

Technological Features of the Production of Granulated Simple Superphosphate According to the Flow Scheme

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Abstract

The classic method of simple ammoniated superphosphate includes: decomposition of phosphate raw materials in sulfuric acid with a concentration of at least 63-68 %, at its norm of 100 % stoichiometry and at a temperature of 70-75 °C. Chamber maturation of superphosphate mass for 1-1,5 hours at a temperature of 115-120 °C; storage ripening for 6 days with 3 times stirring; granulation and ammonization (humidity of superphosphate before granulation 14-15 %); drying and sieving of the product.

That a distinctive feature of the proposed flow method before the known is that the weight of the production cycle of processing natural phosphate is carried out in only two stages. At the first stage, phosphorite is treated with a super stoichiometric flow rate of concentrated sulfuric acid (at least 93 %), under conditions of complete decomposition of phosphorite with the formation of a loose matrix of calcium sulfate crystals, absorbed into it by the liquid phase. At the second stage, a concentrated solution of phosphoric acid in a mixture with sulfuric acid is involved in the reaction with an additional amount of phosphorite introduced, which is the basis of the mechanism of chemical granulation of superphosphate mass.

Keywords: *sulfuric acid, simple superphosphate, granulation superphosphate, monocalcium phosphate.*

1. Introduction

Sulfur deficiency has become more common in the last decades and the demand for S fertilizers has increased. Commercial fertilizers containing elemental S (S⁰ or ES) are usually in granular form, but their efficiency under field conditions has rarely been studied. [1] Phosphoric acid is, mainly, utilized in the production of phosphate fertilizers, which means it is vital for crop production and key economic importance. More than 90 % of phosphoric acid produced worldwide is derived from the wet acid process the phosphate rock digestion by sulphuric acid [2], [3].

Global population growth requires intensification of agriculture, for what a sustainable supply of phosphorus (P) is essential. Since natural P reserves are diminishing, recovering P from wastes and residues is an increasingly attractive prospect, particularly as technical and economic potential in the area is growing. In addition to providing phosphorus for agricultural use, precipitation of P from waste residues and effluents lessens their nutrient loading prior to disposal [4], [5].

Theoretical basis of the process of phosphorite decomposition with concentrated sulfuric acid in the anhydrite mode of phosphoric acid extraction under conditions of minimum water content.

The technology of simple superphosphate from natural phosphates, according to the complexity of its technological processing of raw materials (operations), are usually classified as "simple" or "not complicated", and commercial products are recognized as the cheapest and most affordable phosphorus fertilizer in the world [6]–[8].

Materials and methods

Modern technology for the production of simple and not based on it, neutralized granular superphosphate includes the following stages:

a) Mixing phosphate feed with sulfuric acid under conditions of obtaining a mobile suspension (the use of dilute solutions of sulfuric acid);

b) Curing the resulting suspension of superphosphate by continuing the chemical reaction of the formation of monocalcium phosphate in a solution of phosphoric acid and crystallization of calcium sulfate in a dehydrate form; [8], [9].

c) Final aging of acid superphosphate mass with shoveling, where a significant part of monocalcium phosphate, as it is saturated with its salt, crystallizes into monohydrate and the recrystallization of calcium sulfate dehydrate to hemihydrates is completed;

d) Neutralization of excess acidity of a pre-moistened superphosphate mass by treating it with ammonia or with readily degradable phosphoric acid additives (carbonate phosphate rock, limestone, chalk).

e) Drying the wet granular superphosphate mass.

The concentration, temperature, time conditions and properties of the treated reaction stream in the above stages became decisive in the hardware design of the modern scheme for the production of simple [10]–[12]. For example, for the redistribution of "a", a process is carried out in a mobile pulp medium, for which purpose water is introduced into the reaction mixture from the outside (usually in an aqueous solution of sulfuric acid with a concentration of 65-75 % H_2SO_4). In subsequent stages, this water must be removed. Due to the heat of reaction, the temperature of the medium reaches 110-115 °C. The redistribution duration is short; it lasts for just 2-7 minutes. The upper limit of the residence time is forcedly limited due to the possibility of a quick setting of the reaction mass due to crystallization of calcium sulfate dehydrate and plugging of the mixer [13]–[15]. For such a short period and the properties of the resulting medium, no matter what the modern design of the mixer is chosen, the degree of consumption of the initially introduced sulfuric acid does not exceed 30-40 %. The presence in the reaction mass of the remainder of unreacted sulfuric acid excludes the formation of monocalcium phosphate in its composition [16], [17].

Results and discussion

This process is carried out in series-connected batteries of low-volume tank-type mixers, equipped with high-speed mixing devices [9]. This option for organizing the process of mixing natural phosphate with sulfuric acid is, used mainly in enterprises of the former Soviet Union. Abroad, they use various types of horizontal rotary (drum, screw, and vane) or centrifugal cone type mixers for this purpose, most often Broadfield, Sockett, Forbis or Broadfield rotary mixers.

Redistribution "b" is associated with the formation of a solid-phase reaction mass with a certain ductility and mechanical strength. In the initial phase of this redistribution, the duration of which is 20–40 min, theoretically, the reaction of the formation of phosphoric acid with an almost maximum consumption of sulfuric acid in the mixture and about 70 % of the initially introduced natural phosphate is to be completed. In the final

phase of the redistribution, lasting for 1.2-1.8 hours, phosphoric acid is gradually saturated with monocalcium phosphate, and then, by the end of the redistribution, mass crystallization begins, which will lead to the setting of the reaction mass into a monolith [18]–[23].

This results in a strong inhibition of such processes as the dissolution of phosphate in phosphoric acid, crystallization and recrystallization of calcium salts, which are completely hindered by the low rate of migration (diffusion) of reaction molecules in the solid phase. For this reason, the degree of decomposition of phosphate, even to the completion of redistribution "b", remains still low and does not exceed 85-87 %.

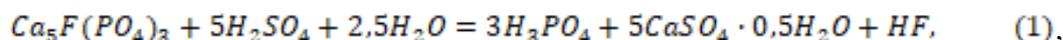
The redistribution of "b" is carried out in special chambers, either cylindrical (circular), slowly rotating in a circle, or rectangular with fixed sides located above the conveyor transport with slow linear motion. The first type of camera is mainly used in enterprises of the CIS. Cameras with linear motion, the so-called Broadfield camera, are widespread in the United States, Europe and other countries.

The redistribution "c" includes a too long technological process in time (from 14 to 21 days), which requires a huge scale of the reaction space (storage facility) in comparison with the working volumes of the remaining stages. Fresh superphosphate from stage "b", having a temperature of 75-80 °C, is constantly subjected to shoveling in the warehouse, while it is cooled to 40-45 °C. About 40-50 % of fluorine, initially introduced by phosphate raw materials, is released at this stage.

The hardware design of the redistribution "c" is almost the same at all plants producing simple superphosphate [24]–[27]. Warehouses for simple superphosphate are everywhere equipped with clamshell cranes or other equipment for periodic shoveling of superphosphate, moving it within the warehouse and to the nutrient hopper of the granular superphosphate workshop.

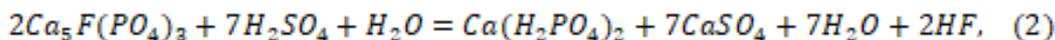
In the redistribution "d" of modern plants, the ripened superphosphate mass is granulated while neutralizing the residual acidity with ammonia (liquid, gaseous or aqueous solution). For granulation, the method of pelletizing a previously moistened mixture with retur in drum, disk or blade granulators is used. More widespread are granulators of drum type. In this case, the optimum moisture content of the material for granulation in the drum is within 15-18 %, and the residence time of the material in them does not exceed 8-12 minutes [19], [28]–[32].

The task of redistributing "a" to the maximum is quantitatively complete, the first stage of decomposition of natural phosphate with sulfuric acid with the conversion of all P₂O₅ raw materials to the liquid phase in the form of free phosphoric acid:



Whose activity should increase as it accumulates in the liquid phase, increases the concentration and increases the temperature of the medium due to the heat of the reactions.

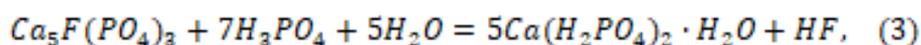
Under real conditions, natural phosphate and an aqueous solution of sulfuric acid are continuously dosed into the reactor-mixer with redistribution "a" in such a mass ratio that the reaction is completed according to the generalized equation:



That is, under conditions of a certain excess of phosphate (or lack of sulfuric acid) according to the stoichiometric reaction (1). Despite the fact that, in the mixer, due to the introduction of water in the composition of the initial sulfuric acid, the necessary

consistency of the reaction mass is maintained, in which the diffusion processes should be intensified and its fluidity should be maintained in a short period of time (5-7 minutes). In the redistribution "a" reaction (1) does not have time to proceed to the end. The reason for this fact is explained by the blocking of the reaction centers of the surface of phosphate particles by calcium sulfate crystals, restricting the access of sulfuric acid molecules to them.

Under these conditions, it can be assumed that passivation of all introduced phosphate by stoichiometric reaction (2) will occur, which should be manifested in a strong inhibition of the reaction of its subsequent decomposition, this time, with the participation of not sulfuric acid, but phosphoric:



The complete completion of reaction (1) can be observed only at the initial stage of redistribution "b" in the superphosphate chamber during the first 20 minutes after pouring the pulp. During this period, the setting of the reaction mass occurs only due to the crystallization of calcium sulfate. From the moment, sulfuric acid disappears in the reaction mixture, free phosphoric acid accumulated in the reaction mass begins to interact with an excess of the initial phosphate according to equation (3).

The main reaction product is monocalcium phosphate, which initially passes into the composition of a concentrated solution of phosphoric acid. Only when it is saturated with this salt, which almost coincides with the end of the maturation period of the superphosphate mass in the chamber, begins to crystallize from it in the form of monocalcium phosphate monohydrate. Thus, the main components of the superphosphate mass, monocalcium phosphate are distributed between two phases: in the liquid - in the form of its solution in phosphoric acid and in the solid - in the form of its crystalline hydrate [33].

Among the serious problems of processing simple superphosphate into its granular form (redistribution "d") is the unsatisfactory granularity of superphosphate mass ripened under storage conditions (high dust fraction in granular superphosphate – 30 % and lower granule strength - less than $1 \text{ kg} \cdot \text{s} / \text{cm}^2$). To a greater extent, this problem manifests itself when starting natural phosphates having a high calcium modulus ($\text{CaO} : \text{P}_2\text{O}_5$) in the range of 2.4-2.7 are used. The ripened phosphorite superphosphate with a calcium module of 2.7 and higher, under normal regulatory production conditions, without the use of special binders, for example, a solution of ammonium sulfate, is not granulated at all [34]–[39].

When identifying the main reasons for the unsatisfactory granularity of ripened superphosphate mass, it is necessary to take into account the special properties of individual particles of the compounds that make up the ripened superphosphate mass. The main one is the ability of particles to form agglomerates between themselves of sufficient strength. According to the data identified by purely experimental means, it was found that particles of natural phosphates, without special binding additives, cannot be agglomerated. Particles of gypsum in all its forms (anhydrite, hemihydrate and dehydrate) also behave this way. Particles of calcium acid phosphates adhere well to each other, and the adhesion forces of monocalcium phosphate particles are much higher than that of dicalcium phosphate. Particles of tricalcium phosphate are completely devoid of these properties. Therefore, the poor granularity of ripened superphosphate is partly due to dilution with calcium sulfate. Its content in superphosphate is greater, the higher the calcium module in the original natural phosphate.

Among the options considered in the following for redistribution "d", innovative may be methods by which phosphorite flour is introduced from the outside to neutralize acidic superphosphate mass, the active centers of particles of which do not contain calcium sulfate crystals. This process is carried out as a separate stage, with the maximum

use of the chemical energy of free phosphoric acid, as a nucleus in a carrier around which, due to its reaction with phosphorite. The layers are layered in the form of a molecular bridge of monocalcium phosphate, and finally, these processes proceed at the same time, in one machine in the rolling mode.

The most interesting, from the point of view of the theory of granule formation, and, productive, practice may be the mechanism by which the growth of the plastic properties of acidic germ particles, consisting of a bulk framework of gypsum crystals, inside which concentrated phosphoric acid is occluded, is formed by repeatedly layering their surface growth material - a reaction product. In this case, the growth material is the product of the chemical interaction of phosphoric acid with phosphorite, that is, monocalcium phosphate.

The efficiency of mass granulation by such a mechanism should be even higher if the following conditions are met:

- at the first stage of decomposition of phosphorite with sulfuric acid, to achieve the most complete yield of phosphoric acid with a minimum contact time of the reacting substances;

- by the beginning of the second stage, it should be accumulated in a framework of calcium sulfate crystals, without any consumption, and its activity is kept as high as possible;

- fine crystalline calcium sulfate formed at the first stage of the process, as a non-granular material, should be isolated from direct participation in the process of increasing the size of the granules in the future;

- the active centers of the contacted portion of the phosphorite flour for the approach of phosphoric acid molecules must be free, that is, not passivated (not shielded) by blocking them with calcium sulfate crystals;

- it is desirable to disintegrate the reaction mass at the exit from the first stage into small germinal particles (centers of granulation) and disperse them evenly in the volume of a continuous medium of granular fine phosphorite.

And the stage of drying granular superphosphate (stage "e") in terms of energy has a peculiar contradiction. The superphosphate mass matured under storage conditions has insufficient moisture (5-10 %) and low temperature (40-45 °C), and to impart plastic properties to the granulated material, it has to be specially moistened at the granulation stage by adding hot water (or steam) to 16-18 % while increasing its temperature to 80-90 °C [28], [40], [41].

As follows from the above points, the technology laid down in the existing production of simple superphosphate is very "far-fetched" to the rank of continuous, and not in the best version of their hardware design. The duration of the redistribution ("a") - ("e"), with slight deviations depending on the origin of natural phosphate, varies significantly among themselves and amounts to: "a" = 2-7 min; "B" = 1.5-2.5 hours, "c" = 14-21 days, "d" = 8-12 minutes, and "c" = 15-20 minutes, which is to choose for all redistributions with a reasonable order the residence time of the streams is very difficult.

Below, we briefly consider the status of work related to the improvement of the production technology of simple granular superphosphate in order to reduce the duration of stages "b" and "c" (ripening and ripening of the mass) or to eliminate them from the technological scheme [22], [42], [43].

The work is devoted to reducing the time of warehouse aging. It is noted that the introduction of sulfuric acid containing a molybdenum-containing spent solution at the stage "b" of the process, the aging of chamber superphosphate from apatite concentrate is reduced from 26 (without additives) to 17-19 hours (with an additive). However, the use at stage "a" of 64% sulfuric acid and a slight reduction in the duration of stage "c" (about 30 %), the proposed method will not lead to a significant intensification of the classical technology for the production of superphosphate.

In the authorship certificate, it was proposed to reduce the time of storage aging by pretreatment of expeditionary superphosphate, aged in storage conditions with a decomposition coefficient of phosphate of less than 90 %, sulfuric acid in the presence or absence of absorption liquid. However, the proposed option leads to a complication of the production scheme and a slight decrease in P_2O_5 in the obtained superphosphate [44]–[46].

The approach to the complete elimination of warehouse ripening is described in the patent [14], which introduced additional stages of processing chamber superphosphate with sulfuric acid and neutralizing the pulp not with ammonia, but with part of the used phosphate feedstock. Fluid pulp is sprayed into a granulation dryer to produce a granular product.

According to the description of the patent in this embodiment, the storage aging of chamber superphosphate is completely excluded. However, this method is also characterized by high energy consumption. In addition, the technological scheme of the process is many times complicated in comparison with the condition proposed by the previous patent [47], [48].

A variant of the complete exclusion from the scheme of chamber maturation and warehouse maturation on the example of the production of simple granular superphosphate from Karatau phosphorites is described in the patent [14]. It is proposed to process phosphorite in two stages: in the first stage, phosphorite is decomposed with diluted 55 % sulfuric acid using for this purpose a standard three or four chamber mixer used in the production of superphosphate (residence time - 5-7 min). Next, the pulp flows into the newly installed reactor with a stirrer, where water is supplied at a ratio of S: L = 1: 1.5 and the resulting non-thickening pulp is kept in it for 1-1.5 hours with constant stirring. Before drying and granulating the product, the non-thickening pulp from the previous step is mixed with a portion of the dried product (retur) in a ratio of 1: 1.5 in the third mixing reactor with a stirrer. A positive aspect of the proposal is the complete exclusion from the scheme of the stage of warehouse aging of superphosphate. However, the hardware design of the process remains complex, high retouring, 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 [49], [50].

A number of works propose the creation of flow schemes with the complete elimination of the problem stage “d” from it. It is according to which the phosphorite flour stream, designed for binding free phosphoric acid, is introduced separately, outside the primary mixing zones of phosphorite with sulfuric acid, chamber and warehouse maturation of superphosphate mass (redistribution of "a", "b" and "c", respectively). The proposals include prior to the decomposition of the main part of the phosphate by sulfuric acid, preliminary mixing of the initial phosphorite with an absorption liquid in the range L: S = 1: 1-2: 1. It proposes neutralizing free phosphoric acid with another part of phosphate, either in an independent reactor or combining this process with the stage of granulation and drying, using apparatuses such as DGA [51]–[54].

A description of a more simplified approach to a two-stage scheme, allowing to exclude the stages of chamber and storage maturation of superphosphate mass, is set forth in the patent. In the first stage, the main part of poor phosphorite (50-70 %) is decomposed with sulfuric acid with a concentration of 25-35 %. The residence time of the pulp in the reactor with an extractor-type stirrer is 6-8 hours. Then, in the second same reactor, the remaining portion (30-50 %) of phosphorite is added to the pulp with constant stirring to completely neutralize phosphoric acid with the formation of monocalcium phosphate, where the residence time of the reaction pulp is 2-4 hours. The pulp is dried and granulated in a drum-type drying granulation apparatus (DGA) [26].

The proposed two-stage scheme for processing phosphate raw materials into fertilizers of the superphosphate class, where in the first stage the main amount of the raw material is treated with sulfuric acid under conditions of its maximum consumption for

the formation of phosphoric acid. This results in acidic reaction mass consisting of high activity phosphoric acid and calcium sulfate, is neutralized Separately, in the second stage of the process, using the remaining part of phosphorite introduced from the outside is promising [55].

In accordance with the descriptions of well-known works on an industrial scale, KyzylKum phosphorites are processed with granular superphosphate, called "ammonium superphosphate", at the Chardzhousk Chemical Plant named after S. Niyazov (Republic of Turkmenistan).

Organization of production according to these proposed schemes requires large capital expenditures. In addition, the neutralized pulp contains about 50 % water, which indicates the inevitability of increased energy consumption [38], [56], [57].

The above brief review of the studies shows that the choice of modes of crystallization of calcium sulfate from phosphoric acid solutions. In the initial stage of decomposition of phosphate, feedstock with sulfuric acid plays an important role, not only in the classical schemes of the production of extraction phosphoric acid. Its main emphasis is on obtaining an increased concentration of P_2O_5 in the liquid phase and crystallization from it of calcium sulfate in large crystalline forms, but also in the organization of the initial stage of the production technology of simple soup phosphate, although in the following. it does not aim at the conclusion of calcium sulfate outside of the reaction medium [58].

In this regard, research aimed at creating a flow technological scheme is of considerable scientific and practical interest. In the initial stage of the process the processing of natural phosphate is carried out with concentrated sulfuric acid, taken in stoichiometric and higher standards, and the temperature and concentration conditions in the reaction mixture correspond to the anhydrite crystallization mode from it calcium sulfate. Issues of testing local Kyzylkum phosphorites in these conditions, which differ in chemical composition from phosphorites of other deposits, the ultimate goal of which is to further increase the volume of their processing on unilateral phosphorus fertilizers available for agriculture [34], [59], [60].

A distinctive feature of our proposed two-stage scheme for the production of simple superphosphate from highly carbonized phosphorites, in comparison with the traditional one, is that at the first stage the main part of phosphorite is decomposed by concentrated sulfuric acid, taken in full and exceeding its consumption rates by stoichiometry of the formation of phosphoric acid. Its sulfate calcium crystallizes in anhydrite, and in the second stage, the acidic reaction mixture obtained in the first stage containing concentrated phosphorus acid, is processed by the second part of phosphorite, where, the processes of neutralizing phosphoric acid to monocalcium phosphate and obtaining a granular product by rolling are combined and carried out in one apparatus.

The decomposition of part of the highly carbonized phosphorite in the first stage with concentrated sulfuric acid at rates of 100-105 % allows the process to be carried out in the anhydrite mode of phosphoric acid extraction (medium temperature 150-200 °C, concentration of P_2O_5 in the liquid phase more than 50-70 %). Which is characterized by a high reaction rate decomposition of raw materials, ending literally in 5-7 minutes.

Within the limits of the applicable acid consumption rates, the $CaSO_4: H_2O$ ratio in the reaction mixture will be 1: 0.15, i.e., sufficient for crystallization in the initial phase of calcium sulfate in the form of a hemihydrate, where the theoretical ratio of $CaSO_4: H_2O = 1: 0.066$. Further, the hemihydrate instantly crystallizes to anhydrite, which is facilitated by both the temperature of the medium (>150 °C) and the concentration of H_3PO_4 (>40 % P_2O_5) [8], [43].

The use of sulfuric acid concentration in the range of 92-93 % H_2SO_4 in the above range of its consumption, due to lack of water, prevents the occurrence of mobile fluid pulp. The new liquid phase that has accumulated towards the end of reaction (1) is exclusively in the anhydrite state that has been occluded in the capillary-porous

framework of agglomerate crystals. This is due to the preservation of the friability of the reaction mass, although it is acid in nature [45], [61], [62].

An excess of sulfuric acid, in addition to the temperature of the medium and its concentration, is a prerequisite for the complete decomposition of phosphorite, but only if there is no excess phosphorite in the mixture.

The proposed two-stage scheme, where instead of redistributing "a" - "d" of the classic version, only two stages are introduced: a) decomposition of the main amount of phosphorite by concentrated sulfuric acid; b) neutralization of the obtained acidic mass with the remaining part of phosphorite with simultaneous granulation, devoid of the disadvantages of traditional technology.

At stage "a" of the new variant, the process is carried out in a certain excess of sulfuric acid in the anhydrite mode of phosphoric acid extraction. The high temperature of the reaction mixture (above 150 °C) and the increased concentration of phosphoric acid in it (above 50 % P₂O₅) cause the mode. Due to the high activity of sulfuric acid, the duration of stage "a" does not exceed 2-7 minutes, at which phosphorite has time to decompose almost completely. During such a treatment time, phosphorite defluorizes up to 70 % and higher, almost decarbonizes. The reaction products are mainly crystallized anhydrite and phosphoric acid.

The possibility of efficient extraction of phosphoric acid with the release of calcium sulfate in the form of stable anhydrite in the temperature and acid concentration range located above the line that separates the existence fields of metastable hemihydrate and stable anhydrite (temperature >107 °C and concentration >52 % P₂O₅) follows from the solubility diagram in the system CaO-P₂O₅-SO₃-H₂O [20], [63].

The physical properties of the reaction mixture from stage a largely depend on the ratio of H₃PO₄: CaSO₄ in it and the shape of the anhydrite crystals.

The mass ratio of H₃PO₄: CaSO₄ in the products of the sulfuric acid decomposition of natural phosphates depends on the calcium module (CaO:P₂O₅) of the feed. With the complete decomposition of different types of raw materials, the theoretical mass ratio of CaSO₄: H₃PO₄ in the products of their decomposition will be:

Type of natural Phosphorite	Module CaO:P ₂ O ₅	Ratio CaSO ₄ :H ₃ PO ₄
Apatite concentrate – phosphorite Karatau	1,32	0,43
from ordinary ore	1,59	0,34
Phosphorite Tashkura washed burnt	2,00	0,28
Phosphorite Tashkura unenriched	2,76	0,20

As can be seen from the above data, the largest amount of phosphoric acid per unit mass of crystallized calcium sulfate occurs in the case of apatite concentrate — 0.43 ppm, which indicates the possibility of excess phosphoric acid in the reaction mass over its occluded amount of interagglomeration pores of the precipitate that is, pulp is obtained. The lowest value of CaSO₄:H₃PO₄ (0.20) is possessed by the product obtained from crude Tashkur phosphorite, where the holding capacity of the framework of anhydrite agglomerates increases, and in them the concentrated phosphoric acid is almost completely in the occluded state.[64], [65]

The first stage of the process is carried out in turbopaste mixers. The outer surface of the mixer body must be reliably insulated. At the outlet of the mixer, the product is a dynamic loose mass with particle sizes of 0.1-2 mm.

The second stage of the innovation project includes the following two technological processes: neutralization of free phosphoric acid with another part of

phosphorite and granulation of the resulting product. These two processes are carried out in one apparatus - a drum-type granulator.

The temperature of the reaction mixture achieved in the first stage should be used to the maximum in the second stage of the process.

When acidic particles, consisting of a porous skeleton of solid anhydrite crystals, containing mixtures of phosphoric and sulfuric acids, are treated with another part of highly carbonated phosphorite with vigorous stirring, the surfaces of acidic fine-grained particles are enveloped in phosphoric flour. At the beginning of the process, first of all, the excess sulfuric acid in phosphoric acid enters the reaction, as a result of which an additional amount of phosphoric acid and anhydrite are formed. After complete consumption of sulfuric acid, mobilization of free phosphoric acid immediately begins, as a result of which the layering of the surface of acidic particles with a solid monocalcium phosphate crust begins. The process of increasing particle size begins, the basis of the mechanism of which is a purely chemical act. Monocalcium phosphate, which passed into a concentrated solution of phosphoric acid, instantly crystallizes into the solid phase in the form of $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ monohydrate [22], [66].

It can be assumed that in the liquid-solid phase section, formed as a result of the contact of the initial grains in the form of acid-saturated clusters of calcium sulfate crystals and phosphate rock particles from the reaction volume. Two processes opposite to each other are likely to proceed simultaneously. On the one hand, the motion of the liquid phase along the capillary pores, directed from the center of the particle to their surface (occurrence of a concentration gradient in the liquid phase at these points), and the resistance opposite to this movement, with increasing Thickness of the newly formed calcium phosphate crust around these particles - on the other. It must be assumed that the depth of penetration of the phosphate crust deep into the wet particles will be limited by the property of the medium, where the diffusion rate of phosphate particles through these crusts is practically zero. However, the process of acid neutralization in these peculiar reservoirs can continue to a certain extent, only due to the compressive forces exerted on these particles, aimed at squeezing the liquid from the inside to their surface. Such forces can act as the mass of the overlying layer of the granulated product into particles during its rolling in the drum, and the temperature in the layer of the same product. These factors are probably necessary and sufficient conditions for continued growth of the thickness of phosphate crusts due to the freshly crystallized monocalcium phosphate particles on the outer surface of these particles [67]–[69].

A distinctive feature of the proposed method before the known is that the weight of the production cycle of processing natural phosphate is carried out in only two stages. In the first stage, highly carbonized phosphorite is treated with a superstoichiometric flow rate of concentrated sulfuric acid, under conditions of complete decomposition of phosphorite with the formation of a loose matrix of calcium sulfate crystals, absorbed into it by the liquid phase. In the second stage, a highly concentrated solution of phosphoric acid mixed with sulfuric acid is involved in the reaction with an additional amount of highly carbonized phosphorite, which is the basis of the mechanism of chemical granulation of superphosphate mass. The next phase of the increase in the size of the granules proceeds already under the conditions of material pelletizing, where agglomeration of individual particles that survived chemical granulation between themselves occurs [69].

Conclusions

Thus, the acid neutralization reaction with phosphorite flour at the second stage of the process is actually the beginning of the granulation process, where the granulation center is a phosphoric acid-saturated framework of calcium sulfate crystals, on the spherical surface of which crystallization of monocalcium phosphate is continuously

ongoing, followed by their close packing on the surface this area. The agglomeration of small particles into spherical granules is significantly accelerated because these spheres are open for reunification by neighboring particles (agglomeration), at the surface of which the same processes occur. Thus, the granulation process of superphosphate mass occurs simultaneously with the continuous crystallization of monocalcium phosphate from the solution is almost until phosphoric acid disappears in it, and not crystallized even before salt granulation, as is the case in the granulation of acidic superphosphate mass according to the classical scheme.

Obtained by the proposed method, the granular product is characterized by low dispersion, and the granules have a high resistance to dynamic abrasion.

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

- the scheme has processing time optimized processing times for highly carbonized phosphorites, as a prerequisite for creating with their use high-performance production lines for the production of simple granular superphosphate;
- on the basis of the developed technology lies the most simplified scheme due to the exclusion from its composition of overly time-consuming redistributions such as chamber maturation and warehouse maturation;
- the technology consumes less energy resources, both due to the use of energy-saving equipment, and the exclusion from its structure of energy-intensive stages of the process, such as warehouse maturation and drying.
- the production line of the installation according to the proposed scheme with selected equipment is significantly 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, it is characterized by the possibility of maximum distillation of harmful fluorine-containing gases from phosphorite and their organized capture;
- the exception of the input of neutralizing agents from the outside (lime flour, liquid or gaseous ammonia, etc.) and binding agents (phosphoric acid, phosphate and sulfate salts of ammonium, etc.).

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