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NITROGEN-SULPHURIC FERTILIZERS BASED ON AMMONIUM NITRATE MELT AND PHOSPHOGYPSUM

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Annotation. *To obtain samples of nitrogen-sulphur fertilizers, the mass ratio of AS : FG was varied from 100 : 0.5 to 100 : 20. It was shown that the crystallization temperature of the nitrate melt decreases from 165 to 152°C. In the products, an increase in the water-soluble form of calcium from 0.06 to 2.86% indicates the reaction of ammonium nitrate with calcium sulfate dehydrate to form calcium nitrate and ammonium sulfate. At the studied ratios of AS : FG = 100 : (0.5 ÷ 20), the strength of the product granules increases from 4.09 to 7.67 MPa. At the same time, the caking of the product decreases from the initial 5.62 kg / cm2 to 1.83 kg / cm2 in the product, almost 3.1 times. Granules of gypsum-containing AS dissolve in water much more slowly than pure AS. Phosphogypsum in the composition of saltpeter promotes its conversion, and with an increase for additive, it increases.*

Keywords. *Ammonium nitrate, phosphogypsum, crystallization temperature, nitrogen-sulfur fertilizer, composition, strength and caking of granules, conversion.*

АЗОТНО-СЕРНЫЕ УДОБРЕНИЯ НА ОСНОВЕ ПЛАВА АММИАЧНОЙ СЕЛИТРЫ И ФОСФОГИПСА

Аннотация. *Для получения образцов азотносерных удобрений массовое соотношение АС : ФГ варьировалось от 100 : 0,5 до 100 : 20. Показано, что температура кристаллизации плава селитры понижается с 165 до 152°С. В продуктах увеличение водорастворимой формы кальция с 0,06 до 2,86% свидетельствует о прохождении реакции взаимодействия нитрата аммония с дигидратом сульфата кальция с образованием нитрата кальция и сульфата аммония. При изучаемых соотношениях АС : ФГ = 100 : (0,5÷20) прочность гранул продукта повышается от 4,09 до 7,67 МПа. При этом слёживаемость продукта снижается с исходного 5,62 кг/см^2 до 1,83 кг/см^2 в продукте, почти в 3,1 раза. Гранулы гипсосодержащей АС растворяются*

в воде значительно медленнее, чем чистая АС. Фосфогипс в составе селитры способствует её конверсии, причем с увеличением количества добавки она возрастает.

Ключевые слова. *Нитрат аммония, фосфогипс, температура кристаллизации, азотносерное удобрение, состав, прочность и слёживаемость гранул, конверсия.*

AMMONIY NITRAT SUYUQLANMASI VA FOSFOGIPS ASOSIDA AZOT-OLTINGUGURTLI O’G’ITLAR

Annotatsiya. *Azot-oltingugurtli o'g'itlar namunalarini olish uchun AS : FG ning massa nisbati 100 : 0,5 dan 100 : 20 gacha o'zgartirildi. Bunda, selitra eritmasining kristallanish harorati 165 dan 152°C gacha pasayadi. Mahsulotlarda kaltsiyning suvda eruvchan shaklining 0,06 dan 2,86% gacha oshishi ammiakli selitraning kaltsiy sulfat dihidrat bilan kaltsiy nitrat va ammoniy sulfat hosil qilish reaktsiyasini ko'rsatadi. O'rganilayotgan AC : FG = 100 : (0,5÷20) nisbatlarda mahsulot granulalarining mustahkamligi 4,09 dan 7,67 MPa gacha oshadi. Shu bilan birga, mahsulotning yopishqoqligi dastlabki 5,62 kg/sm^2 dan mahsulotdagi 1,83 kg/sm^2 gacha, deyarli 3 marta kamayadi. Gipsli AS ning granulalari suvda sof AS ga qaraganda ancha sekin eriydi. AS tarkibidagi FG miqdorining oshib borishi bilan uni konversiyasiga kirishishi ham ortadi.*

Kalit so'zlar. *Ammiakli selitra, fosfogips, kristallanish harorati, azotli oltingugurtli o'g'it, granulalarning tarkibi, mustahkamligi, yopishqoqligi va konversiya.*

Introduction. In 2015, our republic produced 942.72 thousand tons of nitrogen, 148.42 thousand tons of phosphorus and 143.24 thousand tons of potassium mineral fertilizers. Our industrial enterprises produce nitrogen fertilizers such as urea, ammonium nitrate (AN), UAN, ammonium sulfate and others. Among them, ammonium nitrate is considered one of the most effective agrochemical fertilizers. Therefore, it is used in agricultural crops [1].

However, the disadvantages of AN include its granules' strong caking and explosiveness. The above-mentioned problem of caking of AN granules can be eliminated by adding sulfate, sulfate-phosphate, phosphate-sulfate-borate, caustic magnesite or brucite additives to the flour composition, there by obtaining nitrogen fertilizer [2]. In addition, non-caking nitrate is obtained by adding a modifying additive to the AN melt, obtained during the processing of bentonite gel [3].

The explosiveness of AN is much more serious than the problem of caking of its granules. Scientists recommend adding calcium carbonate, limestone, dolomite, potassium sulfate and chloride, ammonium sulfate, ammonium polyphosphates, natural gypsum, phosphogypsum and other inorganic substances to it to reduce its detonation properties [4].

In developed European countries, calcium ammonium nitrate (CAN) is produced by adding calcium carbonate, dolomite and limestone to the smelt or its concentrated solution of AN as inorganic modifiers [5-9].

That is why CAN is very effective only in European soils with an acidic environment. In Russia, the production of potassium ammonium nitrate was first launched in 1999 by adding potassium chloride to AN [10].

In 2002, heat-stabilized AN (32.3% N, 5.2% P_2O_5) was obtained in Russia by adding ammonium polyphosphates, a mixture of orthophosphoric acid, to nitrate as a modifying additive [11, 12].

However, orthophosphoric acid is a very scarce and expensive inorganic compound. Therefore, in our republic, the processes of obtaining fertilizers based on the introduction of Kyzylkum phosphorite flour, natural gypsum and bentonite gel into ammonium nitrate were studied. Based on the results obtained, the production of nitrogen-phosphorus fertilizer (NPF) was organized and bentonite nitrate was introduced into practice [13-16].

Today, waste-free production, and especially the production of finished products from waste, is very important. Phosphogypsum, which is a waste product of ammophos production, makes up 80 million tons. more than a ton has accumulated. In our current study, we aimed to obtain nitrogen-sulfur fertilizers by adding FG waste to ammonium nitrate as a modifier, and to determine their composition and properties.

Methods and materials. The FG, the moisture content of which was about 18-20%, was thoroughly dried and ground in a porcelain mortar to a particle size of 0.25 mm. First, 100 g of AN was converted into a liquid state in a stainless steel reactor glass at a temperature of 170°C. Then, the phosphogypsum-nitrate melt, prepared by adding FG in a mass ratio of AN : FG = from 100 : 0.5 to 100 : 20, was stirred for 2-3 minutes. In the process of mixing by the perilization method, samples of nitrogen-sulfur fertilizers were obtained. The chemical composition and properties of the resulting fertilizer granules were determined using known methods [17, 18]. Addition of FG powder – $CaSO_4$ H_2O to “pure” NH_4NO_3 at 170°C leads to some extent to the following exchange reaction:

$2NH_4NO_3 + CaSO_4\ 2H_2O \leftrightarrow Ca(NO_3)_2 + (NH_4)_2SO_4 + 2H_2O$.

In this case, water-soluble salts of FG – $Ca(NO_3)_2$, $(NH_4)_2SO_4$ are formed. Therefore, we determined the conversion of NH_4NO_3 in phosphogypsum-nitrate melt [19]. We also determined the total salt composition of the nitrogen-sulfur fertilizer samples.

The results obtained are presented in the table and in Figures 1 and 2.

Results and discussion. It was found that the addition of PG to the AN melt in the ratio AN: PG = 100: (0.5-20) leads to a decrease in the crystallization temperature of phosphogypsum-nitrate melts from 165 to 152°C (Fig. a).

In NS fertilizer samples, with an increase in the FG content, the total nitrogen content decreases from 34.81 to 29.04%, while the amounts of sulfur and calcium increase from 0.10 to 3.62% and from 0.17 to 6.23%.

Table

Composition and property of NS-fertilizers

Weight ratio of AN:PG	Content in the products, weight. %				pH of 10 % solution of the product	The time for complete dissolution of granules, sec.
	$N_{total.}$	S	CaO_{total}	CaO_{water}		
NH_4NO_3 brand “pure”	34.96	–	–	–	5.50	44.60
100 : 0.5	34.81	0.10	0.17	0.06	5.16	65.08
100 : 1.0	34.56	0.22	0.36	0.13	5.12	65.92
100 : 1.5	34.42	0.31	0.54	0.20	5.09	66.76
100 : 2.0	34.27	0.42	0.72	0.27	5.05	67.64
100 : 2.5	34.11	0.53	0.90	0.34	5.02	68.56
100 : 3.0	33.94	0.62	1.08	0.41	5.0	69.38
100 : 3.5	33.75	0.75	1.24	0.47	4.95	70.44
100 : 4.0	33.63	0.84	1.49	0.59	4.91	71.26
100 : 4.5	33.50	0.93	1.61	0.66	4.87	72.38
100 : 5.0	33.26	1.02	1.86	0.76	4.83	73.2
100 : 7.0	32.68	1.41	2.45	1.02	4.80	74.0
100 : 10	31.79	1.96	3.35	1.41	4.76	74.86
100 : 12	31.21	2.33	4.0	1.72	4.72	75.64
100 : 15	30.35	2.80	4.87	2.14	4.69	76.78
100 : 18	29.57	3.31	5.68	2.55	4.65	77.56
100 : 20	29.04	3.62	6.23	2.86	4.62	78.60

The sulfur element also plays an important role in achieving high crop yields. That is why sulfur ranks fourth in physiological function after nitrogen, phosphorus and potassium [20].

The strength of the NS fertilizer samples obtained in the studied mass ratios (AN : PG = 100 : (0.5-20)) increases from 4.09 to 7.67 MPa (Fig. b), and the caking of the granules decreases from 2.68 to 1.83 kg/cm^2 (Fig. c).

The stronger the granules of the AN-based fertilizer, the less caking of the granules. From this point of view, FG has proven itself to be effective. The dissolution rate of NS fertilizer samples in water with the addition of 0.5 to 20 g of FG per 100 g of AN melt is from 65.08 to 78.6 sec. (Table 1). For AN granules of the "P" brand, this figure is 44.6 sec.

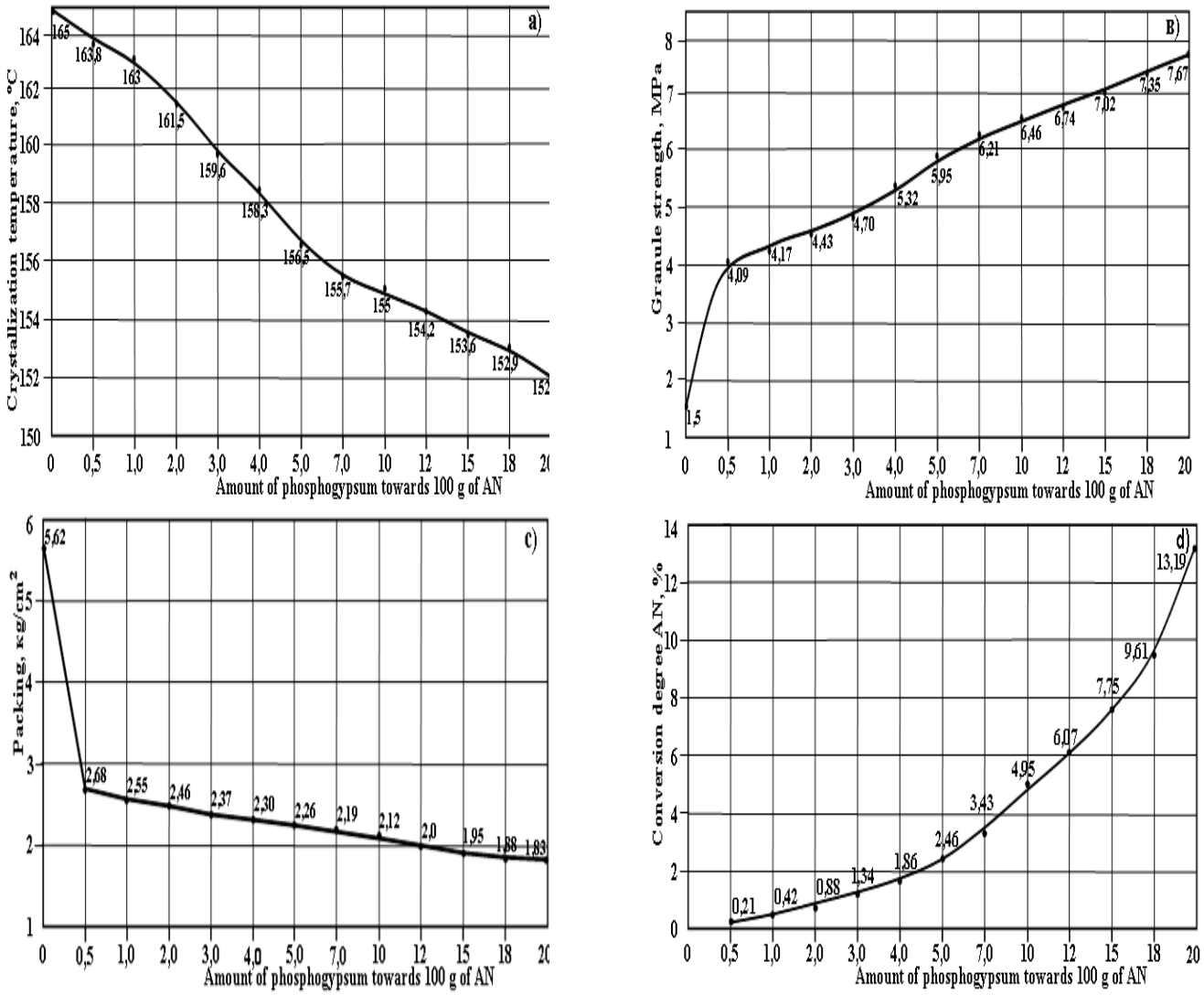

Fig.1. Effect of weight ratio of AN:PG on crystallization temperature of ammonium nitrate (a), granule strength (b), granule packing (c), and conversion rate of NH_4NO_3 (d).

Thus, the presence of FG additive in the composition of nitrate ensures slow leaching of the nitrogen element from the composition of NS fertilizer samples. The pH value of a 10% solution of AN "P" grade and FG waste is 5.50 and 3.42, respectively. Thus, with an increase in the content of PG in the composition of new types of fertilizer samples, the pH value is 5.16-4.62. Therefore, ammonium nitrate – AN modified on the basis of phosphogypsum – FG can be used on any soils.At a temperature of 170°C, a reaction occurs between FG – $CaSO_4$ $2H_2O$ and AN melts, resulting in the formation of $Ca(NO_3)_2$ and $(NH_4)_2SO_4$. In this case, NH_4NO_3 undergoes conversion. In the sample obtained at the ratio AN: PG = 100: 0.5, the

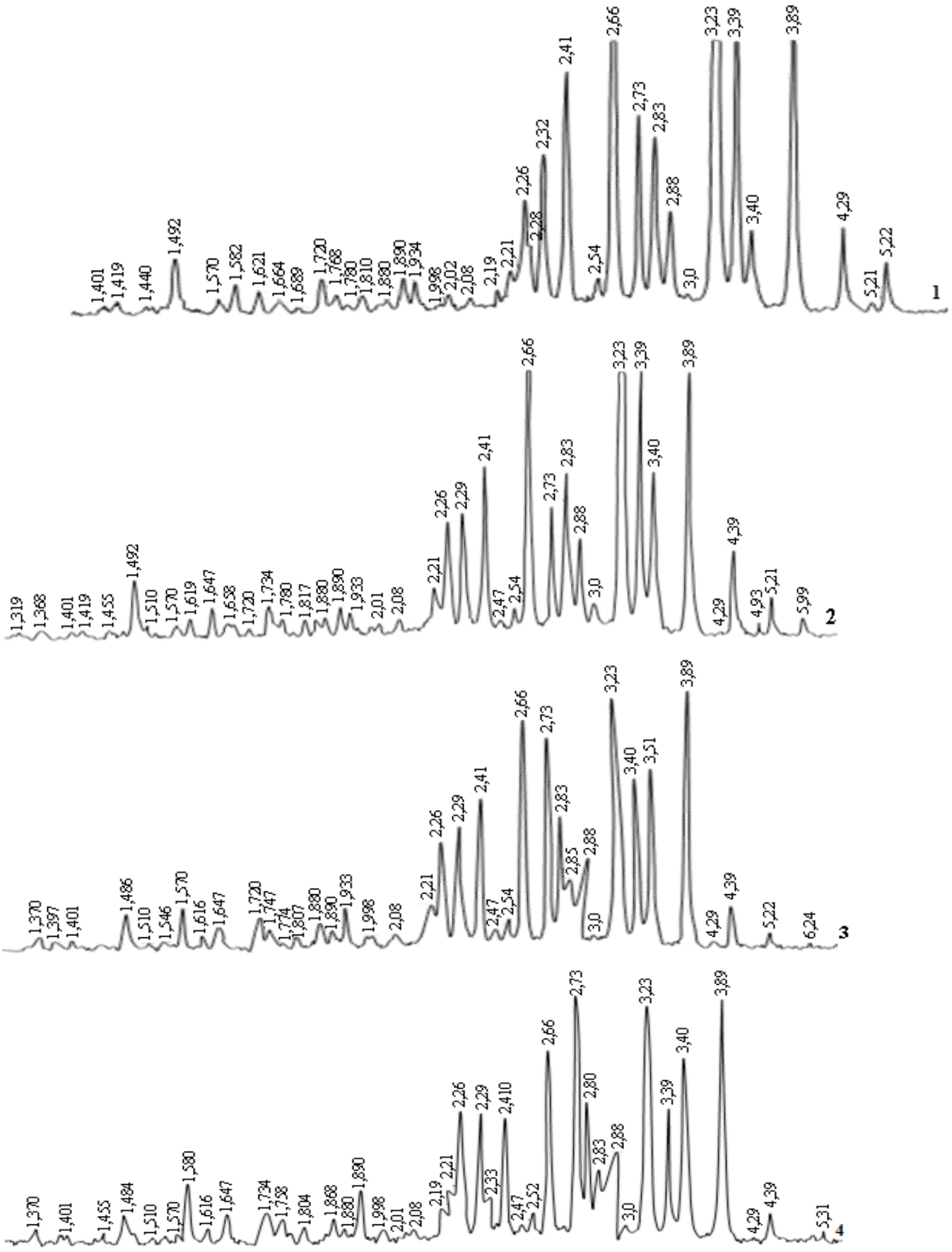

Fig. 2. Radiograph of nitrogen-sulphuric fertilizers obtained on a basis of the ammonium nitrate melt and phosphogypsum.

AN : PG = 1-100 : 1.0; 2-100 : 5.0; 3-100 : 10; 4-100 : 15.

conversion of NH_4NO_3 is 0.21%, at AN: PG = 100 : 20 – 13.19% (Fig. d). Thus, the AN melt activates FG, converting it into water-soluble (CaO_{water} 0.06-2.86%) calcium nitrate (Table 1).

X-ray structural analysis of NS fertilizers showed that it contains the original AN – NH_4NO_3 (2.26-100%; 2.73-76%; 3.08-67%; 3.96-45%; 4.95-44% Å) and FG – CaSO4 2H2O (4.30-100%, 3.07-63%, 7.69-50%, 2.48-20%; 3.81-15% Å) reaks indicating the formation of $Ca(NO_3)_2$ – 3.39; 3.40; 5.20; 5.21 Å and $(NH_4)_2SO_4$– 4.33; 3.89; 4.39; 5.22; 5.31 Å.

Conclusion. By adding powdered phosphogypsum to the ammonium nitrate melt, it is possible to obtain granulated NS fertilizers with good commercial properties. In this case, the resulting complex fertilizer contains, in addition to nitrogen, elements of sulfur and calcium.

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