Nanostructured dolomite flour for soil liming

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Abstract. The nanostructured dolomite flour is produced by ultrasonic dispersion of dolomite flour. It is a suspension of evenly distributed mineral particles in deionized water. The visualized surface showed that the minerals had particles of various sizes and shapes. The structure of dolomite flour was represented by a conglomerate of 0.25–1.0 µm. The particle size of nanostructured dolomite flour ranged from 40.0–120.0 nm, the average size was 50.04 nm. The highly dispersed crushing of dolomite flour conglomerates contributed to an increase in the contact area of particles and the soil; it accelerated their interaction. Shift pH unprotected by 0.3 units, and an increase in the grain of spring wheat by 2.0% using a nanostructured analogue in doses of 0.1 g. and 0.05 Hr. were comparable at a flow rate of 10 and 20 times less compared with dolomite flour at a dose of 1.0 Hr respectively.

1. Introduction
This paper presents priority data on the development of a new form of lime fertilizer to reduce soil acidity. Monitoring of arable lands of the Russian Federation suggests that 30.5 million hectares of soils are acidic; 2.6% of these soils are highly acidic out of 87.4 million hectares of surveyed territories. Moreover, the areas of acidic soils are constantly growing, due to the leaching of calcium: with infiltration waters, the expenditure on the neutralization of physiologically acidic mineral fertilizers, the removal of crops. At the same time, the annual crop shortage is about 10 - 12 million tons of products in terms of grain [1].

The chemical melioration is the foundation on which all the technological methods of cultivating agricultural crops with obtaining high-quality products are manifested with maximum efficiency [2-4]. The liming is used for acid soils. It involves the application of lime fertilizers with a given level of calcium and magnesium in the form of carbonate, oxide and hydroxide to neutralize acidity. Soils with high acidity have poor agrochemical and agrophysical properties. They are characterized by an insufficient content of mobile forms of macro- and microelements, low biological activity. The colloidal part of such soils is poor in calcium and magnesium, but it is rich in hydrogen and mobile cations of aluminum, manganese, and iron. The high concentration of the latter violates carbohydrate and protein exchanges, makes it difficult to feed the plants. A sufficient level of calcium and magnesium in the soil-absorbing complex ensures an optimal response of the soil environment.
The best lime fertilizers that are important to apply where magnesium is required are dolomite flour and dolomitic limestone. Liming neutralizes organic acids in the soil and displaces hydrogen ions $\text{H}^+$, from the absorbing complex, which leads to the elimination of the exchangeable acidity and a decrease in hydrolytic acidity. The cation composition of the soil absorbing complex is improved due to the replacement of hydrogen and aluminum ions with calcium and magnesium cations. Both soil saturation with bases increases and its absorption capacity increase [5].

In the conditions of the development of high-technological agricultural production of great interest is the high reactivity of nanostructured materials. As the long-term practice shows, nanostructured minerals obtained from nonmetallic raw materials of natural origin (agrominerals) are environmentally safe and they contain a wide range of biogenic macro and microelements [6, 7].

In this connection, the purpose of the work was a comparative estimation of the agrochemical activity of dolomite flour and a nanostructured analogue.

2. Materials and methods

The objects of research were soil (gray forest medium-medium), and cultures (spring wheat of the variety Esther, dolomite flour from the Mokro-Savaleevsky deposit of the Republic of Tatarstan with a mass fraction of calcium and magnesium carbonates in the field 91.6%).

The granulometric composition of the rock characterized by the size of fractions was $<$0.25 mm - 19.0%, 0.25-1.0 mm - 33.0%, 1.0-3.0 mm - 26.0%, 3.0-5.0 mm - 10.0%, 5.0 mm $<$ 12.0 percent. The proportion and size of the dolomite flour fractions were $<$0.25 mm - 21.0%, 0.25-1.0 mm - 79.0 percent.

The doses of dolomite flour and nanostructured analogue, providing an optimal response of the soil environment, favorable for soil microorganisms and the physiological development of cultivated crops, were calculated from the hydrolytic acidity (Hr) of the soil. The total calculated dose of dolomite flour in the active substance is equivalent to 1.0 hydrolytic acidity (Hr) [5].

The decisive factor determining the agronomic value of liming is the quality of the lime material is the grain size distribution or the fineness of the grinding. The surface of contact between the particles of lime fertilizers and the soil increases carbonate rocks have poor solubility due to the increase in the grinding fineness. It contributes to the enhanced reaction of their interaction.

The ultrasonic treatment method was used to obtain nanostructured dolomite flour. For this, agrominer in powder form was placed in deionized water and then subjected to dispersion in the recirculating aquaculture system (RAS) of 28/200 MP RELTEC (Russia) with an output power of 100 W for 20 minutes at a frequency of 15.0 kHz (± 10%). The topography of the surface structures of dolomite flour and its nanostructured analogue was studied by intermittent contact atomic force microscopy (AFM) using Veeco (USA) scanning probe microscope [8]. The particle size measurements of dispersed dolomite flour were carried out on a Brookhaven 90Plus / MAS instrument (USA) using disposable plastic cuvettes with a side of 10 mm and a volume of 4 ml.

In order to assess the toxicity and bioactivity of dolomite flour and its nanostructured analogue under laboratory conditions, phytotesting was performed (MU 1.2.2968-11 “The order of biological estimation of plant nanomaterials by morphological features”). Test objects were spring wheat (Esther variety), rye (Radon), barley (Raushan), buckwheat (Cheremshanka), corn (Moldavskaya 215). According to the international standard ISO 11269-1, the seeds of the crops were presoaked in doses of 0.25; 0.50; 0.75; 1.25; 5.0 and 10.0 kg / t for further germination on Petri dishes. For comparison, the seeds were soaked in distilled water (control).

The estimation of the efficiency of the studied forms of dolomite flour was produced by studying the dynamics of acidity of soil samples every thirty days. The investigations coincided with the phases of the development of spring wheat i.e., stem elongation, milk and wax ripeness.

3. Results and discussions

It was found that images were represented by a conglomerate of micrometer-size stuck particles when studying the scanned image of the surface of dolomite flour (figure 1).
Ultrasound exposure caused the crushing of conglomerates of dolomite flour and the formation of particles with the maximum number of chemically active bonds that contributed to an increase in their surface energy and contact area. The structure of the particles had two forms in the form of grains i.e., polygonal, rounded and elongated (figure 2).

It should be noted that, in contrast to dolomite flour, the particles of the nanostructured analog were evenly distributed. The range of particle sizes ranged from 40.0-120.0 nm, there were single conglomerates with sizes greater than 2.0 µm.

The analysis of the histogram of the multimodal distribution of particles in nanostructured dolomite flour found that the average particle size was 50.04 nm (figure 3).
When biotesting crops on phytotoxicity, their growth and morphological characteristics were taken into account when exposed to dolomite flour and a nanostructured analogue. Testing results showed that on all variants of the experiment, seed germination reached 88.0-94.0%. The shoots were healthy; they had a healthy form, well-developed roots and sprouts, without visible deviations in development. No significant differences in germination rates, germination energy and root length were noted.

It is well known that mineral fertilizers contribute to acidification of the soil. In our studies, the reaction of the soil environment under the influence of mineral fertilizers alone decreased to a weakly acidic reaction of the environment, and the shift in $\text{pH}_{\text{salt}}$ is to 0.1 units. (a phase of milky ripeness of spring wheat) (Table 1).

### Table 1. The effect of dolomite flour and nanostructured analogue on the acidity of the gray forest soil in the vegetation phases of spring wheat.

| Variants          | $\text{pH}_{\text{salt}}$ | $H_r$, pitch(eq.)/kg. |
|-------------------|---------------------------|------------------------|
|                   | stem elongation | milky ripeness | wax ripeness | stem elongation | milky ripeness | wax ripeness |
| Control           | 5.6           | 5.6            | 5.6          | 1.4           | 1.5             | 1.7         |
| Background – NPK, 60 kg/ha | 5.6 | 5.5 | 5.5 | 1.7 | 1.7 | 1.8 |
| Background + 1.0* Hr | 5.6 | 5.6 | 5.8 | 1.7 | 1.7 | 1.5 |
| Background + 0.0125** Hr | 5.6 | 5.6 | 5.5 | 1.7 | 1.7 | 1.8 |
| Background + 0.025 Hr | 5.7 | 5.7 | 5.6 | 1.4 | 1.5 | 1.7 |
| Background + 0.05 Hr | 5.7 | 5.7 | 5.6 | 1.3 | 1.5 | 1.7 |
| Background + 0.1 Hr | 5.8 | 5.8 | 5.7 | 1.2 | 1.3 | 1.5 |
| HCP$_{0.5}$       | 0.07          | 0.02            | 0.03         | 0.06          | 0.04            | 0.09        |

Note: 1.0 * Hr is a dose of dolomite flour; 0.0125-0.1 ** are doses of nanostructured dolomite flour.

The reaction of the soil environment has decreased to close to neutral, $\text{pH}_{\text{salt}}$ increased by 0.1 and 0.1-0.3 units respectively to the background using dolomite flour in a dose of 1.0 Hr and nanostructured analogue in doses of 0.0125-0.1 Hr.

The maximum shift in under the influence of dolomite flour 1.0 Hr was to 0.2 units to the background. It was noted in the phase of wax ripeness of spring wheat. By this time, the effect of nanostructured dolomite flour decreased slightly. It contributed to an increase in soil acidity. Relative to the previous vegetation phase of spring wheat, the shift in $\text{pH}_{\text{salt}}$ was to 0.1 units, the background was 0.1-0.2 units $\text{pH}_{\text{salt}}$ respectively doses of 0.025-0.1 Hr.

### Table 2. The effect of dolomite flour and nanostructured analogue on the yield of spring wheat.

| Variants          | Grain yield, cwt/ha | Increment, +/-% |
|-------------------|---------------------|-----------------|
|                   | to control | to background | to dolomite flour |
| Control           | 14.0       | 0              | -7.9             |
| Background – NPK, 60 kg/ha | 14.8 | +5.7 | 0 | -2.6 |
| Background + 1.0* Hr | 15.2 | +8.6 | +2.7 | 0 |
| Background + 0.0125** Hr | 14.8 | +5.7 | 0 | -2.6 |
| Background + 0.025 Hr | 14.9 | +6.4 | +0.7 | -2.0 |
| Background + 0.05 Hr | 15.1 | +7.9 | +2.0 | -0.66 |
| Background + 0.1 Hr | 15.9 | +13.4 | +7.4 | +4.6 |
| HCP$_{0.5}$       | 0.27       |                |                 |
Mineral fertilizers contributed to an increase in hydrolytic acidity, by 0.30 resin(EQ)/kg of soil. Under the influence of dolomite flour 1.0 Hr the greatest decrease in hydrolytic acidity was 0.2 resin(EQ)/kg of soil. Similarly, the best action of agrominerals was observed in the phase of wax ripeness of the culture. Indicators of the investigated acidity of the soil under the influence of nanostructured dolomite flour at doses of 0.025; 0.05 and 0.1 Hr were below the background by 0.1; 0.1 and 0.3 resin(EQ)/kg of soil, respectively. The maximum effect of nanostructured dolomite flour at doses of 0.025-0.1 g. noted in the phase of spring wheat stem elongation, hydrolytic acidity decreased by 0.3-0.5 resin(EQ)/kg of soil, respectively, to the background.

Liming nanostructured dolomite flour 0.0125-0.1 Hr contributed to obtaining reliable increases in grain yield, compared with the control, they were 5.7-13.4%. The increase in yields was noted in the variants with doses of 0.05 and 0.1 kg, i.e., by 2.0 and 7.4% to the background, respectively compared to the background. With the consumption of nanostructured analogue is ten times less (0.1 Hr compared to dolomite flour (1.0 Hr), the grain increment was 4.6%.

The increase in the functional activity of calcium and magnesium cations can be explained by a change in the physicochemical properties of dolomite flour as a result of dispersion that is confirmed by the high rate of stimulation of low doses of the nanostructured analogue. A similar mechanism is noted in the work of Carneiro Laisa R. S. (2018). It was shown that the reactivity of pozzolan nanostructured silica, which has a large specific surface area, was high in comparison with silicon dioxide [9].

The introduction of resource-saving technologies in primary tillage into agriculture provides for a reduction in the number of deep treatments. Traditional liming is designed for plow tillage, with the costs paid off in one or two years. In the conditions of tillage-free tillage, the annual introduction of nanostructured dolomite flour with a wide-cap sprayer is an effective and low-cost technological method. In this case, the effect of nanostructured dolomite flour is noted already at the beginning of the vegetative period of growth and development of agricultural crops. Thus, the use of dolomite flour in nanostructured form can make a significant contribution to improving the efficiency of agricultural production. In the future, nanofertilizers can potentially contribute to an increase in food production, since the high availability of their nanoparticles will allow controlling the concentration of fertilizers in the ideal range [10-12].

4. Conclusion
From natural dolomite, a highly efficient mean for soil liming, nanostructured dolomite flour with a particle size of 50.04 nm (range 40.0-120.0 nm) was developed. Phytotesting of dolomite flour and nanostructured analogue on plants by morphological features showed that there were no visible developmental deviations or differences in germination rates (88.0-94.0%). Under the influence of nanostructured dolomite flour at doses of 0.05 and 0.1 g. respectively shift pH, by 0.1 and 0.2 units, in the first thirty days was noted. High ameliorative effect of nanostructured analog at a dose of 0.1 g. contributed to a significant increase in yield by 7.4% to the background.

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