety) were used as test-cultures.

The experiment options:

1. Control (substrate without additives).
2. Substrate + AN (0.005% of the substrate weight).
3. Substrate + GAN (0.0062% of the substrate weight).
4. Substrate + glauconite (0.0012%).

The AN addition in an amount of 0.005% of the substrate weight is equivalent to soil application of nitrogen with a mass of 75–80 kg per hectare.

The substrate phytotoxicity was detected by inhibition of test cultures' seed germination and seedlings development. The prepared substrate was loaded into plastic containers and moistened with deionized water. The wet substrate surface was covered with filter paper of grade F (GOST 12026-76), the test-cultures seeds were laid there. The containers with seeds were covered with a microperforated polypropylene film and placed in a thermostat to ensure optimum moisture. Germination was carried out at a temperature of 20±1 °C for 7 days.

The germination energy and rate, seedling vigor and also the seedlings' initial growth intensity were indicators of the fertilizers phytotoxicity assessment [20].

Experimental studies were performed in three replications. The results were statistically processed using the Microsoft Excel program.

Results and discussion

The data on the glauconite chemical composition (the content of the basic substance is 96±1%) used for the experiments are presented in Table 1.

In accordance with the chemical analysis, the glauconite inclusion in the AN composition pose no risk of environmental pollution with toxic elements. At the same time, relatively high potassium content (more than 4%) and a number of micronutrients increase the GAN agrochemical value.

The thermogravimetric analysis results indicate that the AN and GAN decomposition begins at the same temperature (Fig.), since the starting temperatures of the mass decrease for both samples coincide. The endothermic peaks, which correspond to the phase transitions at studied samples heating, on the DTA curves are also identical for both samples. Thus, the glauconite addition does not reduce fertilizer thermostability.

Laboratory tests results give reason to assume the possibility of obtaining more homogeneous suspension for granulation due to glauconite powder introduction into AN fusion cake with vigorous stirring (300 rpm and 12 kW drive per 1 m^3 of the mixer reaction volume). In the conditions of sufficient uniformity glauconite will act as a dephlegmatizing addition and an adsorbent released while the AN decomposition to nitrogen oxides. The main AN decomposition product in the fusion cake is nitrous oxide:

$$NH_4NO_3 \rightarrow N_2O + 2H_2O + 36.8\ kJ$$

However, other products (in addition to N_2O) are formed while the above-mentioned decomposition, such as nitrogen dioxide NO_2, that may catalyze the AN thermal decomposition [21]. Nitrogen dioxide binding of due to adsorption may increase GAN thermostability

Table 1

Glauconite chemical composition

Common Name	Formula	Content. mass. share. % *	Method of analysis **
Sodium in terms of oxide	Na_2O	0.086	AE
Magnesium in terms of oxide	MgO	2.02	AE
Aluminum in terms of oxide	Al_2O_3	4.34	AE
Silicon in terms of oxide	SiO_2	69.9	AE
Potassium in terms of oxide	K_2O	4.17	AE
Calcium in terms of oxide	CaO	1.89	AE
Manganese in terms of oxide	MnO	0.0098	AE
Iron total in terms of oxide	Fe_2O_3 total	13.3	AE
Loss on ignition	–	3.98 g	gravimetric
Chrome	Cr	279.3	MS, AE
Cobalt	Co	10.6	MS, AE
Copper	Cu	10.9	MS, AE
Zinc	Zn	70.1	MS
Arsenic	As	5.75	MS
Plumbum	Pb	4.58	MS, AE
Cadmium	Cd	0.078	MS, AE
Molybdenum	Mo	6.54	MS

*Note: * – The results for an absolutely dry assay. The definitions error corresponds to the standards of error in determining the mineral raw materials chemical composition in accordance with category III accuracy. GOST 41-08-212-04; ** – MS – mass spectral method with inductively coupled plasma, AE − atomic emission method with inductively coupled plasma.*

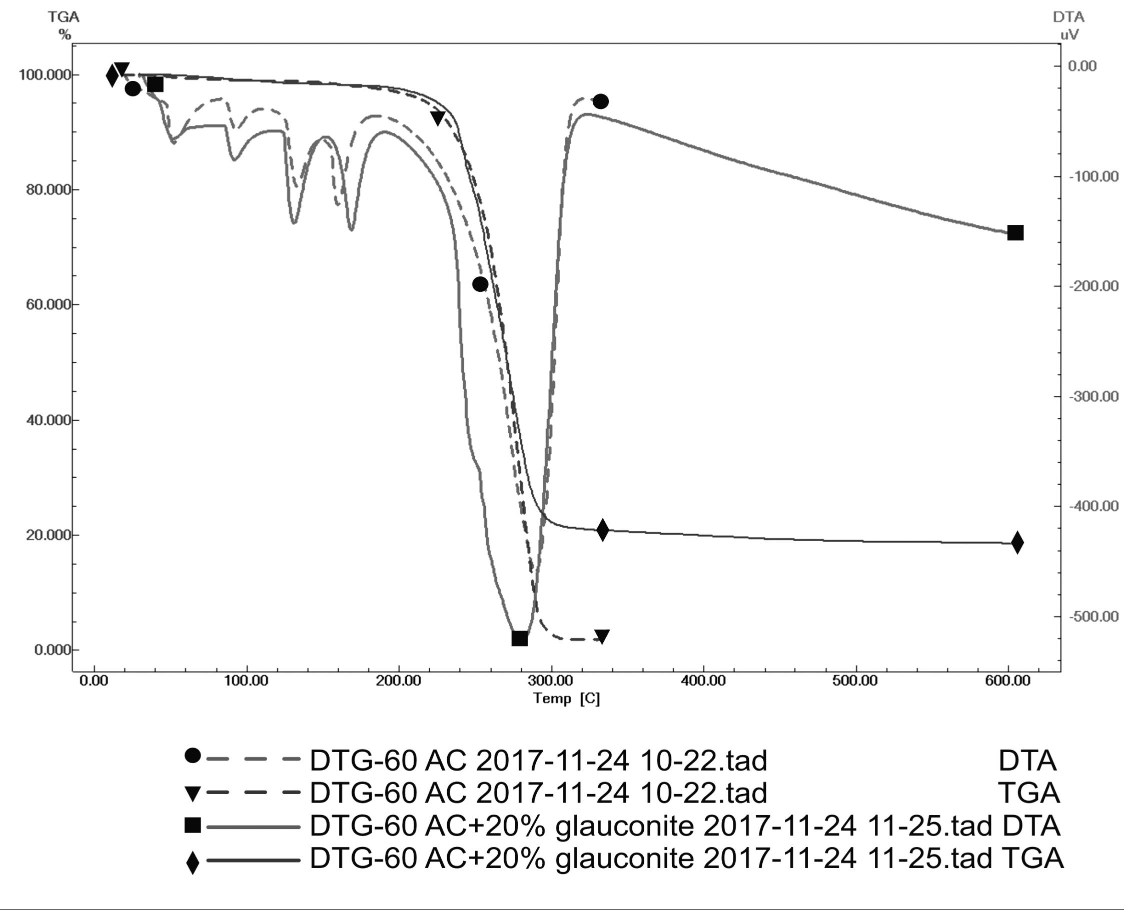

Fig. The thermogravimetric analysis results

Table 2

Results of AN and HAN biotesting

Index		Substrate (control)	Substrate + AN 0.005%	Substrate + GAN 0.0062%	Substrate + glauconite 0.0012%
Roots length, cm	1	5.1±0.3	4.9±0.3	4.8±0.5	4.5±0.3
	2	1.2±0.5	2.1±0.1	2.3±0.2	2.2±0.2
Seedlings length, cm	1	8.2±1.1	8.6±1.6	12.5±0.9	6.2±0.7
	2	1.8±0.3	3.6±0.5	3.8±0.4	4.6±0.7
Seedling vigor, %	1	73.3±9.4	82.2±5.1	93.3±5.8	76.7±8.8
	2	30.0±4.7	74.4±12.6	83.3±5.7	78.9±5.1
Germinating energy, %	1	83.3±11.8	84.4±1.9	95.6±1.9	87.8±6.9
	2	75.0±16.5	82.2±15.0	86.7±5.8	91.1±5.1
Germinating capacity, %	1	91.7±7.1	87.8±1.9	98.9±1.9	91.1±3.8
	2	93.3±4.7	93.3±5.8	96.7±3.3	92.2±5.1

Note: 1 – Secale cereale L., 2 – Raphanus sativus var. radicula Pers.

in comparison with the AN. Pilot-industrial tests are required to confirm this assumption. Table 2 shows the results of AN and HAN biotesting.

The obtained results demonstrate radish high sensitivity to the AN and glauconite additives. Radish seeds are characterized by a twofold increase in such indicators as roots length, seedlings length and seedling vigor when AN adding to the substrate. Practically rye seeds have no reaction for used in the experiment AN and glauconite doses.

The small glauconite doses (55–60 kg/ha) applying into substrate also has a positive effect on radish seeds germination. This effect may be due to the exchange potassium and micronutrients complex in glauconite [22]. The plants' need in potassium is especially great at the early stages of seedlings development; this element is predominantly concentrated in young organs and tissues. The substrate enrichment with glauconite improves the mineral nutrition of seedlings and promotes their development.

The optimal results are observed when applying HAN into the substrate. This experiment option demonstrated higher or at the level of control values (indicator of rye root length) biotested parameters, i. e., the AN and glauconite co-applying into the substrate provides a synergistic effect.

Conclusion

The conducted studies show the prospects of glauconite using as an additive in the AN composition. Granulated composition containing 80% of AN and 20% of glauconite allows to decrease the nitrogen content in the fertilizer finished form to 27–28%, which provides the fire-safety and explosion-safety required level and eliminates the risk of pellets caking during storage.

According to the biotesting results, the glauconite addition to the AN composition favorably effects the seeds germination and the seedlings development. The AN enrichment with glauconite promotes an increase in fertilizer's agrochemical efficiency and allows to decrease the fertilizer's application rates and, consequently, to reduce the environmental burden.

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