Processing of Local Agro Ores of Karakalpakstam for High-Efficiency Fertilizer

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Abstract

The chemical composition of glauconite sands and zhelvak phosphorites of Karakalpakstan used as raw materials for production of complex mixed fertilizers has been studied. Physical and mechanical characteristics and chemical compositions of raw materials - glauconite sand and gelvac phosphorites of Krantau, Khujakul and Beshtyubinsk deposits are given. Several methods of introducing glauconite sand and gelvac phosphorites into the soil have been studied. Thermal analysis of the studied complex glauconite-containing fertilizers consisting of glauconite, monoammonium phosphate and potassium chloride is also provided.

Keywords: *Karakalpakstan, Krantau, Khudjakul, glauconite, glaukonite sands, phosphorite, phos flour, mineral fertilizer.*

Introduction

In Uzbekistan, the main phosphate raw materials for plants producing phosphate fertilizers are granular phosphorites of the Kyzylkum deposit. Currently, the Kyzylkum phosphorite complex carries out thermal enrichment of this carbonate raw material. The complex annually produces 716 thousand tons of washed calcined concentrate with an average content of 26% P2O5 (186.2 thousand tons of P2O5). But this volume is very far from being satisfied. The fact is that in 2018, the need of agriculture of the Republic for phosphate fertilizers amounted to 688.4 thousand tons of P2O5.

In terms of expanding the phosphate base for the production of phosphate fertilizers, nodular phosphorites of Karakalpakstan may be promising, the reserves of which are large (more than 70 million tons with a content of 10-15% P2O5). From a technological point of view, the Khudzhakul, Khodzheyli, Chukai-

Tukai and Nazarkhan deposits are considered promising.

They are in close proximity to the consumer; processing does not require large investments; production can be introduced in a short time; products (raw-ground phosphorites) are much cheaper than any other phosphate products. In agricultural chemistry, the criterion for the assimilation of phosphorus from its compounds is the proportion of P2O5 extracted into a solution of 2% citric acid; the latter in terms of dissolving power is close to soil humic acids. In nodular phosphate - kurskite, the relative content of lemon-soluble P2O5 is 25-35%, much more than, for example, in Karatau or, especially, apatite ores [1].

Materials

Glauconite is a greenish monoprismatic mineral from the group of layered water silicates, with a specific gravity of 1.7-1.9 g/cm3. 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 applications of glauconite are proposed:

1. As micronutrient fertilizers.

2. As a hard water softener. One ton of glauconite softens 810 m3 of water of any hardness. Glauconite can withstand over 500 regenerations per year.

3. For wastewater treatment from heavy metals. According to the Institute of Botany of the Academy of Sciences of the Republic of Uzbekistan, during the treatment of 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. Limiting absorption capacity in relation to heavy metals: Cu - 781.2; Ni - 342.4; Fe - 1317 mg/eq per 1 kg of the 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 Ce-137 and Zr-90 radionuclides, reducing the total β-activity of water by 28-203 times, and is used to decontaminate 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 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 cereals 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, corn, increases the germination (up to 40%) of legumes and cereals, reduces the incidence of plants.

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

The chemical formula of conditioned glauconite can be represented as: (R2O +RO)*R2O3*4SiO2*H2O, where – R2O-K2O; Na2O RO-MgO, CaO, FeO; R2O3-Fe2O3, Al2O3.

All this convincingly indicates that the local agricultural ores of Karakalpakstan can be processed by acid-free methods into highly effective fertilizer preparations at the lowest cost. In this regard, physiologically acidic salts

play an important role: such as ammonium nitrate, sulfate and phosphates, urea, potassium chloride, etc. reducing the radius of transportation of raw materials or finished products.

Nodular phosphorites occupy a special place among the agronomic ores of Karakalpakstan. In nodular phosphorite, the relative content of lemon-soluble P2O5 reaches up to 40%, which is much higher than in Karatau and Kyzylkum or, moreover, apatite ores [1].

This predicts the prospects for its use as a mineral fertilizer in the form of phosphate flour or as part of standard mineral fertilizers [2]. The properties and efficiency of natural phosphates from various deposits were studied [3], using a Guinier FR-552 focusing monochromator, a precise determination of the structural characteristics of a phosphate substance was carried out without its fractional isolation.

In this work, a 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 is determined. According to the obtained values of “AO”, phosphorites are arranged in ascending order: the 1st group includes nodular, the 2nd granular, the 3rd shell phosphorites, the 4th group apatites. The minimum values of the cell parameter are found in nodular phosphorites, and the maximum in apatites. It is concluded that the smaller the size of the crystals, the higher the agrochemical efficiency [3]. Based on this, it can be concluded that nodular phosphorites can be directly used as fertilizer in the form of ground flour, without resorting to many years of testing.

Methods

In table. Figures 1 and 2 show the chemical composition of glaconite sands and nodular phosphorites of Karakalpakstan, used as raw materials for the production of complex fertilizers. The content of P2O5 in the samples is relatively low and is in the range of 6.19-22.84%. The highest content of P2O5 is observed in the ore of the Khudzhakul and Sultan-Uizdag manifestations. The sample from Beshtyube is the poorest phosphate mineral in terms of phosphorus. The content of P2O5 in them ranges from 5.8 to 7.98%. Calcite reaches 55-58% by weight of the ore. Phosphorites are characterized by high R2O3:P2O5 and Fe2O3:P2O5 ratios

Table 1 Chemical composition of glauconites from Karakalpakstan deposits

Samples place birth	SiO_2	Fe_2O_3	FeO	TiO_2	MnO	P_2O_5	Al_2O_3	CaO	MgO	Na_2O	K_2O	CO_2	SO_3	ZnO	VO	H_2O	ппп	%
Krantau	68,91	5,59	1,15	0,44	0,04	0,15	8,95	1,15	1,25	1,71	2,89	0,41	0,24	0,011	0,02	2,29	4,31	99,5
Khudzhakul	72,31	2,27	1,55	0,29	0,17	0,12	9,07	2,32	2,38	2,51	2,86	0,31	-	0,012	0,02	0,21	3,19	99,5
Beshtube	72,46	3,47	0,31	0,51	0,02	0,35	9,84	2,81	0,91	1,79	3,85	0,01	0,71	0,012	0,02	0,87	1,80	99,7

Table 2 Chemical composition of phosphorites from deposits of Karakalpakstan

Samples place birth	Component content %														
	P_2O_5	CaO	SiO_2	CO_2	MgO	F	R_2O_3	Fe_2O_3	Al_2O_3	SO_3	TiO_2	H_2O	орг. вещ-во.	Na_2O	K_2O
Khudzhakul	18,05	33,50	26,45	10,45	0,30	1,27	5,96	3,25	2,71	1,38	0,23	0,42	0,12	0,98	0,54
Beshtube	5,80	39,70	16,80	8,10	0,50	0,71	7,68	2,53	4,45	0,01	0,19	0,35	0,09	1,15	0,60
Sultan Uizdag	19,99	20,40	39,70	7,70	0,35	2,05	4,68	2,09	2,60	1,23	0,25	0,45	0,15	0,86	0,40

Table 3 Physical and mechanical properties of glauconites of Karakalpakstan

Technical indicators	**Technical specifications**		
	Krantausky	**Khudzhakul**	**Beshtube**
Initial humidity, %	2,0	2,19	2,28
Bulk density, g/cm3	0,99	1,21	1,02
Density with seal, g/cm3	1,28	1,48	1,35
Tilt angle, 0C.	25	22	26
Flowability, sec.	18,04	19,17	18,26
Hygroscopic point, %	37,3	39,9	38,7
Moisture capacity, %	6,24	6,72	7,52
pH 10% suspension	6,92	7,41	7,95

To develop a technology for obtaining complex fertilizers from glauconites of Karakalpakstan, information on physical and mechanical properties is needed. These properties include: humidity, bulk density, angle of repose, fluidity, pH, hygroscopicity and moisture capacity. The results of these properties are shown in table. 3 [4].

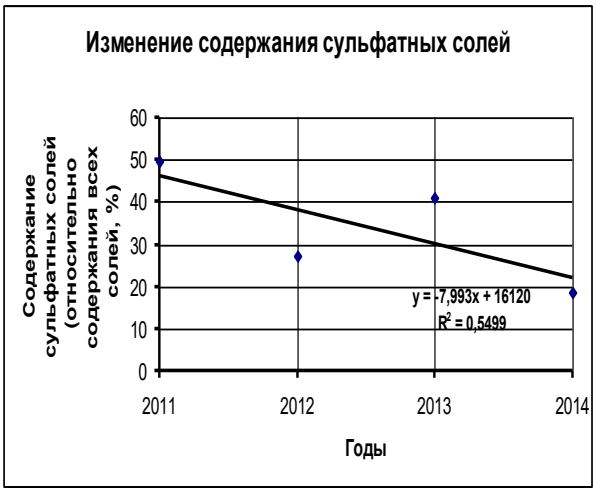
So, at a moisture content of 2.0-2.28%, the free bulk density for Krantausky is 0.99 g/cm3; for Beshtyubinsky - 1.02 g / cm3; for Khudzhakul glauconite - 1.21 g / cm3, and with compaction it is 1.28; 1.48; 1.35, respectively. The slope angle for the Krantau glauconite is 25 degrees; for the Khudzhakul and Beshtyubin glauconites, this figure is 22-26 degrees. Their flowability is 18.04-19.17 sec. The definition 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

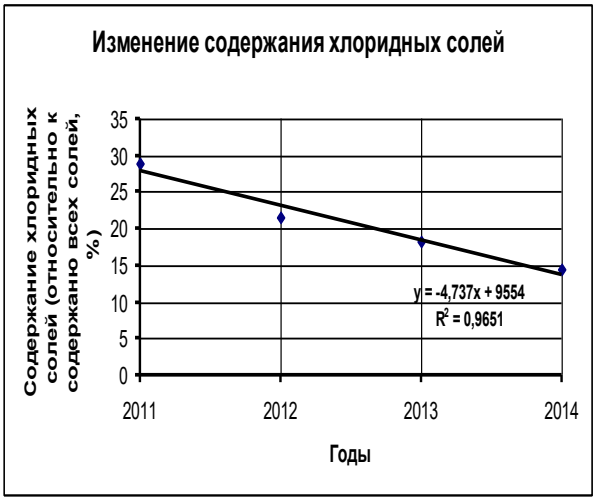
the ability to swell glauconite in water and retain it in large quantities in interplanar spaces. The limiting moisture capacity of glauconite clays is 6.24-7.52%, and at higher humidity, the raw material loses its friability. Glauconites with a pH of 6.92 to 7.95 normalize the acid-base balance of the soil. It should be noted that the dispersed composition and physical and mechanical properties of different samples for different grades of glauconites differ slightly from each other [4].

Results

Due to the continued drying of the Aral Sea, the quality of soils is deteriorating, as the salt layer is growing (chlorine, sulfate, carbonate and other salts).

Our studies have shown that when the fertilizers obtained by us are applied to the soil, the easily soluble salts of the soil are adsorbed into fertilizers, as a result of which they are retained in the structure of the fertilizer and become difficultly soluble, as a result of which they do not have such a strong detrimental effect on the cultivated crops.

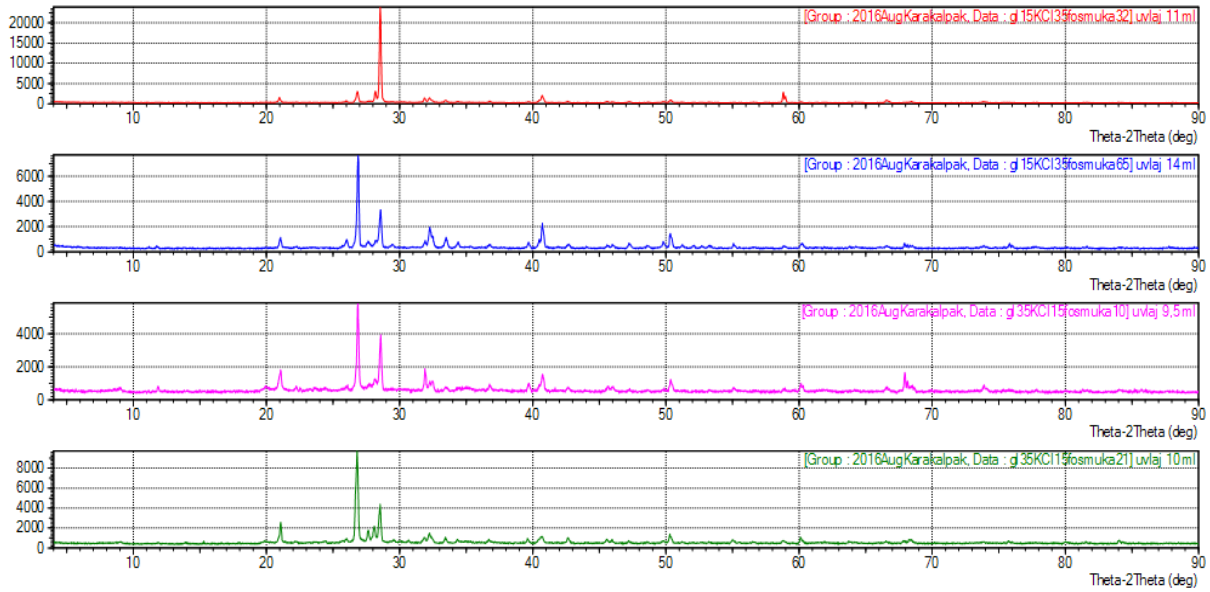




The content of chloride salts decreases by 1/3, 1/6 times, carbonate ions of salts decreases by the same order. The structure and quality of the soil improves, the incidence of wilt decreases by 40-50%.

The resulting fertilizers can be considered as a plant growth and development stimulator, i.e. the assimilation by plants of the phosphorus, potassium and nitrogen they need is improved [4].

Pic.1 Radiographs of samples of fertilizers glauconite, phos flour, potassium chloride,



It has been shown that fertilizers change the physicochemical and mechanical properties of finished products, while the amount of P2O5 of phosphorus increases. This proves that an exchange chemical reaction occurs during the preparation of glauconite-containing complex fertilizers [4].

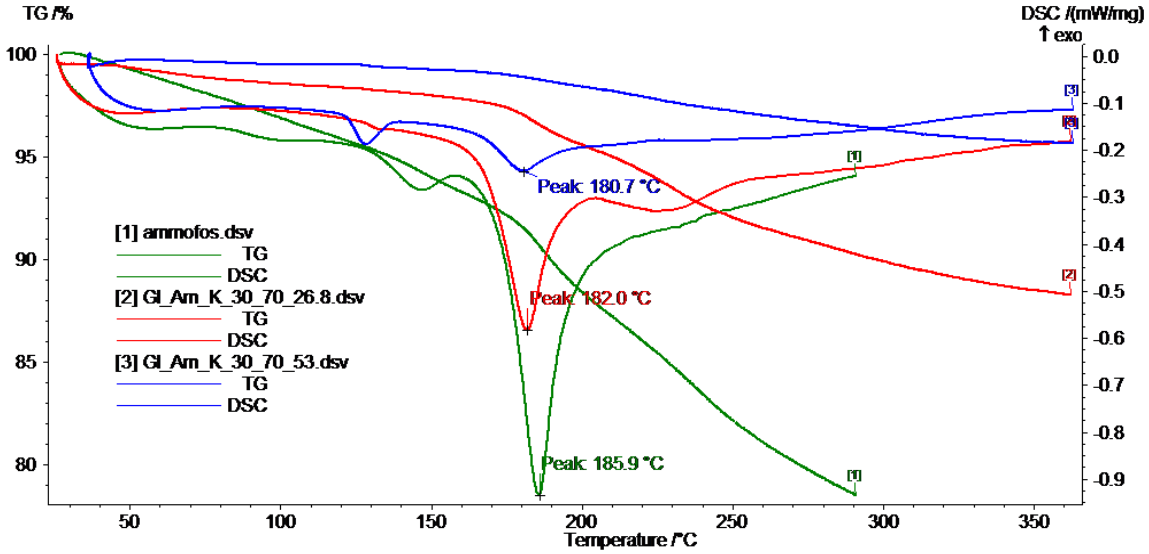
The mineralogical composition of complex fertilizers was also studied using X-ray phase and thermal methods of analysis. According to the results of X-ray phase analysis, the quantitative composition of the developed fertilizers is given in Table. four.

These calculations were carried out with the computer program Profex-3.9.2 [5] developed by the employees of Nicola Doebelin of the Geological Institute (University of Bern, Switzerland) and Reinhard Kleeberg of the Institute of Mineralogy (TU of the Mining Academy, Freiberg, Germany). The calculations take into account only the crystalline phases in the samples under consideration.

Table 4 Quantitative analysis of complex fertilizer composition glauconite: ammophos: KCl-1:2,33:0,89 (а); и 1:2,33:1,79 (б)

A) Glauconite: Ammophos:KCl 1:2,33:0,89			**B)) Glauconite: Ammophos:KCl 1:2,33:1,79**	
Mineral %			Mineral %	
quartz	8.00		Quartz	7.00
anorthite	12.02		Lizardite	9.37
Microint	3.00		Anorthite	4.39
Muscovite	0.49		Microint	3.07
Illit	3.33		Muscovite	0.77
Halite	1.86		Illit	1.83
KCl	3.37		Halite	0.72
Ammophos	9.18		KCl	0.78
calcium phosphate	2.19		Ammophos	0.58
Talc	1.66		calcium phosphate	1.07
Hydroxyapatite 2	8.14		Talc	1.99
brushite	1.22		Hydroxyapatite 2	1.02
CalciteMg	5.80		Brushite	1.01
CaCl2	0.39		CalciteMg	0.48
Lizardite	0.34		CaCl2	65.85
Amorphous part	38.91			

Pic 2. Thermal analysis of the studied complex fertilizers of the composition glauconite: ammophos:KCl-1:2.33:0.89 (red line), glauconite:ammophos:KCl-1:2.33:1.79 (blue line), pure industrial ammophos (green Line).



On Figure 2 also shows the TG-DSC curves of complex glauconite-containing fertilizers consisting of glauconite, monoammonium phosphate (MAP) and potassium chloride at Gl : MAP : KCl = 1:2.33:0.89 and 1:2.33:1.79 and clean MAF. The TG curve of these samples shows the weight loss of bound water and the decomposition of MAP (at 185.90C). But the decomposition temperature of MAP is lower than that of ammophos, and with the addition of glauconite and potassium chloride, the depth of the endothermic effect decreases simultaneously with a decrease in temperature minima to 180.70C [6].

Discussion

Agro-ores of Karakalpakstan can be developed for the needs of agriculture of the district, regional and regional scales, which will quickly solve the issues of providing microelement phosphorus and potash fertilizers. This convincingly indicates that in Karakalpakstan it is possible to arrange the production of such fertilizers for local needs.

In this connection, conducting systematic research on the creation of a technology for obtaining complex microelement-containing fertilizers based on glauconites and phosphorites of Karakalpakstan with the addition of mineral fertilizers is a very urgent task.

Taking into account the positive results of numerous studies, it can be argued that the fertilizers obtained by us can be very effective and, importantly, economical for our region, because they were tested on local soils of the Republic of Karakalpakstan and produced from local raw materials.

Conclusion

The possibility of obtaining glauconite phosphorite-containing fertilizers based on glauconite, nitrogen and potassium fertilizers is shown.

1. The process of obtaining complex glauconite-containing fertilizers based on glauconite, nodular phosphorite of

Karakalpakstan and fertilizer salts has been studied. At the same time, it should be noted that physiologically acidic salts make it possible to activate phosphate raw materials, that is, to convert the indigestible form of phosphorus into a form assimilable for plants.

2. Using physical and chemical methods of analysis, it was shown that the mineralogical composition of the composition consists of glauconite, phosphorite and fertilizer salts, as a result of which new compounds are formed in the systems that are not present in the original components, in particular, calcium sulfate, brushite, chloride -calcium, etc.

3. Agrochemical efficiency of glauconite-containing fertilizers, showing the water-holding capacity of glauconite, reducing the negative impact of chloride and sulfate salinity with an increase in humus in the soil, and optimizing the growth and development of plants in hot climatic conditions.

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