Mineral Composition of Nodular Phosphorite of Karakalpakstan and its Processing into Simple Superphosphate

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Abstract. The possibility of simple superphosphate fabricate by sulfuric acid activation of nodular phosphorites of Karakalpakstanwas considered. At the same time, the chemical and mineralogical composition of phosphate raw materials was established using X-ray diffraction. The raw material mainly consists of 27.09% kurskite and 26.19% francolite, as well as quartz. The norm of sulfuric acid for the decomposition of phosphate, including impurity minerals, has been calculated. Under the optimal activation condition (70% H_2SO_4 of stoichiometry for the formation of monocalcium phosphate), the product was prepared with grades of P_2O_{5free} – 1.48%; P_2O_{5total} – 14.67%; $P_2O_{5assim.}$: P_2O_{5total} = 97.88%; $P_2O_{5water\ soluble}$: P_2O_{5total} = 61.35%. CaO_{total} – 25.72%; CaOassim.: CaO_{total} = 68.12%.

1 Introduction

The continuous growth of the world's population predetermines the aggravation of the problem of food supply. The current forecast shows that in 2050 the world population will grow from the current 6.9 billion to 9.1 billion people [1]. This means that the demand for food is growing sharply, and, according to forecasts, food production in the world will increase by 70%, and in developing countries - by 100%. However, both land and water resources, which are the basis for our food production, are not unlimited and are already experiencing hard times. Thus, the area of arable land per capita will be reduced: instead of 22.8 acres in 2000, and by 2050 there will be 7 acres.

Therefore, the intensification of agriculture depends on the level of its chemicalization, i.e. the use of mineral fertilizers, plant protection chemicals, the introduction of mineral additives into animal feed rations, the use of chemical preservatives in feed production, etc.

In 2018the chemical industry of Uzbekistan produced 908.5 thousand tons of nitrogen, 138.2 thousand tons of phosphorus and 188.4 thousand tons of potash fertilizers in terms of 100% nutrient components. Concerningthe republic's demand, 963.7 thousand tons per year of nitrogen, 688.4 thousand tons of phosphorus and 313.6 thousand tons of potash fertilizers were produced. It turns out that the industry will satisfy the needs of agriculture in nitrogen

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fertilizers by 94%, in phosphate fertilizers by 20% and in potash fertilizers by 60%. The lack of phosphorus and potash fertilizers led to the fact that the average cotton yield in 2015 was only 26.1 q/ha. But the Uzbek Research Institute of Cotton Growing has long shown that cotton without fertilizers yields a crop of 12 centners per hectare, and when 225 kg/ha N, 150 kg/ha P_2O_5 and 100 kg/ha K_2O are applied for it, a guaranteed yield of 30-35 c/ha [2].

The Kyzylkumphosphorite complex annually produces 716 thousand tons of washed calcined concentrate with an average grades of 26% P_2O_5. At present, «Ammophos-Maxam» JSC receives from it ammophos (10% N, 46% P_2O_5) and Suprefos-NS (8-15% N, 20-24% P_2O_5), enriched superphosphate (2.5% N; 18-26% P_2O_5) and partially feed ammonium phosphate (12% N; 53-55% P_2O_5). At the same time, «Qo'qonsuperposfatzavodi» JSC produces simple ammoniated superphosphate (1.5% N; 11.5% P_2O_5). However, its volume in physical terms does not exceed 100 thousand tons per year. Some studies were conducted on preparation of phosphate fertilizers (ammophosphate, complexed fertilizers) based on wet phosphoric acid and phosphorite powder of Kyzylkum deposit [3, 4].

In conditions of drawback of phosphorus-containing fertilizers, it is necessary to begin the development of local deposits of agronomic ores, which have not been developedyet on an industrial scale. In this case phosphate rock such as the nodular phosphorites of Karakalpakstan, there are dozens of deposits. These Khudzhakul, Sultan-Uizdag, Khodzheyly, Nazarkhan, Chukay-Tukay, etc. They can be developed for agricultural needs and will quickly solve the issue in a case providing local phosphate fertilizers. If we start processing the phosphorites of Karakalpakstan, then for many years it will be possible to satisfy the region's need for phosphorus-containing fertilizers.

According to the mineralogical composition, the ore of Karakalpakia is close to the phosphates of the Egorievsk, Vyatsko-Kamsk and Chilisai deposits [5-9]. It is distinguished by fine intergrowth of phosphate mineral and quartz, and contains a significant amount of microimpurities. But Karakalpak phosphorites due to the low content of phosphorus (from 10 to 17% P_2O_5) and the high content of gangue such as sesquioxides (up to 10% R_2O_3) and quartz (up to 50% SiO_2) are unsuitable for obtaining fertilizers by known technological methods.

The difference between nodular phosphorites and types of phosphate raw materials is, firstly: they contain a large amount of quartz, and secondly, the phosphate mineral in them is represented by kurskite and francolite, with the former predominating; thirdly, in nodular phosphorite - kurskite, the relative content of the lemon-soluble form of P_2O_5 is 25-35%, much more than, for example, in Karatau or, especially, apatite ores [10].

This property, due to the imperfection of the crystalline structure of kurskite, makes it possible to use them for direct application to the soil in the form of phosphorite powder. According to GOST 5716-74, the dispersed composition of phosphorite powder after crushing must meet the following requirement - the residue on a sieve with a mesh size of 0.18 mm is not more than 10% [11].

By N.N. Bushuev [12] used a focusing camera-monochromator Guinier FR-552 to carry out a precise determination of the structural characteristics of a phosphate substance 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 „a_o" and „c_o" of the unit cell was determined.

According to the obtained values of „a_o", phosphorites are arranged in ascending order: the 1st group includes nodular, the 2nd granular, the 3rd shell phosphorites, and the 4th group apatites. The minimum values „a_o" 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 greater their interaction with soil solutions, therefore, the higher the agrochemical efficiency [12]. Therefore, nodular phosphorites can be directly used as fertilizer in the form of crushed powder.

The use of finely ground phosphorite as a direct fertilizer (slow release fertilizer), without any chemical processing, would provide agriculture with the cheapest phosphorus fertilizer [13].

But phosphorite flour is successfully used in large quantities on acidic soils [14], and it is ineffective on neutral and alkaline soils of Uzbekistan.

Indeed, in this case, the so-called mechanochemical activation is suitable, when the conversion of the form of P_2O_5 indigestible for plants into raw materials into an assimilable form is carried out mechanically in the presence of any chemical reagents [14]. This provides an increase in the citrate solubility of the phosphate mineral.

To obtain water-soluble phosphorus-containing fertilizers from low-grade phosphate raw materials, sulfuric acid activation (reduced acid rate) is suitable to derive simple superphosphate.

The acceptability of superphosphate can be explained by the following reasons:

availability of raw materials for its production, including low-grade natural phosphorites;

a relatively low consumption of sulfuric acid makes it possible to obtain a fertilizer with the lowest cost per unit of P_2O_5 in comparison with all other known methods;

the simplicity oftechnology and the absence of waste;

low capital investment;

low energy intensity of production and cheapness of products, i.e. cost effective approach;

can be used in conjunction with organic composts;

fertilizer has a long-term effect, which can befed 1-2 times in one season;

the product range includes fertilizer with a variety of micro-additives: manganese, zinc, boron, magnesium, calcium;

It can be successfully applied for backyard farms, where best results are achieved when growing potatoes, vegetables, fruit crops and flowers.

In this regard, the development and implementation of a rational and economical technical solution that ensures the processing of low-grade phosphate raw materials and the reduction of acid consumption is challenging.

The purpose of this work is to study the mineralogical composition and the process of its sulfuric acid processing to derive simple superphosphate.

2 Materials and methods

Phosphorite powder of the Khodjakul deposit (upper layer) was chosen as an object of the composition (wt. %): P_2O_{5total} – 19.11; $P_2O_{5assim.}$ by citric acid: P_2O_{5total} = 63.26; $P_2O_{5assim.}$ by trilon B: P_2O_{5total} = 35.85; CaO – 32.83; MgO - 0.30; CO_2 – 4.03; Fe_2O_3 – 3.50; Al_2O_3 – 1.54; SO_3 - 1.10; F – 1.58; acid-soluble SiO_2 – 28.0; insoluble residue – 1.64; H_2O – 2.62; CaO_{total} : P_2O_{5total} = 1.72. Sieve analysis in terms of fineness is characterized as follows: class (-5+3) – 7.65%; (-3+2) – 24.43%; (-2+1 mm) – 18.29%; (-1+0.5 mm) – 3.0%; (-0.5+0.25 mm) – 22.73%; (-0.25+0.16 mm) – 10.07%; (-0.16 + 0.1 mm) – 4.11%; (-0.1+0.05 mm) – 6.20%; (-0.05 mm) – 3.51%.

Analysis of phosphate rock for the content of various forms of components was carried out according to known methods [16].

The mineralogical composition of powder was determined by X-ray pattern taken on an XRD-6100 diffractometer (Shimadzu, made in Japan). Powder diffraction XRD data werecollected with CuKα radiation (β filter, Ni, tube current and voltage 30 mA, 30 kV) and a constant detector rotation speed of 4 deg/min, and the scanning angle varied from 4 to 80°. Mineral phases were assessed using the 2013 International Center for Diffraction Data database.

3 Results and discussion

The X-ray diffractogram of the nodular phosphorite powder of the Khudzhakul deposit is shown in Fig.1.

Diffraction fringes 1.72; 1.74; 1.79; 1.83; 1.93; 2.24; 2.62; 2.69; 2.77; 2.79; 3.18; 3.44A° belong to fluorocarbonate apatite. Interplanar distances 1.88; 2.28; 3.05A° characterizes calcite. Stripes 1.37; 1.54; 4.02A° refers to dolomite. The most intense peaks are 1.82; 1.98; 2.13; 2.45; 3.23; 3.34; 4.24A° indicates the presence of a large amount of silicon oxide in the phosphate raw material.

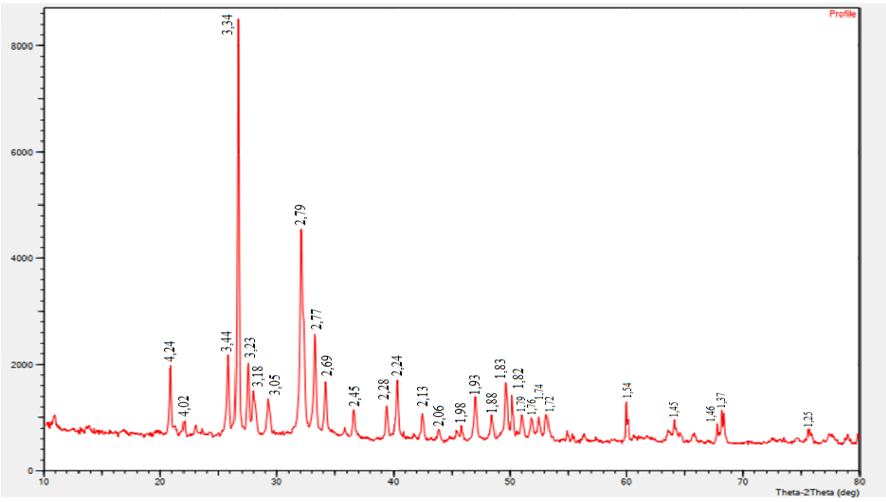

Fig. 1. X-ray diffractogram of nodular phosphorite flour of Karakalpakstan.

Bands 1.37 and 1.93 A° refer to calcium fluoride, while bands 2.06; 2.45 and 3.23A° can be attributed to calcium silicates.

Based on the results of chemical analysis and X-ray studies is givenin Table 1, reflecting the mineral composition of the nodular phosphorite of Karakalpakstan.

Table 1. Mineralogical composition of nodular phosphorite flour of Karakalpakstan

Mineral components of phosphate raw materials	Quantity, wt.%	Mineral components of phosphate raw materials	Quantity, wt.%
$Ca_{10}P_{4.8}C_{1.2}O_{22.8}F_2(OH)_{1.2}$ (kurskite)	27.09	$(K,H_2O)(Fe^{3+},Fe^{2+},Mg)_2$ $[Si_3A1O_{10}]xH_2O$ (glauconite)	3.61
$Ca_{10}P_{5.2}C_{0.8}O_{23.2}F_{1.8}OH$ (francolite)	26.19	CaF_2 (feldspath)	0.82
CaF2 (fluorite)	0.31	Mg_2SiO_4 (magnesium silicate)	0.02
$CaMg(CO_3)_2$ (dolomite)	0.69	SiO_2 (quartz)	28.0
$CaCO_3$ (calcite)	3.05	Ca_2SiO_4 (wollastonite)	2.66
$CaSO_4 \cdot 2H_2O$ (gypsum)	1.15	NaC1 (gallite)	0.02

FeS_2 (pyrite)	0.99	Organicmatters	0.04
$Fe_2O_3 \cdot nH_2O$ (limonite)	1.99	Insolubleresidue	1.64
FeO(OH) (goethite)	0.55	H_2O	1.20

Thus, the main phosphate minerals of nodular phosphorite are kurskite and francolite. They are quite suitable as phosphate raw materials for the production of simple superphosphate intended for topical use.

To study the process of obtaining simple superphosphate, the total consumption of sulfuric acid for the treatment of nodular phosphorite with the formation of monocalcium phosphate and gypsum was calculated. In this case, the main impurities of phosphate raw materials were taken into account.

The production of simple superphosphate is based on the process of decomposition of phosphate raw materials with sulfuric acid, which can be represented by the following overall reaction equation:

$$2Ca_5(PO_4)_3F + 7H_2SO_4 + 6.5H_2O = 3Ca(H_2PO_4)_2 \bullet H_2O + 7CaSO_4 \bullet 0.5H_2O + HF \quad (1)$$

Calculations on the consumption of sulfuric acid for the decomposition of calcium oxide of phosphate raw materials with the formation of monocalcium phosphate are follows as:

$$CaO + P_2O_5 \rightarrow Ca(H_2PO_4)_2$$

$$m(CaO) = \frac{19.11 \cdot 56}{142} = 7.5363g$$

where, 19.11 is the amount of P_2O_5 in 100 g of phosphate raw material, g; 56 isM(CaO), g/mol; 142 – M(P_2O_5), g/mol.

$$CaO + SO_3 \rightarrow CaSO_4$$

$$m(CaO) = \frac{1.10 \cdot 56}{80} = 0.77g$$

where, 1.10 is the amount of CaO in 100 g of phosphate raw material bound in the form of $CaSO_4$, g; 56 – M(CaO), g/mol; 80 – M(SO_3), g/mol.
Thus, the amount of CaO used for acid decomposition is:

$$32.83 – 7.5363 -0.77 = 24.5237g$$

From here comes the required consumption of sulfuric acid for the total amount of CaO:

$$CaO + H_2SO_4 \rightarrow CaSO_4 + H_2O$$

$$m(H_2SO_4) = \frac{24.5237 \cdot 98}{56} = 42.9164g$$

where, 56 is M(CaO), g/mol; 98 – M(H_2SO_4), g/mol.
For the decomposition of magnesium oxide, the amount of acid consumed:

$$MgO + H_2SO_4 \rightarrow MgSO_4 + H_2O$$

$$m(MgO) = \frac{0.3 \cdot 98}{40} = 0.735g$$

where, 0.3 is the amount of MgO in 100 g of phosphate raw material, g; 24 – M(MgO), g/mol; 98 – M(H_2SO_4), g/mol.

For the decomposition of sesquioxides, sulfuric acid is consumed:

$$Al2O3 + 3H2SO4 \rightarrow Al2(SO4)3 + 3H2O$$

$$m(H_2SO_4) = \frac{1.54 \cdot 3 \cdot 98}{102} = 4.4388g$$

where, 1.54 is the amount of Al_2O_3 in 100 g of phosphate raw material, g; 102 – $M(Al_2O_3)$, g/mol; 98 – $M(H_2SO_4)$, g/mol.

$$Fe2O3 + 3H2SO4 \rightarrow Fe2(SO4)3 + 3H2O$$

$$m(H_2SO_4) = \frac{3.50 \cdot 3 \cdot 98}{160} = 6.43125g$$

where, 3.50 is the amount of Fe_2O_3 in 100 g of phosphate raw material, g; 160 – $M(Fe_2O_3)$, g/mol; 98 – $M(H_2SO_4)$, g/mol.

Thus, the total consumption of sulfuric acid for the decomposition of 100 g of nodular phosphorite in terms of monocalcium phosphate and gypsum in the presence of impurity compounds (100% norm of H_2SO_4):
$m(H_2SO_4) = 42.9164 + 0.735 + 4.4388 + 6.43125 = 54.52145$г
or in terms of 93% concentration of H_2SO_4:

$$m(H_2SO_4) = \frac{54.52145 \cdot 3 \cdot 98}{0.93} = 58.6252\text{г}g$$

Thereafter, the process of simple superphosphate preparation was studied. The order of the process of decomposition of phosphate raw materials with sulfuric acid and obtaining the final product was as follows: a calculated amount of 93% sulfuric acid was slowly poured into a glass thermostatic beaker, in which there was a phosphorite powder, at its norms of 50 to 100% of the stoichiometry for the formation of monocalcium phosphate. The mixture was thoroughly mixed. The duration of contacting the components of the reaction mass was 30 min at a temperature of 70°C. Then the resulting mass, together with the beaker, was placed in an oven, where it was dried at 90-1000C to a constant weight.

Chemical analysis of products for the grades of various forms of P_2O_5 and CaO was carried out according to known methods [16]. The content of P_2O_5free. was determined by titration with 0.1 N NaOH using methyl orange and phenolphthalein indicators. The assimilable form of P_2O_5 was determined by solubility both in 2% citric acid and in 0.2 M solution of Trilon B. The assimilable form of CaO was determined only by 2% citric acid. The pH of the product was determined after an hour of shaking its 10% aqueous suspension. There sultsareshownin Table 2.

Dates table 2 shows that with an increase in the norm of sulfuric acid in the products, the content of the total form P_2O_5 decreases from 15.42 to 13.08%, and P_2O_{5free} on the contrary, it increases from 0.91 to 6.60%.

The water-soluble form of P_2O_5 indicates the formation of monocalcium phosphate in the products. Assimilate forms of P_2O_5 and CaO also indicate the presence of dicalcium phosphate in the products. The relative content of the digestible form of P_2O_5 less than 100% indicates that a certain amount of non- decomposed phosphate mineral remains in the composition of the products.

Table 2. Composition of products obtained by sulfuric acid decomposition of nodular phosphorite flour of Karakalpakstan

H_2SO_4 norm, %	productpH	Contentofcomponents, wt. %						
		P_2O_{5free}	P_2O_{5total}	$P_2O_{5assim.}$bycitricacid	$P_2O_{5assim.}$bytrilonB	P_2O_{5water}	CaO_{total}	$CaO_{assim.}$bycitricacid
60	2.36	0.91	15.42	14.55	10.33	7.74	27.82	18.28
70	2.29	1.48	14.67	14.36	10.48	9.00	25.72	17.52
75	2.22	2.95	14.31	14.09	10.35	9.39	24.58	16.78
80	2.06	3.46	14.14	13.98	10.37	9.91	23.97	16.35
90	1.90	4.68	13.61	13.48	10.45	10.30	23.38	15.93
100	1.76	6.60	13.08	12.99	10.14	9.99	22.47	15.28

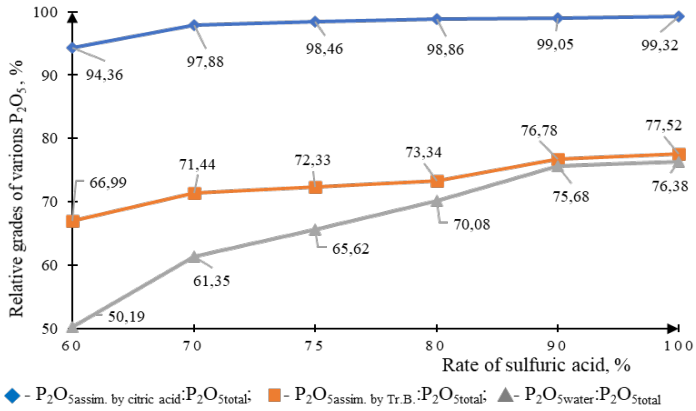

Fig. 2. Relative contents of assimilate and water-soluble forms of P_2O_5 of finished products depending on sulfuric acid

Agrochemists and soil scientists consider the best phosphorus fertilizer to be one in which the content of the water-soluble form of P_2O_5 is at least 50% of the total form of P_2O_5. We consider the optimal rate of acid for processing phosphorite powder to be 70% of the stoichiometric rate for the formation of monocalcium phosphate, since it is at this rate that the relative content of the water-soluble P_2O_5 rate in the products exceeds 50%. (Fig. 2).

In this case, the product contains P_2O_{5free} – 1.48; P_2O_{5total} – 14.67%; $P_2O_{5assim.}$ by citric acid – 14.36; $P_2O_{5assim.}$ by trilon B – 10.48%; P_2O_{5water} – 9.0%; CaO_{total} – 25.72%; $CaO_{assim.}$ – 17.52; pH – 2.29 (Table 2). At the same time $P_2O_{5assim.}$ by citric acid: P_2O_{5total} = 97.88; $P_2O_{5assim.}$ by trilon B : P_2O_{5total} = 71.44; P_2O_{5water} : P_2O_{5total} = 61.35% (Fig. 2).

It should be noted that the relatively high acidity in the products is most favorable for the carbonate soils of Uzbekistan. Acid superphosphate as an intermediate product is also of practical interest in the production of PK and NPK fertilizers.

Thus, the results of laboratory studies indicate the possibility of fabrication of simple superphosphate, bypassing the stages of ripening and ammonization. The proposed method will reduce the rate of deficient sulfuric acid to obtain 1 ton of P_2O_5 compared to simple ammoniated superphosphate by 30-40%.

4 Conclusion

The mineral composition of the nodular phosphoritepowder of Karakalpakstan was determined by the methods of chemical and XRD analysis. The results show that the main phosphate mineral of the raw material is kurskite and francolite, and calcite, dolomite, glauconite, wollastonite, gypsum, silicon, etc. are present as gangues.

The norm of sulfuric acid was calculated for the production of simple superphosphate, where the stages of storage ripening and ammoniation of the finished product are excluded.

The optimal rate of sulfuric acid for processing phosphate raw materials was considered to be 60% of the stoichiometry, since it is at this rate that the relative content of the water-soluble P_2O_5 rate in the products exceeds 50%. In addition, at a relatively high rate of acid, a rather high content of H_3PO_4free is obtained.

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