Granular nitrogen and nitrogen-potassium fertilizers containing sulfur from the spent acid mixture of nitrocellulose production

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Abstract. In the production of cellulose nitrates, waste is formed of mixtures of sulfuric and nitric acids. Regeneration of these mixtures involves large capital, energy costs and emissions of toxic substances in the air. To solve the environmental problem and improve the efficiency of nitrocellulose production, a method for obtaining granular nitrogen and nitrogen-potassium fertilizers with a sulfur content from spent acid mixtures has been developed. Six variants of fertilizer compositions from the spent acid mixture of nitrocellulose production and two samples of a simple salt mixture with an elemental composition identical to the composition of two samples from spent acids were obtained at the laboratory facility. A complex of studies of the obtained granular fertilizers without adding binders was carried out. To improve the quality characteristics of the granulated fertilizer, repeated preparation of fertilizers with the addition of bentonite clay to the salt mixture before granulation was carried out. As a result, strong, moisture-resistant granules of nitrogen and nitrogen-potassium fertilizer with a sulfur content with low acidity and high bulk density were obtained. The qualitative characteristics of granules obtained from the spent acid mixture showed better results in all experiments, compared to samples of a similar elemental composition obtained by simple mixing of salts.

1. Introduction
Currently, due to the growth of chemical production, the volume of industrial waste and harmful gas emissions into the air is increasing, and as a result, the environmental situation is becoming more acute. In these conditions, it is necessary to create new cost-effective methods of waste disposal and reduce the amount of harmful substances in the waste gases. In particular, at nitrocellulose production plants, after the production cycle, 100 % of the sulfuric acid and more than 90% of the nitric acid volume remains as a spent acid mixture. This acid mixture is partially reused in the production cycle, but the main part of it undergoes regeneration with the production of 98% nitric and 92% sulfuric acids. The regeneration process is characterized by high capital, energy costs and the release of toxic substances into the atmosphere.

Acid regeneration costs significantly more than buying new acids and increases the cost of production. With the existing technology of spent acid mixture regeneration, it is impossible to completely capture acid gas emissions (NOₓ, SO₂), and some of the gases inevitably enter the atmosphere. Historically, the main production of nitrocellulose in Russia is located within the city
limits (for example, the Kazan gunpowder plant was founded in 1788 and is located in the historical part of the city with a population of more than a million people). The rejection of the spent acid mixture regeneration process and the production of target products in demand from them will lead to an increase in the efficiency of nitrocellulose production and improve the environmental situation.

The most promising solution for recycling of spent acid mixture from nitrocellulose production is their processing into granular mineral nitrogen (N(S)) and nitrogen-potassium (NK(S)) fertilizers with a sulfur content. If regeneration is completely abandoned and replaced with the production of fertilizers, there is no need to build a new production, one can use existing equipment (tanks, dispensers, pumps, waste gas cleaning system), replacing only acid regeneration devices with devices for neutralization, evaporation and granulation of fertilizer.

It is known that the ammonium form of nitrogen improves photosynthesis, the nitrate form increases the leaf area and promotes the development of the root system [1]. The advantage of the developed N(S) and NK(S) fertilizers is the nitrogen content in two forms: nitrate and ammonium.

Also, the advantage of this fertilizer is the content of sulfur in the form of ammonium sulfate. Sulfur contributes to better nitrogen uptake by plants and reduces nitrogen losses as a result of volatilization from the soil [2, 3]. Ammonium sulfate as an inert compound prevents the potential risk of using ammonium nitrate as an explosive [4]. Sulphur in the fertilizer increases the yield of agricultural crops [5].

The addition of bentonite provides strength and moisture resistance of the fertilizer [6-8]. Also, the addition of bentonite allows to prolong the release of nutrients from the fertilizer granules [9].

In this paper, we investigated the possibility of obtaining granular N(S) and NK(S) fertilizers based on spent acid mixture of nitrocellulose production and their qualitative characteristics (granule strength, pH of 5% solution and moisture absorption). Additional experiments were performed with the addition of 1% of the mass bentonite clay before granulation.

The study of moisture absorption was carried out additionally, since it is assumed to store the produced fertilizer in warehouses with an average annual temperature of 8-12 °C and a relative humidity of 50 %. However, in the middle Volga region in spring and autumn, there are long periods of high humidity (up to 2 weeks) due to a large amount of precipitation in the fall and active snowmelt in the spring. During these periods, relative humidity can increase up to 80% in temporary storage warehouses.

2. Materials and methods
Granulated fertilizer was obtained at a laboratory facility. The quality of fertilizers was assessed by the content of the main elements of nutrition, moisture absorption, strength of granules, hydrogen pH, bulk density. Additionally, the qualitative characteristics of one of the nitrogen fertilizer compositions were determined.

2.1. Method of obtaining
To obtain mineral fertilizer were used:

- spent acid mixture of nitrocellulose production. Mixture composition consists from 39,5 % H₂SO₄, 18,5 % HNO₃ and 42 % H₂O.
- 50 % nitric acid. Dilute nitric acid is a waste product of nitrocellulose production, namely, NO₃ vapors captured from waste gases. The acid is added to the spent acid mixture to increase the nitrogen content of the fertilizer. In parallel, the problem of its utilization is being solved.
- potassium hydrate of technical oxide GOST 9285-78 (the standard fully complies with international standards ISO 992-75, ISO 995-75, ISO 2466-73).
- technical aqueous ammonia GOST 9-92.
- fine bentonite clay was added before granulation to check changes in quality characteristics in some experiments.
Neutralization was carried out before obtaining a slightly alkaline solution. The block diagram for obtaining mineral fertilizers is shown in figure 1.

![Block diagram for obtaining granular N(S) and NK (S) fertilizers](image)

Figure 1. Block diagram for obtaining granular N(S) and NK (S) fertilizers.

Pre-prepared a mixture of acids, namely, spent acid mixture of cellulose nitrate production with 50% nitric acid and 50% potassium hydroxide solution. The neutralization process was carried out in a continuous mode. The resulting salt solutions were dried at 100 °C in a heated agitator. When the humidity reached 5-6%, the mixture was cooled to 60 °C and granulated on a screw granulator with a hole diameter of 2.5 mm. To check the effect of the addition of bentonite clay on the quality characteristics of granulated fertilizer, during repeated experiments, bentonite clay was added as a binder before granulation at the predrying stage in an amount of 1% by weight. After granulation, additional crushing of granules exceeding the diameter of 4 mm was performed and the fraction with a diameter of less than 1 mm was returned as a return for re-granulation. The product fraction with a diameter of granules from 1 to 4 mm was subjected to convective drying heated to 60 °C with air for 40 minutes and sent to the warehouse to gain strength.

2.2. Verification methods
After the granulation and drying processes, the samples were stored in trays at a constant temperature of 12 °C and a constant humidity of 50%. The quality of samples of mineral N(S) and NK(S) fertilizers was evaluated after full strength of all samples. The strength of granules was evaluated according to GOST 21560.2-82 (Mineral fertilizers. Method for determination of granules static strength). The study of the strength of granules was carried out by the MIP-10-1 device. Measurements were carried out every 2 days until the full strength of all samples.

The change in moisture absorption was carried out within 14 days after the strength set at a temperature of 20 °C and relative humidity of 60%, 70% and 80%.

The hydrogen pH of all samples was determined in a 5% aqueous solution. A pH-150MA device was used to determine the pH of the solution.
The bulk density was determined according to GOST EN 1237-2013 identical to the European regional standard EN 1237:1995 "Fertilizers - Determination of bulk density (tapped)"

The granulometric composition of bentonite clay up to a fraction of 50 microns was determined by a set of sieves. The granulometric composition of the bentonite fraction below 50 microns was determined using the HORIBA LA-950 device in distilled water, after a preliminary 3-minute ultrasound treatment of the sample.

Qualitative analysis of N(S) and NK(S) samples of mineral fertilizer was performed using the Rigaku Smartlab x-ray diffractometer.

Classification of granules of the received fertilizer by size was carried out by a set of sieves from sieve cloths with round holes.

### 3. Results and discussion

According to this method, 6 samples of granular fertilizer were obtained. 3 samples of N(S) fertilizer and 3 samples of NK(S) fertilizer. Table 1 shows the conditions for obtaining and composition of the samples obtained.

Table 1. Raw substances for production, % composition of fertilizer and the ratio of the main and general elements of nutrition.

| sample | spent acid mixture composition | raw substance, g | elements of nutrition, % | ratio of the elements of nutrition |
|--------|--------------------------------|------------------|--------------------------|----------------------------------|
|        | spent acid mixture | HNO3 (80 %) | KOH (96 %) | NH4OH (25 %) | N | K2O | S | NK | NK-S | (NK-O)S | ΣNK | ΣNKS |
| N1     | 1000 | 0 | 0 | 747,9 | 25,5 | 0 | 16,8 | 1:0:0,66 | 1:0,65 | 25,5 | 42,3 |
| N2     | 1000 | 635 | 0 | 1090,6 | 28,7 | 0 | 11,0 | 1:0:0,38 | 1:0,38 | 28,7 | 39,7 |
| N3     | 1000 | 1100 | 0 | 1341,3 | 30,0 | 0 | 8,8 | 1:0:0,29 | 1:0,29 | 30,0 | 38,8 |
| NK1    | 1000 | 0 | 134,53 | 591,0 | 19,9 | 13,3 | 15,8 | 1:0,67:0,78 | 1:0,48 | 33,2 | 49,0 |
| NK2    | 1000 | 650 | 208,3 | 855,8 | 23,0 | 13,3 | 10,3 | 1:0,58:0,45 | 1:0,28 | 36,3 | 46,6 |
| NK3    | 1000 | 635 | 312,5 | 726,3 | 20,3 | 19,6 | 10,0 | 1:0,95:0,49 | 1:0,25 | 39,9 | 49,9 |

It is obvious that the obtained samples of fertilizers containing potassium have a higher percentage of the main elements of nutrition (N and K) in their composition, and they can be attributed to highly concentrated fertilizers.

In order for nitrogen fertilizer to be considered highly concentrated, it is necessary that the nitrogen content in it is at least 30 %. This can be achieved by adding nitric acid to the spent acid mixture in a ratio of at least 1:1:1.

In the samples NK(S) of fertilizer, the amount of the main elements to sulfur (NK:S) is more optimal and already when added to the spent acid mixture of 50% nitric acid in the ratio 1:0.65 becomes equal to 1:0.28, while the nitrogen fertilizer should be diluted spent acid mixture in the ratio of not less than 1:1.1 to the amount of sulfur does not exceed 0.30 from the weight of the main batteries.

Additionally, a mixture of pure N0 and NK0 salts with an element composition NK(S) identical to that of N3 and NK3 was granulated.

The ratio of substances for making the mixture is shown in table 2.

Table 2. Artificial mixtures similar to manufactured fertilizers N3 and NK3.

| sample | pure substances, mass. % | elements of nutrition, % |
|--------|--------------------------|--------------------------|
|        | NH4NO3 | (NH4)2SO4 | KNO3 | K2SO4 | N | K2O | S |
| N0     | 63,7 | 36,3 | 0 | 0 | 30,0 | 0 | 8,8 |
| NK0    | 16,9 | 40,5 | 41,5 | 1,1 | 20,3 | 19,6 | 10,0 |
Table 3 shows the quality assessment of all 8 samples of the obtained granules. The complete strength of the NK(S) fertilizer granules was achieved in 6-8 days, and the N(S) fertilizer granules in 8-10 days. The table shows the results of strength measurement on day 14, taken simultaneously from all samples.

**Table 3. Qualitative analysis of the obtained samples of granular fertilizer.**

| sample | ρ_{BULK}, kg/m³ | σ_{COMP}, MPa | pH (5 % solution) | W=80 %, % | W=70 %, % | W=60 %, % |
|--------|-----------------|----------------|-------------------|------------|------------|------------|
| N0     | 0.624           | 1.12           | 5.17              | 8.0        | 6.3        | 0.7        |
| N1     | 0.691           | 1.51           | 5.21              | 5.8        | 3.7        | 0.2        |
| N2     | 0.653           | 1.15           | 5.16              | 6.0        | 3.6        | 0.1        |
| N3     | 0.629           | 1.36           | 5.12              | 6.1        | 3.9        | 0.2        |
| NK0    | 0.718           | 1.24           | 5.23              | 6.7        | 5.4        | 0.4        |
| NK1    | 0.737           | 1.87           | 5.07              | 2.5        | 1.1        | 0.1        |
| NK2    | 0.755           | 2.32           | 5.07              | 3.1        | 1.2        | 0.1        |
| NK3    | 0.796           | 2.91           | 5.05              | 2.1        | 1.0        | 0.0        |

According to the results presented in table 3, samples of N(S) fertilizer are significantly inferior in quality to samples of NK(S) fertilizer, with the exception of the hydrogen index, which is higher by 0.05-0.15 units. Samples of NK(S) fertilizers obtained by spent acid mixture neutralization are more durable (1.24-2.60 times), with a higher bulk density (1.13-1.27 times) and less moisture absorption (1.87-2.90 times). Samples obtained by simple mixing of N0 and N0 salts are much inferior to similar samples of N3 and NK3 in terms of strength and moisture absorption. Samples N0 and N2 do not meet the strength requirements for granular fertilizers and require additional strengthening by the introduction of binders.

The pH of all samples is higher than 5 units, so they can be considered weak acid fertilizers.

For testing the influence of bentonite clay on the quality characteristics of granulated fertilizer, a second series of experiments was conducted, which differs from the first in that at the pre-drying stage all samples were introduced bentonite in the amount of 1% mass from the mass sent for granulation. The granulometric composition of bentonite clay is shown in table 4.

**Table 4. Granulometric composition of bentonite clay.**

| Substance | ≤1 | 1-2 | 2-5 | 5-10 | 10-20 | 20-40 | 40-50 | 50-63 | 63-80 | 80-140 | ≥140 |
|-----------|----|-----|-----|------|-------|-------|-------|-------|-------|--------|------|
| Bentonite | 4.69 | 4.01 | 14.49 | 8.80 | 7.50 | 4.25 | 0.54 | 21.65 | 8.72 | 23.93 | 1.11 |

The granulometric composition of bentonite clay is quite heterogeneous.

Table 5 shows the assessment of the quality of pellets with the addition of bentonite clay. The complete strength of the NK(S) fertilizer granules has been achieved in 6 days, and the N(S) fertilizer granules in 8-10 days. Table 5 shows the results of strength measurement on day 12, taken simultaneously from all samples.

**Table 5. Qualitative analysis of fertilizer samples with the addition of 1% of the mass bentonite clay.**

| sample | ρ_{BULK}, kg/m³ | σ_{COMP}, MPa | pH (5 % solution) | W=80 %, % | W=70 %, % | W=60 %, % |
|--------|-----------------|----------------|-------------------|------------|------------|------------|
| N0b    | 0.754           | 1.89           | 5.82              | 5.2        | 3.1        | 0.4        |
With the introduction of 1% mass bentonite clay quality indicators of all samples have significantly improved. Although the quality indicators of samples obtained by mixing N0b and NK0b salts also improved, but did not reach the indicators of spent acid mixture samples. For samples obtained by spent acid mixture neutralization, relative to similar samples without binders, the strength increased by 1.51-2.31 times, the bulk density increased by 1.11-1.24 times, the moisture absorption decreased by 1.19-1.45 times at 80% relative humidity (not exceeding 5.0% for N(S) and 2.6% for NK(S) fertilizers). The pH of all samples increased by 0.53-0.74 units, the fertilizer became more neutral and will less acidify the soil when applied in the fields.

Additionally, x-ray phase analysis of samples N3 (figure 2) and 1 (figure 3) was performed. The quantitative composition of samples is shown in the figures:

![Figure 2. X-ray phase analysis of the N3 sample.](image)

![Figure 3. X-ray phase analysis of the NK1 sample.](image)
The composition of the samples shows that most of the substance is in the form of complex, double and triple salts. The N3 sample is dominated by the double salt ammonium sulfate-nitrate (67.7%), while the NK1 sample contains more than 62% of the substance in complex and double salts.

It can be assumed that the characteristics of the samples obtained from spent acid mixture are much better than the characteristics of the samples obtained by simple mixing of salts, due to the presence in them of a significant amount of complex, double and triple salts.

4. Conclusion
Granulated slightly acidic N(S) and NK(S) fertilizers with good bulk density, low moisture absorption (less than 6.1% at a relative humidity of 80%), high content of nutrients (all nutrients: more than 39% for N(S) and more than 46.7% for NK(S) fertilizers, for the main elements: more than 25.5% and more than 33.2%, respectively) were obtained. Without the additional binder the samples of N(S) fertilizers showed low strength of granules, samples of NK(S) fertilizers on the contrary are characterized by high strength and better moisture absorption and bulk density relative to N(S) fertilizers.

When adding a binder of bentonite clay in the amount of 1% mass for all samples, the bulk density increases by more than 11%, strength by more than 51%, pH by more than 0.53 units, and moisture absorption decreases by more than 1.2 times. When adding a binder, the pH of the fertilizer becomes more neutral, which is more preferable when used on neutral and slightly acidic soils.

In experiments with the addition of a binder and without a binder, the granules obtained from the spent acid mixture showed better results than those obtained by simple mixing of salts, which is due to the presence of a large number of complex, double and triple salts in them.

Although the addition of bentonite significantly improved the quality characteristics of all samples, however, for NK(S) fertilizers, there is no need to use a binder, since their characteristics meet the requirements for fertilizers, and have low moisture absorption. In experiments without a binder and with the addition of bentonite clay, all samples of NK(S) fertilizer obtained from spent acid mixture showed significantly better characteristics relative to N(S) fertilizer.

Upon refusal to regenerate spent acid mixture for nitrocellulose production and to send them to fertilizers, the amount of harmful emissions will be significantly reduced, the cost of the main production will be decreased and additional profit will be generated from the sale of new products – granular nitrogen and nitrogen-potassium fertilizers with sulfur content.

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