

Development of Mineral Fertilizers From Agricultural Resources of Karakalpakstan for use in the Creation of the Forests on the Dried Bottom of the Aral sea

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Abstract

This article discusses the intensive processes of production of mineral fertilizers by acidifying glauconite sand with nitric acid, followed by processing low-grade phosphate raw materials with acidification products. This study proved that the introduction of phosphorites in the system improves the particle size distribution and quality of the finished product. When processing glauconite with incomplete norms of nitric acid, a complex fertilizer is obtained

Keywords: *Production, glauconit, calcium carbonate, nitric acid, phosphorit, system, IR spectrum, filtration, fertilizer, crystallization.*

1. Introduction

Currently taking a number of measures on creation of forests and maintaining ecological balance in the arid region of the Aral sea. From the dried bottom of the Aral sea rises to 700-800 tonnes of salt storms per year, it is necessary to reduce the negative impact of rising particles of sand, salt and dust [1, 207].

Measures are being taken to continue the creation of protective forests from desert plants in arid areas of the Aral sea and to mitigate the negative impacts of global climate change. For events to create "green cover" on the dry bottom of the Aral sea it is necessary to determine the soil composition of the land.

The chemical analysis of soils can be used mainly in analytical methods, which are divided into two groups-chemical and instrumental. Chemical methods in turn are divided into gravimetric and titrimetric consisting of acid-base, redox, chelatometric and non-solvent aqueous titration. Among the instrumental methods of chemical analysis of soils are the most widely used electrochemical and spectrochemical methods.

The study of saline soils are paying a lot of attention, as they are widely distributed, and address any issues of land reclamation is based on the information about the salinity. To are saline soils containing soluble salts in quantities that adversely affect plant development.

This category includes soils that contain at least one horizon of the soil profile of soluble salts in quantities that exceed the emission threshold-the minimum allowable number salts which is inhibited. All soluble salts are considered toxic to plants. They increase the osmotic pressure of the soil moisture, reducing its availability to plants, adversely affect soil properties and, in addition, may have specific toxic effects on plants, disrupting the normal ratio of mineral nutrients or by increasing the alkalinity of the solution. Soil salinity is evaluated by analysing soil solutions, the filtrates from water saturated soil paste and water extract. Analysis of soil solutions and filtrates from water saturated soil pastes allows to get an idea of the salt concentration in the liquid phases of real soils. Method of aqueous extract allows to evaluate the total content of soluble salts in soils. In the evaluation of salinity, as a rule, determine anions (CO_3^{2-} , HCO_3^- , Cl^- , SO_4^{2-}) and cations (Ca^{2+} , Mg^{2+} , Na^+ , K^+) soluble salts. To the assessment of soil salinity using two methods. The degree of soil salinity or estimate for the total content of soluble salts in the soil or on the concentration of salts in soil slurries or effluents from water saturated soil pastes. To include saline soils, where concentration of soluble salts in the soil solution exceed 5-7 g/l or soils containing 0.05% to 0.15% of soluble salts depending on their composition.

Qualitative tests of salinity carried out before you begin cooking the aqueous extract. This makes the sample for the presence in the soil of Cl^- , SO_4^{2-} , and Ca^{2+} . A qualitative test is performed as follows: to 5 g of soil poured 25 ml of distilled water, shaken for 3 min, filtered [2].

2. Methodology.

Determination of soluble salts and evaluation of soil salinity conduct the method of the aqueous extract. The method is based on extraction of soluble salts 5-fold relative to the mass of soil to volume of distilled water. Water is added to the sample soil suspension is agitated and filtered. The result is water extraction. The aqueous extract analysed immediately after receiving them. As over time they may change the pH, the concentration of carbonate IO-new, in connection with the absorption by extracts CO_2 from ambient air. If the soil is saline soluble salts, we get a transparent drawing, as in the presence of salts and soil colloids coagulated [3].

pH of saline extracts reveal the degree of acidity of the soil and depending on it set a dose of lime in reclamation of acidic soils. Often pH is measured in soil suspensions prepared from air-dry soil samples. As the standard ratio when measuring pH take the ratio of soil: 1 M KCl is equal to 1:2,5.

Reserves of such minerals as potassium and phosphoric acid, adding to the need of plants for nutrients. In low salinity groundwater is dominated by carbonates, the growth of salinity begins to increase the content of sulfates, then chlorides. Valid for plants and soil content of soluble salts is from 0.1 to 0.15% (from 1 to 1.5 g/l) [4].

Another serious problem of our agriculture is related to provision of fertilizers. There is a significant gap between the volume of production of phosphoric fertilizers industry of the Republic and the volumes they are made by agricultural producers. The Ministry of agriculture of the Republic of Uzbekistan annually declared the need for phosphorus fertilizers is 660 thousand tons in calculation on 100 % P_2O_5 . In 2019, it produced about 150 thousand tons of phosphate fertilizers. This is due to the lack of quality phosphate rock, which is washed calcined concentrate (26% P_2O_5). At the same time in the Kyzylkum phosphorite complex in the dumps have accumulated more than 10 million tons of mineralized mass (MM) (12-14% P_2O_5 .) and 5 million tonnes of phosphorite slurry (10-12% P_2O_5), which are waste of enrichment of phosphorite of Central Kyzylkum (CC). In the General case, with them is lost each year 42% P_2O_5 from the original ore [5].

Based on the foregoing, we have studied the processes of obtaining mineral fertilizers from locally glauconitic ores, waste, Kyzylkum phosphorite complex (mineralizovannyh weight (MM) (12-14% P_2O_5) and phosphate slurry (10-12% P_2O_5).

Table 1

Soil Test Results										
№	Depth, cm	Cl, %	SO ₄ , %	Ca %	Mg, %	P ₂ O ₅ , %	Na+K		pH	Note
							mg/ekv	%		
1	0-10	0.029	0.054	0,021	0.005	2.56	1,17	0,027	8,20	Weakly salted
2	10-20	0.037	0.112	0.032	0.012	3.57	0,98	0,024	8,12	Weakly salted
3	20-30	0.067	0.059	0.021	0.011	3.68	1,89	0,046	8,11	Medium Chlorine Populated

Table 2

№	Depth, cm	Sum of salts, %	P ₂ O ₅ mg/kg	Humus, %
1	0-10	2,658	68,5	0,13
2	10-20	1,346	63,6	0,14
3	20-30	1,217	75,4	0,06

Made sampling the soil in some areas dried out bottom of the Aral sea. Tests were conducted according to the methodology [2].

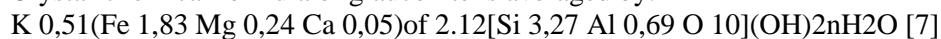
These saline areas are mostly chlorine (table 1). Therefore there is a need of measures to reduce the amount of chlorine ions in the soil.

In such areas the drylands of the Aral sea basin to create a "green cover" of saxaul, karabuak and kandym. [6]

The purpose of our research is to develop fertilizers from local agroores of Karakalpakstan for these purposes. Developed fertilizer is required at planting seedlings and, if necessary, during the next agricultural activities.

Of local agroores of Karakalpakstan in the experiments used Kraniauskas glauconite deposits. The study of glauconite showed the presence in them of such important nutrients as potassium, aluminum, iron, magnesium, calcium, phosphorus. The composition of glauconitic sand (glauconite - 35-40%, quartz - 33-55%, feldspar – 6,4-6,9%, phosphorus - 0,7-0,9%, ferric hydroxide - 3,5-4,0%, gypsum - 0,4-0,5% mica - 0,2-0,3; calcite - 0,1-0,2%) will improve the productivity and quality of agricultural crops. One of the alternative methods of desalinization of soils is the use of glauconite, since the introduction of glauconite reduces the content of salts harmful to plants. Due to the rather high content of potassium dioxide (6-7%) and phosphorus pentoxide (to 3.0%), glauconite can be used to produce potash fertilizer, or as a natural fertilizer without any treatment.

Crystal-chemical formula of glauconite is averaged by:



In particular, the soil glauconitic flour increases the yield of several grain crops and potatoes by 10-20%. Revealed a stimulating effect of glauconite on the development of beneficial microflora of the soil, a prerequisite for this is the high content in glauconite of potassium oxide, the ability to quickly break down in the soil to release potassium in the form of easily digestible compounds. The reactivity of glauconite can be improved by heating to a temperature of 500°C and above. An important fact is that in glauconite often in significant quantities are the trace elements (Mn, Cu, Co, Ni, B, etc.), and many deposits of glauconitic rocks contain P_2O_5 and even include phosphorite horizons. All this gives grounds to consider glauconite as a natural fertilizer, allowing not only to enrich the soil with potassium, but also improve its structure, retain moisture, stimulate growth and reduce the incidence of plants [5].

The results of agricultural research is the positive impact of a glauconitic concentrate on the growth and development of seed. In dry soil at concentrations of 3...9 g/m² 2.6...of 8.6 % increases the germination and 3,4...10% energy of germination, while at low and medium concentrations (3 and 6 g/m²) there is an increase in green mass of plants compared to the control variant of 8.2 and 11.7 %, respectively. Soaking seeds in a solution of glauconite with concentrations of 0.001...0.1% on ...1,4 7,4 % increases the germination rate by 2...4 %. When watering the soil glauconitic solution with concentrations of 0.03...0.09 percent, the growth and development of plants took place at the level of the control variant. To assess the impact on soil microporisma contained in glauconitic concentrate, were carried out corresponding tests. It is established that the amount of harmful substances (As, Pb, V, Mn, Sb) in soils after application of glauconite in the sand does not exceed their number in the source soils, while also unchanged in comparison with the background value remains the total radioactivity. [6].

Studied intensive processes of production of mineral fertilizers by acidification glauconitic sand with nitric acid with the follow-ing treatment of low-grade phosphate raw material products of acidification. Sample substances placed in a porcelain mortar and crushed them for 15 min until a homogeneous mass. Sample were transferred to volumetric flasks 250 ml and thereto was added 100 ml of distilled water. The flask contents were shaken on a rotating apparatus for 6 hours, and then the volume of the solutions was adjusted to the mark with water, mixed and left at room temperature for 24 hours. Then the solutions were filtered and in the filtrate was determined by the number of water soluble forms of P_2O_5 . Precipitation filters were transferred to same volumetric flasks, dissolved in 0.2 M Trilon B solution and determined the amount of assimilable forms of P_2O_5 .

The control pH was controlled in the range of 7.0 – 8.0 by adding a slurry of phosphorite, and mineralized masses (MM).

In this work we present the results of IR spektroskopicheskoe and x-ray source of low-grade phosphate rock, Glauco-Nita and the resulting products.

3. Research results

Radiographic analysis was performed on the apparatus XRD-6100 control-operated computer. Phase identification was performed using the literature [7, 8]. IR spectra were determined on the spectrometer Irtacer 100 (Shimadzu) in the frequency range 400-4000 cm^{-1} .

Chemical compositions of the mineralized mass and the slurry of phosphate rock are given in table 3.

Table 3.

The chemical composition of phosphorites

Views phosphorite	Component content, weight. %									P ₂ O ₅ as. / P ₂ O ₅ co %
	P ₂ O ₅	CaO	Al ₂ O ₃	Fe ₂ O ₃	MgO	F	CO ₂	SO ₃	H ₂ O	
Sludge phosphorite	10,87	40,27	1,94	1,48	0,64	1,54	20,93	0,49	14,8	9,34

The sludge phosphorus (Fig.1.) there are also diffractive strips with values 2,77; 2,70; 2,62; 2,28; 1,93; 1,83 JSC that belong to percarbonate, and the interplanar distance 3,86; 3,03; 2,49; 2,28; 2,09; 1,91; 1,87; 1,62; 1,60 AO - calcite, of 2,84; 2,77; 1,42 AO gypsum, 3,45; 2,49 AO to tricalcium phosphate, 3,35; 2,49; 1,93; 1,87; 1,42 AO - quartz [9-10].

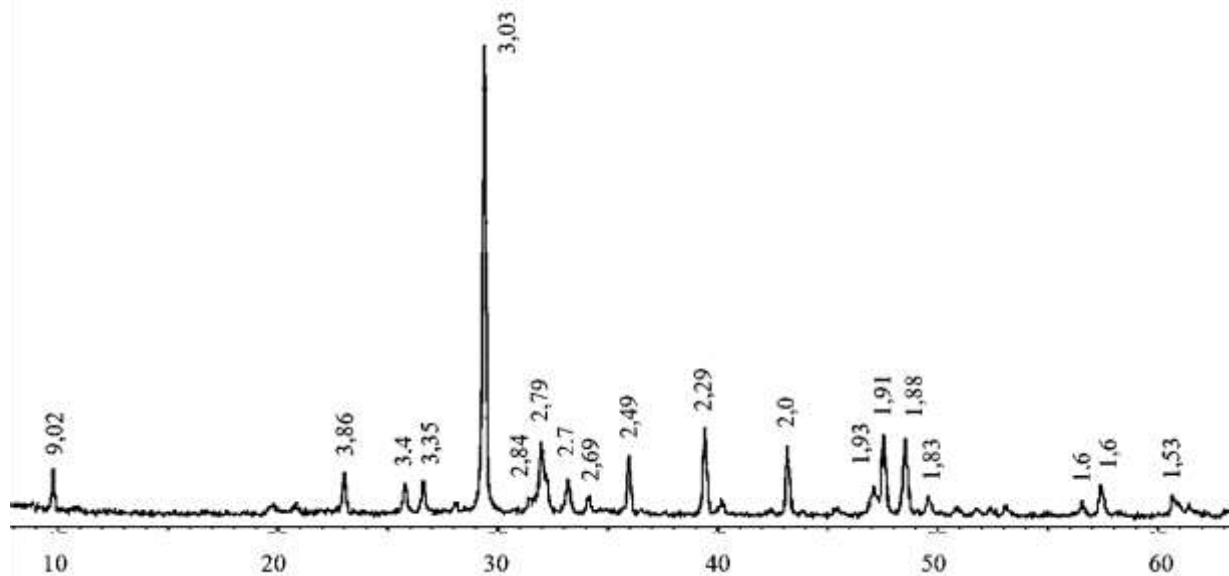


Fig. 1 – Radiograph of a slurry of phosphorite

The IR spectrum of SHF show obvious absorption bands corresponding to antisymmetric stretching and deformation vibrations of ion PO_4^{3-} in the frequency 570-605 cm^{-1} and 1026-1066 cm^{-1} [11]. In the spectra of the NF frequency vibrations 713; 875; 1427; cm^{-1} belong to the carbonate - ion. Region 1041, 798, and 470 cm^{-1} , characteristic of valence vibrations of Si-O-Si-bonds of the silicates. The replacement of ion PO_4^{3-} in the molecule of fluorapatite on CO_3^{2-} group probably can be judged from the shift of maxima of band of fluctuation PO_4^{3-} in high frequency region due to the overlap of the carbonate absorption bands in the composition of the phosphate mineral. Also, the absorption band of the tetrahedron PO_4^{3-} overlaps with the absorption band of silicates (area 1041-1068 cm^{-1}). In region 1620, and 3529 cm^{-1} there are absorption bands, characteristic of valence and deformation vibrations of crystallization, as well as physically adsorbed on the surface of mineral grains water (Fig. 2).

X-ray diffraction analysis showed (Fig.3) that the glauconitic Sands are varieties of feldspar, where the maximum peaks are at $2\theta=27.49^\circ$ ($d/n=3.24 \text{ \AA}$) and $2\theta=27.92^\circ$ ($d/n=3.19 \text{ \AA}$). These peaks are the main peaks of microcline and anortite (analbite). The strongest peak belongs to quartz with the

corresponding values of $2\theta=26.64^\circ$ ($d/n=3.342 \text{ \AA}$). The weak peak at $2\theta=12.29^\circ$ ($d/n=7.19 \text{ \AA}$) corresponds to the basal reflections of kaolinite.

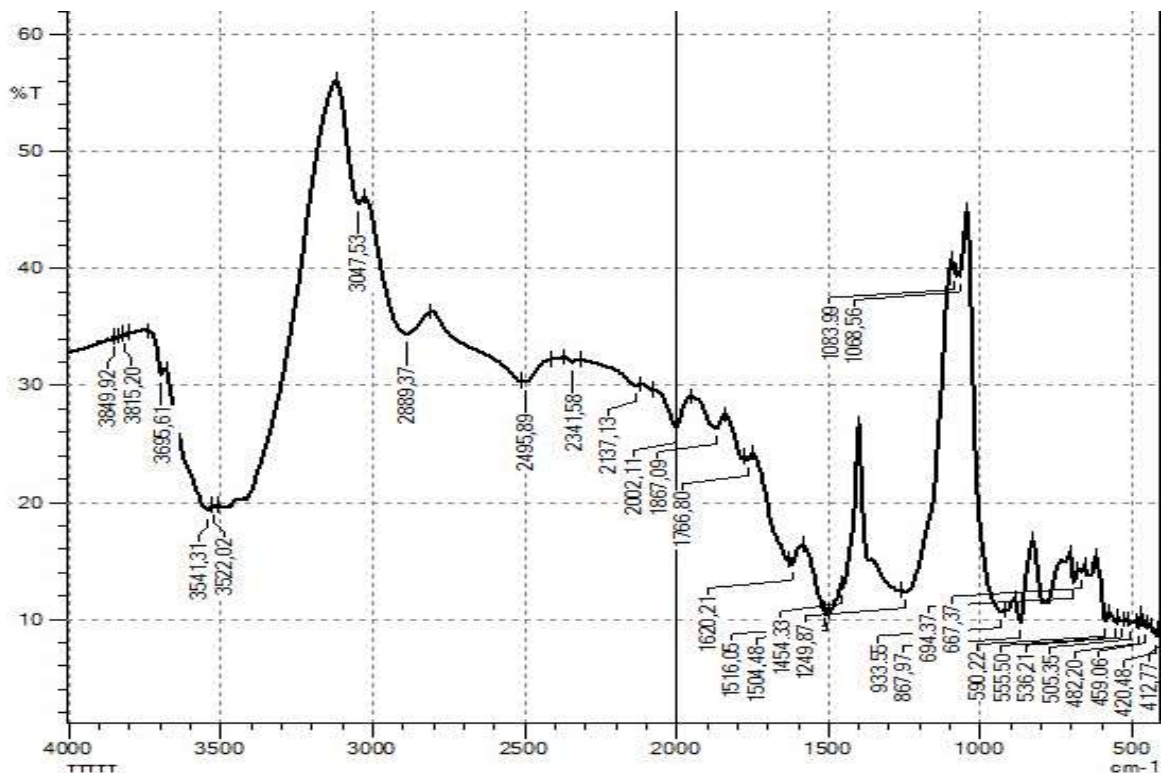


Fig. 2 – IR spectrum of a slurry of phosphorite

A pronounced reflection of Muscovite in the diffraction pattern is not noticeable, which would correspond to $2\theta=8.81^\circ$ ($d/n=10.03 \text{ \AA}$). The presence of the mineral illite shows a basal peak at $2\theta=20.70^\circ$ ($d/n=4.29 \text{ \AA}$). The presence of halite is not always evident even in the samples from one point in the samples of glauconite, sifted through sieves of different sizes (n), the position of the peak is equal to $2\theta=31.73^\circ$ ($d/n=2.82 \text{ \AA}$). Amorphous-crystalline glauconite is not manifested by severe reflections, But his presence with the montmorillonite can be seen due to the tubercle $2\theta=5-8^\circ$.

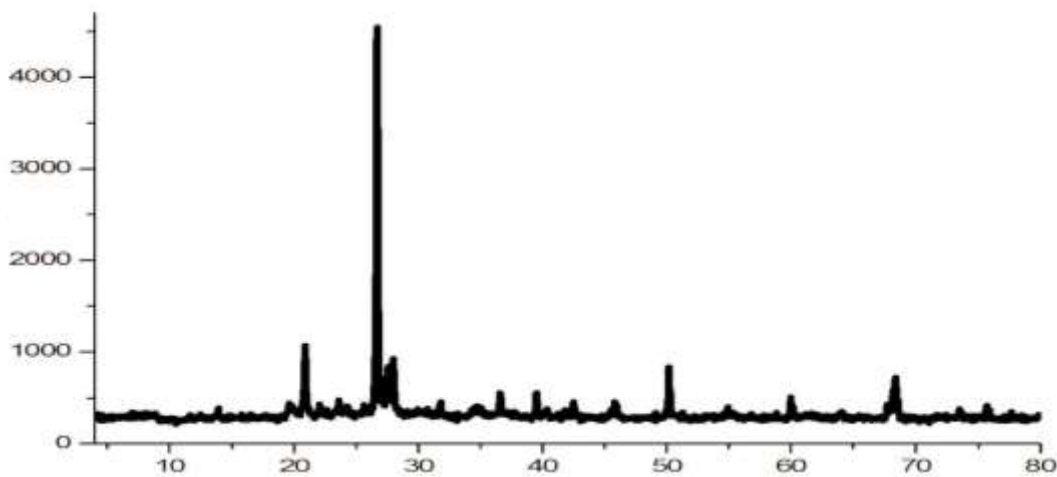


Fig. 3. The diffraction pattern of glauconite sand Kraniauskas field

In samples glauconitic Sands in addition to the glauconite and quartz are the minerals feldspar (microcline, orthoclase, albite, anortite), hydrology (illite, Muscovite), kaolinite, montmorillonite, halite and phosphates.

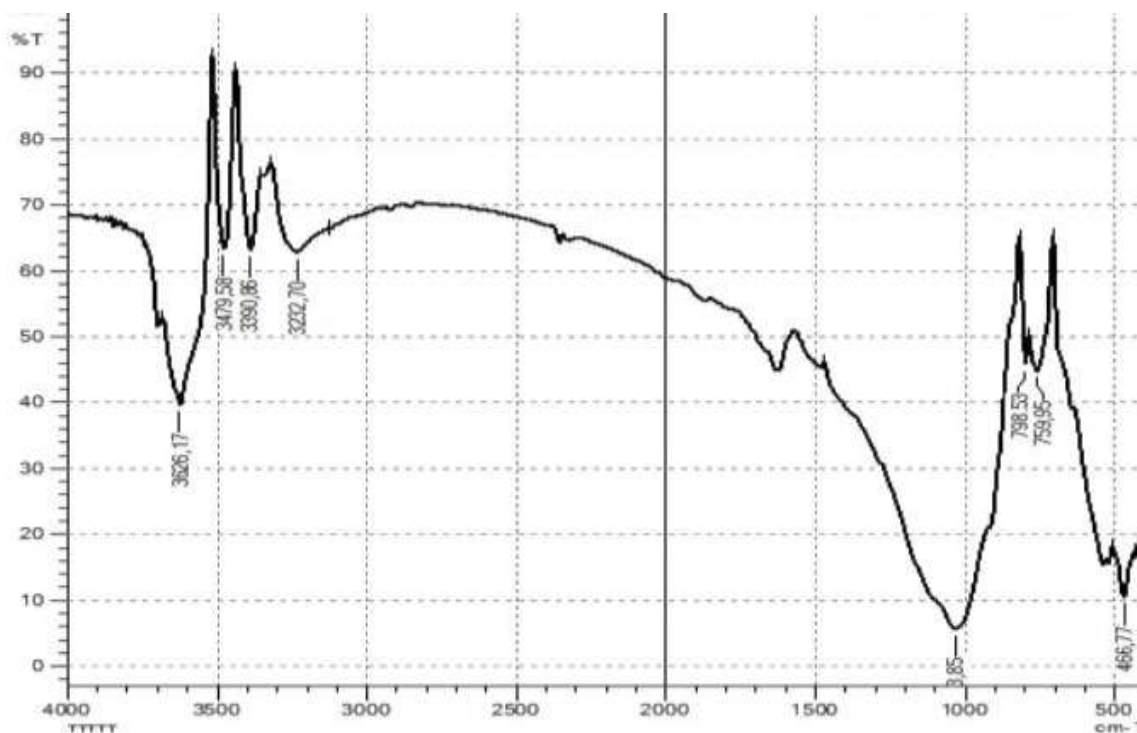


Fig. 4 – IR spectrum of glauconitic sand

In the low frequency region of the spectrum, there are absorption bands with maxima at 466 cm⁻¹ and a broad asymmetric band with a maximum at 1050 cm⁻¹. More detailed correlation of the frequency spectrum showed that the absorption 466 cm⁻¹ corresponds the vibrations of Fe-O bonds.

The main band of stretching vibrations of bridging Si-O-Si(Al) and the bridging Si-O linkages appear at 1050 cm⁻¹. The width of a maximum of 1050 cm⁻¹ due to substitution of trivalent ions Al³⁺ in the nodes of Si⁴⁺ with tetrahedral coordination, causing an increase in the average distance (Si,Al)-O and the change in effective mass of the respective oscillators due to the interaction of particles with atoms adsorbed on the interlayer space with water molecules. It is known that the frequency of stretching vibrations of the relations Si-O decreases linearly with increasing fraction of aluminum ions in position with tetrahedral coordination.

In the middle region of the spectrum observed absorption band with a maximum at 1637 cm⁻¹ which attributed to the deformation vibrations of the groups HE is in peaks of silica oxide tetrahedra, the stretching vibrations C-O of carbonate group, when CO₃²⁻ CO₃²⁻, the absorption band of the deformation vibration of which is observed in the field 759-798 cm⁻¹. It should also be noted that the relevant absorption bands of the nitrate ion, NO₃ is also observed in these regions of the spectrum.

In the region of stretching vibrations of OH-groups is observed an intensive band with a maximum at 3232 cm⁻¹. From the literature it is known that in glauconite are present OnP-groups of the two forms (H₂O), one of which is a associated with the exchange cations from the interlayer space of the water molecule and the other SiOH groups. Communication O-H belonging to the water molecules and hydroxyl groups have different force constants, and consequently different frequencies of oscillation. The frequency of deformation vibrations of O-H, in contrast to valence, varies in a very narrow interval, and thus its value depends not only on the strength of hydrogen bonds. The calculated frequencies of stretching vibrations of OH-groups associated hydrogen bond have frequencies 3550-3450 cm⁻¹ (dimers) and 3400-3200 cm⁻¹ (associates), whereas the unbound OH-groups 3650-3580 cm⁻¹. Consequently, the absorption band at 3626 cm⁻¹ can be attributed to valent fluctuations OHn-groups of water molecules of the interlayer space. Water molecules in cavities of the crystal is the number of possible States according to the number of hydrogen bonds: H₂O with one, same or different force constant two, three and four-connected hydrogen molecule. It turned out that even without a hydrogen bond with the surroundings, water molecules show a small low-frequency shift compared to the frequency in the free state. In addition to hydrogen, water molecules in the interlayer space and form through the oxygen atom bond with an alkaline cation, which also leads to changes in the frequencies of stretching vibrations. Consequently, the broad and asymmetric profile of this absorption band

associated with high dispersion of the mineral and the presence in its structure of the smectite interlayer spacing (Fig.4).

Thus, a comparative analysis of IR spectra of the glauconite samples showed that the observed in the IR spectrum major absorption bands, characteristic of hydrous (silica oxide groups), have significant differences.

Structural analysis of the IR spectra is reduced to finding the characteristic absorption bands and their assignment to the respective structural elements. The assignment takes into account the numerical values of the frequencies of the absorption maxima, contour and intensity of the bands.

To decrypt the bands in the region 1500 cm^{-1} further information was required on the relevant groups (information about the origin, composition, structure of analyte), because in this area the overlap of the bands of such groups as the Halogens, CH_2 , NO_2 , SO_2 , hydrogen atoms with double bonds.

The figure shows that the IR spectra have a large activity band corresponding to the valence antisymmetrical and the diffraction oscillations of the ion PO_4^{3-} ($960\text{-}1032\text{ cm}^{-1}$) and ($550\text{-}617\text{ cm}^{-1}$) in the phosphate substance.

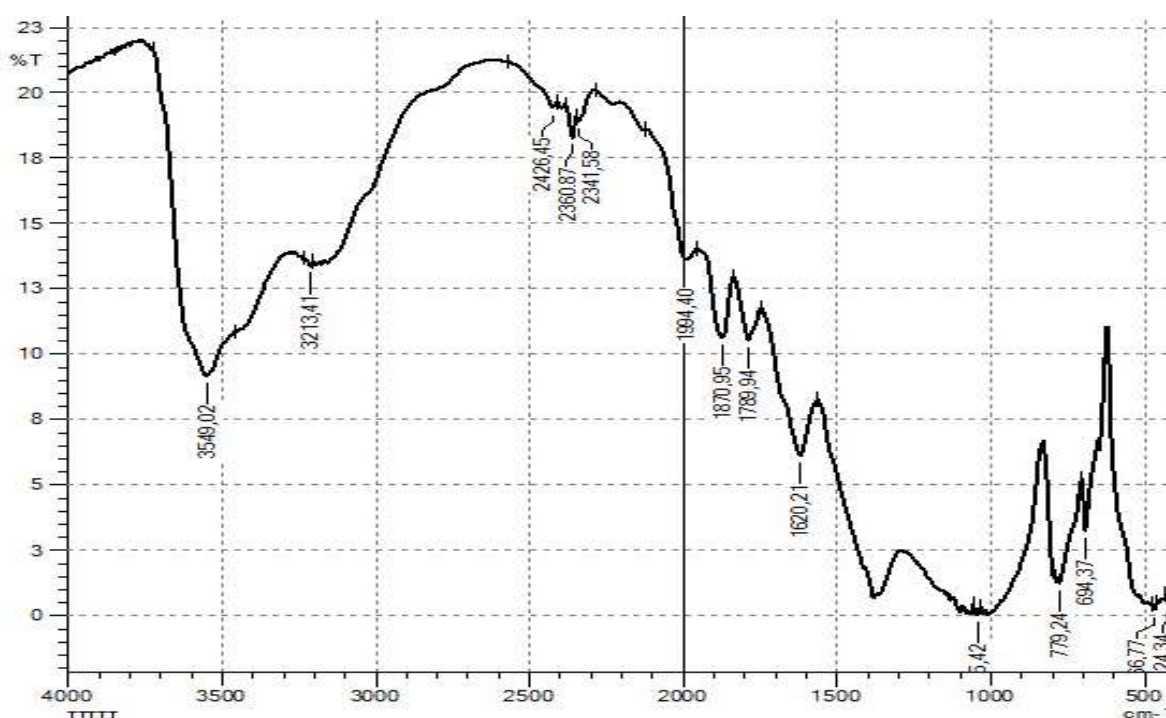


Fig. 5 – IR spectrum of the composition of glauconitic sand and slurry of phosphorite

The purity fluctuations at $1411\text{-}1870\text{ cm}^{-1}$ are characteristic valent and deformation vibrations of water of crystallization. Medium intensity absorption band at $3200\text{-}3540\text{ cm}^{-1}$ characterize the main stretching vibrations of water in the composition of clay minerals, the crystalline, as well as physically adsorbed water on the surface of mineral grains. Major fluctuations of the ion (region 1032 cm^{-1}) overlap with strong absorption bands of the anion PO_4^{3-} (Fig.4).

4. Conclusion

The study shows that the introduction of the system of phosphates improves the particle size distribution and the quality of the finished product. During the processing of a glauconite with 30-60% of governmental regulations nitric acid, it turns out granulier-ized complex fertilizer in which more than 68-86% P_2O_5 is in a digestible form.

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