Simple superphosphate by two-stage acid treatment of phosphate raw materials

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Abstract. The distinguishing feature of the proposed flow method before the classical (chamber) method is that the entire production cycle of natural phosphate processing is carried out in two stages. At the first stage, the phosphorite is treated with a stoichiometric flow rate of concentrated sulphuric acid (at least 93%), under conditions of complete decomposition of phosphorite to form phosphoric acid and crystals of anhydrite (calcium sulfate). The reaction temperature is 122 °C. In the second stage, the resulting concentrated solution of phosphoric acid in a mixture with sulphur is involved in a reaction with an additional input of phosphorite, which is the basis for the mechanism of chemical formation of monocalciumphosphate and granulation of superphosphate mass. The processes for neutralizing phosphoric acid on monocalciumphosphate and for granulating the product by coagulation are combined in one apparatus. The drying stage of the product is excluded from the scheme.

1. Introduction

Phosphorus is the second most important macronutrient for plant growth, crop production and human nutrition. Application of P fertilizers is vital for sustaining desired crop yield and quality, and phosphate fertilization has been practiced massively since the end of World War II [1-3]. Use of P in agriculture accounts for nearly 90% of the total world demand; however, world reserve of phosphates is limited and high-grade phosphate rock is rapidly depleted [4]. The need to feed the world population of 7.2 (now) to 10 billion (2050) at decreasing reserves of mineable phosphate raises great urgency of exploiting new P fertilizers [5-8] and improving management of soil P [1].
Central Kyzylkum phosphorites are the main phosphate raw material for Uzbek factories producing phosphorus-containing fertilizers [9]. Open-pit phosphate reserves have been approved in three deposits: Jeroi Sardara, North Jetymtau and Karakata. Table 1 shows the reserves of phosphate raw materials of the Kyzylkum deposit.

| Deposit            | Approved ore stocks, thous. t | reserve P₂O₅, thous. t | Average content P₂O₅ in ore, % | Note                                      |
|--------------------|-------------------------------|------------------------|-------------------------------|------------------------------------------|
| 1. Jeroi-Sardara.  | 291168                        | 55516                  | 19.1                          | All three plots are on the balance       |
| In the case of, i.e. plots: |                   |                        |                               |                                          |
| Tashkur            | 116619                        | 21255                  | 18.2                          | sheet. Mining                           |
| Kurukkuduk         | 90141                         | 17294                  | 19.2                          | takes place at the Jeroi the South       |
| Jeroi the South    | 84408                         | 16967                  | 20.1                          | Tashkur site.                           |

2. North Jetymtau

| Deposit            | Approved ore stocks, thous. t | reserve P₂O₅, thous. t | Average content P₂O₅ in ore, % | Note                                      |
|--------------------|-------------------------------|------------------------|-------------------------------|------------------------------------------|
| 3. Karakata        | 43052                         | 8236                   | 19.1                          | Stocks approved and on balance           |
| In the case of, i.e. plots: |                   |                        |                               |                                          |
| Aznek              | 26947                         | 4928                   | 18.3                          | pending development.                     |
| Ayakkuduk          | 16105                         | 3308                   | 20.5                          |                                           |

Total: 384413          | 73916                         | 19.5                   |

Kyzylkum phosphorites are granular phosphorites, the main mineral of which is francolite. To compare them, briefly refer to the mineral constituents of some natural phosphates [10, 11]. The phosphorus substance in phosphorites is the minerals of the apatite group with the common formula \(3M_3(PO_4)_2\cdot CaX_2\) where \(M\) is represented by \(Ca^{2+}\), and \(X^-\) is represented by fluorine, chlorine, OH group, CO₃. Calcium, which is a component of the phosphate part of the molecule, can be isomorphically substituted by strontium, rare earth elements; the ion \(PO_4^{3-}\) ions \(SO_4^{2-}\) and \(SiO_4^{2-}\) ions. The most common calcimfluorapatite is \(3Ca_3(PO_4)_2\cdot CaF_2\) or \(Ca_5F(PO_4)_3\), and hydroxylapatite \(3Ca_3(PO_4)_2\cdot Ca(OH)_2\) or \(Ca_5(PO_4)_3OH\). A phosphate substance of phosphate other than fluoroapatitecan be represented by fluorocarbononapatite in the form of franklite or courgetti.

The work [12, 13] states that the higher the CO₂ content in the phosphate grid, the higher the specific surface and the defect of the phosphate lattice; the lower the parameter "a" of the crystalline lattice, and the higher the reaction capacity of the phosphate.

A characteristic feature of granular phosphorites is the stability of mineral composition. All phosphate deposits have a three-component composition [14].
The main mineral of granulated phosphate is Francolite. It has elemental cell parameters \( a_0 = 9.33\text{Å}, c_0 = 6.89\text{Å} \) and contains 37% \( \text{P}_2\text{O}_5 \), 3.5% \( \text{CO}_2 \), and 3% \( \text{SO}_3 \) isomorphic to its crystalline structure.

The second important mineral, calcite, forms cement and are included in the granular material of phosphorite ores. Together with Francolite, they make up 75-80 to 93-95% of the ore’s mass. The distinctive feature of the Kyzylkum phosphorites is the presence in them of three forms of carbonates: a calcite relict preserved from phosphate substitution within phosphate shells - «endocalcite»; cement calcite - «exocalcite»; carbonate groups isomorphically included in the crystalline lattice of phosphate mineral [15]. The relationship between calcite and fluorocarbonapatite affects the technological properties of ores.

The third, in quantitative terms, mineral component of phosphate ores - clay is usually incorporated into cement. In addition to these main minerals, phosphate ores are always present as impurities of gypsum and hydrohetite, and in raw ores, organic matter and pyrite are present. Of the minerals, impurities with a content of not more than one-hundredth of a percent are zeolites (clinopytylolit), polygorskite, alevrite quartz and others.

The ores of the Jerois-Sardarin deposit have the following average mineral composition, %: Francolite – 56.0; Calcite – 26.5; Quartz – 7.5 – 8.0; Hydro-mixtic minerals and field spurs – 4.0 – 4.5; Gypsum – 3.5; Hetite – 1.0; Zeolite - less than 1; Organic matter - about 0.5 [16].

The average sample of phosphorite from the Jeroy-Sardarin deposit comprises (weight. %): 16.2 \( \text{P}_2\text{O}_5 \); 46.2 \( \text{CaO} \); \( \text{CaO} : \text{P}_2\text{O}_5 = 2.85 \); 17.7 \( \text{CO}_2 \); 0.6 MgO; 2.9 \( (\text{Al}_2\text{O}_3+\text{Fe}_2\text{O}_3) \); 1.5 \( (\text{K}_2\text{O}+\text{Na}_2\text{O}) \); 2.65 \( \text{SO}_3 \); 1.94 F; 0.1 Cl; 7.8 insoluble residue. Low phosphorus content, high calcium module value, high carbonate and chloride content make such raw materials unfit for sulfuric acid extraction [9]. To get high-quality phosphorus fertilizers from it, it has to be enriched. When the carbonate content is high, thermal roasting [17] is the best way to enrich the phosphate raw material. Therefore, the Kyzylkum phosphorite complex (KPhC) has undergone multi-grade enrichment: crushing, dry enrichment in order to produce ordinary phosphorus, washing off chlorine and burning to remove \( \text{CO}_2 \).

Since 2016, the KPhC has annually produced soaked, burnt concentrate with an average content of 26% \( \text{P}_2\text{O}_5 \) in the volume of 716 thousand tons. The KPhC has been producing a new product. It is the raw material for the production of extractive phosphoric acid and ammophos. KPhC also produces ordinary phosphate flour with a content of 17-18% \( \text{P}_2\text{O}_5 \). It can be converted into a simple local super phosphate.

Simple superphosphate is one of the most famous phosphorus fertilizers. This fertilizer is a product consisting of a mixture of monocalcium phosphate and gypsum. Simple superphosphate is produced by sulfuric acid decomposition of natural phosphates by chamber, flow or chamber flow methods.
Its production is based on the reactions of sulphuric acid with phosphate raw material and subsequently phosphoric acid with the partially decomposed part of the phosphate raw material during the warp maturation process:

\[
\begin{align*}
\text{Ca}_5(\text{PO}_4)_3F + 5\text{H}_2\text{SO}_4 + 2,5\text{H}_2\text{O} &= 3\text{H}_3\text{PO}_4 + 5\text{CaSO}_4 \cdot 0,5\text{H}_2\text{O} + \text{HF} \quad (1) \\
\text{Ca}_5(\text{PO}_4)_3F + 7\text{H}_3\text{PO}_4 + 5\text{H}_2\text{O} &= 5\text{Ca(H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O} + \text{HF} \quad (2)
\end{align*}
\]

They are summarized as follows:

\[
2\text{Ca}_5(\text{PO}_4)_3F + 7\text{H}_2\text{SO}_4 + \text{H}_2\text{O} = \text{Ca(H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O} + 7\text{CaSO}_4 + 7\text{H}_2\text{O} + 2\text{HF} \quad (3)
\]

In simple superphosphate production, these two stages are sequential. This is because the co-existence of \(\text{H}_2\text{SO}_4\) and \(\text{Ca(H}_2\text{PO}_4)_2\) in aqueous solutions is not possible due to an exchange reaction with the formation of low soluble calcium sulphate:

\[
\text{H}_2\text{SO}_4 + \text{Ca(H}_2\text{PO}_4)_2 = \text{CaSO}_4 + 2\text{H}_3\text{PO}_4 \quad (4)
\]

So, there’s only one chemical reaction at each stage. At the end of the reaction, the resulting super-phosphate mass is fed into a warehouse ripening, where the decomposition reaction of the phosphate raw material by phosphoric acid is completed within a few days [18].

This long process of decomposition of the phosphate raw material is explained by the fact that the reaction with \(\text{H}_2\text{SO}_4\) produces a surface crust of \(\text{CaSO}_4\) crystals on the surface of the phosphorite grains [19]. Another layer of calcium phosphate crystal is formed during the reaction with \(\text{H}_3\text{PO}_4\). Thus, in both sulfuric and phosphoric acids, it is necessary to cross a layer of crystal grains on the surface in order to react with the phosphate grain itself. Since at the chamber and stock maturation stages the limiting stage of the process is the rate of diffusion of the acid through the formed salt crust [20].

In addition, the presence of large amounts of impurities in the phosphate raw material degrades the main reaction, that is, it binds a part of the useful \(\text{P}_2\text{O}_5\) and results in a significant consumption of the acid necessary for the complete decomposition of the raw material [19].

The sulfuric acid degradation of natural phosphate raw materials produces a hygroscopic product characterized by low granule strength and high traceability. This is because the vapour pressure above the phosphoric acid is considerably lower than the saturated monocalcium phosphate solution. Since absorbed moisture dissolves some monocalciumphosphate, causing its decomposition into dicalciumphosphate and phosphoric acid:
\[
Ca(H_2PO_4)_{2} \cdot H_2O + H_2O = CaHPO_4 + H_2PO_4 + 2H_2O \quad (5)
\]

The release of additional free phosphoric acid further increases the hygroscopy value of the superphosphate, which results in poor physical properties, and in the reduction and dissipation of the product.

One way to improve the quality of acidic superphosphate is to neutralize free \(H_3PO_4\) with ammonia. Neutralization is usually combined with the process of granulation. Ammonized superphosphate is not comfortably and is not tracked, has low humidity and an elevated \(P_2O_5\) content; it can be introduced into the soil by means of simple soils, resulting in a more even distribution and better use. When neutralized by free \(P_2O_5\) gaseous ammonia, monoammonium phosphate is formed:

\[
H_3PO_4 + NH_3 = NH_4H_2PO_4 \quad (6)
\]

Due to the separation of the neutralization heat, the temperature rises to 80-90°C and the superphosphate is slightly dried.

In the process of ammonium conversion of the super phosphate mass, \(P_2O_5\) is retrograded - the water-soluble monocalcium phosphate is converted to citrate-soluble dicalciumphosphate by reaction:

\[
Ca(H_2PO_4)_{2} + NH_3 = CaHPO_4 + NH_4H_2PO_4 \quad (7)
\]

It should be noted that when \(Ca(H_2PO_4)_{2}\) is retrograded to form \(CaHPO_4\), although the water-soluble form content decreases but the content of the form to be assimilated does not change. It is on this phenomenon that the prolonged action of fertilizer [21-22] is based.

The Kokand superphosphate plant currently produces a simple ammonized superphosphate chamber method [23]. This method includes: decomposition of soap dried Kyzylkum concentrate (18-19% \(P_2O_5\)) with 60% sulfuric acid at its rate of 100% and 70-75°C; chamber ripening of superphosphate mass for 1-1.5 h. at 115-120°C; Stock ripening for 6 days at 3-time refining; granulation and ammonium, drying and dispersion of the product. The finished product comprises 12% \(P_2O_{\text{total}}\), 1.5% N, and \(P_2O_5\)water.: \(P_2O_{\text{total}} = 50\%\) and strength of granules of 1.5MPa.

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

a) Six days of warehousing ripening and three times of refining, passivation of active centres of all expendable fluorocarbonate apatiteandincomplete extraction of \(H_3PO_4\) into liquid phase;
b) Diffusion inhibition of the formation of Ca(H$_2$PO$_4$)$_2$ and high content of free H$_3$PO$_4$ in the chamber product;

c) Unsatisfactory granulation of superphosphate mass and high retention rate;

d) The unorganized release of harmful substances and the high level of dust in the production rooms, as warehousing ripening is a potent source of fluoride emissions to the atmosphere.

An analysis of the working conditions of workers and the main professions involved in the production of superphosphate has been conducted in [24]. In addition, work places have recorded exceedances of the maximum allowable concentrations of industrial aerosols, deterioration of microclimatic parameters and exceedance of vibration levels. For general hygiene assessment of the classes of working conditions of the scraper driver and the loading operator, it corresponds to the 3rd harmful 2nd degree; crane driver and packing-packing machines, apparatus operator - 3rd harmful 3rd degrees.

The option of excluding chamber maturation and storage maturation and ammonium from the production of simple superphosphate from Karatau phosphate is described in the patent [25] where it is proposed to treat phosphate in two stages: In the first step, phosphate is degraded by diluted 55 % sulphuric acid using three or a four-chamber mixer used in the production of superphosphate (residence time 5-7 min). The pulp is then supplied with water at a ratio of S : L = 1 : 1.5, and the resultant non-polluting pulp is held in it for 1-1.5 hours when stirring. Prior to drying and granulation, the unpolluted pulp shall be mixed with a portion of the fine dried product (less than 1 mm) in a ratio of 1 : 1,5. A positive point is the complete elimination of the stage of warehouse ripening. However, the hardware design is complex, high recycle rate, and, in addition, the technology is energy-intensive due to the need to evaporate a significant amount of water from the diluted pulp at the stage of its drying and granulation.

The proposed two-stage method for processing phosphate raw materials into superphosphate, where at the first stage the main amount of raw materials is treated with sulfuric acid to form phosphoric acid, and the resulting acidic reaction mass, consisting of phosphoric acid and calcium sulfate, is neutralized in the second stage of the process with the help of highly reactive phosphorite. Ability or other neutralizing agent can become encouraging, both in terms of the possibility of intensifying its individual stages, and creating on their basis a more rational flow production technology different from the classical version.

A more simplified approach to the two-stage scheme, allowing for the exclusion of chamber and warehouse maturation phases of superphosphate, is described in the patent [26]. In the first stage, most of the poor dolomitized phosphorite (50-70%) is degraded with sulphuric acid at a concentration of 25-35%. The duration
of the pulp in the reactor by an extractor type mixer is 6-8 hours. In the second reactor, in the case of constant mixing, the remaining part (30-50%) of phosphorite is added to the pulp in order to completely neutralize the phosphoric acid, thus forming a monocalcium phosphate, where the reaction pulp has a residence time of 2-4 hours.

The pulp is dried and granulated in a drum-type drying and granulation apparatus (DGA). Lack of the same need for evaporation of the diluted pulp and long decomposition process.

The patent [27] describes a similar sulphuric acid extraction regime for phosphoric acid as the first stage in the two-stage treatment of natural phosphates. The phosphate raw material is decomposed in two stages: in the first stage 70-90% of the phosphate raw material of the total quantity is used, the sulphuric acid is decomposed in a mode corresponding to the dehydrate mode for producing the extractive phosphoric acid (EPhA) in the resulting phosphorous acid suspension the ratio S : L is equal to 1 : (1,7-2,5). In the second stage, the rest of the raw material, in the form of phosphate, is introduced into the suspension. The neutralization is carried out up to NH₃ : H₃PO₄, which is equal to 0.95-1.3. The resulting product contains mainly ammonium monophosphate and calcium sulphate.

The time of the phosphorous acid suspension in the reactor at 80°C is 1,5 h. (first stage). The duration of the second stage of neutralization at 60-80°C - 20 min. The temperature at both stages of the process is maintained by the heat of the reactions.

According to the above-mentioned method at the Chardzhou chemical plant named after S. Niyazova (Republic of Turkmenistan) our Kyzylkumphosphorites are processed on granulated superphosphate, called «ammonium superphosphate» [28]. The organization of production under these proposed schemes requires a high capital investment. In addition, the neutralized pulp contains about 50% of the water, which results in increased energy consumption.

A brief review shows that the choice of modes of crystallization of calcium sulfate from phosphoric acid solutions at the initial stage of decomposition of phosphate raw materials with sulfuric acid plays an important role, not only in the classical schemes of EPhA production technology, where the main emphasis is on the production of phosphoric acid with an increased concentration of P₂O₅ and crystallization from it CaSO₄ in large-crystalline forms, but also in the organization of the initial stage of the technology for the production of simple superphosphate, although the latter does not aim at removing CaSO₄ from the reaction medium.

In order to intensify the initial stage of the two-stage treatment scheme for natural phosphates, options for regulating the conditions of the sulphuric acid extraction regime were considered [22, 29-31].
Depending on the concentration of phosphoric acid in the system and temperature, the resulting calcium sulphate in the reaction equation (1) can be precipitated in the form of anhydrite \((n = 0)\), hemihydrates \((n = 0.5)\) and dihydrate \((n = 2)\). These are the basis for three options for the extraction method for the production of EPhA: anhydrite, hemihydrate and dihydrate [32].

For example, in the dihydrate method, \(\text{CaSO}_4\) is precipitated in the form of dihydrate (at 70-80°C and the acid concentration in the reaction mixture of 20-32% \(\text{P}_2\text{O}_5\)), in the form of hemihydrates (at 90-100°C and at 35-42% acid). Crystalization fields above 110°C and \(\text{P}_2\text{O}_5\) concentrations above 50% [33] correspond to the anhydritic mode.

Under real conditions of sulfuric acid extraction (temperature 80-90°C, concentration 20-38% \(\text{P}_2\text{O}_5\)), gypsum (dehydrate) is a stable form, where phase transformations occur according to the scheme:

\[
\text{CaSO}_4\cdot0.5\text{H}_2\text{O} \rightarrow \text{CaSO}_4 \rightarrow \text{CaSO}_4\cdot2\text{H}_2\text{O} \leftarrow \text{CaSO}_4\cdot0.5\text{H}_2\text{O}
\]

that is, gypsum can crystallize by watering both anhydrite and hemihydrate. Then, under temperature (>110°C) and concentration \((\text{P}_2\text{O}_5>50\%)\) conditions for the production of simple superphosphate, anhydrite will become a stable form, where these transformations occur according to the following scheme:

\[
\text{CaSO}_4\cdot0.5\text{H}_2\text{O} \rightarrow \text{CaSO}_4\cdot2\text{H}_2\text{O} \rightarrow \text{CaSO}_4 \leftarrow \text{CaSO}_4\cdot2\text{H}_2\text{O}
\]

that is, the hemihydrate turns into anhydrite not directly, but through watering it into gypsum.

There are also fields of crystallization of calcium sulfate with boundaries in temperature (110°C and above) and concentration (52% \(\text{P}_2\text{O}_5\) and above), where anhydrite is also a stable phase, and the scheme of phase transformations proceeds according to the scheme:

\[
\text{CaSO}_4\cdot2\text{H}_2\text{O} \rightarrow \text{CaSO}_4\cdot0.5\text{H}_2\text{O} \rightarrow \text{CaSO}_4 \leftarrow \text{CaSO}_4\cdot0.5\text{H}_2\text{O}
\]

that is, in the initial stage of crystallization, only hemihydrate is formed (lack of water for watering), which instantly transforms into anhydrite.

This area is an unexplored part of the \(\text{CaSO}_4\) crystallization field; under temperature and concentration conditions, it can manifest itself if natural phosphate is decomposed by concentrated sulfuric acid (93-98% \(\text{H}_2\text{SO}_4\)), without water input from outside. Due to the high temperature of the phosphate decomposition reaction with concentrated sulfuric acid, the water introduced by its solution (2-7% \(\text{H}_2\text{O}\)) instantly evaporates at the very beginning of the process,
and the source for the formation of crystalline hydrate CaSO$_4$·0.5H$_2$O can be molecular water released by the reactions (1, 3) for its crystallization.

If we talk about the size of crystals of hemihydrate and anhydrite released from concentrated solutions of phosphoric acid at elevated temperatures, then anhydrite is released in the form of larger crystals that form irregular square plates in the case when the solution in the superphosphate mass has a concentration of 45-55% P$_2$O$_5$, containing some excess of sulfuric acid (3-5% SO$_3$).

A feature of our proposed method for producing granular superphosphate from carbonate phosphorites in comparison with the classical one is that the technological process is carried out in two stages:

1) The main part (70-80% of the total mass) of phosphorite is decomposed by 92-93% H$_2$SO$_4$ taken at 100-105% rates of stoichiometry to form 45-50% P$_2$O$_5$ phosphoric acid, where calcium sulfate crystallizes in the form anhydrite;

2) The acidic reaction mass obtained in the first stage, containing concentrated phosphoric acid (45-50% P$_2$O$_5$) and the anhydrite is treated with the rest (20-30%) of phosphorite, the process of neutralizing phosphoric acid into monocalcium phosphate takes place.

The duration of the first stage is 15-20 minutes at 120-125°C. The processes of neutralization and granulated product by pelletizing are combined, and they are combined in one apparatus. Duration 25-30 minutes. In this case, the stage of product drying is excluded from the scheme.

To elucidate the mechanism of decomposition of phosphate raw materials in two stages, the present study was performed.

2. Methods

For experiments as raw materials were taken phosphorite flour of the composition (wt.%): P$_2$O$_5$ – 17.54; CaO – 47.75; MgO – 1.79; CO$_2$ – 16.5; Fe$_2$O$_3$ – 0.73; Al$_2$O$_3$ – 0.95; SO$_3$ – 4.06; F – 1.7; SiO$_2$ – 1.24; insoluble residue – 4.03; CaO : P$_2$O$_5$ – 2.72 and 93% - H$_2$SO$_4$.

Experiments on the decomposition of phosphate rock were carried out in a thermostated reactor equipped with a paddle stirrer at 122°C (The required temperature for the anhydrite regime was maintained by the heat of reaction). The rate of sulfuric acid was taken as 100% of the stoichiometry for the formation of H$_3$PO$_4$ (reaction 1), taking into account the decomposition of impurity components of phosphate raw materials. Content P$_2$O$_5$ free in the reaction mixtures and finished products was determined by titration with 0.1 n NaOH using indicators of methyl orange and phenolphthalein.

First, we studied the kinetics of decomposition of phosphate raw materials. In this case, the contact time of the components was 2; 5; 10; 20; 40 and 60 minutes. The results are shown in Figures 1-3.
3. Results and Discussions

It can be seen from it that with an increase in the duration of the interaction of phosphate with sulfuric acid from 2 to 60 minutes, the decomposition coefficient of phosphate raw materials increases, that is, the relative content of the watersoluble form of P$_2$O$_5$ in relation to its total form from 90.02 to 92.32% (Figure 1.).

In this case, the total content of P$_2$O$_5$ in the reaction mass increases from 9.42 to 9.90% (Figure 2.), and the free acidity (the sum of sulfuric and phosphoric acids), on the contrary, decreases from 16.68 to 15.39% (Fig.3.). From the data, it can be concluded that from a technological point of view, the decomposition time of phosphate raw materials is sufficient for 20-30 minutes. A further increase in time does not lead to a significant increase in the decomposition coefficient. And with a processing time of less than 20-30 minutes, there is no sufficient formation of a thixotropic mass necessary for further processing of the reaction mass.

In the second stage, experiments were carried out to obtain finished superphosphate by neutralizing the acidic reaction mass with phosphorite flour (the second stage of processing). The rate of phosphate was varied from 105 to 220% of the stoichiometry for the formation of monocalcium phosphate (reaction 2). At the same time, the general rate of H$_2$SO$_4$ (including the 1st and 2nd stages of decomposition of phosphate raw materials) is from 84 to 102% for monocalcium phosphate, taking into account the decomposition of impurity
components. The neutralization time of the reaction mass is 30; 40; 60; 80 and 120 minutes at 122°C. The reaction of neutralization of the acid mass with phosphorite flour at the second stage of the process is actually the beginning of the granulation process, where the skeleton of calcium sulfate crystals saturated with phosphoric acid acts as a granulation center. Granulation of the neutralized product was carried out by the pelletizing method. Obtained by the proposed method, the granular product is characterized by low dispersion, and the granules have high resistance to dynamic abrasion.

Figure 2. The decomposition coefficient of phosphate rock by 93% sulfuric acid depending on the interaction time

In finished products, the assimilable form of P₂O₅ was determined by its solubility in 2% citric acid. The chemical analysis results are shown in Table 2.

The table shows that the higher the norm of phosphorite flour and the longer the period of interaction of phosphoric acid with phosphorite flour, the lower the content of P₂O₅_free and the higher is P₂O₅_total in superphosphate. So, for the norm of phosphorite flour - 105% (norm of H₂SO₄ - 98.5% of stoichiometry for the formation of Ca(H₂PO₄)₂) with an increase in the interaction time from 30 to 120 minutes, the content of P₂O₅_free in the product decreases from 10.45 to 9.56%, for the norm 110% (norm H₂SO₄ - 97.5%) from 9.95 to 9.38%, for the norm 120% (norm H₂SO₄ - 96%) from 9.51 to 8.18%, for norm 180% (norm H₂SO₄ - 88.5%) from 6.02 to 5.32%, for the norm 190% (norm H₂SO₄ - 87.5%) from 5.35 to
5.03%, for norm 200% (norm H₂SO₄ - 86%) from 4.81 to 4.26% and for norm 220% (norm H₂SO₄ - 84%) from 2.89 to 2.46%.

* Free acid content was determined as the sum of free sulfuric and phosphoric acids.

**Figure 3.** Free acidity content in the reaction mass, wt. %

**Table 2.** The composition of the products of neutralization of phosphoric acid in the reaction mixture (the initial rate of 93% H₂SO₄ is 100% of the stoichiometry for the formation of H₃PO₄, the reaction time is 20 minutes) at rates of phosphoric acid - 105-220% for the formation of Ca(H₂PO₄)₂, depending on the interaction time components

| Time of interaction of H₃PO₄ with phosphate, min. | P₂O₅ content in the reaction mass, wt. % | P₂O₅assim. / P₂O₅total ·100, % | P₂O₅free. / P₂O₅total ·100, % |
|-----------------------------------------------|--------------------------------------|----------------------------------|----------------------------------|
|                                               | P₂O₅total | P₂O₅assim. | P₂O₅satur. | P₂O₅free. | P₂O₅assim. / P₂O₅total ·100, % | P₂O₅free. / P₂O₅total ·100, % |
| 30 at the rate of phosphate rock - 105%        | 10.58     | 9.92      | 9.41      | 10.45     | 93.76                        | 88.94                        |
| 40 at the rate of phosphate rock - 105%        | 10.60     | 9.96      | 9.61      | 10.34     | 93.96                        | 90.66                        |
| 60 at the rate of phosphate rock - 110%        | 10.67     | 10.07     | 10.03     | 10.14     | 94.37                        | 94.00                        |
| 80 at the rate of phosphate rock - 110%        | 10.72     | 10.16     | 10.10     | 9.95      | 94.77                        | 94.22                        |
| 120 at the rate of phosphate rock - 110%       | 10.84     | 10.35     | 10.24     | 9.56      | 95.48                        | 94.46                        |

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|   |   |   |   |   |   |   |
|---|---|---|---|---|---|---|
|   | 10.66 | 10.07 | 9.49 | 9.86 | 94.46 | 89.02 |
|   | 10.73 | 10.17 | 9.86 | 9.66 | 94.78 | 91.89 |
|   | 10.79 | 10.27 | 10.00 | 9.47 | 95.18 | 92.68 |
|   | 10.92 | 10.46 | 10.28 | 9.08 | 95.78 | 94.14 |
|   |   |   |   |   |   |   |
| 30 | 10.69 | 10.14 | 9.18 | 9.51 | 94.85 | 85.87 |
| 40 | 10.73 | 10.20 | 9.34 | 9.36 | 95.06 | 87.04 |
| 60 | 10.81 | 10.33 | 9.68 | 9.06 | 95.56 | 89.55 |
| 80 | 10.88 | 10.42 | 9.89 | 8.77 | 95.77 | 90.90 |
| 120| 11.03 | 10.58 | 10.36 | 8.18 | 95.92 | 93.92 |

at the rate of phosphate rock - 120%

|   |   |   |   |   |   |   |
|---|---|---|---|---|---|---|
|   | 10.92 | 10.66 | 9.00 | 6.02 | 97.62 | 82.42 |
|   | 10.95 | 10.66 | 9.01 | 5.99 | 97.35 | 82.28 |
|   | 11.03 | 10.67 | 9.02 | 5.93 | 96.73 | 81.77 |
|   | 11.11 | 10.69 | 9.05 | 5.72 | 96.21 | 81.45 |
|   | 11.43 | 10.71 | 9.09 | 5.32 | 93.70 | 79.52 |

at the rate of phosphate rock - 180%

|   |   |   |   |   |   |   |
|---|---|---|---|---|---|---|
|   | 11.13 | 10.47 | 8.92 | 5.35 | 94.07 | 80.14 |
|   | 11.14 | 10.48 | 8.93 | 5.31 | 94.07 | 80.16 |
|   | 11.17 | 10.49 | 8.94 | 5.24 | 93.91 | 80.03 |
|   | 11.20 | 10.50 | 8.95 | 5.17 | 93.75 | 79.91 |
|   | 11.63 | 10.54 | 8.97 | 5.03 | 90.62 | 77.12 |

at the rate of phosphate rock - 190%

|   |   |   |   |   |   |   |
|---|---|---|---|---|---|---|
|   | 11.17 | 10.21 | 8.80 | 4.81 | 91.41 | 78.78 |
|   | 11.26 | 10.25 | 8.82 | 4.75 | 91.03 | 78.33 |
|   | 11.45 | 10.33 | 8.85 | 4.63 | 90.22 | 77.29 |
|   | 11.63 | 10.40 | 8.89 | 4.50 | 89.42 | 76.44 |
|   | 12.01 | 10.56 | 8.96 | 4.26 | 87.93 | 74.60 |

at the rate of phosphate rock - 200%

|   |   |   |   |   |   |   |
|---|---|---|---|---|---|---|
|   | 11.66 | 10.43 | 8.99 | 2.89 | 89.45 | 77.10 |

at the rate of phosphate rock - 220%
Table 2 shows that at a 200% rate of phosphate rock (the rate of H$_2$SO$_4$ is 87.5%) and a neutralization time of 30 minutes, the composition of the finished product is as follows (wt.%): P$_2$O$_5$free. – 4.81%, P$_2$O$_5$total. – 11.17%, P$_2$O$_5$assim.: P$_2$O$_5$total. = 91.41% and P$_2$O$_5$water.: P$_2$O$_5$total. = 78.78%, and its granule strength exceeds 2 MPa.

4. Conclusions

Thus, the proposed version of the in-line method of simple superphosphate over the current one based on the classical scheme has the following advantages:

- the scheme has time-optimized processing stages of high-carbonate phosphorites, as a prerequisite for the creation of high-performance production lines for the production of simple granular superphosphate using them;
- on the basis of the proposed method is the most simplified scheme, due to the exclusion from its composition of redistributions that are too prolonged in time, such as chamber maturation and warehouse maturation;
- the technology consumes less energy resources, both due to the use of energy-saving equipment and exclusion from its composition of the scheme of energy-intensive process stages, such as warehouse ripening and drying;
- the technological line of the installation according to the proposed scheme with the selected equipment is much compact, easier to install and simple to operate than expected to reduce capital and operating costs for their maintenance;
- the technology is environmentally friendly: less unorganized dust and gas emissions, is distinguished by the possibility of maximum distillation of harmful fluorinated gases from phosphorite and their organized collection;
- exclusion of the introduction of neutralizing agents from the outside (lime flour, liquid or gaseous ammonia, etc.) and binding additives (phosphoric acid, phosphate and sulphate ammonium salts, etc.).

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