DOI: 10.6060/rcj.2024683.16

УДК: 631.632:14

ПЕРЕРАБОТКА ЖЕЛВАКОВЫХ ФОСФОРИТОВ КАРАКАЛПАКИИ В ПРОСТОЙ СУПЕРФОСФАТ

Р.К. Курбаниязов[1], Ж.Х. Худойбердиев[2], А.М. Реймов[1], Ш.С. Намазов[3], А.Р. Сейтназаров[3], У.К. Алимов[3]

[1]Рашид Калбаевич Курбаниязов**,** Ахмед Мамбеткаримович Реймов
Каракалпакский государственный университет, ул. Ч. Абдиров, 1, Нукус, Республика Каракалпакстан, Узбекистан, 230100
E-mail: kurbaniyazov-rk@mail.ru
[2]Жалолиддин Хасанович Худойбердиев
Кокандский государственный педагогический институт, улица Турон, 23, г. Коканд, Ферганский обл., Узбекистан, 713000
[3]Шафоат Саттарович Намазов, Атаназар Рейпназарович Сейтназаров, Умарбек Кадирбергенович Алимов
Лаборатория Фосфорных удобрений, Институт общей и неорганической химии АН Республики Узбекистан, ул. Мирзо Улугбек, 77-а, Ташкент, Узбекистан, 100170

Отличие желвакового фосфорита месторождения Ходжакуль (Каракалпакстан) от других видов фосфатного сырья заключается в том, что во-первых: в его составе имеются большое количество кварца, а во-вторых: фосфатный минерал в нем представлен курскитом и франколитом с преобладанием первого; в-третьих в желваковом фосфорите – курските относительное содержание усвояемой формы P_2O_5 составляет 35-40%. Определен химический и дисперсный состав фосфоритной муки. Рассчитан минералогический её состав, главными фосфатными минералами которой являются курскит (27,09%) и франколит (25,89%) почти на равных количествах. В качестве примесей присутствуют кварц (28%), кальцит (3,05%), глауконит (3,61%), гипс (1,15%), лимонит (1,99%), волластонит (2,66%) и прочие. Это сырье, хотя не пригоден для производства аммофоса, но представляет интерес, для получения активированного простого суперфосфата, предназначенного для местного применения. Рассчитана норма серной кислоты для полного разложения фосфоритовой муки, включительно примесных минералов с получением простого кислоты суперфосфата (13-16% P_2O_5). Обработку сырья проводили 93%-ной серной кислоты при температуре 70 °С в течение 30 мин.

Для обработки Ходжакульской фосмуки оптимальной нормой серной кислоты является 70% H_2SO_4 от стехиометрии на образование монокальцийфосфата, при котором относительное содержание водорастворимой нормы P_2O_5 в продукте превышает 50%. При этом активированный суперфосфат содержит $P_2O_{5своб.}$ – 1,48%; $P_2O_{5общ.}$ – 14,67%; $P_2O_{5усв.}$: $P_2O_{5общ.}$ = 97,88%; $P_2O_{5водн.}$: $P_2O_{5общ.}$ = 61,35%. С целью придания гранулообразования и достаточной прочности гранул проведен процесс обработки порошков простого суперфосфата растворами аммонийных солей различных их концентрации. При этом получались достаточно прочные гранулы с максимально высокими выходами товарного продукта.

Рентгенограмма сырья и готового продукта снята на дифрактометре XRD-6100 (Shimadzu, пр-во Япония). Размеры частиц сырья сняты на растровом электронном микроскопе (СЭМ) Evo MA10 (Zeiss, Германия).

Ключевые слова: желваковый фосфорит, серная кислота, активация, грануляция, химический и минералогический составы

Для цитирования:
Курбаниязов Р.К., Худойбердиев Ж.Х., Реймов А.М., Намазов Ш.С., Сейтназаров А.Р., Алимов У.К. Переработка желваковых фосфоритов каракалпакии в простой суперфосфат. *Рос. хим. ж. (Ж. Рос. хим. об-ва)*. 2024. Т. LXVIII. № 3. С. 106–119. DOI: 10.6060/rcj.2024683.16.

For citation:
Kurbaniyazov R.K., Xudoyberdiev J.X., Reymov A.M., Namazov Sh.S., Seytnazarov A.R., Alimov U.K. Processing of karakalpak nodular phosphorites into simple superphosphate. *Ros. Khim. Zh.* 2024. V. 68. N 3. P. 106–119. DOI: 10.6060/rcj.2024683.16.

PROCESSING OF KARAKALPAK NODULAR PHOSPHORITES INTO SIMPLE SUPERPHOSPHATE

R.K. Kurbaniyazov[1], J.X. Xudoyberdiev[2], A.M. Reymov[1], Sh.S. Namazov[3], A.R. Seytnazarov[3], U.K. Alimov[3]

[1]Rashid Kalbaevich Kurbaniyazov, Akhmed Mambetkarimovich Reymov Karakalpak State University, Ch. Abdirov st., 1, Nukus, Karakalpakstan, Uzbekistan, 230100
E-mail: kurbaniyazov-rk@mail.ru
[2]Jaloldin Xasanovich Xudoyberdiev
Kokand State Pedagogical Institute, Turon Street, 23, Kokand, Ferghana region, Uzbekistan, 713000
[3]Shafoat Sattarovich Namazov, Atanazar Reypnazarovich Seytnazarov, Umarbek Kadirbergenovich Alimov
Laboratory of Phosphate Fertilizer, Institute of General and Inorganic chemistry of Uzbek Academy of Sciences, Mirzo Ulugbek st., 77-a, Tashkent, Uzbekistan, 100170

The difference of nodular phosphorite of Khodjakul deposit (Karakalpakstan) from other types of phosphate raw materials is that firstly: it contains a large amount of quartz, and secondly: phosphate mineral in it is represented by kurskite and francolite with predominance of the former; thirdly, in nodular phosphorite - kurskite relative content of assimilable form of P_2O_5 is 35-40%. The chemical and disperse composition of phosphate powder (like-flour) was determined. Its mineralogical composition was calculated, the main phosphate minerals of which are kurskite (27.09%) and francolite (25.89%) in almost equal amounts. Quartz (28%), calcite (3.05%), glauconite (3.61%), gypsum (1.15%), limonite (1.99%), wollastonite (2.66%) and others are present as gangues. This raw material, although not suitable for the production of ammophos, but is of interest for the production of activated simple superphosphate, applied for local agriculture using. The consumption norm of sulphuric acid to decompose completely of phosphate powder, including impurity minerals with obtaining simple acid superphosphate (13-16% P_2O_5) was calculated. Feed stock phosphate ore was treated with 93% sulphuric acid at a temperature of 70 °C for 30 min. Yet, optimal condition for decomposition as sulphuric acid's norm is 75% from stoichiometry on monocalcium phosphate formation, at which the relative content of water-soluble P_2O_5 in the product to be exceeded 50%. Thus activated superphosphate contains P_2O_{5free} - 1.48%; P_2O_{5total} - 14.67%; P_2O_{5accep}: P_2O_{5total} = 97.88%; P_2O_{5water} : P_2O_{5total} = 61.35%. In order to obtain fertilizers as beads in form of granule with sufficient strength, the process of treatment simple superphosphate powders was exercised using solutions of ammonium salts of different concentrations. At the same time sufficiently strong granules with maximum high yields of commercial product were obtained. X-ray diffractograms of raw materials and finished product were taken on diffractometer XRD-6100 (Shimadzu, Japan). The particle sizes of raw materials were taken on a scanning electron microscope (SEM) Evo MA10 (Zeiss, Germany).

Keywords: nodular phosphorite, sulfuric acid, activation, granulation, chemical and mineralogical compositions

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 increasing sharply, and according to forecasts, food production in the world will increase by 70%, and in developing countries - by 100%. However, both the land and water resources that underpin our food production are finite and are already facing difficult times. Thus, the area of arable land per capita will decrease: instead of 22.8 hectares in 2000, and by 2050 there will be 0.07 hectares left.

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

In 2019, Uzbekistan's industry produced 898.3 thousand tons of nitrogen fertilizers, 119.4 thousand tons of phosphorus and 199.1 thousand tons of potash based on 100% nutritional components. Whereas, the republic's agricultural needs for this year amounted to 1075.8 thousand tons of nitrogen fertilizers (N), 759.3 thousand tons of phosphate fertilizers (P_2O_5) and 373.9 thousand tons of potassium fertilizers (K_2O).

The drawback of phosphoric and potassium fertilizers led to the fact that the average cotton yield in 2015 was only 26.1 c/ha. But the Uzbek Research Institute of Cotton Growing has long shown that cotton without fertilizers produces a yield of 12 c/ha, and when 225 kg/ha of N, 150 kg/ha of P_2O_5 and 100 kg/ha of K_2O are applied to it, a guaranteed yield of 30-35 c/ha [2].

The Kyzylkum phosphorite complex annually produces 716 thousand tons per year of washed calcined concentrate with an average content of 26% P_2O_5. Currently, Ammofos-Maxam JSC prodices from it ammophos (10% N, 46% P_2O_5) and Suprefos (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'qon superposfat zavodi JSC produces simple ammoniated superphosphate (1.5% N; 11.5% P_2O_5). But its volume in physical terms does not exceed 100 thousand tons per year.

In conditions of a shortage of phosphorus-containing fertilizers, it is necessary to begin the development of local deposits of agronomic ores, which have not yet been developed on an industrial scale. An example is the nodular phosphorites of Karakalpakstan, of which there are dozens of deposits. These are Khujakul, Sultan-Uizdag, Khojeyly, Nazarkhan, Chukai-Tukai, etc. They can be developed for agricultural needs and will quickly solve the issues of providing phosphate fertilizers for local application. If we start processing phosphorites in Karakalpakstan, we can satisfy the region's need for phosphorus-containing fertilizers for many years.

In terms of mineralogical composition, the ore of Karakalpakstan is close to the phosphates of the Egoryevsk, Vyatsko-Kama and Chilisay deposits [3-7]. It is distinguished by fine germination of phosphate mineral and gangue minerals such as quartz, and contains a significant amount of microimpurities. But Karakalpak phosphorites, due to their low phosphorus content (from 10 to 17% P_2O_5) and high content of sesquioxides (up to 10% R_2O_3) and quartz (up to 50% SiO_2), are unsuitable for producing fertilizers using conventional technological methods.

The difference between nodular phosphorites and other types of phosphate raw materials is that, firstly: they contain a large amount of quartz, and secondly: the phosphate mineral in them is represented by kurskite and francolite with a predominance of the former; 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 [8].

This property, due to the defectiveness of the crystalline structure of kurskite, allows them to be used for direct application to the soil in the form of phosphate rock. According to Statestandard 5716-74, the dispersed composition of phosphate after crushing must meet the following requirement - the residue on a sieve with a mesh size of 0.18 mm is no more than 10% [9].

N.N.Bushuev [10], using a Guinier FR-552 focusing camera-monochromator, 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 "a_o" and "c_o" of the unit cell was determined.

According to the obtained "a_o" values, phosphorites are arranged in increasing order: the 1st group includes nodular phosphorites, the 2nd group includes granular phosphorites, the 3rd group contains shell phosphorites, and the 4th group includes apatites. 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 crystals, the greater their interaction with soil solutions, therefore, the higher the agrochemical efficiency [10]. Therefore, nodular phosphorites can be directly used as fertilizer in the form of milled powder.

The use of finely ground phosphorite as a direct fertilizer, without any chemical processing, would provide agriculture with the cheapest phosphorate fertilizer [11].

Yet phosphate rock is successfully used in large quantities on acidic soils [12], but it is ineffective on neutral and alkaline soils of Uzbekistan.

In this a case, it is necessary to use the so-called mechanochemical activation, when the transfer of the P_2O_5 form, indigestible for plants, in the raw material into an assimilable form is carried out mechanically in the presence of any chemical reagents [13].

This ensures increased citrate solubility of the phosphate mineral.

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

The acceptability of superphosphate can be listed in the following circumstances: availability of raw materials for its production, including low-grade natural phosphorites; the relatively low consumption of sulfuric acid makes it possible to obtain fertilizer with the lowest cost per unit of P_2O_5 compared to all other conventional methods; simplicity of its production technology and absence of waste; low capital investment; low energy intensity of production and low cost of products; can be used in conjunction with organic composts; the fertilizer has a slow release effect, which can fertilize it 1-2 times in one season; the product range includes fertilizers with various microadditives: manganese, zinc, boron, magnesium, calcium; can be approached ideality for household plots, the best results are achieved when growing potatoes, vegetables, fruits and berries and flowers.

In this regard, the development and implementation of a rational and economical technical solution that ensures the processing of poor phosphate raw materials and reducing acid consumption is an urgent task.

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

MATERIALS AND METHODS

Phosphorite powder (flour-likely) of the Khodzhakul deposit (upper layer) of composition (wt. %): P_2O_5 – 19.11; $P_2O_{5acceptable}$. for citric acid: P_2O_{5total}. = = 63.26; $P_2O_{5acceptable}$. according to 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 shows that its dispersion 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%.

Chemical analysis of phosphate rock for the content of various forms of components was carried out according to known methods [14].

To roughly determine the mineralogical composition of the powder, its X-ray diffraction pattern was taken using an XRD-6100 diffractometer (Shimadzu, made in Japan). CuKα radiation was used (β-filter, Ni, tube current and voltage mode 30 mA, 30 kV) and a constant detector rotation speed of 4 deg/min, and the scanning angle varied from 4 to 80°. Identification of mineral phases was carried out using the 2013 International Center for Diffraction Data database.

RESULTS AND DISCUSSION

Mineralogical properties of nodular phosphorite powder of Khodjakul

An X-ray diffraction (XRD) of nodular phosphorite powder from the Khudzhakul deposit is shown in Fig. 1.

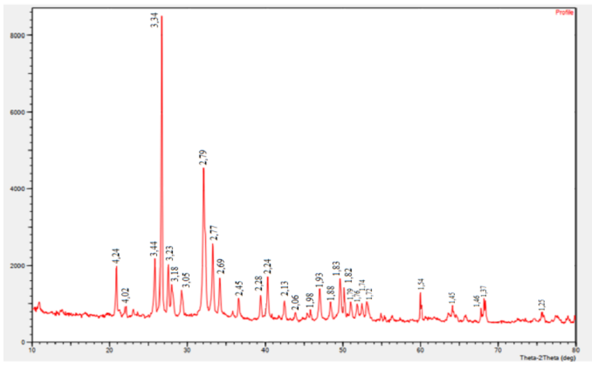

Fig. 1. XRD of phosphorite powder of Khodjakul

Diffraction bands 1.72; 1.74; 1.79; 1.83; 1.93; 2.24; 2.62; 2.69; 2.77; 2.79; 3.18; 3.44 Å belong to fluorocarbonate apatite. Interplanar distances 1.88; 2.28; 3.05 Å characterizes calcite. Stripes 1.37; 1.54; 4.02 Å belong to dolomite. The most intense peaks are 1.82; 1.98; 2.13; 2.45; 3.23; 3.34; 4.24 Å indicates the presence of a large amount of silicon oxide in the phosphate raw material. Bands 1.37 and 1.93 Å belong to calcium fluoride, and 2.06; 2.45 and 3.23 Å can be attributed to calcium silicates.

Images of the nodular powders were obtained using an Evo MA10 scanning electron microscope (SEM) (Zeiss, DE). As seen from Fig. 2, there is an image of a powder in the sample, where particles of various sizes are visible (on a scale of 50 µm). Using a microscope and an energy dispersive analyzer (Inca, Oxford Instruments, UK) (EDX analysis), the elemental composition of this sample was simultaneously determined.

In addition, the microstructure and elemental composition observed at 50-fold magnification of the studied sample of phosphate rock from the Khodzhakul deposit are shown in Fig. 2.

From the microstructure and elemental composition of phosphorite powder, recalculated in terms of the oxides, it follows that its main components are oxides of calcium (CaO), phosphorus (P_2O_5), silicon

(SiO_2), aluminum (Al_2O_3), iron (Fe_2O_3), potassium (K_2O) and sodium (Na_2O).

As can be seen from Fig. 2, Khodjakul phosphate rock is characterized by fine-grained minerals. Here, the phosphate component of the ore - square minerals, expressed in gray color - is represented by inclusions of siliceous minerals, irregular fragmentary hexahedrons and colorless rhombic crystals. Siliceous components are characterized by a predominance of phosphated silicates.

Based on the results of chemical analysis, the mineral composition of the raw materials was calculated by radiography and scanning electron microscope.

The content of phosphorus and fluorine in the sample confirms that the Khodjakul phosphate rock is represented by francolite and kurskite:

In francolite $\frac{F}{P2O5} = \frac{3.44}{37.14} = 0.09262$ and in kurskite $\frac{F}{P2O5} = \frac{3.85}{34.52} = 0.11152$

In our case it was revealed as:

$\frac{F}{P2O5} = \frac{2.09}{19.11} = 0.10936.$

The following are calculations in terms of the mineral components of phosphate with taking account some additions to the differences in values for the content of components. This means that the calculation was performed for 100g of phosphorite powder.

The chemical formula of kurskite and francolite in phosphorite powder is as follows:

$$Ca_{10}P_{4.8}C_{1.2}O_{22.8}F_2(OH)_{1.2(kursite)} +$$
$$+ Ca_{10}P_{5.2}C_{0.8}O_{23.2}F_{1.8}OH_{(francolite)} \rightarrow$$
$$\rightarrow 5P_2O_5 + 18.1CaO + 2CO_2 + 1.9CaF_2 + 1.1H_2O$$

$$m(\text{kurskite + francolite}) = \frac{19.11 \cdot 1979{,}6}{5 \cdot 142} = 53.2819 \text{ g}$$

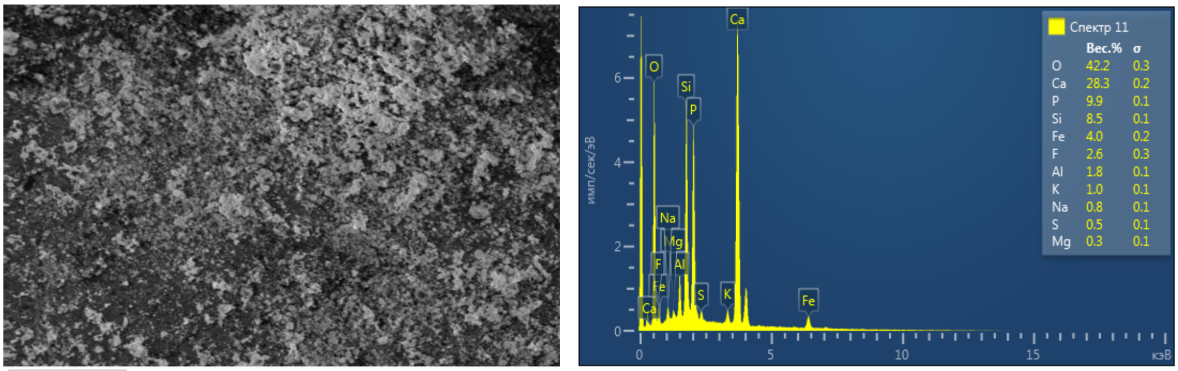

Fig 2. Microstructure and elemental composition of Khodjakul phosphate rock, obtained at 50 times magnification

Distribution of components over kurskite and francolite in phosphorite powder.

First in terms of P_2O_5 CaO content. F and CO_2 in phosphorite powder, the amount of francolite and kurskite is calculated:

in francolite:

$$\underset{m_1}{\underset{993.2\text{ g/mol}}{Ca_{10}P_{5.2}C_{0.8}O_{23.2}F_{1.8}OH}} \rightarrow \underset{x}{\underset{369.2\text{ g/mol}}{2.6P_2O_5}} +$$

$$+ 9.1CaO + 0.8CO_2 + 0.9CaF_2 + 0.5H_2O$$

in kursite:

$$\underset{m_2}{\underset{986.4\text{ g/mole}}{Ca_{10}P_{4.8}C_{1.2}O_{22.8}F_2(OH)_{1.2}}} \rightarrow \underset{19.11-x}{\underset{340.8\text{ g/mol}}{2.4P_2O_5}} +$$

$$+ 9CaO + 1.2CO_2 + CaF_2 + 0.6H_2O$$

$$\begin{cases} x = \frac{2.6 \cdot 142 \cdot m_1}{993.2} = 0.3714 m_1 \\ 19.11 - x = \frac{2.4 \cdot 142 \cdot m_2}{986.4} = 0.3455 m_2 \\ 19.11 - 0.3714m_1 = 0.3455m_2 \end{cases}$$

In this case, the total mass of francolite and kurskite:

$m_1 = 53.28\text{g} - y$

$m_2 = y$

$19.11 - 0.3714 \cdot (53.28 - y) = 0.3455y$

$19.11 - 19.7882 + 0.3714y = 0.3455y$

$- 0.6782 = 0.3455y - 0.3714y$

$- 0.6782 = - 0.0259y$

$y = 26.1853$

$m_2 = y = 25.89$ (kurskite)

$m_1 = 53.28 - 26.1853 = 27.0947$ (francolite)

$$x = \frac{2.6 \cdot 142 \cdot m_1}{993.2} = 0.3714 m_1 =$$
$$= 0.3714 \cdot 27.0947 = 10.07 \ \ (P_2O_5 \text{ francolite})$$

$19.11 - x = 19.11 - 10.0718 = 9.04$ (P_2O_5 kurskite)

CaO, CO_2 and F in the composition of francolite were determined as follows:

$$Ca_{10}P_{5.2}C_{0.8}O_{23.2}F_{1.8}OH \rightarrow$$
$$\rightarrow \underset{2.6\cdot142}{2.6P_2O_5} + \underset{9.1\cdot56}{9.1CaO} + \underset{0.8\cdot44}{0.8CO_2} + \underset{0.9\cdot78}{0.9CaF_2} + 0.5H_2O$$

$$m(CaO) = \frac{10.07 \cdot 9.1 \cdot 56}{2.6 \cdot 142} = 13.90g$$

$$m(CO_2) = \frac{10.07 \cdot 0.8 \cdot 44}{2.6 \cdot 142} = 0.96g$$

$$m(CaF_2) = \frac{10.07 \cdot 0.9 \cdot 78}{2.6 \cdot 142} = 1.91g$$

$0.9CaF_2 \rightarrow 0.9CaO + 1.8F$

0.9·78 0.9·56 1.8·19

$$m(CaO) = \frac{1.91 \cdot 0.9 \cdot 56}{0.9 \cdot 78} = 1.37g$$

$$m(F_2) = \frac{1.91 \cdot 1.8 \cdot 19}{0.9 \cdot 78} = 0.93g$$

CaO, CO_2 and F in the composition of kurskite were determined as follows:

$Ca_{10}P_{4.8}C_{1.2}O_{22.8}F_2(OH)_{1.2} \rightarrow$

$\rightarrow 2.4P_2O_5 + 9CaO + 1.2CO_2 + CaF_2 + 0.6H_2O$

2.4·142 9·56 1.2·44 78

$$m(CaO) = \frac{9.04 \cdot 9 \cdot 56}{2.4 \cdot 142} = 13.37g$$

$$m(CO_2) = \frac{9.04 \cdot 1.2 \cdot 44}{2.4 \cdot 142} = 1.40\ g$$

$$m(CaF_2) = \frac{9.04 \cdot 78}{2.4 \cdot 142} = 2.07\ g$$

$CaF_2 \rightarrow CaO + 2F$

56 2·19

$$m(CaO) = \frac{2.07 \cdot 56}{78} = 1.49\ g$$

$$m(F) = \frac{2.07 \cdot 2 \cdot 19}{78} = 1.01\ g$$

The stoichiometric amount of fluorine in phosphorite powder is 2.09%.

2.09 – m(F^- francolite) - m(F^- kurskite)=m(CaF_2).

This means that 2.09-0.93-1.01 = 0.15 g of fluorine will be bound in the form of CaF_2

$CaF_2 \rightarrow CaO + 2F^-$

fluorite 56 2·19

$$m(\text{fluorite}) = \frac{0{,}15 \cdot 78}{2 \cdot 19} = 0{,}31\ \text{г}$$

$$m(CaO) = \frac{0{,}15 \cdot 56}{2 \cdot 19} = 0{,}22\ \text{г}$$

Phosphorite powder contains dolomite:

$CaCO_3 \cdot MgCO_3 \rightarrow MgO + CaO + 2CO_2$

dolomite 0.15 0.21 0.33

$$m(dolomite) = \frac{0.15 \cdot 184}{40} = 0.69\ g$$

$$m(CaO) = \frac{0.15 \cdot 56}{40} = 0.21\ g$$

$$m(CO_2) = \frac{0.15 \cdot 2 \cdot 44}{40} = 0.33\ g$$

The stoichiometric amount of CO_2 in phosphorite is 4.03%.

$m(CO_2)$=4.03 - $m(CO_2)_{francolite}$ -

- $m(CO_2)_{kurskite}$ - $m(CO_2)_{dolomite}$

$m(CO_2)$ = 4.03-0.96-1.40-0.33 = 1.34 g

$CaCO_3 \rightarrow CaO + CO_2$

calcite 1.705 1.34

$$m(calcite) = \frac{1.34 \cdot 100}{44} = 3.44\ g$$

$$m(CaO) = \frac{1.34 \cdot 56}{44} = 1.705\ g$$

$CaSO_4 \cdot 2H_2O \rightarrow CaO + SO_3 + 2H_2O$

gypsum 0.30 0.53

$$m(gypsum) = \frac{0.53 \cdot 172}{80} = 1.14\ g$$

$$m(CaO) = \frac{0.53 \cdot 56}{40} = 0.371\ g$$

$2FeS_2 \rightarrow Fe_2O_3 \cdot 4SO_3$

pyrite 0.66 0.33

$$m(pyrite) = \frac{0.33 \cdot 2 \cdot 120}{80} = 0.99\ g$$

$$m(Fe_2O_3) = \frac{0.33 \cdot 160}{80} = 0.66\ g$$

$2Fe(OH)_3 \cdot Fe_2O_3 \rightarrow 3Fe_2O_3 + 3H_2O$

limonite 1.79

$$m(limonite) = \frac{1.79 \cdot 2 \cdot 267}{3 \cdot 160} = 1.99\ g$$

$2FeO(OH) \rightarrow Fe_2O_3 + H_2O$

goethite 0.49

$$m(goethite) = \frac{0.49 \cdot 2 \cdot 89}{160} = 0.545\ g$$

The amount of glauconite in phosmuc was found:

$(Na_2O + MgO)\ Fe_2O_3 \cdot 4SiO_2 \cdot 2H_2O \rightarrow$

$\rightarrow Na_2O + MgO + Fe_2O_3 + 4SiO_2 + 2H_2O$

0.22 0.14 0.56

$$m(MgO) = \frac{0.56 \cdot 40}{160} = 0.14\ g$$

$$m(Na_2O) = \frac{0.56 \cdot 62}{160} = 0.14\ g$$

$$m(SiO_2) = \frac{0.56 \cdot 4 \cdot 60}{160} = 0.84\ g$$

$(Na_2O + CaO)\ Al_2O_3 \cdot 4SiO_2 \cdot 2H_2O \rightarrow$

$\rightarrow Na_2O + CaO + Al_2O_3 + 4SiO_2 + 2H_2O$

$$m((Na_2O + CaO)Al_2O_3 \cdot 4SiO_2 \cdot 2H_2O) = \frac{0.195 \cdot 496}{56} = 1.73\ g$$

$$m(Al_2O_3) = \frac{0.195 \cdot 102}{56} = 0.355\ g$$

$$m(Na_2O) = \frac{0.195 \cdot 62}{56} = 0.2158\ g$$

$$m(SiO_2) = \frac{0.195 \cdot 4 \cdot 60}{56} = 0.8357\ g$$

The amount of feldspar in phosphorite powder was found:

$$2(Na, K)\ AlSi_3O_8 \rightarrow$$
$$\rightarrow K_2O + Na_2O + Al_2O_3 + 6SiO_2$$

$$m((Na, K)AlSi_3O_8) = \frac{0.16 \cdot 2 \cdot 262}{162} = 0.82\ g$$

$$m(K_2O) = \frac{0.16 \cdot 94}{102} = 0.15\ g$$

$$m(Na_2O) = \frac{0.16 \cdot 62}{102} = 0.097\ g$$

$$m(SiO_2) = \frac{0.16 \cdot 6 \cdot 60}{102} = 0.56\ g$$

The amount of mica (or hydromica) in phosphorite powder was found:

$$(OH)_4K_2(Si_6Al_2)Al_4O_{20} \rightarrow$$
$$\rightarrow K_2O + 3Al_2O_3 + 6SiO_2 + 2H_2O$$
$$1.025$$

$$m(\text{слюда}) = \frac{1.025 \cdot 796}{3 \cdot 102} = 2.66\ g$$

$$m(K_2O) = \frac{1.025 \cdot 94}{3 \cdot 102} = 0.314\ g$$

$$m(SiO_2) = \frac{1.025 \cdot 6 \cdot 60}{3 \cdot 102} = 1.206\ g$$

The amount of magnesium silicate was found:

$$Mg_2SiO_4 \rightarrow 2MgO + SiO_2$$
$$0.01$$

$$m(Mg_2SiO_4) = \frac{0.01 \cdot 140}{2 \cdot 40} = 0.0175\ g$$

$$m(SiO_2) = \frac{0.01 \cdot 60}{2 \cdot 40} = 0.0075\ g$$

The amount of gallite in phosphorite powder was found:

$$2NaCl \rightarrow Na_2O + 2Cl$$
$$0.01$$

$$m(gallite) = \frac{0.01 \cdot 2 \cdot 585}{2 \cdot 35.5} = 0.016\ g$$

$$m(Na_2O) = \frac{0.01 \cdot 62}{2 \cdot 35.5} = 0.0087\ g$$

Thus, the main phosphate minerals of nodular phosphorite are kurskite and francolite. It is quite suitable as a phosphate raw material for the production of simple superphosphate intended for local use [15, 16].

To study the process of obtaining simple superphosphate, the total consumption of sulfuric acid for processing 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.

Based on the data obtained, Table 1 was compiled, reflecting the mineralogical composition of the nodular phosphorite powder of Khodjakul.

Thus, this raw material belongs to the nodular type, the main minerals of which are kurskite and francolite in almost equal quantities. It is quite possible to obtain simple superphosphate from it for topical use.

Table 1

Mineralogical composition of phosphate ore Khodjakul

Mineral components of raw materials	Quantity, wt.%	Mineral components of raw materials	Quantity, wt.%
$Ca_{10}P_{5.2}C_{0.8}O_{23.2}F_{1.8}OH$ (francolite)	27.09	$(K,H_2O)(Fe^{3+},Fe^{2+},Mg)_2[Si_3A1O_{10}]xH_2O$ (glauconite)	3.61
$Ca_{10}P_{4.8}C_{1.2}O_{22.8}F_2(OH)_{1.2}$ (kurskite)	25.89	CaF_2 (field spar)	0.82
CaF_2 (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	Organic matter	0.04
$Fe_2O_3 \cdot nH_2O$ (limonite)	1.99	Insoluble residue	1.64
FeO(OH) (goethite)	0.55	H_2O	1.20

Calculation of the rate of sulfuric acid to obtain simple superphosphate.

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:

$$2Ca_5(PO_4)_3F + 7H_2SO_4 + 6.5H_2O =$$
$$= 3Ca(H_2PO_4)_2{\cdot}H_2O + 7CaSO_4{\cdot}0.5H_2O + HF$$

The consumption of sulfuric acid for the decomposition of calcium oxide of phosphate raw materials with the formation of monocalcium phosphate was calculated:

$$CaO + P_2O_5 \rightarrow Ca(H_2PO_4)_2$$
$$\mathrm{m(CaO)} = \frac{19.11 \cdot 56}{142} = 7.5363\text{г}$$

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

$$CaO + SO_3 \rightarrow CaSO_4$$
$$\mathrm{m(CaO)} = \frac{1.10 \cdot 56}{80} = 0.77\text{ g}$$

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 available for acid decomposition is:

$$32.83 – 7.5363 -0.77 = 24.5237\text{ g}$$

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

$$CaO + H_2SO_4 \rightarrow CaSO_4 + H_2O$$
$$\mathrm{m(H_2SO_4)} = \frac{24.5237 \cdot 98}{56} = 42.9164\text{ g}$$

where, 56 – M(CaO), g/mol; 98 – M(H_2SO_4), g/mol.

To decompose magnesium oxide, the amount of acid consumed:

$$MgO + H_2SO_4 \rightarrow MgSO_4 + H_2O$$
$$\mathrm{m(MgO)} = \frac{0.3 \cdot 98}{40} = 0.735\text{ g}$$

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.

Sulfuric acid is used to decompose sesquioxides:

$$Al_2O_3 + 3H_2SO_4 \rightarrow Al_2(SO_4)_3 + 3H_2O$$
$$\mathrm{m(H_2SO_4)} = \frac{1.54 \cdot 3 \cdot 98}{102} = 4.4388\text{ g}$$

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

$$Fe_2O_3 + 3H_2SO_4 \rightarrow Fe_2(SO_4)_3 + 3H_2O$$
$$\mathrm{m(H_2SO_4)} = \frac{3.50 \cdot 3 \cdot 98}{160} = 6.43125\text{ g}$$

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 with the formation of monocalcium phosphate and gypsum in the presence of impurity compounds (100% H_2SO_4 consumption norm):

$$\mathrm{m(H_2SO_4)} = 42.9164 + 0.735 + 4.4388 +$$
$$+ 6.43125 = 54.52145\text{ g}$$

or in terms of 93% concentration of H_2SO_4:

$$\mathrm{m(H_2SO_4)} = \frac{54.52145}{0.93} = 58.6252\text{ g}$$

The process of obtaining simple superphosphate.

Further, the process of obtaining simple superphosphate was studied. The procedure for carrying out the process of decomposing phosphate raw materials with sulfuric acid and obtaining the finished product was as follows: the calculated amount of 93% sulfuric acid was slowly poured into a thermostated glass beaker, in which there was a sample of phosphate, at its rates of 60 to 100% of the stoichiometry for the formation of monocalcium phosphate.

The mixture was thoroughly mixed. The duration of contact between the components of the reaction mass was 30 min at a temperature of 70 °C. Then the resulting mass together with the glass was placed in a drying cabinet, in which it was dried at 90-100 °C until constant weight.

Chemical analysis of the products for the content of various forms of P_2O_5 and CaO was carried out according to known methods [14]. P_2O_{5free} content was determined by titration with 0.1 N NaOH using the indicators methyl orange and phenolphthalein. The digestible form of P_2O_5 was determined by solubility in both 2% citric acid and 0.2 M solution of Trilon B. The acceptable form of CaO was determined only by 2% citric acid. The pH of the product was determined after shaking its 10% aqueous suspension for an hour. The results are shown in Table. 2.

Table 2

Composition of products obtained by sulfuric acid decomposition of Khodjakul nodule phosphorite powder

Consumption norm of H_2SO_4, %	Component content, weight. %						
	P_2O_{5free}	P_2O_{5total}	$P_2O_{5accep.}$ by citric acid	$P_2O_{5accep.}$ by EDTA	P_2O_{5water}	CaO_{total}	$CaO_{accep.}$ by citric acid
1	2	3	4	5	6	7	8
50	0.29	16.08	14.09	9.67	6.81	28.70	18.92
60	0.91	15.42	14.55	10.33	7.74	27.82	18.28

Продолжение таблицы

70	1.48	14.67	14.36	10.48	9.00	25.72	17.52
75	2.95	14.31	14.09	10.35	9.39	24.58	16.78
80	3.46	14.14	13.98	10.37	9.91	23.97	16.35
90	4.68	13.61	13.48	10.45	10.30	23.38	15.93
100	6.60	13.08	12.99	10.14	9.99	22.47	15.28

Table 2 shows that with an increase in the consumption norm of sulfuric acid in products, the content of the total form of 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. Acceptable forms of P_2O_5 and CaO indicate the presence of dicalcium phosphate in products. The relative content of the acceptable form of P_2O_5 is less than 100%, indicating that a certain amount of non-decomposed phosphate mineral remains in the composition of the products.

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 has to be at least 50% of the total form of P_2O_5. We consider the optimal acid consumption norm for processing phosphate rock to be 70% of the stoichiometric rate for the formation of monocalcium phosphate, since it is at this norm that the relative content of the water-soluble P_2O_5 in products exceeds 50% (Fig. 3).

In this case, the product contains P_2O_{5free} – 1.48; P_2O_{5total} – 14.67%; $P_2O_{5accep.}$ by citric acid – 14.36%; $P_2O_{5accep.}$ by Trilon B – 10.48%; $P_2O_{5water.}$ – 9.0%; CaO_{total} – 25.72%; $CaO_{accep.}$ – 17.52; pH – 2.29 (Table 2). At the same time, $P_2O_{5accep.}$ by citric acid: P_2O_{5total} = = 97.88%; $P_2O_{5accep.}$ by trilon B: P_2O_{5total} = 71.44%; $P_2O_{5water.}$: P_2O_{5total} = 61.35% (Fig. 3).

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

To ensure the identification of the composition of superphosphate fertilizers, XRD methods were used.

In Fig. 4 it is shown an XRD pattern of the product obtained from the decomposition of phosphorite powder with 75% sulfuric acid. Obviously, that the main components of simple superphosphate are monocalcium phosphate, characterized by diffraction maxima of 3.01, 2.86, 2.69, 2.09, 1.75, 1.55Å, dihydrate dicalcium phosphate, having diffraction minima of 3.75, 2.47, 2.25, 2.17, 1.94, 1.87, 1.82 Å, anhydrous dicalcium phosphate with diffraction maxima of 2.20 AO, calcium sulfate dihydrate with diffraction maxima of 3.80, 2.22, 2.14, 1.99 Å, and calcium sulfate hemihydrate with a diffraction maximum of 2.77 Å.

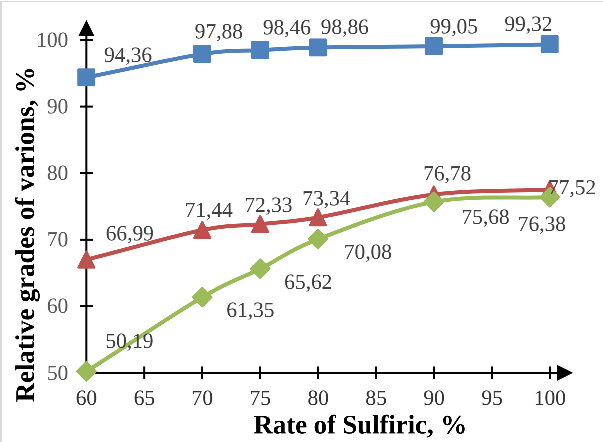

Fig. 3. Relative contents of acceptable and water-soluble forms of P_2O_5 via consumption norm of sulfuric acid

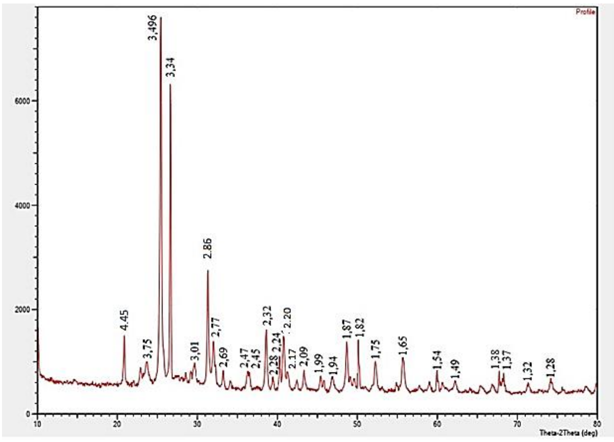

Fig. 4. XRD pattern of products obtained by sulfuric acid decomposition of Khodjakul nodule phosphorite

Study of the granulation process of simple superphosphate obtained from Khodjakul nodule phosphate.

It is known from practice that phosphoric acid from granulated superphosphate is used by plants more fully than from powdered fertilizer, and most importantly, it imparts a long-lasting effect to the product. Granules have a smaller bulk volume compared to the same volume of powder, which makes them more stable both physically and chemically. The structure of the granules ensures a lower level of hardening.

The process of obtaining activated simple superphosphate for local use depending on the concentration (68-93% H_2SO_4) and the rate of sulfuric acid (60-100% of the stoichiometry for the monocalcium phosphate formation) was studied [15, 16]. The optimal acid concentration turned out to be 93%, allowing the formation of a superphosphate mass that can be easily supplied for granulation process. The optimal consumption norm of sulfuric acid can be taken as 70-75%, at which the relative content of the water-soluble P_2O_5 in products exceeds 60% (must be at least 50%), and the content of P_2O_{5free} no more than 2-3%. Such as fertilizer is quite suitable as a single fertilizer for application under fallow soil.

Granulation is a complex technological process and is characterized by many factors - physical and chemical properties, cohesive-adhesive abilities and others [17-22]. To decompose phosphate raw materials, 93% sulfuric acid was used. The procedure for carrying out the process of decomposition of phosphate raw materials and obtaining granulated simple superphosphate was as follows: the calculated amount of sulfuric acid was slowly poured into a thermostated glass beaker containing a sample of phosphorite. In this case, the variable parameter was the acid consumption norm (from 60 to 75% of the stoichiometry for the monocalcium phosphate formation). The mixture was thoroughly mixed. The stirring duration time of the reaction mass was 30 min at 70 °C. Granulation of the product was carried out using the method of intensive balling. In order to impart granulation and sufficient strength to the granules, we have studied the process of granulation of powdered simple superphosphate by spraying them with a spray bottle to a certain amount of binding solutions (indicated below), allowing the formation of a dough-like superphosphate mass that is easily supplied for granulation.

The following were used as binding reagents: 25% NH_4OH (State standard 9-92), $(NH_4)_2SO_4$ (State standard 9097-82) $NH_4H_2PO_4$ (State standard 3771-74). Aqueous solutions of various concentrations were prepared from them (for NH_4OH, $(NH_4)_2SO_4$, $NH_4H_2PO_4$ - 5; 10; 15; 20; 25%).

When superphosphate powder is treated with binding solutions of the above substances, the following reactions occur:

$$Ca(H_2PO_4)_2 + NH_4OH =$$
$$= CaHPO_4 + (NH_4)_2HPO_4 + H_2O$$
$$Ca(H_2PO_4)_2 + (NH_4)_2SO_4 + H_2O =$$
$$= CaSO_4 + 2NH_4H_2PO_4$$
$$Ca(H_2PO_4)_2 + NH_4H_2PO_4 = CaHPO_4 + (NH_4)_2HPO_4$$

The new compounds formed in this case should contribute to the formation of granules and obtain sufficiently strong granules of the product. Depending on the degree of granule formation, the granulation process time ranged from 5 to 10 min.

The concentration of binding solutions NH_4OH, $(NH_4)_2SO_4$ and $NH_4H_2PO_4$ varied from 2 to 25%. In this case, moist round-shaped particles were formed. The mass of granular particles was dried at 100°C. The result was fairly strong granules, which were cooled and then classified according to size. The particle size distribution of the product was determined by sieve analysis. Particles measuring 3-4 mm were analyzed for the strength of granules according to State standard 21560.2-82. Chemical analysis of the products was carried out according to known methods [14]. The results on the chemical and granulometric compositions, as well as the strength of product granules are given in Table 3 and in Fig. 4.

Using the method of chemical analysis, the chemical composition and granulometric samples of simple superphosphate were compared, without treatment and with treatment with binding solutions. So, if in an unprocessed product with a norm of H_2SO_4 - 75% the content of P_2O_{5total}, P_2O_{5free}, $P_2O_{5accep.}$: P_2O_{5total}, $P_2O_{5water.}$: P_2O_{5total} are 14.31, 2.95, 98.46, 65.62, then with an increase in the concentration of binding solutions for NH_4OH (from 5 to 25%), these indicators vary from 13.10 to 13.95, 2.50 to 2.72, from 95.05 to 99.08, from 58.42 to 69.16%, for $(NH_4)_2SO_4$ (from 2 to 20%) from 13.67 to 14.04, from 2.98 to 3.98, from 92.52 to 97.51, from 64.39 to 67.37% and for $NH_4H_2PO_4$ (from 2 to 20%) from 14.21 to 15.29, from 1.36 to 1.72, from 96.97 to 99.22, from 64.11 to 65.27%, respectively (Table 3).

During the granulation process of acidic superphosphate (pH about 3), the binders, being in the liquid phase, bind small particles of superphosphate, thereby ensuring maximum granulation of the finished product. For example, the yield of the commercial fraction (-5+1 mm) of the original superphosphate without a binding additive is ~15 and ~20%. And when using 5-20% solutions of NH_4OH, this figure is 91.56-95.38 and 91.36-94.18%, $(NH_4)_2SO_4$ - 93.85-96.44 and 94.16-96.11%, $NH_4H_2PO_4$ - 95.52-97.14 and 94.32-96.78%, respectively for H_2SO_4 – 60 and 75% of stoichiometry norm (Table 3).

An increase in salt concentration leads to a decrease in the degree of granule formation, although only slightly. Yet, most importantly, binding solutions ensure the production of granules whose strength meets the requirements of State standard 5956-78 (must be at least 1.4 MPa).

Relatively strong granules were obtained as a sulfuric acid norm of 60%. In regards in the optimal norm of H_2SO_4 - 75% (with a relative content of the water-soluble form of P_2O_5 more than 60%), the strength of simple superphosphate granules for solutions of NH_4OH, $(NH_4)_2SO_4$, and $NH_4H_2PO_4$ reaches 2.18-2.45, 1.35-2.12 and 1.09- 1.95 MPa, respectively (Fig. 5).

The proposed method of granulating superphosphate powder makes it possible to ensure a commercial product yield of up to 92-98%, while simultaneously increasing the strength of the granules by more than 2 MPa. The method used makes it possible to reduce dust in the production of simple superphosphate and improve environmental protection in workplaces.

Thus, the results of laboratory studies convincingly indicate the possibility of obtaining activated simple superphosphate, bypassing the stages of ripening and ammonization. The proposed method will reduce the consumption norm of sulfuric acid to produce 1 ton of P_2O_5 compared to simple ammoniated superphosphate by 30-40%.

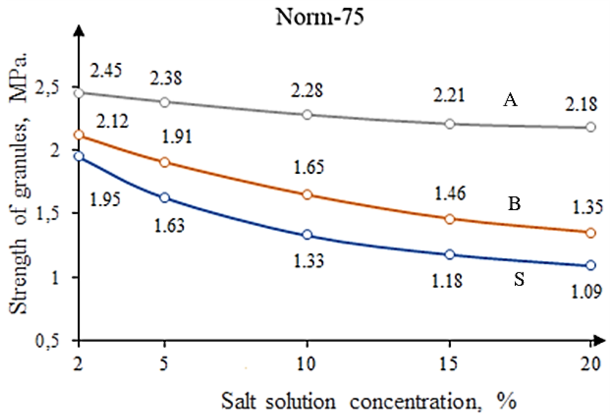

Fig. 5. The strength of activated simple superphosphate granules and treated using A - NH_4OH; B - $(NH_4)_2SO_4$; S - $NH_4H_2PO_4$ Solutions

Table 3

Chemical granulometric composition of samples of simple superphosphate treated with solutions of ammonia, sulfate and ammonium phosphate (Sulfuric acid consumption norm - 75%)

Salt concentration %	The amount of salt solution in relation to 100 g of product,	P_2O_{5total}, %	P_2O_{5free}, %	$P_2O_{5accep.}/P_2O_{5total}$, %	$P_2O_{5water.}/P_2O_{5total}$, %	Yield of granule fraction, % +5+1 mm	Yield of granule fraction, % -1 mm
Without binding solution		14.31	2.95	98.46	65.62	~20	~80
NH_4OH							
5	6.52	13.10	2.72	99.08	69.16	94.18	5.82
10	6.03	13.19	2.64	98.94	67.25	93.52	6.48
15	5.41	13.28	2.55	98.80	65.36	92.78	7.22
20	5.10	13.62	2.53	96.84	61.82	92.06	7.94
25	4.80	13.95	2.50	95.05	58.42	91.36	8.64
$(NH_4)_2SO_4$							
2	5.95	14.04	2.98	92.52	64.39	96.11	3.89
5	5.72	13.98	3.91	93.56	64.95	95.78	4.22
10	5.24	13.86	3.93	95.09	65.87	95.13	4.87
15	4.90	13.75	3.96	96.36	66.69	94.80	5.20
20	4.60	13.67	3.98	97.51	67.37	94.16	5.84
$NH_4H_2PO_4$							
2	4.04	14.21	1.36	96.97	64.11	96.78	3.22
5	5.48	14.44	1.51	97.30	64.47	96.05	3.95
10	4.16	14.78	1.65	98.03	64.61	95.63	4.37
15	6.12	15.03	1.68	98.74	64.94	95.09	4.91
20	5.09	15.29	1.72	99.22	65.27	94.32	5.68

CONCLUSION

The mineral composition of the nodular phosphorite flour of Karakalpakstan was determined using chemical and XRD analysis methods. The results show that the main phosphate minerals of the raw materials are kurskite and francolite, and calcite, dolomite, glauconite, wollastonite, gypsum, silicon, etc. are present as impurities.

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

The optimal norm of sulfuric acid for processing phosphate raw materials is considered to be 75% of the stoichiometry, since it is at this norm that the relative content of the water-soluble P_2O_5 in products exceeds 50%. In addition, at a relatively high acid rate, a fairly high content of H_3PO_4 free is obtained.

From 2 to 25% solutions of NH_4OH, $(NH_4)_2SO_4$ and $NH_4H_2PO_4$ were used to improve the process of granule formation of simple superphosphate. The granulometric compositions of the initial (untreated superphosphate) and the final product (treated with solutions of ammonium salts) were compared. The results show that the processing of powdered simple superphosphate makes it possible to obtain 100% friable granules of the finished product, a particle size distribution (1-4 mm - more than 92%, must be at least 85%) and a strength of at least 2 MPa.

The authors declare the absence a conflict of interest warranting disclosure in this article.

Авторы заявляют об отсутствии конфликта интересов, требующего раскрытия в данной статье.

ЛИТЕРАТУРА

1. *Курбаниязов Р.К., Худойбердиев Ж.Х., Реймов А.М., Намазон Ш.С., Раджапов Р., Сейтназаров А.Р.* Характеристика желваковых фосфоритов каракалпакстана и их переработка в гранулированный простой суперфосфат. Изв. вузов. Химия и хим. технология. 2025. Т. 68. Вып. 1. С. 109-119. DOI: 10.6060/ivkkt.20256801.7007.
2. *Темиров У.Ш., Намазов Ш.С., Усанбаев Н.Х.* Интенсивная технология переработки птичьего пометав органоминеральныеудобрения. Изв. вузов. Химия и хим. технология. 2020. Т. 63. Вып. 12. С. 85-94. DOI: 10.6060/ivkkt.20206312.6210.
3. *Xudoyberdiev J., Reymov A., Kurbaniyazov R., Namazov Sh., Badalova O., Seytnazarov A.* Mineral Composition of Nodular Phosphorite of Karakalpakstan and its Pro cessing into Simple Superphosphate. E3S Web Conf. Inter national Scientific and Practical Conference “Priority Direc tions of Complex Socio-Economic Development of the Region” (PDSED 2023). 2023, V. 449. P. 1-9. DOI: 10.1051/e3sconf/202344906005.
4. *Otaboev Kh.A., Sherkuziev D.Sh., Badalova O.A., Radjabov R., Namazov Sh.S., Seytnazarov A.R.* Mineralogical Compo sition of Kyzylkum Washed Dry Concentrate and Its Processing into Simple Superphosphate. Russ. J. Gen. Chem. 2022. V. 92. N 3. P. 505–517. DOI: 10.1134/S1070363222030203.
5. *Локшин Э.П., Тареева О.А., Седнева Т.А., Елизарова И.Р.* Получение фосфорной кислоты сорбционной кон версией апатитового концентрата с использованием сульфокатионита в натриевой или калиевой формах. Изв. вузов. Химия и хим. технология. 2020. Т. 63. Вып. 1. С. 78-85. DOI: 10.6060/ivkkt.20206301.5851.
6. *Ткачук В.А., Лютова Е.С., Бузаев А.А., Борило Л.П., Спивакова Л.Н.* Получение композитов TiO_2-SiO_2 P_2O_5/ZnO, исследование их свойств и возможностей при менения в качестве биоматериала. Изв. вузов. Химия и хим. технология. 2024. Т. 67. Вып. 5. С. 70-76. DOI: 10.6060/ivkkt.20246705.6953.
7. *Khurmamatov A.M., Auesbaev A.U., Ismaylov O.Y., Begzhanova G.B.* Effect of temperature on the physico-

REFERENCES

1. *Kurbaniyazov R.K., Khudoberdiev J.X., Reymov A.M., Namazov Sh.S., Radjapov R., Seytnazarov A.R.* Characteristics of nodular phosphorites of karakalpakstan and their processing into granular simple superphosphate. ChemChemTech [Izv. Vyssh. Uchebn. Zaved. Khim. Khim. Tekhnol.]. 2025. V. 68. N 1. P. 109-119. (in Russian). DOI: 10.6060/ivkkt.20256801.7007.
2. *Temirov U.Sh., Namazov Sh.S., Usanbayev N.Kh*. Intensive technology for processing bird litter in organomineral fertilizers. ChemChemTech [Izv. Vyssh. Uchebn. Zaved. Khim. Khim. Tekhnol.]. 2020. V. 63. N 12. P. 85-94 (in Russian). DOI: 10.6060/ivkkt.20206312.6210.
3. Xudoyberdiev J., Reymov A., Kurbaniyazov R., Nama zov Sh., Badalova O., Seytnazarov A. Mineral Composi tion of Nodular Phosphorite of Karakalpakstan and its Pro cessing into Simple Superphosphate. E3S Web Conf. In ternational Scientific and Practical Conference “Priority Directions of Complex Socio-Economic Development of the Region” (PDSED 2023). 2023, V. 449. P. 1-9. DOI: 10.1051/e3sconf/202344906005.
4. *Otaboev Kh.A., Sherkuziev D.Sh., Badalova O.A., Radjabov R., Namazov Sh.S., Seytnazarov A.R.* Mineralogical Compo sition of Kyzylkum Washed Dry Concentrate and Its Processing into Simple Superphosphate. Russ. J. Gen. Chem. 2022. V. 92. P. 505–517. DOI: 10.1134/S10703632 22030203.
5. *Lokshin E.P., Tareeva O.A., Sedneva T.A., Elizarova I.R.* Production of phosphoric acid by sorption conversion of ap atite concentrate using sulfocationite in sodium or potassium forms. ChemChemTech [Izv. Vyssh. Uchebn. Zaved. Khim. Khim. Tekhnol.]. 2020. V. 63. N 1. P. 78-85 (in Russian). DOI: 10.6060/ivkkt.20206301.5851.
6. *Tkachuk V.A., Lyutova E.S., Buzaev A.A., Borilo L.P., Spivakova L.N.* Preparation of TiO_2-SiO_2-P_2O_5/ZnO com posites, investigation of their properties and application pos sibilities as a biomaterial. ChemChemTech [Izv. Vyssh. Uchebn. Zaved. Khim. Khim. Tekhnol.]. 2024. V. 67. N 5. P. 70-76 (in Russian). DOI: 10.6060/ivkkt.20246705.6953.
7. *Khurmamatov A.M., Auesbaev A.U., Ismaylov O.Y., Begzhanova G.B.* Effect of temperature on the physico-

chemical properties of n-methyldiethanolamine. Process. Petrochem. OR. 2023. V. 24. N 1. P. 99-107.

8. *Karshiev B., Seytnazarov A., Alimov U., Reymov A., Rasulov A.* Purification of wet process phosphoric acid by desulfurization and ammonization. Vopr. Khim. Khim. Tekhnol. 2021. N 1. P. 24-34. DOI: 10.32434/0321-4095 2021-134-1-24-34.
9. *Otaboev Kh., Sherkuziev D., Namazov Sh., Radjabov R., Seytnazarov A.* Flow of simple superphosphate using two stage decomposition of phosphorite. IOP Conf. Ser.: Earth and Environ. Sci. 2021. V. 939. N 1. P. 012055. DOI: 10.1088/ 1755-1315/939/1/012055.
10. *Ismaylov O.Y., Khurmamatov A.M., Ismaylov M.K., Auesbaev A.U., Utegenov U.A.* Investigations of the impact of the magnetic field on the process of formation of scaling in thermal devices. Nafta-gaz. 2024. N 2. P. 115-121. DOI: 10.18668/NG.2024.02.07.
11. *Khurmamatov A.M., Auesbaev A.U.* Analysis of the oper ating mode of the existing desorber and its modernization using additional contact devices. Nafta-gaz. 2023. N 6. P. 412-419. DOI: 10.18668/NG.2023.06.05.
12. *Сейтназаров А.Р., Турдиалиев У.М., Намазов Ш.С., Беглов Б.М., Дехканов З.К., Курбаниязов Р.К.* Фосфоритовая мука – бескислотная форма фосфорных удобрений. Химический журнал Казахстана. 2017. Т.59. Вып. 3. С. 157-173.
13. *Seitnazarov A.R., Musaeva S.A., Namazov Sh.S.; Beglov B.M.* Mechanochemical activation of ordinary phosphorite powder of Central Kyzylkum mixed with urea nitrate and am mobium carbonate salts. Russ. J. Appl. Chem. 2007. V. 80. P. 1973–1976. DOI: 10.1134/S1070427207110432.
14. *Khurmamatov A.M., Yusupova N.K., Auesbaev A.U., Abdurakhimov S.S.* Results of a study on the treatment and separation of water from hydrocarbon waste. Process. Petrochem. OR. 2023. V. 24. N 3. P. 421-430. DOI: 10.36719/1726-4685/95/421-430.
15. *Худойбердиев Ж.Х., Реймов А.М., Курбаниязов Р.К., Намазов Ш.С., Каймакова Д.А., Сейтназаров А.Р.* Простой суперфосфат на основе сернокислотной активации желваковых фосфоритов Каракалпакстана. Химическая промышленность. 2021. Т.98. Вып. 4. С. 198-205.
16. *Худойбердиев Ж.Х., Реймов А.М., Курбаниязов Р.К., Намазов Ш.С., Бадалова О.А., Сейтназаров А.Р.* Активированной суперфосфат на основе желваковой фосфоритовой муки Каракалпакстана. Научный вестник ФерГУ. 2022. Вып. 2. С. 29-35. DOI: 10.56292/SJFSU/vol28_iss2/a45.
17. *Khurmamatov A.M., Matkarimov A.M., Auesbaev A.U., Utegenov U.A.* Results of experiments on studying the composition and purification of technical water of oil and gas processing plant. Process. Petrochem. OR. 2023. V. 24. N 4. P. 671-678. DOI: 10.36719/1726-4685/96/671-678.
18. *Otaboev Kh.A., Sherkuziev D.Sh., Badalova O.A., Radjabov R., Namazov Sh.S., Seytnazarov A.R.* Mineralogical Composition of Kyzylkum Washed Dry Concentrate and Its Processing into Simple Superphosphate // Russian Journal of General Chemistry volume, 2022, V. 92. P. 505–517. DOI: 10.1134/S1070363222030203.
19. *Самедов М.М., Мустафа-заде Д.М., Мамедова Г.М., Джавадова С.Г.* Исследование процесса получения су перфосфата разложением фторапатита серной кислотой в присутствии интенсифицирующих добавок. Вестн. Кузбас. Гос. техн. Ун-та. 2022. Т. 152. № 4. С. 23-32. DOI: 10.26730/1999-4125-2022-4-23-32.

chemical properties of n-methyldiethanolamine. Process. Petrochem. OR. 2023. V. 24. N 1. P. 99-107.

8. *Karshiev B., Seytnazarov A., Alimov U., Reymov A., Rasulov A.* Purification of wet process phosphoric acid by desulfurization and ammonization. Vopr. Khim. Khim. Tekhnol. 2021. N 1. P. 24-34. DOI: 10.32434/0321-4095 2021-134-1-24-34.
9. *Otaboev Kh., Sherkuziev D., Namazov Sh., Radjabov R., Seytnazarov A.* Flow of simple superphosphate using two stage decomposition of phosphorite. IOP Conf. Ser.: Earth and Environ. Sci. 2021. V. 939. N 1. P. 012055. DOI: 10.1088/1755-1315/939/1/012055.
10. *Ismaylov O.Y., Khurmamatov A.M., Ismaylov M.K., Auesbaev A.U., Utegenov U.A.* Investigations of the impact of the magnetic field on the process of formation of scaling in thermal devices. Nafta-gaz. 2024. N 2. P. 115-121. DOI: 10.18668/NG.2024.02.07.
11. *Khurmamatov A.M., Auesbaev A.U.* Analysis of the oper ating mode of the existing desorber and its modernization using additional contact devices. Nafta-gaz. 2023. N 6. P. 412-419. DOI: 10.18668/NG.2023.06.05.
12. *Seytnazarov A.R., Turdialiev U.M., Namazov Sh.S., Beglov B.M., Dekhkanov Z.K., Kurbaniyazov R.K.* Phosphorite flour is an acid-free form of phosphate fertilizers. Chemical Journal of Kazakhstan. 2017. V. 59. N. 3. P.157-173.
13. *Seitnazarov A.R., Musaeva S.A., Namazov Sh.S.; Beglov B.M.* Mechanochemical activation of ordinary phosphorite powder of Central Kyzylkum mixed with urea nitrate and am mobium carbonate salts. Russ. J. Appl. Chem. 2007. V. 80. P. 1973–1976. DOI: 10.1134/S1070427207110432.
14. *Khurmamatov A.M., Yusupova N.K., Auesbaev A.U., Abdurakhimov S.S.* Results of a study on the treatment and separation of water from hydrocarbon waste. Process. Petrochem. OR. 2023. V. 24. N 3. P. 421-430. DOI: 10.36719/1726-4685/95/421-430.
15. *Khudoiberdiev Zh.Kh., Reimov A.M., Kurbaniyazov R.K., Namazov Sh.S., Kaimakova D.A., Seitnazarov A.R.* Simple superphosphate based on sulfuric acid activation of nodule phosphorites of Karakalpakstan. Chemical industry. 2021. V.98. N. 4. P. 198-205.
16. *Khudoiberdiev Zh.Kh., Reymov A.M., Kurbaniyazov R.K., Namazov Sh.S., Badalova O.A., Seytnazarov A.R.* Activated superphosphate based on nodule phosphorite flour of Karakalpakstan. Scientific Bulletin of Ferguson State University. 2022. N. 2. P. 29-35. DOI: 10.56292/SJFSU/ vol28_iss2/a45
17. *Khurmamatov A.M., Matkarimov A.M., Auesbaev A.U., Utegenov U.A.* Results of experiments on studying the composition and purification of technical water of oil and gas processing plant. Process. Petrochem. OR. 2023. V. 24. N 4. P. 671-678. DOI: 10.36719/1726-4685/96/671-678.
18. *Otaboev Kh.A., Sherkuziev D.Sh., Badalova O.A., Radjabov R., Namazov Sh.S., Seytnazarov A.R.* Mineralogical Compo sition of Kyzylkum Washed Dry Concentrate and Its Processing into Simple Superphosphate. Russ. J. Gen. Chem. 2022. V. 92. N 3. P. 505–517. DOI: 10.1134/S1070363222030203.
19. *Samedov M.M., Mustafa-zade D.M., Mammadova G.M., Javadova S.G.* Study of the process of superphosphate pro duction by decomposition of fluorapatite with sulfuric acid in the presence of intensifying additives. Vestn. Kuzbas. Gos. Tekhn. Univ. 2022. V. 152. N 4. P. 23-32 (in Russian). DOI: 10.26730/1999-4125-2022-4-23-32.
20. *Kolpakov V.M., Norov A.M., Pagaleshkin D.A., Fedotov P.S., Kochetova I.M., Petropavlovskiy I.A.* Effect on de gree of

20. *Колпаков В.М., Норов А.М., Пагалешкин Д.А., Федотов П.С., Кочетова И.М., Петропавловский И.А.* Влияние степени нейтрализации фосфорной кислоты на свойства нитратсодержащих азотно-фосфорно-калийных удобрений. Изв. вузов. Химия и хим. технология. 2021. Т. 64. Вып. 3. С. 52-58. DOI: 10.6060/ivkkt.20216403.6289.
21. *Auesbaev A.U., Khurmamatov A.M., Ismaylov O.Y., Khametov Z.M.* Study of the thickness of the boundary layer of hydrocarbons in horizontal tubes of heat exchangers. Process. Petrochem. OR. 2024. V. 25. N 3. P. 931-941. https://doi.org/10.62972/1726-4685.2024.3.931.
22. *Shomansurov F.F, Auesbaev A.U., Ismaylov O.Y., Khurmamatov A.M., Khametov Z.M., Muminov J.A.* Optimization of the process of heating an oil and gas condensate mixture by light naphtha vapor in heat – exchanger condenser 10E04. Nafta-gaz. 2024. N. 8. P. 501-510. DOI: 10.18668/NG.2024.08.05.

phosphoric acid neutralization on properties of ni trate-containing nitrogen-phosphorus-potassium fertilizers. ChemChemTech [Izv. Vyssh. Uchebn. Zaved. Khim. Khim. Tekhnol.]. 2021. V. 64. N 3. P. 52-58 (in Russian). DOI: 10.6060/ivkkt.20216403.6289.

21. *Auesbaev A.U., Khurmamatov A.M., Ismaylov O.Y., Khametov Z.M.* Study of the thickness of the boundary layer of hydrocarbons in horizontal tubes of heat exchangers. Process. Petrochem. OR. 2024. V. 25. N. 3. P. 931-941. https://doi.org/10.62972/1726-4685.2024.3.931.
22. *Shomansurov F.F, Auesbaev A.U., Ismaylov O.Y., Khur-mamatov A.M., Khametov Z.M., Muminov J.A.* Optimization of the process of heating an oil and gas condensate mixture by light naphtha vapor in heat – exchanger condenser 10E04. Nafta-gaz. 2024. N. 8. P. 501-510. DOI: 10.18668/NG.2024.08.05.

Поступила в редакцию (Received) 12.02.2024
Принята к опубликованию (Accepted) 18.04.2024