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THE COMPOSITION AND PROPERTIES OF GLAUCONITE SANDS AND NODULAR PHOSPHORITES OF KARAKALPAKSTAN AND THE PRODUCTION OF FERTILIZERS BASED ON THEM

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Abstract

The article presents the physical and mechanical characteristics and chemical composition of the initial raw materials – glauconite sand and nodular phosphorites of the Krantau, Khojakul, Beshtyu be and Sultan-Uizdag deposits. The methods of determining the chemical composition and commercial quality, as well as conducting physico-chemical studies of raw materials – glauconite sand and nodular phosphorites of Karakalpakstan and finished products using modern research instruments (X-ray, electron microscopic, thermal, optical emission spectrometer with inductively coupled argon plasma – ECO with ISP, HPLC-mass-spectrometry, ESI mass spectrometry studies, elemental analysis).

Keywords: *chemical composition, commercial quality, physico-chemical research of raw materials, phosphate flour, RA fertilizers*

Glauconite – monoprismatic greenish mineral from the group of layered hydrous silicates, with a specific gravity of 1.7–1.9 g/cm ^{3}. Its ion exchange capacity is 0.1–0.4 mol/ kg; porosity 20–25%; hardness 1.3–2.0; Density – 1.8–3.0.

The cation exchange capacity of glauconite concentrate varies from 390 to 550 mg/ eq per 1 gram of sample. According to its structural and geochemical properties, glauconite is a multi-purpose mineral raw material. The following areas of application of glauconite are offered:

1. As microelement-containing fertilizers.

2. As a hard water softener. One ton of glauconite softens 810 m^{3} of water of any hardness. Glauconite can withstand more than 500 regenerations per year.

3. To purify wastewater from heavy metals. According to the Institute of Botany of the Academy of Sciences of the Republic of Uzbekistan, when treating wastewater from the Tashkent Cable Plant, the content of metal salts decreased: Cu from 114.5 to 4.6 mg/l; Sn from 375 to 2 mg/l; Zn from 380 to 40 mg/l. Maximum absorption capacity in relation to heavy metals: Cu – 781.2; Ni – 342.4; Fe – 1317 mg/ eq per 1 kg of mineral. The

ability of glauconite to extract heavy metals from solutions is (in% of the initial content): Pb –99, Hg –64, Co –97, Cd –96, Mn –95, Cr –92, Ni –90, Zn –90, Fe – 99.

4. Glauconite effectively absorbs radionuclides Ce –137 and Zr-90, reducing the total β-activity of water by 28–203 times, and is used for decontamination of waters and soils with increased radioactivity. Moreover, glauconite is an active absorber of various organophosphorus, organofluorine and sulfur-containing pesticides, sharply reducing their content in the soil and aquatic environment.

5. Glauconite increases the accumulation of nutrients in the soil, improves the water-physical regime and soil structure, and activates the activity of soil microflora. As a result, the yield of grains and legumes increases by 10–40%, root crops by 30–35%. Glauconite has a positive effect on the yield of green mass of annual grasses and corn, increases the germination rate (up to 40%) of legumes and cereals, and reduces the incidence of plant diseases.

6. In livestock and poultry farms, glauconite can be used as a feed additive.

The chemical formula of conditioned glauconite can be presented as: $(R_2O + RO) * R_2O_3 * *4\ SiO_2 * H_2O$, where – R_2O – K_2O; Na_2-RO - MgO, CaO, FeO; R_2O_3 – Fe_2O_3, Al_2O_3.

The properties and effectiveness of natural phosphates from various deposits were studied (Beskrovny Yu.V., Veretennikov G.G., Galkina N.V., Ibadullaev E.I., Mirkhodzhaev I.M., 1970) using a Guinier focusing camera monochromator FR–552 carried out a precision determination of the structural characteristics of a phosphate substance without its fractional isolation. In this work, the linear dependence of the agrochemical characteristics of known types of phosphate raw materials from various deposits on the value of the parameter "ao" and "co" of the unit cell was determined. According to the obtained ao values, phosphorites are arranged in increasing order: group 1 includes nodular phosphorites, group 2 granular, group 3 shell phosphorites, and group 4 apatite. The minimum cell parameter values are found in nodular phosphorites, and the maximum values are found in apatites. It is concluded that the smaller the crystal size, the higher the agrochemical efficiency (Bushuev N.N., 2008). Based on this, we can conclude that nodular phosphorites can be directly used as fertilizer in the form of crushed flour, without resorting to many years of testing.

Among the agronomic ores of Karakalpakstan, nodular phosphorites occupy a special place. In nodular phosphorite, the relative content of lemon-soluble P_2O_5 reaches up to 40%, much more than in the Karatau and Kyzylkum ores, especially apatite ores (Veiderma M.A., 1977) This predicts the prospects for its use as a mineral fertilizer in the form of phosphate or as part of standard mineral fertilizers (Seitnazarov A.R., Turdialiev U.M., Namazov Sh.S., Beglov B.M., Dekhkanov Z.K., Kurbaniyazov R.K., 2017).

In table 1 and 2 show the chemical composition of glaconite sands and nodular phosphorites of Karakalpakstan, used as raw materials for the production of organomineral fertilizers. The content of P_2O_5 in the samples is relatively low and ranges from 6.19–22.84%. The highest content of P_2O_5 is observed in the ore of the Khodzhakul and Sultan- Uizdag occurrences. The sample from Beshtyube is the poorest phosphate mineral in phosphorus. The P_2O_5 content in them ranges from 5.8 to 7.98%. Calcite reaches 55–58% of the ore mass. Phosphorites are distinguished by high ratios $R_2O_3 : P_2O_5$ and $Fe_2O_3 : P_2O_5$.

To develop a technology for producing organomineral fertilizers based on agricultural ores of Karakalpakstan, information on physical and mechanical properties is needed. These properties include: humidity, bulk density, angle of repose, fluidity, pH, hygroscopicity and moisture holding capacity. The results of these properties are given in Table 3.

So, at a humidity of 2.0–2.28%, the free bulk density for Krantausky is 0.99 g/cm ^{3}; for Beshtyubinsky – 1.02 g/cm^3; for Khodzhakul glauconite – 1.21 g/cm^3, and with compaction it is 1.28; 1.48; 1.35, respectively. The angle of repose for the Krantau glauconite is 25 degrees; for the Khodzhakul and Beshtyubinsk glauconites, this figure is 22–26 degrees. Their flowability is 18.04–19.17 seconds. Determination of fluidity showed that they are equal to 10 points for all samples. The hygroscopic point for the 1st sample was equal to 37.3%; 2nd – 39.9%; 3rd – 38.7%. Their low value is explained by the ability of glauconite to swell in water and retain it in large quantities in the

interplanar spaces. The maximum moisture capacity of glauconite clays is 6.24–7.52%, and at higher humidity the raw material loses its friability. Glauconites with a pH from 6.92 to 7.95 normalize soil acid- base balance. It should be noted that the dispersed composition and physical and mechanical properties of various samples for different times from the Krantau deposit as an additive.

During the reporting period, organomineral fertilizers were obtained in laboratory conditions by chemical activation of phosphorites and glauconites of Karakalpakstan with ammonium sulfate and nitrate. Phosphorus in the soil is in the form of tricalcium phosphate, which does not dissolve in the soil solution. As a result of using the new fertilizers we have received, phosphorus in the soil turns into a soluble form.

Based on the chemical activation of Khodzhakul phosphate rock and glauconite from the Krantau deposit, phosphorus-containing fertilizers were obtained. Applying these phosphorites directly, as fertilizers, without prior activation is not effective.

The mechanism of the process of activation of phosphorites with solutions of ammonium sulfate and ammonium nitrate proceeds according to the following scheme. Under the influence of solutions of ammonium salts, the main minerals (calcium fluorapatite and calcite) of phosphorite decompose. An exchange reaction occurs between the components of phosphorite and the activating reagent. As a result of the dissociation of ammonium sulfate, an acidic environment is formed in the solution. The resulting acid ions react primarily with calcite. At the next stage, with the entry of ions into fluorocarbonate -apatite, the diffusion process is accelerated and their specific effective surface area increases. In the solution, aqueous and plant-assimilated forms of P_2O_5 phosphate minerals are formed.

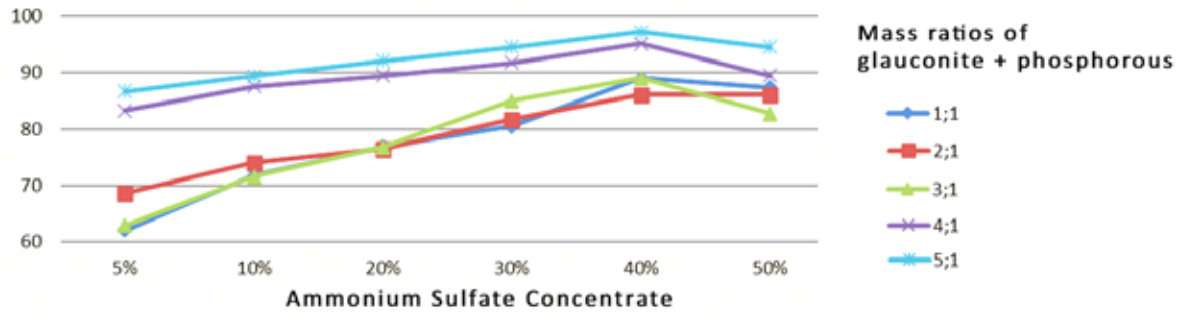
The study established that the process of activation of FM with a solution of ammonium nitrate (pH = 4.4 – 4.8) compared to ammonium sulfate proceeds more slowly. When 2 rFM is processed in a 2% solution of ammonium nitrate, the content of the digestible form of P_2O_5 is 31.5%, and 11.6% R_2O_5 is in water-soluble form. With an increase in the concentration of ammonium nitrate solution from 5 to 20%, the content of the digestible form of P_2O_5 increases by an average of 1.35 times. After activation, the reaction medium becomes almost neutral. The weight ratios of phosmuca and glauconite were 10(10 : 1; 10 : : 2; 10 : 3; 10 : 4; 10 : 5).

Phosphate rock and different weight ratios of glauconite were taken10 gr

No.	1	2	3	4	5
	10 + 10 1 : 1	10 + 20 1 : 2	10 + 30 1 : 3	10 + 40 1 : 4	10 + 50 1 : 5

In the first version, the mixture was stirred in a porcelain cup and moistened with water, after which, stirring vigorously, it was poured onto a sieve, where granules were formed. The resulting granules were dried in a thermostat for 2 hours at a temperature of 80–100 °C. The external shape of the product granules is similar to the shape of ammonium nitrate granules. After that, the strength of the resulting granules of size 2 was measured 3 мм and a chemical analysis was carried out for the digestible form of P_2O_5. Experimental data are shown in Table 4.

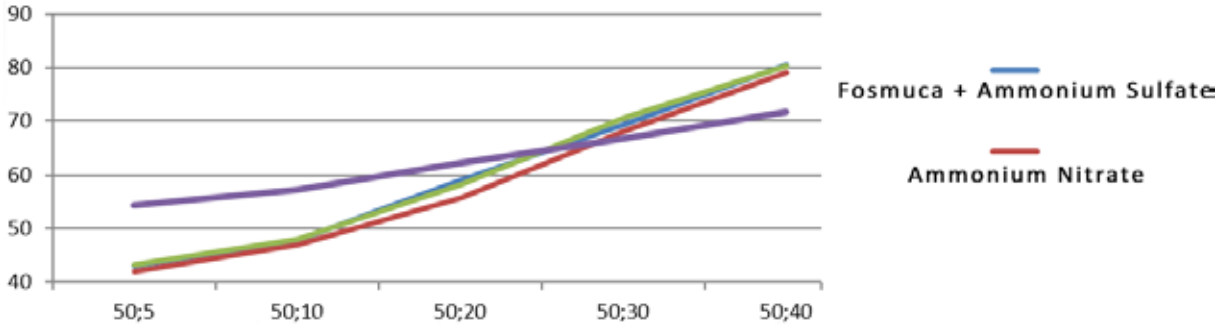
Figure 1. *Phosphorus content and its relative digestibility in fertilizer made from glauconite and phosmuca Khodzhakul deposit in various mass ratios (ammonium sulfate)*



It should be noted that recently microelement-containing fertilizers are practically not used in the cultivated areas of the Republic, although plants need them only in very small quantities, but without them plants cannot develop normally. This is explained by the fact 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.

Phosphorus and glauconite sand as additives, due to the fact that glauconite, a clay mineral of variable composition, has a high content of a complex of macro and microelements. The beneficial effect of glauconite on increasing plant productivity is manifested in various directions. It improves the soil structure, increasing its permeability, which is especially important on heavy soils. Possessing high selectivity towards large cations, glauconite accumulates such essential plant nutrition elements as nitrogen, phosphorus and potassium in the form of bulk cations and sorbs NH 3, and then slowly releases them during plant growth, playing the role of a prolongator. Digestible forms of fertilizers adsorbed by glauconite are preserved from leaching; the loss of ammonia nitrogen due to nitrification and volatilization is reduced.

Table 2. *Phosphorus content and its relative digestibility in phosphate fertilizer Khodzhakul deposit and glauconite in various mass ratios*



Therefore, we carried out its granulation in laboratory conditions using the rolling method. To do this, the dust-like product was placed in a porcelain cup, the required amount of water was dosed and vigorously stirred with a glass rod. In this case, moist round- shaped particles were formed; the mass of these particles was dried at 80 °C, and solid granules were obtained. They cooled and then dispersed particle 3 ммsize 2 – were analyzed for granule strength.

Experiments were carried out with various mineral salts at different ratios with phosphate flour and glauconite.

The results show that the mechanochemical activation of phosphate flour with potassium dihydrogen phosphate and potassium chloride produces highly concentrated RA fertilizers containing from 16.97–25.78% of the total form of P_2O_5.

The amount of nutritional components in the products ranges from 67.81 to 84.80% for citric acid; the granules of the resulting products have sufficient strength (2.17––5.19 MPa).

With the addition of glauconite, the relative content of the digestible form of P_2O_5 increases relative to the total, ranging from 80.26–96.60% granule strength (from 2.59––3.72 MPa) and meets the requirements of agriculture.

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