Obtaining Sapropel-Based Organomineral Fertilizers from the Mixed Acids Spent in Producing Nitrocellulose

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Abstract. Basic nitrocellulose wastes are spent mixed acids. Neutralizing them with potassium hydroxide and/or ammonia, or ammonia water produces nitrogen or nitrogen-potash mineral fertilizers sought after in the agro-industrial complex of the Russian Federation. However, using a crystalline fertilizer leads to some difficulties with transporting, storing, or applying them to the fields. Granulation is the preferable solution aimed at reducing the caking ability and uniformly dosing the fertilizers. This present study is aimed at granulating mineral nitrogen and nitrogen-potash fertilizers mixed with lake sapropel in different proportions. Sapropel is a natural binder in the mixture, it is also a source of organic and additional mineral substances, and it reinforces mineral fertilizers. Technology used to manufacture granulated organomineral fertilizers includes neutralizing the mixed acids spent in producing nitrocellulose, mixing with sapropel in given proportions, followed by granulating the obtained mixture on a screw granulator. In terms of containing In terms of nutrients contained in them, the most optimal is the mass relation of mineral fertilizer: sapropel in a mixture as 70-80 : 20-30, while in case of using the fertilizer as an ameliorant, it should be 10-20 : 80-90. Different component proportions in the mixture were considered.

In 2018, the global market of artificial polymers based on cotton or wood cellulose amounted to 215,000 t in physical quantities [1]. One of large Russian enterprises manufacturing nitrocellulose is located in the Republic of Tatarstan [2]. Polymers manufactured are predominantly represented by colloxylin and its derivatives. Producing nitrocellulose, particularly colloxylin, requires large quantities of nitric and sulfuric acids. As a result, manufacturing nitrocellulose causes producing large amounts of spent mixed acids of no demand, namely 1 to 3.5 t per 1 t of nitrocellulose, depending on its grade. Currently, these mixed acids are restored to concentrated nitric and sulfuric acids. Restoring them is accompanied by emitting much SO₂ and nitration gases NOₓ, which provides adverse effect upon the ecology around the manufacturing enterprise. Restoring also consumes much energy and requires large capital investments into purchasing and repairing/maintaining the machinery [3, 4]. Therefore, new solutions are needed to recycle the spent mixed acids without damage to environment or large financial expenditures.
In 2016, the needs of Russian manufacturers for agricultural products were satisfied in the amount of 3,222,000 t. However, according to the regulatory evaluations from various sources, the real need ranges from 8,500,000 to 17,500,000 t [5].

Considering the above, the most rational solution is to obtain mineral nitrogen and nitrogen-potash fertilizers from spent mixed acids [6, 7]. Spent mixed acids are neutralized by potassium hydroxide and/or ammonia water. Resulting from neutralization and dehydration, a concentrated crystalline nitrogen (N = 20-25 %) or nitrogen-potash (N=14-20 %, K=8-20 %) fertilizer is obtained.

However, using a crystalline fertilizer is accompanied by difficulties. It is difficult to dose it uniformly when applying, while it becomes set up and clumped if its package loses its tightness due to relative humidity fluctuations. In the Republic of Tatarstan, average values of relative humidity vary from 60-70 % in summer to 80-85 % in winter.

To reduce caking ability and ensure uniformly applying the fertilizers together with crop seeds, the fertilizers must be granulated. That is, the higher is the strength of granules, the lower is their caking ability and the less deformable are the granules when moving or transporting packages. To enhance the strength of granules, various additives can be used as binders. For example, various organic, organomineral, or synthetic substances [8], or bentonite [9] can be utilized.

Bottom settings named sapropels, rich in organic substances, can also be used as binders. Using sapropel for this purpose is well known in manufacturing construction materials [10, 11] and briquetting lignite [12]. Sapropel has adhesive properties, high shape stability, and plasticity.

It is also known that sapropel is used as ameliorant. Due to its containing various nutrients, sapropel can be used along with mineral fertilizers to feed plants. Share of mineral fertilizers in sapropel is usually 5-20 % to achieve a balanced content of nutrients [13, 14, 15]. In the amounts of 40-200 t/ha, using sapropel may completely replace applying mineral fertilizers [16, 17]. With smaller doses, below 6 t/ha, there is no explicitly positive effect detected without applying it together with mineral fertilizers [18, 19].

With the development of lakes, sapropel is gradually accumulated in bottom settings and, as the time progresses, ensures the high level of nutrients in the water body, which leads to weeding the lake surface with aquatic higher plants [20, 21]. High sapropel content in lakes worsens their environmental status and requires recultivation. Extracting sapropel can be considered as a tool to improve the ecological status of lakes and restore their natural conditions. In recultivating lakes, sapropel can be considered as a recultivation waste. When using sapropel as a fertilizer or ameliorant after cleaning up lakes, synergetic effect will be achieved.

Mineral fertilizers market in Russia is considered to be promising, but still not sustainable. Cost of organic fertilizers, particularly sapropel, remains high; therefore, applying sapropel as an independent fertilizer is still unprofitable. Farmers prefer applying mineral fertilizers, in which the price per a kilogram of active substance is by an order lower than that of sapropel. Granulating fertilizers also involves additional expenditures in manufacturing; however, they are reasonable for mineral fertilizers that are applied in considerable smaller quantities than organic ones.

About 50 sapropel deposits have been proven in the Republic of Tatarstan. Their reserves in categories A, B, and C2 are evaluated as 16,800,000 t. However, only one deposit is being developed currently [22, 23].

**Table 1. Compositions of mixed acids spent in producing nitrocellulose (NC)**

| Nitrocellulose   | SMA composition, %wt. H₂SO₄ | HNO₃ | H₂O | SMA weight per 1 t of NC |
|------------------|-----------------------------|------|-----|--------------------------|
| Pyroxylin #1     | 71.25                       | 19.80| 8.95| 1.0-1.2                  |
| Pyroxylin #2     | 66.23                       | 15.93| 17.77| 1.0-1.2                  |
| Colloxylin       | 39.50                       | 18.50| 42.00| 3.0-3.5                  |
| Entrapped acid   | 0.50                        | 50.00| 50.00| 0.1-0.2                  |
This study was aimed at obtaining granulated fertilizers from the products of neutralizing the spent mixed acids that represent nitrocellulose and sapropel waste, i.e., organominal waste of lake recultivation, mixed in different proportions, and investigating their properties.

A scheme was previously developed and tested for obtaining mineral fertilizers from spent mixed acids composed as follows: \( \text{HNO}_3 - 18.5 \% \), \( \text{H}_2\text{SO}_4 - 39.5 \% \), and \( \text{H}_2\text{O} - 42 \% \). To obtain a granulated mineral nitrogen fertilizer, sulfate nitrate (SN), spent mixed acids were neutralized with ammonia water, and the mixture obtained was evaporated and granulated [24]. To obtain a granulated nitrogen-potash fertilizer (NPF), part of ammonia water was replaced with potassium hydroxide. Process flow diagram of obtaining the granulated nitrogen fertilizer is shown in Figure 1:

![Diagram of process flow](image-url)

**Figure 1.** Process flow diagram of obtaining a nitrogen fertilizer from SMA.

Scheme was slightly changed for obtaining organominal fertilizers. Before the granulation stage, mineral fertilizer obtained upon neutralizing the spent mixed acids was mixed with sapropel in predefined proportions. To achieve plasticization required for granulating, water was added to the mixture.

As a binder for granulating, we used sapropel, i.e., bottom settings formed by the debris of water animals and plants. We used sapropel of the Beloye Lake, the largest sapropel deposit of the Republic of Tatarstan (as of Jan. 1, 1997 the Category A sapropel reserves were 6,112 thousand \( \text{m}^3 \) (3,316 thousand t) at 60% of moisture). Organo-limy and limy sapropel, ash contents 53.6–62%, pH 6.7–7.1. Contents (in %): \( \text{CaCO}_3 - 24.7 \); \( \text{Fe}_2\text{O}_3 - 2.4 \); \( \text{N} - 1.86 \); \( \text{P}_2\text{O}_5 - 0.7 \); \( \text{K}_2\text{O} - 0.6 \); and \( \text{S} - 1.25 \). Size distribution of the original sapropel is not uniform, it contains agglomerated particles exceeding 3 mm in diameter. To achieve uniform composition, sapropel was homogenized in a high-speed mixer-disperser before mixing. Mineral fertilizer and homogenized sapropel were mixed in a 5-blade mixer with the shaft rotation speed of 6-7 rps.

Granulation was performed on a screw granulator by pressing through conical nozzles with the output diameter of 2.5 mm. Granules represent 2-4 mm long cylinders with the diameter of 2.5 mm. Granules were dried at the temperature of 20-25°C and relative humidity of 60 % within 2 weeks, and then their physical and chemical properties were investigated.
Bulk density Measuring the bulk density upon densification was defined by GOST 28512.1-90. Moisture absorption was performed by exsiccation technique, using sulfuric acid of different concentrations (GOST 24816-81). Static strength of granules was measured by spring testing machine MIP-10-1 (GOST 21560.2-82).

We investigated the organomineral fertilizer (OMF) samples obtained through mixing followed by granulating from SN or NPF and sapropel taken at the initial moisture content of 5 % for the mineral component and 22 % for sapropel.

Granulating all samples on a screw granulator caused no difficulties, provided that the humidity was selected properly. Contents of particles sized less than 1 mm or more than 4 mm ranged from 0.2 to 0.5 %wt. All measurements were made after the material had been dried and hardened for 14 days. Figure 2 shows the results of studying the static compressive strength of granules.

![Figure 2. Compressive strength of granules on the 14th day.](image)

Contents of original components before mixing in the diagrams correspond with the sapropel content with the humidity of 22% and mineral fertilizer with the humidity of 5 %. Component ratios on a dry basis differ to increase the mineral fertilizer content in the mixture.

Strength of mineral fertilizers and sapropel without additives are approximately comparable, i.e., 3.69 MPa for SN, 5.18 MPa for NPF, and 3.68 MPa for sapropel). Strength of all the samples of mineral fertilizers mixed with sapropel is higher than that of the components without any additives. Compression strength of mineral fertilizers with sapropel added increases strongly and reaches its maximum at the ratio of MF:S = 80:20 (3.3 times higher than the sapropel strength for SN and 3.4 times for NPF). With the amount of sapropel further increasing in the mixture, the strength decreases gradually, but remains higher than that of the granulated sapropel.

To compute the dimensions of packing materials, warehouses, and storages, it is necessary to know the bulk density of a fertilizer. Figure 3 shows the bulk density after densification depending on the sapropel contents:
Figure 3. Bulk density of samples.

Bulk density of a mineral fertilizer rapidly increases at the ratio of MF:S = 90:10 by 16.5 % for SN and by 19.1 % for NPF, after which the growth slows, while for SN, upon slightly growing, it even falls to the local minimum at the ratio of MF:S = 40:60. The highest density for NPF is achieved at the ratio of MF:S = 30:70 (growth of 27 % as compared to the bulk density of the mineral fertilizer without any additives), while for SN the maximum is at MF:S = 20:80 (growth by 34 %).

Hygroscopic points are found for all samples by N.E. Pestov’s technique (Fig. 4), while moisture absorption is detected (Fig. 5 for SN and Fig. 6 for NPF) by the static exsiccation method:

Figure 4. Hygroscopic point.

For granulated sapropel, hygroscopic point is 25 % of relative humidity. With the mineral fertilizer content increasing, the hygroscopic point for NPF grows and reaches 74 % if no sapropel is added. However, SN mixtures manifest a different behavior: If SN is added to sapropel, hygroscopic point
reduces to 15 % at MF:S = 30:70, and only after that it starts growing. For all SN samples, except for those without any additives, hygroscopic point is below 60 %.

![Figure 5](image1.png)
**Figure 5.** Moisture absorption by the OMF samples of NPF and sapropel.

![Figure 6](image2.png)
**Figure 6.** Moisture absorption of OMF samples of SN and sapropel.

At the relative humidity of 70 %, water content in the OMF NPF samples with the ratio of MF:S from 100:0 to 40:60 has not exceeded 1.87 % over 21 days, while for other component ratios, the moisture content is slightly higher (3.4-5.5 %). At the relative humidity of 80 %, water contents ranged within 4.92-8.3 % in all samples. At the relative humidity of 90 %, the measured moisture content in sapropel made 8 %; where it was diluted with NPF, it increased up to the highest value at MF:S = 90:10 and made 28.2 %, i.e., 3.5 times higher.

For the OMF SN samples, water contents of no higher than 1.88 % is observed at the relative humidity of 60 % and the ratio of MF:S from 100:0 to 50:50, while at the higher sapropel contents increases by up to 5.5 % at MF:S=80:20. At 70, 80, and 90 %, the moisture absorption of SN increases
considerably. At 90%, moisture content grows from 8% in sapropel to 44.2% in SN without additives.

Granulated mixtures of mineral fertilizer and sapropel have shown high compression strength exceeding that of the granulated sapropel by up to 3.3-3.4 times at a ratio of MF:C = 80:20.

At 50-60% of relative humidity for SN with sapropel and at 50-70% of humidity for NPF, moisture absorption reduces with decreasing the sapropel share in the mixture, while at 90% of relative humidity, vice versa, moisture absorption increases. As a result, at increasing the relative humidity from 50% to 90%, moisture content of sapropel grows from 4.1% to 8%, SN without sapropel from 0% to 44.2%, and NPF without sapropel from 0% to 28.8%. Hygroscopic point of sapropel is much lower than that of MF; however, moisture absorption of sapropel is within a narrow range, and humidity fluctuations affect granulated sapropel to a lesser extent. Mixtures of mineral fertilizer with sapropel take intermediate values between sapropel and a mineral fertilizer without sapropel. Adding sapropel reduces the moisture absorption of the mixture.

In general, mixtures of NPF and sapropel demonstrate better performance, such as lower moisture absorption and higher strength, bulk density, and hygroscopic point as compared to the mixture of SN and sapropel.

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