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## **DEVELOPMENT OF TECHNOLOGY FOR OBTAINING NEW TYPES OF MICROELEMENT-CONTAINING FERTILIZERS BASED ON GLAUCONITES AND BENTONITES OF KARAKALPAKSTAN**

**Abstract.** The climatic and geographical features of Uzbekistan, including the Republic of Karakalpakstan and the special zone of the Aral Sea region, its unique ecosystems with rare species of flora and fauna, which are of great importance for the entire global ecosystem of the planet, have led to the inclusion of tasks to ensure environmental sustainability among the national priorities. One of the alternative ways to restore soil fertility is the use of organic-mineral fertilizers. The results of the existing experience in the use of organic-mineral fertilizers in agriculture show that they have the property of restoring soil fertility due to the content of various microelements in them. Along with this, the water-retaining property of organic fertilizers based on manure, among other things, allows for a more rational use of water.

**Keywords:** Republic of Karakalpakstan, bentonites, glauconites, organic, organomineral, ammonium nitrate.

In order to prevent dehydration of the soil cover, preserve and even increase the humus content in the soil, mobilize soil phosphates, and protect the environment, by eliminating waste from the production

of mineral resources, two types of microelement-containing fertilizers have been created based on local mineral raw materials and plant waste of Karakalpakstan.

The climatic and geographical features of Uzbekistan, including the Republic of Karakalpakstan and the special zone of the Aral Sea region, its unique ecosystems with rare species of flora and fauna, which are of great importance for the entire global ecosystem of the planet, have led to the inclusion of tasks to ensure environmental sustainability among the national priorities. Given the high rates of economic growth over recent years, Uzbekistan recognizes the need to balance measures aimed at ensuring further economic growth with actions to protect the environment, including the rational use of natural resources and their preservation for future generations.

Insufficient application of organic fertilizers led to a sharp decrease in the amount of humus in the soil. Scientific research data show that intensive chemicalization of agricultural production with the use of mineral fertilizers leads to an increase in emissions of carbon dioxide, methane and nitrogen into the atmosphere, which are formed as a result of the destruction of soil humus. Research scientists show that the formation of carbon dioxide leads to climate change. It has been established that 20–25% of the total accumulated carbon dioxide in the atmosphere is the result of the destruction of soil humus due to the use of mineral fertilizers.

Studies show that more than 95% of the irrigated lands of the Republic of Karakalpakstan (the total area of irrigated lands is 500 thousand hectares) are saline. Practice shows that even weak salinization of soils leads to the loss of at least 15% of the yield of cotton and other crops. Currently, soil desalination is carried out by washing. The scarcity of fresh water complicates the application of this method.

One of the alternative ways to restore soil fertility is the use of organic-mineral fertilizers. The results of the existing experience in the use of organic-mineral fertilizers in agriculture show that they have the

property of restoring soil fertility due to the content of various microelements in them. Along with this, the water-retaining property of organic fertilizers based on manure, among other things, allows for a more rational use of water.

Regular monitoring of the state of the soil in the Aral Sea zone shows that from year to year the soils are subject to degradation processes: dehumification, desiccation, salinization, deterioration of water-physical properties, and more. The predominance of the removal of nutrients over their return, more intense mineralization of organic matter in comparison with humus formation is the main reason for the decline in fertility and an increase in the rate of regression of agro-ecosystems.

Therefore, along with the need to develop effective measures for desalinization and improvement of soils, a promising direction is the creation of agro-ore-containing fertilizers based on animal and poultry waste (30–40 t/he or more per year) with complex-forming, ion-exchange and sorption properties that would help plants grow on saline soils. Such properties are possessed by complex fertilizers obtained on the basis of agricultural ores of Karakalpakstan.

It should be emphasized that it is the decrease in the content of organic matter in the soil that is the root cause of its salinization, which, in turn, leads to a complete loss of structure and further to deflation and erosion.

The problem of soil degradation poses urgent challenges for the entire world community. In this regard, the FAO expert panel report *The State of the World's Soil Resources* identifies 10 major threats to soils: erosion, loss of soil organic carbon, nutrient imbalances, soil acidification, pollution, waterlogging, soil compaction, soil sealing, salinization and loss soil biodiversity. There are four priority measures to combat degradation (UN General Assembly resolution 64/201): 1) minimizing further degradation and restoring the productivity of soils that have already degraded in regions where the population is

most vulnerable; 2) stabilization of global stocks of organic matter in soils, such as organic carbon and soil organisms; 3) stabilization or reduction of global fertilizer use in regions where there is a shortage of nutrients; 4) improving knowledge about the state of soils and the main trends in this area.

The soil cover of the arid zones of Uzbekistan (including Karakalpakstan) is also subject to degradation and desertification processes, which leads to a reduction in the area of agriculturally suitable land. Taking into account the above priority measures to combat the degradation of arid soils, the Institute of General and Inorganic Chemistry of the Academy of Sciences of the Republic of Uzbekistan is developing new types of fertilizers that would optimize the nutrient regime of soils, increase the efficiency of nitrogen and phosphorus fertilizers through modification and giving them new properties.

So, thanks to the addition of local minerals – bentonites in an amount of 15–20% to the melt of nitrogen and phosphorus fertilizers, modified fertilizer granules acquire new qualities: slowly soluble properties, the ability to swell and water retention, to change the physical and chemical properties of soils due to the stabilization of soil aggregates and, as a result, the optimization of biological processes.

Three-year vegetation studies of the Laboratory of Agrochemistry of the Institute of General Chemistry of the Academy of Sciences of the Republic of Uzbekistan and the Laboratory of Chemistry of Mineral Fertilizers of the Karakalpak Research Institute of Natural Sciences made it possible to deeply study the properties of new bentonite-modified nitrogen and phosphorus fertilizers of prolonged action, intended for irrigation conditions on typical gray soil. A complex of physicochemical, agrochemical and microbiological studies was carried out, which made it possible to: 1) assess the degree and rate of release of nutrients from granules of bentonite-containing fertilizers; 2) to study the change in the physicochemical and agrochemical properties of the soil under the influence of slow-acting fertilizers;

3) evaluate the effectiveness of their influence on the growth, development and productivity of cotton plants; 4) identify patterns of microbial activity in the soil, including the dynamics of the number of microorganisms involved in the transformation of nitrogen and phosphorus and the level of activity of soil transformation of nitrogen phosphorus and the level of activity of soil enzymes.

The material briefly presents the results of studying the physicochemical and agrochemical properties of fertilizers and their agrochemical effectiveness on cotton crops. The composition of the studied fertilizers: bentoammonium nitrate (BAN) in%: bentonite – 15; N – 28.9; CaO – 0.6;  $\text{Al}_2\text{O}_3$  – 1.9;  $\text{SiO}_2$  – 6.5;  $\text{SO}_3$  – 0.19;  $\text{K}_2\text{O}$  – 0.3, granule strength – 4.77 MPa; bentoammophos BAM in%: bentonite – 20; N – 8.65; P – 38.5; CaO – 0.5;  $\text{Al}_2\text{O}_3$  – 1.4;  $\text{SiO}_2$  – 5.6;  $\text{SO}_3$  – 0.12;  $\text{K}_2\text{O}$  – 0.23, granule strength – 7.50 MPa. The experiment was carried out on a typical gray soil (Calciol, WRB, 2006) with the following characteristics: C – 0.5%;  $\text{N}_{\text{total}}$  – 0.09%;  $\text{P}_{\text{total}}$  – 0.14%; pH 7.2.

A model laboratory experiment with soil columns found that the presence of bentonite in the composition of fertilizers, prolonged BAN and BAM, and the ability to adsorb and retain moisture can increase soil moisture capacity (by 0.42–0.65%), reduce the dissolution rate of fertilizer granules by 1.1–2.5 times (in the first days of the experiment up to 4–10 times), reduce the intensity of leaching of  $\text{NH}_3^+$ ,  $\text{N-NO}_3^-$  and  $\text{P}_2\text{O}_5$  – ions by irrigation water.

Laboratory and vegetative experiments showed that BAN and BAM showed a positive effect on the phenological and biometric characteristics of the development of cotton plants, stimulating both the energy of seed germination (by 2.4–28.1%) and the growth of plant organs (the main stem by 1.7–4.7%); leaves by 2.3–4.1%; sympodial branches 2.5–12.7%; buds and fruit elements 2.1–12.9%) with an increase in yield by 9.4–15.2%. It should be especially noted that the number of immature fruit elements in the

variants with BAN and BAM was 2.3–1.6 times less than in the control.

The study of the agrochemical characteristics of a typical serozem under the influence of prolonged BAS and BAM fertilizers recorded a small but stable change in indicators (by the end of the third year of research): an increase in the amount of humus by 3.2–4.4% (compared to control), an increase in ammonium nitrogen under exposure to BAS (1.12–3.7 times), with a decrease in the content of the nitrate form (by 1.9–47%) and an increase in mobile phosphorus by 20.5–32.5% in the soil due to a more gradual and uniform release nutrients.

The involvement in the production of fertilizers of new types of agrochemical raw materials (local minerals and agro-ores, in particular bentonites) is one of the reserves for increasing the yield of irrigated crops and the quality of agricultural products, maintaining and increasing soil fertility in conditions of moisture deficiency or drought on degraded soils.

It should be noted that in recent years microelements containing fertilizers are practically not used on the sown areas of the republic, although it is known that microelements are part of enzymes, vitamins, hormones and other physiologically active compounds that play an extremely important role in the processes that occur in living organisms. Therefore, along with the need to develop effective measures for soil desalinization, a promising direction is the creation of microelement-containing fertilizers with complex-forming, ion-exchange and sorption properties. Such properties, in our opinion, can be possessed by complex fertilizers obtained from glauconites of Karakalpakstan. In this regard, we used glauconites as additives in order to obtain new nitrogen fertilizers.

Ammonium nitrate is a universal nitrogen fertilizer. The main disadvantages of ammonium nitrate are its caking and thermal instability, to eliminate which various additives are introduced into it. The best effect is achieved when using caustic magnesite. It is known that pure ammonium nitrate is a strong

oxidizing agent capable of sustaining combustion and detonation when subjected to a strong impact load or when initiated by explosives. An important task at present is to reduce the level of potential hazard of ammonium nitrate. For this, research is underway on the selection of highly effective additives that improve the strength of the granules, increase the thermal stability of the fertilizer [1–3].

We used glauconite sand of the Karakalpakstan deposit as an additive. Glauconite is a clay mineral of variable composition with a high content of bi- and trivalent iron, calcium, magnesium, potassium, and also containing a whole complex of microelements. The beneficial effect of glauconite on increasing plant productivity is manifested in various ways. It improves soil structure by increasing its permeability, which is especially important on heavy soils. In addition, the introduction of glauconite into ammonium nitrate makes it possible to reduce its flammable and explosive properties and expand the sales market.

One of the promising deposits is the Khodjakul glauconite deposit, the promising reserve of which is about 10 million tons.

It seems possible to identify those properties of glauconite that can be classified as unique, since they are the determining factors in the manifestation and development of the process of self-organization of the mineral, and among which the high physical and chemical activity of glauconite occupies a special place.

Along with the need to develop effective measures for soil desalinization, a promising direction is the creation of fertilizers with complexing, ion-exchange and sorption properties that will help plants grow on saline soils, as well as solve the problem of the explosive nature of ammonium nitrate.

The results of the research showed that the introduction of glauconite ammonium nitrate into the melt leads to a significant increase in the quality indicators of the resulting fertilizer. Based on the results obtained, for the first time, a technology was developed for obtaining a microelement-containing fertilizer based on the melt of ammonium nitrate

and glauconite, the introduction of which in order to solve the problem of its explosiveness leads to the production of thermostable ammonium nitrate. In this regard, samples of a new fertilizer were obtained at the experimental facility under laboratory conditions, its chemical, physico-chemical, physico-mechanical, and mineralogical compositions were determined.

The objects of research in the work were ammonium nitrate, glauconite of the Khodjakul deposit and the obtained fertilizer.

Since agriculture imposes strict requirements on the quality of fertilizers: all granular fertilizers should not be caked, 100% friability should be maintained for 6 months from the date of their manufacture: the static compressive strength of the granules should be at least 1.2–1.8 MPa. In this regard, we have determined some quality indicators (caking, the rate of dissolution of the granules of the resulting glauconite-containing ammonium nitrate in water).

The caking of ammonium nitrate with the addition of glauconite was determined by the express method, according to which the change in the degree of caking of ammonium nitrate was checked when glauconites were added to its melt in the ratio of ammonium nitrate: glauconite, equal to 100: (3–30). The test results of AS with the addition of glauconite show that with a decrease in its amount, the caking capacity of ammonium nitrate increases from 1.94 to 2.61 kg/cm<sup>2</sup>. With the ratio AC: glauconite equal to 100:30, the caking of the product is 1.94 kg/cm<sup>2</sup>, which is 2.4 times less than the caking of pure ammonium nitrate with the addition of magnesite produced by Maksim-Chirchik JSC (the caking of which is 4.64 kg/cm<sup>2</sup>).

The values of the hygroscopic points of the studied fertilizer with granule sizes of 2–3 mm are equal, in%; for AS-62.2; for fertilizer (AC: glauconite=100:3)-61.2, for fertilizer (AC: glauconite=100:20)-60.44 and for fertilizer (AC: glauconite=100:30)-58.5. According to the hygroscopicity scale, all samples are classified as hygroscopic sub-

stances. When studying the sorption moisture capacity, it was noted that ammonium nitrate at a moisture content of 3.5% strongly caking and loses friability, and samples of glauconite-containing fertilizers up to 5.0–6.0% moisture content retain the ability to sieving.

The rate of dissolution of fertilizer granules determines the caking of fertilizers during storage, therefore it has been experimentally revealed that when glauconite is introduced into the melt of ammonium nitrate, the rate of dissolution of fertilizer granules decreases compared to pure ammonium nitrate. With an increase in the mass fraction of glauconite in fertilizer samples (from 5 to 50), the time for complete dissolution of the granules increases from 48.8 to 96.2 sec. The time of complete dissolution of pure saltpeter granules is 46.8 sec. The data obtained indicate that the leaching of the studied fertilizer from the soil will occur much more slowly than the leaching of pure ammonium nitrate.

Studies on the strength of granules have shown that the more additive is introduced into the composition of the ammonium nitrate melt, the higher the strength of the granules. It was found that already at the AC: Gl ratio of 100:5, the strength of the granules is up to 1.66 MPa, with the strength of the granules of pure ammonium nitrate – 1.6 MPa, and at the ratio of AC: Gl equal to 100:13, the strength of the granules already reaches 2.0 MPa.

All the data obtained from the studies also indicate a decrease in the propensity of the obtained nitrogen fertilizer to detonation, which is explained by a decrease in the size of the crystals, which ensure their denser packing and the presence of calcium in the mixture, which interrupts the uniformity of the properties of ammonium nitrate and the detonation wave propagation zone.

Practice has shown that organic and organomineral, glauconite-bentonite-containing fertilizers have high agrochemical efficiency and mobilizing properties in relation to indigestible phosphates and have growth-active substances in their composition, create

a loose structure, increase the total surface area of the volume of finished products, promote adsorption and retention of moisture, and also nutrients – nitrogen, phosphorus, potassium, calcium, trace elements.

For organic and inorganic substances used as fertilizers, in terms of increasing their functional efficiency, their physical and mechanical state is of great importance, so the first and main effect will be achieved due to their loose structure, and this will affect several indicators [4–9]:

- time of transition to the active functional phase (decomposition phase). The fact is that as a result of oxidative processes in the production of fertilizers or in soil conditions, humification and transformation of organic matter occur and loose, developed structures with a large volume surface are formed;

- looser structures (compounds), when they decompose, and they decompose faster, are in the phase of free radicals, which in itself increases the functional activity of the compounds, as a result of which the rapid penetration of nutrients into soil solutions and plants is ensured;
- to increase the productivity of the process, the development of the contact surface is of great importance, which leads to an increase in the efficiency of the entire process. Due to the development of the contact surface and loose structure, the time of interaction of the reacting substances is reduced, which makes it possible to simplify the technology and improve the quality of the resulting fertilizers;
- loose structures are hydrophilic structures, they promote the adsorption and binding of soil moisture and prevent many of the processes that cause weathering and soil erosion. These are “preservatives” of soils while improving their structure and fertility;
- organic and organomineral fertilizers are capable of adsorbing and retaining nutrients by increasing the total volume surface, and their high ability to adsorb moisture (up to 50% abs.) prevents and eliminates the possibility

of washing out nutrients (nitrogen, phosphorus, potassium, calcium, and others) in sub-surface horizons. All this makes it possible to significantly (by 25–50%) reduce the rate of application of nutrients to the soil. The use of such fertilizers will reduce and eventually remove salinization and increase soil fertility, as well as save the growing season of plants that require irrigation;

- loose and porous structures of organic and organomineral fertilizers allow to increase the possibility of covering soil horizons and improve their interaction with phosphates, soil and plant root system.

The economic component of the production and use of organic, organomineral fertilizers based on organomineral raw materials always has a real and reliable positive value due to:

- simplicity of technological solutions for their production (no high temperatures, pressures, expensive equipment, washing, roasting and other operations);
- the maximum utilization rate of raw materials (conducting the process using non-waste technologies or technologies involving the involvement of waste as additional raw materials);
- a significant reduction in the volume of acidic reagents (by 4 or more times) and energy costs;
- reduction of chemical aggression on the environment and the biosphere (lack of fixation and leaching of nutrients into subsoil horizons and loss of nitrogen into the atmosphere in the form of oxides);
- increasing the efficiency of the nutrient elements of finished products and reducing the hectare norm of fertilizers by 2 or more times;
- optimization of physico-chemical, physical, soil, microbiological processes and other factors;
- improving the quality of grown products (no nitrates, increasing shelf life, increasing the content of vitamin C, protein, starch, gluten, carbohydrates, organic acids, etc.).

Maintaining and increasing the level of soil fertility is becoming a critical issue due to the increasing population density in the world, and the need to increase the yield of food crops. Therefore, the development of effective technologies for the production of organic and organomineral fertilizers and their implementation will allow to comprehensively solve the issues of raw materials, water and soil, animal and plant resources, environmental protection and ensure an increase in the volume and quality of agricultural products.

The lack of mineral fertilizers in the Republic of Kazakhstan is associated with remoteness from the place of their production, high cost. They do not contain trace elements. Standard fertilizers do not heal the saline soils of Karakalpakstan, have little effect on soil moisture retention, do not improve soil structure, do not contribute to the formation of humus in the soil, and increase the content of harmful salts in the soil. The efficiency of standard fertilizers

is not high enough. For example, the efficiency of phosphate fertilizers (ammophos, superphosphate) is 15–20%. Standard fertilizers quickly dissolve in the soil solution and a significant part of the beneficial components are washed out. In this regard, plants do not receive enough nutrients necessary for growth and development.

Establishing the production of fertilizers locally, using cheap local agricultural ores, can change the situation for the better. The composition of enriched agro-ores contains from 15 to 20 micro- and macro-elements necessary for the growth of crops. As a result of our research, it was found that new fertilizers based on local raw materials heal the soil, namely, in the process of interaction with the soil solution, redox reactions occur, which lead to a decrease in soil salinity, help retain moisture in the soil, and increase the humus content in the soil, soil structure formation improves, which leads to an increase in crop yields.

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