

## Technological principles of production of organo-mineral fertilizers from leonardite

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National Scientific Center «Institute for Soil Science The mixture contain easily digestible form all 3 basic and Agrochemical Researches named after O.N. Sonutrients that significantly improve the quality of the kolovsky 4 Chaikovska Str., Kharkiv, 61024, Ukraine

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**Goal.** Improvement of the method of obtaining solid organo-mineral fertilizer with the use of leonardite. **Methods.** Laboratory-analytical, model, statistical. **Results.** Technological approaches to the processing of natural raw materials into organo-mineral fertilizers with the definite composition of nutrients are proposed. The expediency of enriching leonardite with a starting complex of nutrients, which enhances the fertilizer-stimulating effect and allows to obtain fertilizers with improved agro-chemical properties and increased physiological activity, has been scientifically substantiated. The optimal ratio in mixture of components of solid organo-mineral fertilizers is 1:1. Such mixture contains organic (leonardite with a moisture content of at least 40%) and mineral (a complex fertilizer  $N_{16}P_{16}K_{16}$ ) components. The mixture contain easily digestible form all 3 basic nutrients that significantly improve the quality of the final product without decreasing the functionality of mineral and organic components as a nutritional value for plants. The technology of preparation of solid organo-mineral fertilizers provides a separate stage of grinding organic and mineral components, during which they are stabilized. The next technological stage is the enrichment of leonardite in the appropriate ratio of the starting complex of nutrients with the replacement of water with mineral components and the process of saturation of leonardite with subsequent granulation and drying of the finished product. **Conclusions.** The proposed method of obtaining organo-mineral fertilizer is based on the use of available organic and mineral raw materials, which transform into organo-mineral form, balanced in the content of humic substances, macro- and micronutrients.

**Key words:** soil improver,  $N_{16}P_{16}K_{16}$ , processing of natural raw materials, mechanical mixing, activation of carbonaceous raw materials, granulation, drying.

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Today, in the conditions of constant growth of prices for mineral fertilizers and shortage of fertilizers of organic origin in the regions of Ukraine where there are reserves of natural raw materials (peat, leonardite, lignite, sapropel) actively implement technologies for production of organo-mineral fertilizers (OMF) nutrients [1-4].

Leonardite is naturally oxidized brown coal has long attracted the attention of scientists and practitioners as a valuable organic raw material for various sectors of the economy, including agriculture, as a material for the production of organic, OMF and soil improvers. Depending on the direction of use, the maximum ash content of raw materials is accepted: up to 15% - for chemical use and thermal processing, up to 30% - for fuel, 30% or more - for the manufacture of organic fertilizers. A distinctive feature of leonardite is a complex supramolecular structure, where the proportion of humic and fulvic acids determines its value as a raw material for the production of OMF. The natural humidity of leonardite varies widely 25-57%, due to the difference in the characteristics of organic matter and chemical composition of the mineral part. Organic matter contains up to 49% of total carbon, about 10% of the material in the form of plant residues, is characterized by the absence of lignin, high content of humic substances 77-96 g/kg. Humic substances of leonardite are characterized by high carbon content compared to such young caustobiolites as peat and sapropel, the content of hydrogen, nitrogen and oxygen in them, on the contrary, is lower [5-7].

The amount of carbon in the composition of humic substances indicates the depth of the process of transformation of organic matter: the longer this process takes place, the more prone to destruction easily hydrolyzed aliphatic fragments, and the more the molecular structure contains aromatic condensed high-carbon parts, which is characteristic of humus. Significant aromaticity of molecular structures of humic substances of leonardite also testifies to their hydrophobicity. The low nitrogen content that can be traced is also associated with the depletion of their structure by aliphatic fragments, including nitrogen-containing amino sugars and protein components. Fulvic acids, in turn, have a higher acidity, richer in phenolic and alcohol OH groups [8-15].

Due to the low availability of organic matter, in its pure form, leonardite is not used as a fertilizer only as a soil improver, which has a positive effect on the moisture and air retention function of the soil. However, the humic substances contained in these minerals go into a physiologically active state and effectively act as plant growth stimulants and sources of plant nutrients only after the activation of raw materials.

There are two ways to activate carbonaceous raw materials by chemical or physical activation. Chemical activation of leonardite involves the use of an activating extractant ( $ZnCl_2$ ,  $H_3PO_4$ , NaOH, KOH, etc.), which is mixed with raw materials under certain extraction conditions and extract humic substances in the form of water-soluble humates [16-19]. In the case of physical activation, the raw material is activated under the influence of elevated temperatures or mechanical action on the raw material [20, 21]. The application of such elements of

technology reduces the rates of application of mineral fertilizers, and natural raw materials are involved in agriculture in full.

**The purpose of research** is to obtain a new type of fertilizer based on leonardite and a complex mineral fertilizer balanced in the content of humic substances, macro- and microelements.

To date, new technological approaches have been developed for the production of OMF using modern equipment created in Ukraine on the basis of domestic raw materials. Therefore, the relevance of these issues, especially in conditions of shortage of raw materials and energy resources, led to the choice of research topic.

**Materials and methods.** To achieve this goal used a number of experimental studies: laboratory-analytical - to determine the agrochemical composition of leonardite and organo-mineral fertilizers based on it, model - to study the technological process of obtaining solid organo-mineral fertilizers, statistical - to establish the reliability of experimental data using Statistica 10 software.

The research was carried out in the certified laboratory of organic fertilizers and humus NSC «Institute for Soil Science and Agrochemistry Research named after O.N. Sokolovsky» (certificate of compliance of the measurement system with the requirements of DSTU ISO 10012: 2005, № 01-0104 / 2017) in accordance with current standards of Ukraine (DSTU).

Selection and preparation of samples of leonardite and organo-mineral fertilizers for analysis was carried out according to:

- DSTU EN 1482-1 Fertilizers and lime materials. Method of sampling and preparation of samples. Part 1. Sampling.
- DSTU EN 1482-2 Fertilizers and liming materials. Sampling and preparation of samples. Part 2. Preparation of samples.
- DSTU ISO 5306 Fertilizers. Requirements for sampling protocols.

The content of total organic carbon was determined by the Turin method based on the oxidation of organic matter with chromic acid. The total nitrogen content is according to the modified Kjeldahl method. The total phosphorus content was determined by extraction of water-soluble phosphates. The content of total potassium was determined by flame-photometric method.

The content of humic (Cha) and fulvic acids (Cfa) was determined by the Turin method in the modification of Kononova-Belchikova. Extracted NaOH humic substances were separated into humic and fulvic acid fractions by acidifying the extract to pH 1.3-1.5 using 0.5 n. H<sub>2</sub>SO<sub>4</sub> at a temperature of 68-70 °C, and humic acids were separated by filtration. The separated humic acids were redissolved in 0.1 n. NaOH solution. The carbon content in the fractions of humic and fulvic acids was determined by the method of oxidation of organic matter with chromic acid. Determination of pH according to DSTU EN 13037: 2005 Soil and growth medium ameliorants. Determination of pH.

The content of trace elements and heavy metals (Cu, Fe, Zn, Mn, Co, Ni, Cr, Pb, Cd) was determined in acid extract (10% HCl) by atomic absorption method on a Saturn-4 spectrophotometer. All measurements were performed in triplicate.

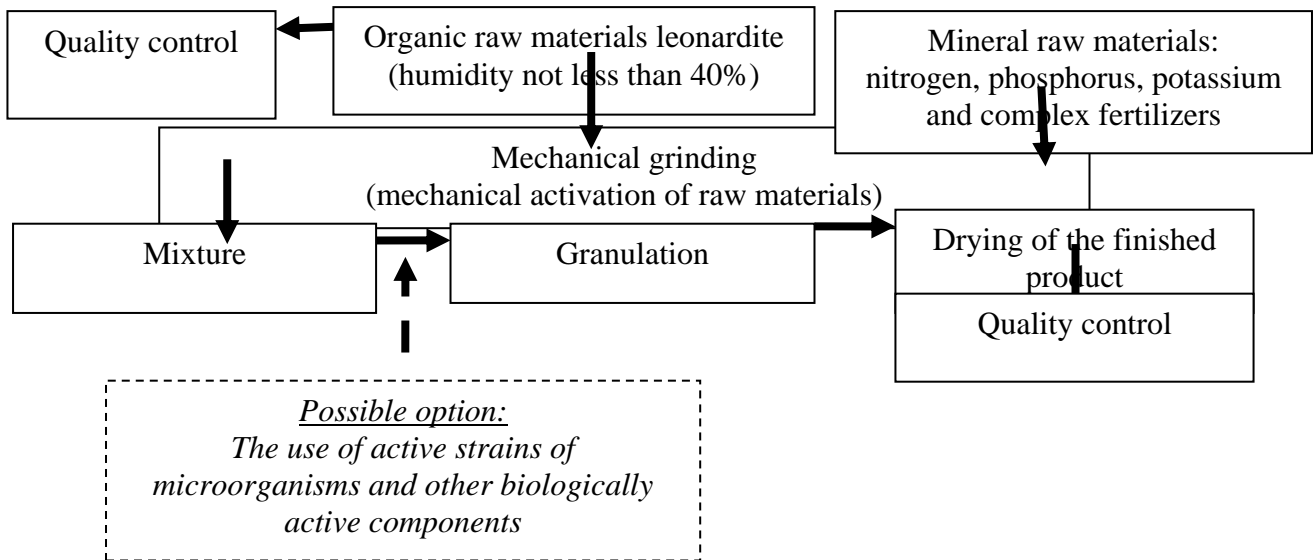
**Results and discussion.** Currently, the main disadvantage of the known methods of obtaining organo-mineral fertilizers is a significant reduction in organic matter during their production, and when adding mineral components, each of them «works» on its own. In addition, mineral nutrients are easily leached from such fertilizers, which significantly reduces their shelf life [17, 18].

Our research is based on the idea of the possibility of including a certain part of mineral nutrients in the organic component due to the formation of chemical or, mainly, physico-chemical bonds. From the point of view of physicochemical mechanics, solid OMF is a composite system, where the role of the matrix is performed by the organic component, and the filler - mineral fertilizers.

Scientific developments in the laboratory of organic fertilizers and humus have proven the possibility of using leonardite for the production of solid OMF, the effectiveness of which is due to the high mobility of humic substances and nitrogen of organic compounds, trace elements and good binder for making granular product [22-24]. This is very important, because the roots do not penetrate into the mineral granule, but bypass it, while in experiments with OMF plant roots penetrated the granules, absorbing nutrients not only from the soil solution, but also directly from fertilizers.

The method of obtaining solid OMF is carried out by mechanical mixing to a homogeneous mixture of leonardite with mineral fertilizers, followed by granulation and drying of the finished product, while as a mineral component take complex nitroammophos fertilizers containing active substance nutrients (about 16%), and mixing and granulation at experimentally received mass ratio of the specified components (fig.).

After agrochemical analysis by technology, the organic and mineral components are ground in a mill to a fraction of 1-2 mm (mechanoactivation) and loaded into the receiving tank of the mixer in a mass ratio of 1: 1, where they are mixed in solid form for 35 min to a homogeneous mixture. During mixing, an organo-mineral complex is formed, the organic part of which is chemically bound to nutrients. At this stage, it is possible to add microorganisms at a certain temperature (not more than 60-65 °C) to save biologically active substances from thermal destruction. Then there is a granulation of the finished product in the extruder and drying with mandatory quality control of natural raw materials and OMF.



**Schematic diagram of the technology of production of solid OMD on the basis of leonardite**

Based on the model experiments, it was found that the best mineral component for enrichment of Leonardite is a complex fertilizer - nitroammophoska (N<sub>16</sub>P<sub>16</sub>K<sub>16</sub>) in a ratio of 1:1, which contains in easily digestible form all three basic nutrients, it significantly improves the quality of the final product without compromising functionality. mineral and organic components as a nutritional value for plants. The results of the experiment on the saturation of leonardite with mineral components are shown in table.

**Agrochemical characteristics of leonardite and organo-mineral fertilizers (OMF) based on it**

Indicator	Actual content, g/kg	
	Leonardite	OMF
Mass fraction of organic matter	697	512
Mass fraction of humic acids	20,62	12,32
Mass fraction of fulvic acids	64,35	48,53
Mass fraction of humic substances	84,97	60,85
Mass fraction of total nitrogen, N	4,47	67,00
Mass fraction of total phosphorus, P <sub>2</sub> O <sub>5</sub>	0,20	71,50
Mass fraction of total potassium, K <sub>2</sub> O	0,57	70,80
The total mass fraction of trace elements (Cu, Mn, Zn, Co, Fe, Ni)	3,91	2,14
pH	5,9	5,2

After adding a complex fertilizer in the form of nitroammophoska significantly increases the content of nutrients in the organo-mineral mixture, nitrogen - 15 times, phosphorus and potassium almost 70 times with a minimum reduction of organic and humic substances by 27%, it significantly improves the quality of the final product. without compromising the functionality of mineral and organic components as a nutritional value for plants.

In the process of developing the technology of obtaining OMF it was found that the moisture content of raw materials before saturation with its mineral components should be not less than 40%, the diameter of leonardite particles and mineral component not more than 2 mm, and the humidity of the fertilizer after granulation up to 15%. This is due to the fact that with strong drying of organic raw materials, the absorption capacity of mineral components decreases sharply, and the solubility of humic acids decreases, when the raw material is wetted more than 50%, the structure of fertilizer is lost and nitrogen losses during drying increase. it with mineral components, reducing the absorption capacity, and the prepared mixture before entering the soil is stratified.

It is also possible to add microorganisms to the OMF to accelerate the process of converting hard-to-reach carbohydrates and nitrogen-containing substances into readily available biological substances: mono and polysaccharides, organic acids, ammonia nitrogen, and others that are well absorbed by microorganisms.

During the production of OMF in granular form, the most important process that affects the quality is the granulation process, the efficiency of which depends on the main operational parameters of the granule. Such parameters include physicochemical, mechanical and commercial properties. Physicochemical properties include the chemical composition and uniform distribution of components in the volume of the granule. The main mechanical parameter is the strength of the granules, the value of the parameter should be  $\geq 10$  N per granule. Commodity properties include fertilizers in the form of cylindrical granules.

To create a solid OMF of a new generation with a given composition of useful components in accordance with agro-climatic conditions, it is necessary to determine the useful effect of each component, placement in the granule and concentration.

For acid soils, it is possible to add a deoxidizing component, such as lime or calcium carbonate, to the OMF. In conditions of arid climate and uneven rain regime, components with certain physicochemical properties with high catalytic activity should be added to the composition of fertilizers. The use of zeolites, which have the properties of sorption of a significant amount of water will retain moisture in the granules for a longer period and save fertilizers from leaching. Bentonite clays also have good catalytic activity, binding and bonding properties, so their use is necessary for moisture sorption. It is also possible to add potassium salts, chalk, phosphorite flour, phosphogypsum and many other useful components to the granules, which are usually applied separately and help provide the plant with all the necessary nutrients and trace elements.

The use of solid OMF allows to increase the soil fertility most effectively and safely for the environment, to provide plants with the most important nutrients, such as nitrogen, phosphorus, potassium, humic compounds, etc. Also a great advantage of granular fertilizers is their convenient use, storage and transportation.

Fertilizers do not contain high concentrations of heavy metals, so their accumulation in the crop does not occur. The positive effect of fertilizers is achieved due to humic acids contained in the organic component of leonardite, the activity of organisms and biological mass, as well as the presence in leonardite in the required number of trace elements. The economic effect of the technology is 20-30% compared to the use of complex fertilizers nitroammophoska.

### Conclusions

*Currently, the scope of application of organo-mineral fertilizers for agricultural production is constantly expanding, which contributes to a number of significant advantages. Significant amounts of humic substances of fossil origin can be involved in the production of fertilizers as a useful organic component. The technological process involves obtaining an organo-mineral complex, the organic part of which is chemically bound to nutrients. Based on model experiments, it was found that the best mineral component for enrichment of Leonardite is a complex fertilizer - nitroammophoska in a ratio of 1:1, which significantly improves the quality of the final product without compromising the functionality of mineral and organic components as nutritional value for plants. Therefore, the development of the production of organo-mineral fertilizers and their introduction into agricultural practice makes it possible to comprehensively address the issues of raw materials, environmental protection and ensure the further development of agricultural production. The work was carried out in the framework of scientific research of the laboratory of organic fertilizers and humus NSC «Institute for Soil Science and Agrochemistry Research named after O.N. Sokolovsky» on the task 01.03.03.04 «Development of new methods of processing natural raw materials into fertilizers and evaluation of the effectiveness of their use in agricultural production» (№ SR 0119U002111).*

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