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# Mineralogical Composition of Kyzylkum Washed Dry Concentrate and Its Processing into Simple Superphosphate

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**Abstract**—The various types of phosphate minerals of the apatite group have been analyzed. The phosphate substance of phosphorites except fluorapatite, can be represented by fluorocarbon apatite—francolite or kurskite. The highest phosphorus content is found in fluorapatite, and the lowest in kurskite. In terms of the unit cell parameters ($a_0$ = 9.33 Å), the phosphate mineral of granular phosphorites of the Kyzylkum desert is francolite. The mineralogical composition of the washed dried concentrate, a granular type of phosphorites of the Central Kyzyl Kum, was studied by X-ray and chemical methods of research. It has been established that the main phosphate mineral of granular phosphorites of the Kyzyl Kum is francolite. Calcite, dolomite, gypsum, quartz, calcium silicate, etc. are present as gangue. The rate of sulfuric acid for the decomposition of washed dried concentrate (25.75% $P_2O_5$) in terms of obtaining simple superphosphate (at least 17% $P_2O_5$) has been calculated. A distinctive feature of the proposed in-line method over the classical one (chamber) is that the entire production cycle of natural phosphate processing is carried out in two stages. At the first stage, the phosphate raw material is treated with a stoichiometric consumption of concentrated sulfuric acid (at least 93%), under conditions of complete decomposition of the washed dried concentrate with the formation of phosphoric acid and anhydrite crystals (calcium sulfate). The reaction temperature is 130°C. At the second stage, the resulting concentrated solution of phosphoric acid in a mixture with sulfuric acid participates in the reaction with an additional introduced amount of washed dried concentrate, which is the basis of the mechanism of chemical formation of monocalcium phosphate and granulation of superphosphate mass. On comparison to the conventional flowsheet, the process excludes the stages of warehouse maturation, ammonization and drying of the product.

**Keywords:** washed dried concentrate, X-ray diffraction, chemical and mineralogical composition, sulfuric acid, decomposition, simple superphosphate

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## INTRODUCTION

Phosphate raw materials are necessary for the production of mineral fertilizers, chemical and metallurgical industries, the production of flotation reagents, detergents, as mineral fertilizing of livestock and poultry, as well as for other purposes [1].

The phosphate industry relies on a powerful raw material base. The identified global reserves of phosphate ores are accounted for in 76 countries and are estimated at 70587.4 million tons of $P_2O_5$, including 65328.4 million tons of phosphorite and 5259 million tons of apatite ores [2]. In ten countries (USA, Mexico, China, Russia, Mexico, Kazakhstan, Peru, South Africa, Western Sahara and Tunisia), 61015.4 million tons of $P_2O_5$ are concentrated, which is 87% of the global reserves. Significant deposits of phosphate rocks have been identified at the bottom of the seas and oceans, mainly on the shelves. They are estimated at 7271 million tons of $P_2O_5$ (approximately 12% of onshore reserves).

Concerning countries, Morocco is the absolute leader, followed by the USA, China, Russia and Kazakhstan [3]. Apatite ores account for about 1/5 of the world's resources of mineral raw materials. Russia, South Africa, Uganda, China, Brazil and Vietnam have the largest reserves.

The countries producing phosphate raw materials (in 2001, their number was 31) can be divided into three groups [4]. The first group (the main producers) are the USA, Morocco, China and Russia (more than 10 million tons/year), which account for 67.7% of total world production; the second group is represented by 10 countries (Tunisia, Jordan, Brazil, Israel, South Africa, Syria, Senegal, Australia, India and Togo), which account for 26% of world production; the third—17 countries—Kazakhstan, Egypt, Algeria, Mexico, Canada, Finland, Vietnam, Christmas Island, Venezuela, Iraq, Nauru, Uzbekistan, the DPRK, Zimbabwe, Colombia, Sri Lanka and Peru, producing 6.3% of phosphate raw materials. It is assumed that by 2050, the annual production and consumption of phosphate raw materials will amount to about 70 million tons of $P_2O_5$ (220 million tons of phosphate raw materials).

According to the accepted classification, according to the content of the useful component, ores are divided into very poor (2–8% $P_2O_5$), poor (8–18% $P_2O_5$), medium (18–28% $P_2O_5$) and rich (over 28% $P_2O_5$). The higher the content of $P_2O_5$ in raw materials, the better the economic indicators of its processing. The best phosphate raw material in the world is Khibiny apatite concentrate (Russia). It contains 39.54% $P_2O_5$. Only for the Khibiny concentrate and similar foreign phosphate raw materials Khuribga 80–82 TPL, Bu Kraa 80 TPL (Morocco), Nauru 84 BPL, there are technologies for obtaining any types of phosphorus-containing fertilizers from it with acceptable technical and economic indicators.

(Note: abroad, the main characteristic of raw phosphate products is considered to be the percentage of tricalcium phosphate Ca3(PO4)2 in them (English—BPL, French—TPL; 1 % BPL corresponds to 0.4576% $P_2O_5$, or 0.1997% P, and, conversely, 1% $P_2O_5$ is 2.185% BPL, or 0.436% P) [5].

However, the reserves of high-quality ores are steadily depleted, there is a tendency to involve poorer phosphorite (15–20% $P_2O_5$) and very poor apatite ores (4–8% $P_2O_5$) in industrial processing. In this regard, the decisive factor in the phosphate industry is the successful enrichment of poor phosphate, especially phosphate-carbonate ores, which reserves account for two-thirds of the world's reserves [6]. Another important technical task is the development and industrial implementation of technological processes for the production of phosphorus-containing fertilizers from low-grade phosphate raw materials.

In Uzbekistan, the main phosphate raw materials are granular phosphorites of the Kyzylkum deposit. Reserves of phosphate raw materials in areas up to a depth of 50 m, that is, suitable for open-pit mining, have been approved for three locations: Jeroy-Sardara, Northern Jetymtau and Karakata. The approved ore reserves amount to 384413 thousand tons (average content of $P_2O_5$ in ore—19.5%) or 74960 thousand tons of $P_2O_5$ [4].

Phosphorite ore has the following average mineral composition, %: francolite—56.0; calcite—26.5; quartz—7.5–8.0; hydrosluidic minerals and feldspar—4.0-4.5; gypsum—3.5; goethite—1.0; zeolite—less than 1; organic matter—0.5 [7]. The average sample of phosphorite contains (wt. %): 16.2 $P_2O_5$; 46.2 CaO; CaO : $P_2O_5$ = 2.85; 17.7 $CO_2$; 0.6 MgO; 2.9 ($Fe_2O_3$ + $Al_2O_3$); 1.5 ($K_2O$ + $Na_2O$); 2.65 $SO_3$; 1.94 F; 7.8 of insoluble residue. This is a phosphorus-poor raw material. Therefore, it is necessary to enrich it. First of all, it is necessary to get rid of excessive amounts of carbonates. The most common method of enrichment is flotation. But the Kyzylkum phosphorites, along with a high degree of carbonation, are characterized by the germination of a phosphate mineral with calcium, and attempts to enrich them with flotation do not lead to positive results [8, 9].

Therefore, it is necessary to develop new flotation enrichment methods: to find new flotation reagents and improve flotation techniques and technology. It is necessary to search for selective solvents that would selectively dissolve calcium and magnesium carbonate in phosphorite without affecting the phosphate mineral [10–15]. However, these results have not yet gone beyond laboratory studies, only some of them have been tested on enlarged model installations.

Naturally, with such a high content of carbonates (17.7% $CO_2$), roasting turned out to be one of the best enrichment methods. It was implemented at the Kyzylkum phosphorite complex as part of a combined technology [16–18], which includes crushing of ore, dry processing to produce ordinary phosphorite flour, deslamation, firing to remove $CO_2$ and washing of raw materials from chlorine. Since 2015, the complex annually produces 716 thousand tons of washed burnt concentrate (WBC-26) with an average content of 26% $P_2O_5$.

It should be noted that in the process of thermal enrichment, phosphorite flour (17–18% $P_2O_5$) and washed dried concentrate (22–24% $P_2O_5$) are obtained as intermediate phosphate materials, and such wastes as

**Table 1.** Chemical characteristics of various types of phosphate minerals

| Type of apatite group | Compound | Component content, wt.% | | | | |
|---|---|---|---|---|---|---|
| | | $P_2O_5$ | CaO | $CO_2$ | $CaF_2$ | $Ca(OH)_2$ |
| Fluorapatite | $Ca_{10}P_6O_{24}F_2$ | 42.43 | 50.05 | – | 7.74 | – |
| Hydroxylapatite | $Ca_{10}P_6O_{24}(OH)_2$ | 42.40 | 50.23 | – | – | 7.37 |
| Carbonatapatite | $Ca_{10}P_6CO_{24}(OH)_3$ | 35.97 | 48.31 | 4.46 | – | 11.26 |
| Francolite | $Ca_{10}P_{5.2}C_{0.8}O_{23.2}F_{1.8}OH$ | 37.14 | 48.52 | 3.54 | 7.07 | 3.73 |
| Kurskite | $Ca_{10}P_{4.8}C_{1.2}O_{22.8}F_2(OH)_{1.2}$ | 34.52 | 47.52 | 5.35 | 7.91 | 4.50 |

mineralized mass (12–14% $P_2O_5$) and slurry phosphorite (8–10% $P_2O_5$) are removed from the enrichment process, which are not yet used in the production of mineral fertilizers. And phosphorite flour is used to produce simple superfosphate (12% $P_2O_5$) at JSC "Navoiazot," "Ferganaazot," and "Kokand superphosphate Plant" (now "Indorama Kokand Fertilizers and Chemicals"). Washed dried concentrate (WDC) is a phosphorous product used to produce WBC-26 by firing at 950–1000°C. WBC-26 is the main raw material for the production of extractive phosphoric acid and ammophos at Ammofos-Maxam JSC. It is necessary to study the possibility of processing this raw material into a simple superphosphate.

The purpose of this work is to study the mineralogical composition and physico-mechanical characteristics of WDC and the process of its sulfuric acid decomposition to obtain a simple superphosphate.

## EXPERIMENTAL

**Characteristics of washed dried concentrate.** The phosphoric substance in phosphorites are minerals of the apatite group with the general formula $3M_3(PO_4)_2 \cdot CaX_2$, where M is represented by $Ca^{2+}$, and X by fluorine, OH group, $CO_3$. Calcium, which is included into the phosphate part of the molecule, can be morphologically replaced by strontium, rare earth elements; $PO_4^{3-}$ ion by $SO_4^{2-}$ and $SiO_4^{2-}$ ions. The most common in nature is calcium fluoroapatite $3Ca_3(PO_4)_2 \cdot CaF_2$ or $Ca_5F(PO_4)_3$ and hydroxypapatite $3Ca_3(PO_4)_2 \cdot Ca(OH)_2$ or $Ca_5(PO_4)_3OH$. The phosphorous substance of phosphorites, in addition to fluorapatite, can be represented by fluorocarbonatapatite—francolite or kurskite. Table 1 presents the comparative chemical and mineralogical compositions of some types of phosphate minerals [19].

It shows that fluorapatite has the highest phosphorus content, and kurskite—the lowest. There are a number of differences in the structure of kurskite from apatite, the main one is the substitution of a part of the $PO_4^{3-}$ tetrahedra by groups of $CO_3^{2-}$. Thus, 20–25% of phosphorus of the apatite structure has been replaced with carbon in it, as a result, the theoretical content of $P_2O_5$ in it is 33–33.5% (at 5.35% $CO_2$). However, in a real mineral, the amount of $P_2O_5$ rarely exceeds 28.5–29%, which is due to contamination of phosphate grains with finely dispersed glauconite, pyrite, goethite and organic matter. By methods of chemical, thermogravimetric, IR spectroscopic and X-ray analysis, it was found that the general formula of kurskite according to Bliskovsky is as follows: $Ca_{10-n/2}(PO_4)_{6-n}(CO_3)_nF_2$, where $n = 1.5$ [20].

Phosphate ores of Central Kyzylkums, including WDC, belong to granular phosphorites, the main mineral of which is francolite. It has unit cell parameters $a_0$ = 9.33 Å, $c_0$ = 6.89 Å and contains 37% $P_2O_5$, 3.5% $CO_2$ and up to 3% $SO_3$, isomorphically included in its crystalline structure.

The WDC with the following composition (wt. %) is selected as the object of the study: $P_2O_5$—25.75; $P_2O_{5assim}$ : $P_2O_{5tot}$ = 13.08; CaO—52.07; MgO—0.30; $CO_2$—10.97; $Fe_2O_3$—0.31; $Al_2O_3$—1.02; $SO_3$—1.48; F—2.76; $SiO_2$—1.78; insoluble residue—1.23; $H_2O$—0.92; $CaO_{tot}$ : $P_2O_{5tot}$ = 2.02. Chemical analysis of raw materials for the content of various components was carried out according to known methods.

The determination of $P_2O_5$ was carried out by a differential method on a KFK-3 device (wavelength $\lambda$ = 440 nm) in the form of a phosphoric vanadium-molybdenum complex. By means of $SO_3^{2-}$ ion weight deposition in the form of $BaSO_4$. Determination of the content of CaO and Mg carried out using volumetric

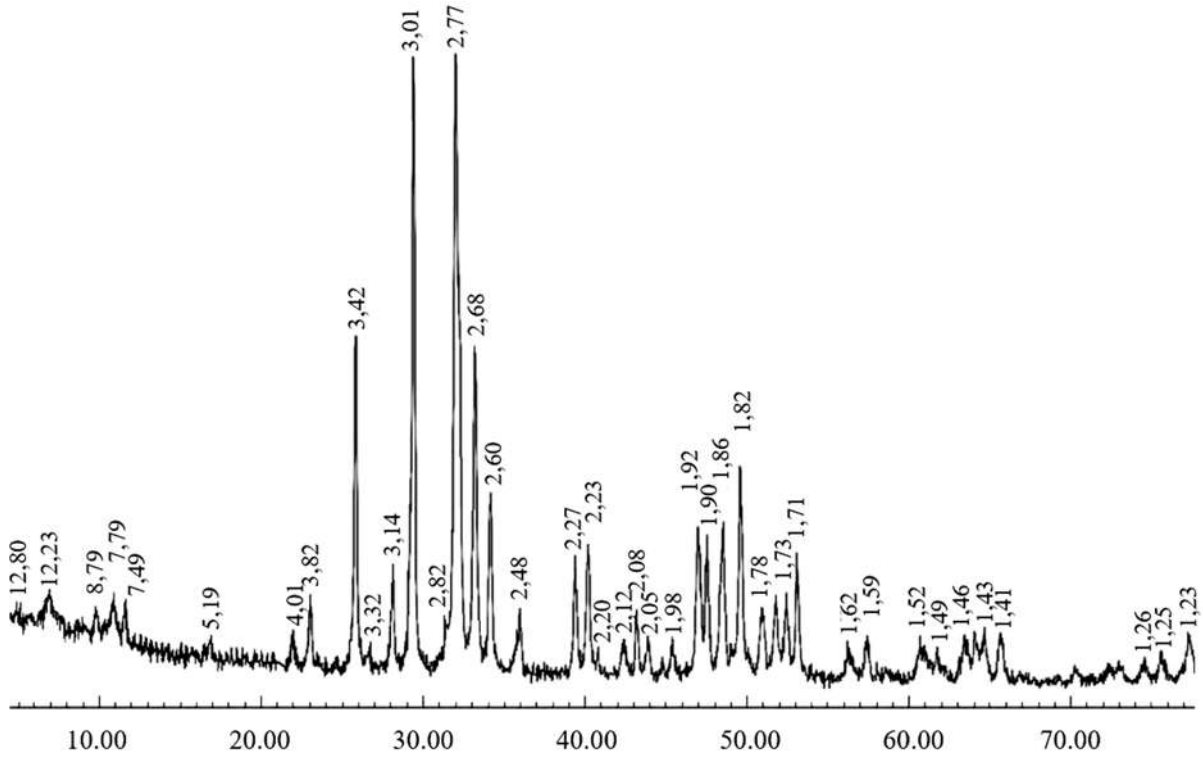


**Fig. 1.** Roentgenogram of washed dried concentrate.

complexometric method: titration with a solution of trilon B (0.05 n) in the presence of the calcein and chrome dark blue indicators, respectively. The analysis for $Al_2O_3$ and $Fe_2O_3$ was also carried out by complexometric titration with 0.05 n solution of trilon B in the presence of the xylenol orange indicator and sulfosalicylic acid, respectively. $CO_2$ content is determined by volumetric decomposition of carbonates with diluted hydrochloric acid. Determination of F was carried out by a potentiometric method using a fluoride selective electrode. $SiO_2$ was determined by means of gravimetric method with silicic acid deposition using gelatin, and an insoluble residue in aqua regia.

In order to develop a technology for obtaining phosphate fertilizers, its physical and mechanical properties (dispersed composition, moisture content, bulk density, slope angle, fluidity, pH, hygroscopicity, moisture capacity) were studied.

## RESULTS AND DISCUSSIONS

Sieve analysis shows that the dispersion of WDC is characterized as follows: class (–2 + 1 mm)—1.4%; (–1 + 0.63 mm)—1.9%; (–0.63 + 0.4 mm)—2.4%; (–0.4 + 0,315 mm) of 7.0%; (–0.31 + 0.25 mm) to 8.3%; (–0.25 + 0.16 mm)—41.1%; (0.16 + 0.1 mm)—26,6%; (–0.1 + 0,05 mm)—8.5%; (–0.05 mm)—2.8%. By studying the properties, it is shown that at the initial humidity (0.92%), the free bulk density of WDC is 1.23 g/cm$^3$, and with a flattening it is 1.56 g/cm$^3$. The value of the natural slope angle is 28 degrees. It dissipates without any difficulties. The hygroscopic accuracy turned out to be 59.2%, and the maximum moisture capacity is 6.2%, but at higher humidity it loses its friability. In this regard, during storage and transportation, it is necessary to protect it from moisture.

For an approximate determination of the mineralogical composition of the WDC, we took its roentgenogram on the XRD-6100 diffractometer (Shimadzu, Japan). Cu$K_\alpha$ radiation (β-filter, Ni, tube current and voltage mode 30 mA, 30 kV) and a constant detector rotation speed of 4 deg/min were used, and the scanning angle varied from 4° to 80°. When taking samples, a rotating camera was used with the rotation speed of 30 rpm. Identification of mineral phases was carried out using the 2013 International Centre for Diffraction Data database. The roentgenogram of WDC is shown in Fig. 1.

Diffraction bands on the roentgenogram, namely, 3.43; 3.14; 2.83; 2.77; 2.68; 2.60; 2.23; 1.92; 1.82; 1.75; 1.73; 1.71 Å belong to fluorocarbonatapatite. The presence of calcite is confirmed by interplane distances 3.82; 3.01; 2.48; 2.27; 2.08; 1.90 Å, of dolomite—by 1.78 Å. Bands 3.32 Å indicate the presence of quartz, but there is very little of it. In smaller quantities, feldspar, glauconite, bentonite, chlorite, etc. can also be present.

The chemical composition and physicomechanical properties of WDC show that this phosphate raw material is quite suitable for producing various grades of phosphorus-containing fertilizers.

To clarify the presence of the quantitative content of these minerals, we performed calculations based on the chemical composition of the WDC.

Below is a calculation to determine the mineral content of phosphate raw materials per 1000 kg.

**Calculation of the mineral composition of washed dried concentrate.** Thus, granular phosphorites of Central Kyzylkum are included in the francolite group of apatite rock.

Judging by the content of phosphorus and fluorine in francolite, there is a concentration of approximately 0.09262 parts of fluorine to one part of $P_2O_2$ by weight:

$$\frac{F}{P_2O_5} = \frac{3.44}{37.14} = 0.09262,$$

in our case this parameter is

$$\frac{F}{P_2O_5} = \frac{2.76}{25.75} = 0.10718.$$

Thus, in this case, the difference is insignificant, just

$$\frac{F}{P_2O_5} = 0.01456.$$

This fact indicates that the Kyzylkum phosphorite contains excessive fluorine in the form of $CaF_2$.

The calculations for the mineral components of the WDC francolite are given below, with some additions to the differences in the values of the components content. That is, the calculation is made for 1000 kg of WDC.

The chemical formula of francolite is as follows:

$$2Ca_{10}P_{2.5}C_{0.8}O_{23.2}F_{1.8}OH \rightarrow$$
$$5.2P_2O_5 + 18.2CaO + 1.6CO_2 + 1.8CaF_2 + H_2O.$$

*I. Distribution of components according to the francolite of WDC.*

First, the amount of francolite contained in the 1st ton of WDC is calculated based on the content of phosphorus pentoxide in WDC:

$$m_{\text{francolite}} = \frac{2 \cdot 993.2 \cdot 257.5}{5.2 \cdot 142} = 692.71 \text{ kg},$$

where 993.2 is $M_{(\text{francolite})}$, g/mol; 257.5 is the amount of $P_2O_5$ in 1000 kg of WDC, kg; 142 is $M(P_2O_5)$, g/mol.

Now, we calculate the amount of CaO present in the francolite:

$$m(CaO_{\text{francolite}}) = \frac{257.5 \cdot 18.2 \cdot 56}{5.2 \cdot 142} = 355.42 \text{ kg},$$

where 56—M(CO), g/mol.

We calculate the amount of $CaO_2$ present in the francolite:

$$m(CaO_{2\text{francolite}}) = \frac{257.5 \cdot 1.6 \cdot 44}{5.2 \cdot 142} = 24.55 \text{ kg},$$

where 44—$M(CO_2)$, g/mol.

The francolite structure contains $CaF_2$:

$$m(CaF_{2\text{francolite}}) = \frac{257.5 \cdot 1.8 \cdot 78}{5.2 \cdot 142} = 48.96 \text{ kg},$$

where 78—$M(CaF_2)$, g/mol.

Hence, we calculate the number of F and CaO coupled in $CaF_2$ according to the following scheme:

$$1.8CaF_2 \rightarrow 1.8CaO + 3.6F^-.$$

First we determine the number of F in the form of $CaF_2$:

$$m(F_{CaF_2}) = \frac{48.96 \cdot 3.6 \cdot 19}{1.8 \cdot 78} = 23.85 \text{ kg},$$

where 19—M(F), g/mol.

Then, out of it, we calculate the amount of CaO coupled in $CaF_2$:

$$m(CaO_{CaF_2}) = \frac{23.85 \cdot 1.8 \cdot 56}{3.6 \cdot 19} = 35.15 \text{ kg}.$$

*II. Prorating of components in impurity compounds of WDC.*

From the above chemical composition it can be seen that the 1st ton of WDC contains 27.6 kg of fluorine, and from the above calculation it follows that 23.85 kg of fluorine is bound in the francolite structure. Hence, 27.6 – 23.85 = 3.75 kg of fluorine in the free state are in the form of $CaF_2 \rightarrow CaO + 2F$.

Therefore, we determine the number of CaO bound in $CaF_2$ in WDC:

$$m(\mathrm{CaO}_{\mathrm{CaF_2}}) = \frac{3.75 \cdot 56}{2 \cdot 19} = 5.526 \text{ kg}.$$

It is equivalent to $CaF_2$:

$$m(\mathrm{CaF_2}) = \frac{5.526 \cdot 78}{56} = 7.696 \text{ kg}.$$

Now we shall calculate the amount of dolomite – $SaMd(CO_3)_2$ in WDC:

$$m_{\text{dolomite}} = \frac{3 \cdot 184}{40} = 13.8 \text{ kg},$$

where 3.0 is the amount of MgO in 1000 kg of WDC, kg; 184—M($SaMg(CO_3)_2$), g/mol; 40—M(MgO), g/mol.

In the dolomite, CaO is present, bound in the dolomite:

$$\mathrm{MgCO_3 \cdot CaCO_3 \rightarrow MgO + CaO + 2CO_2}.$$

Then we determine the amount of CaO in the dolomite:

$$m(\mathrm{CaO}_{\text{dolomite}}) = \frac{3 \cdot 56}{40} = 4.2 \text{ kg},$$

where 56—M(CaO), g/mol; 40—M(MgO), g/mol.

Next step is to find the amount of $CO_2$ in the dolomite:

$$m(\mathrm{CaO}_{\text{2dolomite}}) = \frac{2 \cdot 3 \cdot 44}{40} = 6.6 \text{ kg},$$

where 44—M($CO_2$), g/mol.

According to the results of analytical data, the total amount of $CO_2$ in the 1st ton of WDC is 109.7 kg.

It follows from the above calculations that carbonate anhydride is present in the WDC in the form of the following minerals:

$$m(\mathrm{CO}_{\text{2phosphorite}}) - (m(\mathrm{CO}_{\text{2francolite}}) + m(\mathrm{CO}_{\text{2dolomite}})) = m(\mathrm{CO}_{\text{2calcite}}).$$

Thus, 109.7 – (24.55 + 6.6) = 78.55 kg of $CO_2$ is bound in the calcite mineral:

$$\mathrm{CaCO_3 \rightarrow CaO + CO_2}.$$

Hence, we find the amount of $CaCO_3$ in WDC:

$$m_{\text{calcite}} = \frac{78.55 \cdot 100}{44} = 178.52 \text{ kg},$$

where 100 is M($CaCO_3$).

We determine the amount of CaO in calcite:

$$m(\mathrm{CaO}_{\text{calcite}}) = \frac{78.55 \cdot 56}{44} = 99.97 \text{ kg},$$

Then we find the amount of passive CaO in WDC. It is presented in the form of gypsum: $CaO + SO_3 \rightarrow CaSO_4$.

We determine the amount of CaO in the gypsum:

$$m(\mathrm{CaO}_{\text{gypsum}}) = \frac{14.8 \cdot 56}{80} = 10.36 \text{ kg},$$

where 14.8 is the amount of $SO_3$ in 1000 kg of WDC, kg; 80—M ($SO_3$), g/mol.

From here we calculate the amount of gypsum:

$$m_{\text{gypsum}} = \frac{10.36 \cdot 172}{80} = 31.82 \text{ kg},$$

where 172 is M($CaSO_4 2H_2O$), g/mol.

Now we shall determine the total amount of CaO in WDC, both in active (reactive) and passive (non-reactive) forms:

Reactive (active) forms of CaO include:

$$m(\mathrm{CaO}) = m(\mathrm{CaO}_{\text{francolite}}) + m(\mathrm{CaOCaF}_{\text{2francolite}}) + m(\mathrm{CaOCaF_2}) + m(\mathrm{CaO}_{\text{dolomite}}) + m(\mathrm{CaO}_{\text{calcite}})$$

$$= 355.42 + 35.15 + 5.526 + 4.2 + 99.97 = 500.266 \text{ kg}.$$

And non-reactive (reactive) forms of CaO include:

$$m(\mathrm{CaO}_{\text{gypsum}}) = 10.36 \text{ kg},$$

According to the results of analytical data, the total amount of CaO in the 1st ton of WDC is 520.7 kg. So, the remaining amount of CaO is:

$$m(\mathrm{CaO}) = 520.7 - 500.266 - 10.36 = 10.074 \text{ kg}.$$

**Table 2.** Mineralogical composition of washed dried concentrate

| Mineral components of phosphate raw materials | Quantity, wt. % | Mineral components of phosphate raw materials | Quantity, wt. % |
|---|---|---|---|
| $Ca_{10}P_{5.2}C_{0.8}O_{23.2}F_{1.8}OH$ | 69.27 | $CaF_2$ | 0.77 |
| $CaCO_3$ | 17.85 | $Al_2O_3$ | 1.02 |
| $CaMg(CO_3)_2$ | 1.38 | $Fe_2O_3$ | 0.31 |
| $CaSO_4 \cdot 2H_2O$ | 3.18 | Insoluble residue | 1.23 |
| $SiO_2$ | 1.24 | $K_2O + Na_2O$ (glauconite and organic substances) | 0.1 |
| $Ca_2SiO_4$ | 1.55 | | |
| $H_2O$ | 0.92 | Other | < 1.18 |

The remaining 10.074 kg of CaO is in the form of calcium silicate:

$$Ca_2SiO_4 \rightarrow 2CaO + SiO_2.$$

Next step is to find the amount of $SiO_2$ in calcium silicate:

$$m(SiO_2) = \frac{10.074 \cdot 60}{2 \cdot 56} = 5.396 \text{ kg},$$

where 60 is $M(SiO_2)$, g/mol.

From here we calculate the amount of calcium silicate ($Ca_2SiO_4$):

$$m(Ca_2SiO_4) = \frac{10.074 \cdot 172}{2 \cdot 56} = 15.48 \text{ kg},$$

where 172 is $M(Ca_2SiO_4)$, g/mol; 56 is M(CaO), g/mol.

Based on the data obtained, Table 2 was compiled, reflecting the mineral composition of the WDC.

Thus, washed dried concentrate belongs to granular types, the main mineral of which is francolite. It is quite possible to obtain a simple superphosphate from it for local use.

**Study of the process of two-stage processing of washed dried concentrate into simple superphosphate.** The Kokand superphosphate plant in Uzbekistan produces simple ammoniated superphosphate by the chamber method [21]. This method includes the following stages: decomposition of phosphorite flour (17–18% $P_2O_5$) with sulfuric acid concentration of 60% at its rate of 100% and 70–75°C; chamber maturation of the superphosphate mass for 1–1.5 h at 115–120°C; warehouse maturation for 6 days with triple shoveling; granulation and ammonification, drying and the sieving of the product. At the same time, the finished product contains 12% $P_2O_{5tot.}$, 1.5% N, $P_2O_{5aq.} : P_2O_{5tot.}$ = 50% and the strength of the granules of 1.5 MPa.

The disadvantages of the chamber (classical) technology for the production of simple superphosphate are as follows:

a) six-day maturation in the warehouse and triple shoveling, passivation of the active centers of the entire consumable fluorocarbonate and incomplete extraction of H3PO4 into the liquid phase;

b) diffusion inhibition of the formation reaction of $Ca(H_2PO_4)_2$ and high content of free $H_3PO_4$ in the chamber product;

c) unsatisfactory granulation of the superfosphate mass and high recycling;

d) disorganized emission of harmful substances and high dustiness of industrial premises, since warehouse maturation is a powerful source of fluoride compounds release into the atmosphere.

Such a long decomposition process of phosphate raw materials can be explained by the fact that when reacting with $H_2SO_4$ an upper crust of $CaSO_4$ crystals is formed on the surface of phosphorite grains [22].

During the reaction with $H_3PO_4$, another layer of calcium phosphate crystals is formed. Thus, in both sulfuric and phosphoric acids, it is necessary to overcome the layer of crystals deposited on the surface of the grains in order to react with the phosphate grain itself. The limiting stage of the decomposition process, both for apatite and phosphorite, is the diffusion process [23]. That

is, at the stages of chamber and warehouse maturation, the limiting stage of the process is the rate of acid diffusion through the formed salt crust [24].

In the study [25], an analysis of the working conditions of labor force, the main professions engaged in the production of superphosphate was carried out. At the same time, excess of the maximum concentrations of industrial aerosols, violation of microclimate parameters, preliminary increase in vibration level indicators were registered at the working sites. With a general hygienic assessment of the classes of working conditions, we can state the following degree of noxiousness for certain professions: the scraper driver and the loader operator—3rd harmful of the 2nd degree of noxiousness; the crane operator and packaging machines operator—3rd harmful of the 3rd degree of noxiousness.

**The essence of the proposed method**. The peculiarity of our proposed method for obtaining granular superphosphate from carbonate phosphorites in comparison with the classical one is that the technological process is also carried out in two stages:

1) The main part (70–80% of the total mass) of phosphorite decomposes with 92–93% $H_2SO_4$, taken at 100-105% norms from stoichiometry to form 45–50% phosphoric acid, where calcium sulfate crystallizes as anhydrite;

2) The acid reaction obtained at the first stage is a mass containing concentrated phosphoric acid (45–50% $P_2O_5$) and anhydrite is treated with the remaining part (20–30%) of phosphorite, resulting in the neutralization of phosphoric acid into monocalcium phosphate.

The duration of the first stage of sulfuric acid decomposition is 15–20 min at 120–130°C. And the processes of neutralizing the acid mass and granulating the product by means of pelletization are combined in one device. Duration is 25–30 min. It should be noted that the drying stage of the product is excluded from the scheme.

In order to clarify the mechanism of decomposition of phosphate raw materials in two stages, a current study was conducted.

**Calculation of the consumption rate of sulfuric acid for the treatment of the washed dried concentrate in anhydride mode with the formation of phosphoric acid in the first stage and neutralization of free phosphoric acid with washed dried concentrate with the formation of monocalcium phosphate in the second stage.** *The Ist stage of the process of obtaining a simple superphosphate (complete decomposition of the washed dried concentrate with the formation of phosphoric acid in the anhydride mode).*

The basis for the formation of phosphoric acid is the reaction of sulfuric acid with francolite:

$$Ca_{10}P_{2.5}C_{0.8}O_{23.2}F_{1.8}OH + 10H_2SO_4 \rightarrow 5.2H_3PO_4 + 10CaSO_4 + 0.8CO_2 + 1.8HF + 1.8H_2O.$$

We calculate the consumption rate of sulfuric acid for the decomposition of francolite with the formation of phosphoric acid:

$$m^1(H_2SO_4) = \frac{692.71 \cdot 10 \cdot 98}{993.2} = 683.50 \text{ kg},$$

where 692.71 is the amount of francolite in 1000 kg of WDC, kg; 98—$m(H_2SO_4)$, g/mol; 993.2—$m_{\text{francolite}}$, g/mol.

Consumption of sulfuric acid for the decomposition of $CaF_2$ by the following reaction: $CaF_2 + H_2SO_4 = CaSO_4 + 2HF\uparrow$.

$$m^2(H_2SO_4) = \frac{5.52 \cdot 98}{56} = 9.67 \text{ kg},$$

where 5.52—is the amount of $CaF_2$ in 1000 kg of WDC, kg; 56—$m$(CaO), g/mol.

It should be noted that part of the CaO is bound with MgO in the form of dolomite ($MgCO_3 \cdot CaCO_3$).

Consumption of sulfuric acid for the decomposition of CaO by the following reaction:

$$CaCO_3 + H_2SO_4 = CaSO_4 + CO_2\uparrow.$$

$$m^3(H_2SO_4) = \frac{4.2 \cdot 98}{56} = 7.35 \text{ kg},$$

where 4.2 is the amount of CaO from dolomite in 1000 kg of WDC, kg; 56—M(CaO), g/mol.

The consumption of sulfuric acid for the decomposition of Mg by reaction: $MgCO_3 + H_2SO_4 = MgSO_4 + CO_2\uparrow$:

$$m^4(H_2SO_4) = \frac{3 \cdot 98}{40} = 7.35 \text{ kg},$$

where 3.0 is the amount of MgO from dolomite in 1000 kg of WDC, kg; 40—M(MdO), g/mol.

Consumption of sulfuric acid for decomposition of calcite ($CaCO_3$) in WDC by reaction: $CaCO_3 + H_2SO_4 = CaSO_4 + CO_2\uparrow$:

$$m^5(H_2SO_4) = \frac{99.97 \cdot 98}{56} = 174.94 \text{ kg},$$

where 99.97 is the amount of CaO from calcite in 1000 kg of WC, kg; 56 is M(CaO), g/mol.

Consumption of sulfuric acid for the decomposition of calcium silicate by reaction:

$$2Ca_2SiO_4 + 2H_2SO_4 \rightarrow 2CaSO_4 + SiO_2 + 2H_2O,$$

$$m^6(H_2SO_4) = \frac{15.48 \cdot 2 \cdot 98}{172} = 17.64 \text{ kg},$$

where 15.48 is the amount of $Ca_2SiO_2$ in 1000 kg of WDC, kg; 172—M($Ca_2SiO_2$), g/mol.

We calculate the consumption of sulfuric acid for the decomposition of ferric oxide (III) by reaction:

$$Fe_2O_3 + 3H_2SO_4 \rightarrow Fe_2(SO_4)_3 + 3H_2O,$$

$$m^7(H_2SO_4) = \frac{3.1 \cdot 3 \cdot 98}{160} = 5.69 \text{ kg},$$

where 3.1 is the amount of $Fe_2O_3$ in 1000 kg of WDC, kg; 160 is M($Fe_2O_3$), g/mol.

Then we calculate the consumption of sulfuric acid for the decomposition of aluminum oxide(III) by reaction:

$$Al_2O_3 + 3H_2SO_4 \rightarrow Al_2(SO_4)_3 + 3H_2O,$$

$$m^8(H_2SO_4) = \frac{10.2 \cdot 3 \cdot 98}{102} = 29.4 \text{ kg},$$

where 10.2 is the amount of $A1_2O_3$ in 1000 kg of WDC, kg; 102—M($A1_2O_3$), g/mol.

Thus, at the 1st stage of formation of phosphoric acid, the total consumption of 100% sulfuric acid for the decomposition of acid-degradable components of the WDC is as follows:

$$\sum H_2SO_4 = 683.5m^1 + 9.67m^2 + 7.35m^3 + 7.35m^4 + 174.94m^5 + 17.64m^6 + 5.69m^7 + 29.4m^8 = 935.54 \text{ kg}.$$

Or on conversion to 93% $H_2SO_4$:

$$m(H_2SO_4) = \frac{935.54}{0.93} = 1005.95 \text{ kg},$$

$$Ca_{10}P_{2.5}C_{0.8}O_{23.2}F_{1.8}OH + 10H_2SO_4 \rightarrow 5.2H_3PO_4 + 10CaSO_4 + 1.8H_2O + 0.8CO_2 + 1.8HF.$$

Thus, with 100% sulfuric acid decomposition of 1000 kg of washed dried concentrate (with a content of 25.75% PO), phosphoric acid (100% $H_3PO_4$) is formed in the amount of:

$$m(100\%H_3PO_4) = \frac{257.5 \cdot 5.2 \cdot 98}{2.6 \cdot 142} = 355.42 \text{ kg}.$$

*The IInd stage of the process of obtaining a simple superphosphate (neutralization of phosphoric acid with washed dried concentrate to form monocalcium phosphate).*

The main decomposition reaction of francolite with phosphoric acid:

$$Ca_{10}P_{2.5}C_{0.8}O_{23.2}F_{1.8}OH + 14.8H_3PO_4 + 8.2H_2O \rightarrow 10(H_3PO_4)_2 + 1.8HF + 0.8CO_2.$$

We calculate the consumption of phosphoric acid for the decomposition of francolite to form monocalcium phosphate:

$$m^1(H_3PO_4) = \frac{692.71 \cdot 14.8 \cdot 98}{993.2} = 1011.585 \text{ kg},$$

where 692.71 is the amount of francolite in 1000 kg of WDC, kg; 98—M($H_3PO_4$), g/mol; 993.2—$M_{francolite}$, g/mol.

Phosphoric acid for the decomposition of $CaO_{act}$ in ftouride and calcium silicate, calcite and dolomite is consumed by reaction:

$$Ca_2SiO_4 + 4H_3PO_4 \rightarrow 2Ca(H_2PO_4)_2 \cdot H_2O + SiO_2,$$

$$CaO + 2H_3PO_4 \rightarrow Ca(H_2PO_4)_2 \cdot H_2O,$$

$$CaF_2 + 2H_3PO_4 \rightarrow Ca(H_2PO_4)_2 \cdot H_2O + 2HF.$$

The total amount of active calcium oxide in WDC is:

$$m_{CaOact} = m(CaO_{CaF_2}) + m(CaO_{CaF_2}) + m(CaO_{dolomite}) + m(CaO_{calcite}) + m(CaO_{Ca_2SiO_4}) = 5.52 + 4.2 + 99.97 + 10.08 = 119.77 \text{ kg},$$

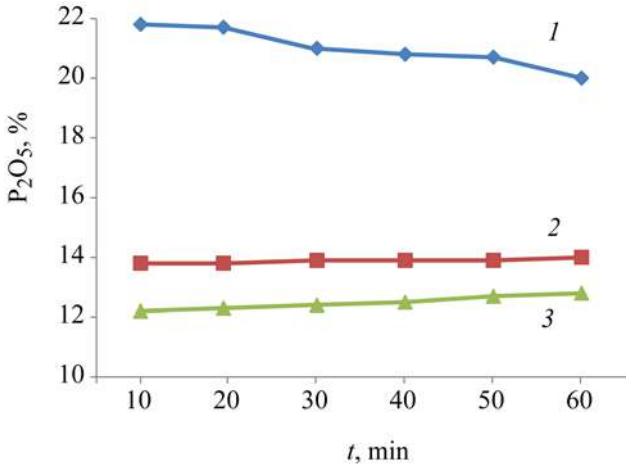


**Fig. 2.** The content of free (*1*) acidity, (*2*) total, and (*3*) aqueous forms of $P_2O_5$ in the acidic superphosphate mass, depending on the contact time of the washed dried concentrate with sulfuric acid.

where 5.52, 4,2, 99.97, and 10.08 is the amount of $CaF_2$; $CaO_{dolomite}$; $CaO_{calcite}$ and $CaO_{Ca_2SiO_4}$ in 1000 kg of WDC:

The total amount of phosphoric acid for the decomposition of $CaO_{act}$ in WDC is:

$$m^2(H_3PO_4) = \frac{119.77 \cdot 2 \cdot 98}{56} = 419.2 \text{ kg}.$$

To decompose MgO in dolomite, $H_3PO_4$ is consumed by the reaction: $MgO + H_3PO_4 = MgHPO_4 + H_2O$

$$m^3(H_3PO_4) = \frac{3 \cdot 98}{40} = 7.35 \text{ kg},$$

where 3 is the amount of MgO in 1000 kg of WDC, kg; 40—M(MgO), g/ mol.

Consumption of $H_3PO_4$ for decomposition of sesquioxides in WDC:

$$Fe_2O_3 + 2H_3PO_4 \rightarrow 2FePO_4 + 3H_2O,$$

$$m^4(H_3PO_4) = \frac{3.1 \cdot 2 \cdot 98}{160} = 3.80 \text{ kg},$$

where 3.1 is the amount of $Fe_2O_3$ in 1000 kg of WDC, kg; 160—M($A1_2O_3$), g/mol.

$$Al_2O_3 + 2H_3PO_4 \rightarrow 2AlPO_4 + 3H_2O,$$

$$m^5(H_3PO_4) = \frac{10.2 \cdot 2 \cdot 98}{102} = 19.6 \text{ kg},$$

where 10.2 is the amount of $A1_2O_3$ in 1000 kg of , kg; 102—M($A1_2O_3$), g/mol.

When calculating 100% decomposition of 1000 kg WDC, the total consumption of phosphoric acid into various components is: $m(H_3PO_4)$ = 1011.585($m^1$) + 419.195($m^2$) + 7.35($m^3$) + 3.80($m^4$) + 19.6($m^5$) = 1461.52 kg.

Thus, at the Ist stage of sulfuric acid decomposition of 1000 kg of WDC, $m(H_3PO_4$, 100%) = 355.42 kg of 100% phosphoric acid is formed.

Then, the amount of WDC (100% of the reaction stoichiometry) required to neutralize 355.42 kg of phosphoric acid with the formation of monocalcium phosphate in the second stage of processing when obtaining a simple superphosphate is calculated:

$$M_{WDC} = \frac{355.42 \cdot 1000}{1461.52} = 243.19 \text{ kg},$$

where 355.42 is the amount of 100% $H_3PO_4$ formed at 100% sulfuric acid decomposition of 1000 kg WDC, kg; 1461.52 is the amount of 100% $H_3PO_4$ required for decomposition of 1000 kg WDC, kg.

**The process of obtaining a simple superphosphate.** Experiments on the decomposition of WDC with sulfuric acid were carried out in a thermostatically controlled reactor equipped with a paddle stirrer at 130°C (necessary to maintain the anhydride regime due to the heat of the reaction). The norm of sulfuric acid was taken 100% of the stoichiometry for the formation of $H_3PO_4$, taking into account the above reactions for decomposition of impurity components of phosphate raw materials (Ist stage of processing). The content of $P_2O_{5free}$ in the reaction masses and finished products were determined by titration of 0.1 N NaOH using indicators of methyl orange and phenolphthalein.

First, we studied the kinetics of decomposition of phosphate raw materials. At the same time, the contact time of the components was 2, 5, 10, 20, 40, and 60 min. The results are shown in Figs. 2 and 3.

It shows that with an increase in the duration of interaction from 2 to 20 min, the coefficient of decomposition of WDC with sulfuric acid increases, that is, the relative content of the water-soluble form of

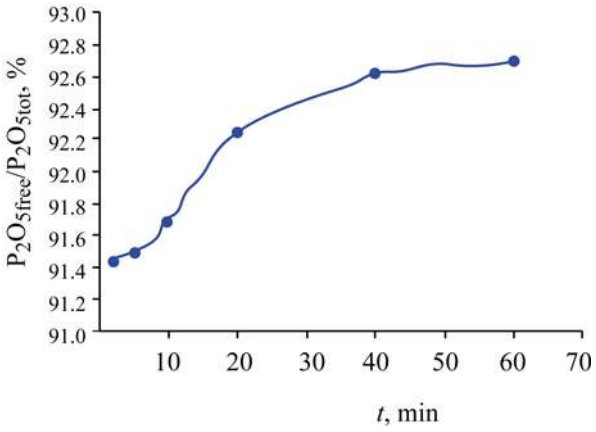


**Fig. 3.** The content of the relative form of $P_2O_5$ in relation to its total content depending on the contact time of the washed dried concentrate with sulfuric acid.

$P_2O_5$ in relation to its total form from 91.44 to 92.24%. With further increase in time from 40 to 60 minutes, this indicator increases slightly, only from 92.61 to 92.7%. At the same time, the total content of $P_2O_5$ in the reaction mass increases from 13.55 to 14.11%, and the free acid content, on the contrary, decreases from 21.42 to 19.77%. The highest concentration of free acidity is explained by the fact that in addition to phosphoric acid, unreacted $H_2SiF_6$, as well as $H_2SiF_6$ and HF, formed during decomposition, are present in the reaction mass.

From the data, it can be concluded that from a technological point of view, the decomposition time of phosphate raw materials is 20–30 min. A further increase in time does not lead to a significant increase in the decomposition coefficient. And with a processing duration of less than 20–30 min, there is not sufficient formation of the thixotropic mass necessary for further processing of the reaction mass.

In the second stage, experiments were carried out to obtain the finished superphosphate by neutralizing the acid reaction mass with WDC (the second stage of processing). At the same time, the rate of WDC varied from 100 to 270% of stoichiometry for the formation of monocalcium phosphate (IInd stage of processing). At the same time, the total rate of $H_2SO_4$ (including the 1st and 2nd stages of decomposition of phosphateraw materials) ranges from 79 to 105% for the formation of monocalcium phosphate, taking into account the above-mentioned decomposition reactions of impurity components.

The neutralization time of the reaction mass is 20 min at 130°C. The reaction of neutralization of the acid mass with WDC at the second stage of the process is actually the beginning of the granulation process, where a

**Table 3.** Composition of products after neutralization and drying of superphosphate mass (the initial norm of 93% $H_2SO_4$ is 100% of stoichiometry for the formation of $H_3PO_4$)

| The WDC norm to form $Ca(H_2PO_4)_2$, % | The initial norm of $H_2SO_4$ (for the Ist and IInd stages) to form $Ca(H_2PO_4)_2$, % | $P_2O_5$ content in the reaction mass, wt % | | | | $P_2O_{5assim}$ : $P_2O_{5otot}$ % | $P_2O_{5aq.}$: $P_2O_{5tot}$ % |
|---|---|---|---|---|---|---|---|
| | | $P_2O_{5tot}$ | $P_2O_{5assim}$ | $P_2O_{5aq}$ | $P_2O_{5free}$ | | |
| After neutralization of the acid reaction mass with washed dried concentrate | | | | | | | |
| 100 | 105 | 15.84 | 13.35 | 13.32 | 12.46 | 84.28 | 84.09 |
| 180 | 91 | 16.76 | 13.79 | 12.76 | 8.00 | 82.28 | 76.13 |
| 200 | 88 | 17.17 | 13.97 | 12.60 | 6.60 | 81.36 | 73.38 |
| 220 | 85 | 17.27 | 14.05 | 12.25 | 5.46 | 81.35 | 70.93 |
| 240 | 83 | 17.28 | 14.05 | 11.85 | 4.50 | 81.30 | 68.57 |
| 260 | 80 | 17.29 | 14.05 | 11.83 | 3.87 | 81.26 | 68.42 |
| 270 | 79 | 17.30 | 14.05 | 11.82 | 3.61 | 81.21 | 68.32 |
| After drying of the wet simple superphosphate | | | | | | | |
| 180 | 91 | 16.86 | 14.03 | 12.68 | 7.08 | 83.21 | 75.20 |
| 200 | 88 | 17.27 | 14.09 | 12.46 | 5.60 | 81.58 | 72.14 |
| 220 | 85 | 17.37 | 14.17 | 12.25 | 4.86 | 81.57 | 70.52 |
| 240 | 83 | 17.38 | 14.17 | 12.22 | 4.15 | 81.53 | 70.31 |
| 260 | 80 | 17.39 | 14.17 | 12.19 | 3.56 | 81.48 | 70.09 |
| 270 | 79 | 17.40 | 14.17 | 12.18 | 3.50 | 81.43 | 70.00 |

phosphoric acid-saturated framework of calcium sulfate crystals acts as the granulation center. The granulation of the neutralized product was carried out by means of the pelletizing method. The granulated product obtained by the proposed method is characterized by low density, and the granules have high resistance to dynamic abrasion.

In finished products, the available form of $P_2O_5$ was determined by solubility in 2% citric acid. The results of the chemical analysis are shown in Table 3.

From the table it can be seen that the higher the WDC norm, the lower the content of $P_2O_{5free}$ and the higher the $P_2O_{5total}$ in superphosphate. Thus, if at the rate of 100% WDC (the general norm of $H_2SO_4$ is 105%) of stoichiometry for the formation of $Ca(H_2PO_4)_2$, contents of $P_2O_{5free}$ and $P_2O_{5total}$ in the product are 12.46 and 15.84%, then at the norm of 200% WDC (the general norm of $H_2SO_4$ is 88%), these indicators have 6.60 and 17.17%, at the norm of 240% WDC (the general norm of $H_2SO_4$ is 83%)—4.50 and 17.28%, and at the rate of 270% WDC (the general norm of $H_2SO_4$ is 79%)—3.61 and 17.30% correspondingly. At the same time, $P_2O_{5assim}$ : $P_2O_{5tot}$. and $P_2O_{5free}$ : $P_2O_{5tot}$. decrease from 84.28 to 81.21% and from 84.09 to 68.32%, respectively.

The table also shows the composition of dried samples of simple superphosphate. According to the regulations, the content of $P_2O_{5free}$ in the finished superphosphate should not exceed 5%. On this basis, at 220% WDC norm (the general norm of $H_2SO_4$ is 85%) the composition of the dry product (wt %) is: $P_2O_{5free}$—4.86%, $P_2O_{5tot}$—17.37%, $P_2O_{5assim}$ : $P_2O_{5tot}$ = 81.57%, and $P_2O_{aq}$ : $P_2O_{5tot}$ = 70.52%, and its granule strength is 1.99 MPa.

## CONCLUSIONS

The mineral composition of granular phosphorite—washed dried concentrate was determined by chemical and radiographic analysis methods. The results show that the main mineral of phosphate raw materials is francolite, and calcite, dolomite, calcium silicate and fluoride, gypsum, silicon, sesquioxide, etc. are present as the gangue.

The norm of sulfuric acid is calculated for obtaining a simple superphosphate from it by means of the two-stage decomposition of washed dried concentrate, at the first stage of which the raw materials are treated with a stoichiometric consumption of 93% sulfuric acid and at 130°C in conditions of complete decomposition with the formation of phosphoric acid and anhydrite (calcium sulfate), and at the second stage, the resulting concentrated solution of phosphoric acid participates in the reaction with an additional amount of phosphate solution, which is the basis of the mechanism of chemical formation of monocalcium phosphate and granulation of superphosphate mass, and out of which the stages of ammonation and drying of the finished product are excluded.

Thus, the proposed method consumes less energy resources, both due to the use of energy-saving equipment and the exclusion of energy-intensive stages of the process, such as warehouse maturation and drying. In addition, the introduction of external neutralizing agents from outside (lime flour, liquid or gaseous ammonia, etc.) and binding additives (phosphoric acid, phosphate and sulfate salts of ammonium, etc.) is excluded.

## CONFLICT OF INTEREST

No conflict of interest was declared by the authors.

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