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ABSTRACT

of the dissertation for the degree of Doctor of Philosophy

SYSTEMATIC ANALYSIS AND INTENSIFICATION OF THE GRANULATION PROCESS OF DUSTY SUBSTANCES

Speciality: 3303.01 – Chemical technology and engineering

Field of science: Technical

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Dissertation work was performed at the Institute of of Catalysis and Inorganic Chemistry named after Academician M. Nagiyev, Azerbaijan National Academy of Sciences.

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General Description of Work

Relevance of the work. The rapid development of the chemical industry in our country, the development of fundamentally new, more modern, and cost-effective production methods, as well as the intensification and modernization of existing traditional processes are important, and conducting new research in this area is a priority for researchers. In this regard, the improvement of the technology of granulation of chemical products and the increase of production efficiency, as well as the quality of the products produced are of scientific and practical interest. Known methods of granulation mainly ensure that the finished product is obtained with traditional quality indicators. The growing demand for product quality indicators highlights the improvement of known methods and rules of the granulation process, the search for newer and more sophisticated methods. Design and apparatus of granulation processes of powdery materials is carried out by mathematical modeling methods on the basis of theoretical analysis and calculations. As the granulation processes of dusty materials are based on many physical phenomena, the size of the droplets of the binder and the efficiency of the aggregation of dust particles into a single system are important.

Despite the fact that the process of granulation of dusty materials is sufficiently studied, there are still a number of shortcomings in the production of granular superphosphate. These include insufficient physical and mechanical properties of the granular material, insufficient study of the relationship between the structure of the granules and process parameters, as well as it can be shown that the amount of powder in the finished product is excessive and the fine fraction is returned to the system in the form of retouching, the mechanical strength of the granules and the yield of the commodity fraction are not high enough. That’s why, theoretical and experimental research on the intensification of the process of granulation of powdered superphosphate and the modification of the obtained granular superphosphate with additional nutrients is of scientific and practical interest. Therefore, the creation of a new effective method of granulation of pulverized materials, the construction of a mathematical model of the process of granulation of pulverized materials, development of new technology for the production of granular superphosphate modified with additional nutrients, with high mechanical strength and high yield of the commodity fraction are relevant and promising issues.

Object and subject of research. Research of the process of granulation of powdered substances with the participation of intensifying additives, production of phosphorus granular mineral fertilizers enriched with nitrogen, potassium, and magnesium, construction of a mathematical model of granulation formation, and development of process technology.

The aim of the research. Theoretical and practical study of the process of granulation of powdered materials in a cylindrical apparatus using intensifying additives, the development of new efficient technology for the production of granular superphosphate modified with additional food and trace elements based on classical technology using natural zeolite, ammonium hydroxide, and manganese oxide. In accordance with the purpose of the research, the following issues were raised:

- ✓ study of the mechanism of particle compaction in the process of granulation of dusty materials;
- ✓ study of the process of obtaining granular superphosphate enriched with nitrogen, potassium and magnesium by granulation of powdered superphosphate in the presence of natural zeolite;
- ✓ development of some kinetic regularities of the process of granulation of dusty materials in a cylindrical apparatus;
- ✓ Construction of a mathematical model of the process of granulation of powdered superphosphate obtained on the basis of classical technology in a cylindrical apparatus with the participation of natural zeolite;
- ✓ Development of a new efficient technology for the production of modified granular superphosphate with additional nutrients based on the obtained experimental evidence.

The goal was achieved as a result of determining the nature of the intensifying additives and the amount of injection into the system, studying the optimal values of the parameters of the technological mode of the granulation process, analyzing the technological conditions of granulation and key parameters of the product.

Research methods. The phase and structural composition of the modified granular phosphorus mineral fertilizer obtained using a suspension prepared from a mixture of natural zeolite and ammonium hydroxide solution have been studied by modern physicochemical analysis methods- X-ray phase and IR-spectroscopic methods. Quality indicators and physical properties of the finished product are determined by photocolorimetric, gravimetric and volume methods according to the standard.

The main provisions submitted to the defense:

a) Determining the degree of compaction depending on the number of other particles in contact with the central particle, ie the relationship between the porosity of the granule and the coordination number by studying the mechanism of particle compaction in the process of granulation of powdered materials; b) obtaining a new type of phosphorous mineral fertilizer modified with nitrogen, magnesium and potassium by granulation of powdered superphosphate using a suspension containing natural zeolite and ammonia water as an intensifying component, in contrast to the classical methods; c) determination of the main parameters of granulation formation by determining the kinetic regularities of the process of granulation of powdered superphosphate in a cylindrical apparatus using a suspension containing natural zeolite and ammonium hydroxide; d) Determining the optimal values of the main parameters that provide an increase in the yield of standard (1-4 mm) granules and increasing the mechanical strength of the granules in the process of granulation of powdered superphosphate in the presence of an intensifying component in a cylindrical granulator and establish a technological scheme of the process.

Scientific novelty of the work A new method of obtaining granular superphosphate enriched with additional nutrients nitrogen, potassium and magnesium has been developed using a suspension consisting of a mixture of natural zeolite and ammonia water as a moisturizing, binding and neutralizing additive. The mechanism of granulation formation was studied with the participation of an intensifying additive, some kinetic regularities of the process were determined and a mathematical model describing the dynamics of asymmetric growth of granules and the function of distribution of granules along the length of a cylindrical apparatus have been obtained. On the basis of theoretical and experimental research, a new technology has been developed to ensure the production of granular superphosphate modified with additional nutrients in the presence of natural zeolite, improving the physical, chemical and mechanical properties of the product, as well as increasing the yield of commodity fractions.

Theoritical and Practical relevance of the work. A new technological method of obtaining granular superphosphate enriched with nitrogen, potassium and magnesium has been proposed in our country using natural zeolite with rich deposits and industrial waste products containing ammonium hydroxide.

Based on this technology, the powder obtained by the classical method is granulated by moistening with a suspension containing natural zeolite, ammonium hydroxide and water. The obtained granular superphosphate is enriched with additional nutrients nitrogen, potassium and magnesium.

This technological method is characterized by simplicity, universality and feasibility on an industrial scale.

Determination of the laws of formation of granules as a result of agglomeration of particles around the nucleus in the process of granulation of powdered substances and obtaining a mathematical relationship that characterizes the relationship between the porosity of the granule and the coordination number.

Physicochemical and mechanical properties of the modified granular superphosphate obtained by the developed new technological method were studied.

Studies have shown that the efficiency obtained by the proposed method:

- ✓ simpler neutralization of free phosphate acid in powdered superphosphate and thus complete elimination of the use of limestone as a neutralizing additive in the classical method;
- ✓ Increasing the value of mineral fertilizers by increasing the number and amount of nutrients in the finished product;
- ✓ It consisted of improving the physicochemical and mechanical properties of the modified granular superphosphate, increasing the

efficiency of the new technology by increasing the yield of the commodity fraction.

Approbation and application of work. The scientific results of the dissertation were discussed at a number of international and national scientific conferences. RSC on the topic “Actual Problems of Chemistry and Ecology” dedicated to the 86th anniversary of National Leader Heydar Aliyev, Baku, ASPU, 2009; RSC dedicated to the 85th anniversary of academician T.N. Shakhtakhtinsky, Baku 2011; VIII ISC on "Ecology and protection of life activities" dedicated to the "Year of Industry", Sumgayit, 2014; RSC dedicated to the 90th anniversary of Academician T.N. Shakhtakhtinsky, Baku 2015; RSC dedicated to the 80th anniversary of the Institute of Catalysis and Inorganic Chemistry named after M. Nagiyev, Baku, 2016; X International scientific-practical conference of young scientists. "Actual problems of science and technology -2017", Russia, Ufa. 2017; Topical issues of applied physics and energy, ISC Sumgayit, 2018; Information Systems and Technologies: Achievements and Prospects ISC, Sumgayit, SSU, 2018; “Nagiyev Graats” ISC, dedicated to the 110th anniversary of Academician M. Nagiyev, Baku, 2018; Chemistry. Ecology. Urbanistics. All-Russian. SPC with international participation, Perm, 2019; Modern problems of chemistry RSC, Sumgayit, 2021.

Publications. 22 scientific works on dissertation work, including 10 scientific articles, 5 conference materials, 6 abstracts were published and a patent of the Republic of Azerbaijan was obtained for one invention. The results of the dissertation are used by students majoring in chemical engineering in teaching the process and apparatus of the chemical industry.

Organization where dissertation work is performed. It was performed at the Institute of Catalysis and Inorganic Chemistry named after academician M.N. Nagiyev of the National Academy of Sciences of Azerbaijan.

Personal presence of the author. Determining the purpose and direction of the dissertation, problem statement, performance of experiments and analyzes, analysis, generalization of the obtained experimental evidence, interpretation of logical results and preparation of the dissertation belong to the applicant.

Structure of the dissertation. The total volume of the dissertation with a sign, indicating the volume of the structural units of the dissertation separately. The dissertation consists of an introduction part, 4 chapters, a conclusion, a list of references, and appendices with 179 references, and is published on 157 pages, including 12 tables, 6 figures, 11 graphs. The total volume of the dissertation, excluding tables, pictures, and bibliography, is 208,306 characters.

In the introductory part, the materials on the topicality of the topic, the purpose of the dissertation, scientific novelty, practical significance, reliability of the results, approbation, structure and scope of the work are briefly explained.

The first chapter examines the sources of literature on the topic of the dissertation, collects information from authoritative scientific journals and patent materials, and comprehensively analyzes the information on the granulation of powdered substances and identifies their pros and cons. Based on the analysis of the literature, the urgency of the problem was substantiated and the purpose and direction of the dissertation were determined.

In the second chapter, a hierarchical sequence of system analysis for the experimental study of the process of granulation of powdered substances in a cylindrical apparatus is defined (Figure 1) and interpreted. It also provides preliminary indications of powdered superphosphate used for the production of modified granular mineral fertilizers with standard compositions of raw materials, reagents and intensifying additives and additional nutrients used for research. As well as, the method of research was developed, analytical methods were determined according to the standard to determine the quality indicators of the product obtained by granulation of powdered materials in a cylindrical type apparatus..

The third chapter describes the results of theoretical and experimental research on the granulation of dusty materials. Some kinetic regularities of the process of granulation of powdered materials in a cylindrical apparatus with mineral additives were studied, the function of longitudinal distribution of granules inside the cylindrical apparatus in the process of granulation was determined. The mechanism of particle compaction in the process of granulation, the rheological model of compaction and disintegration of granules and the mathematical model of granulation in the process of granulation have also been developed here.

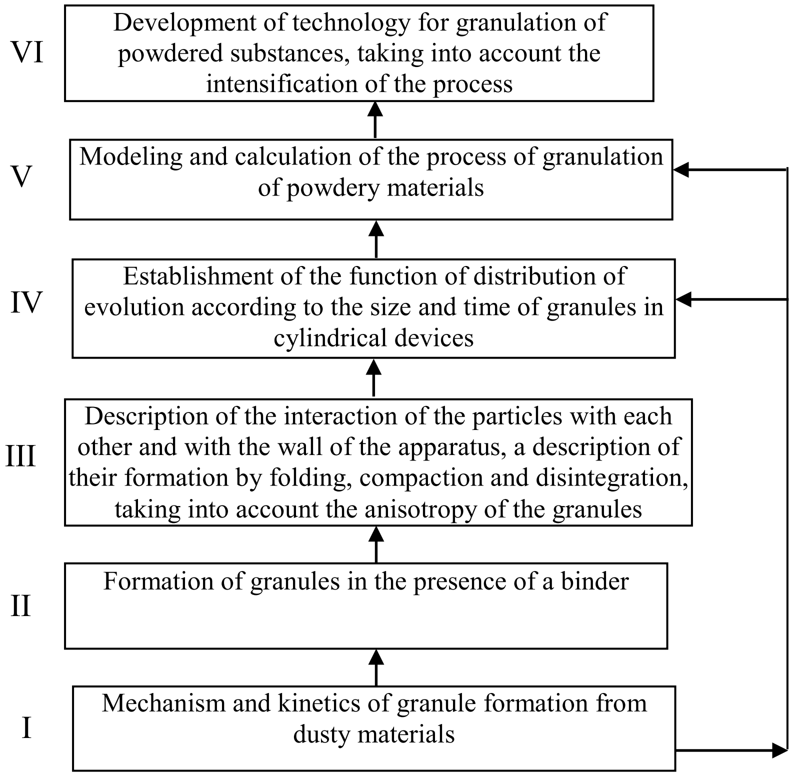


Figure 1. Hierarchical structure of the process of granulation of dusty materials.

In the fourth chapter, a new technology for the production of granular superphosphate modified with nitrogen, potassium, and magnesium was developed, the quality characteristics and mechanical properties of a new type of granular mineral fertilizer obtained in the laboratory were determined, the advantages of the new method of granular mineral fertilizer over the classical method (Patent of the Republic of Azerbaijan I 2017 0068) of granular superphosphate have been identified. Based on the results of the research, the technology of production of modified granular superphosphate has been developed.

MAIN CONTENT OF THE DISSERTATION

1. Theoretical and experimental study of the process of granulation of powdered materials with the participation of intensifying components

The study of the process of granulation of powdered materials was carried out by granulation of superphosphate obtained by the classical method in a cylindrical type apparatus. A suspension containing natural zeolite and ammonia water was used as a moisturizing, neutralizing, binding and intensifying reagent. The main results of the research are presented in a systematized form in separate sections.

1.1. Investigation of the process of granulation of dusty materials with the participation of natural zeolite

Granulation of flowing materials begins with a small amount of water. Such greed for granulation is due to the discovery of the van der Waals joining forces of particles in a very fine dusty material. It is known that under the influence of these forces, small particles smaller than 1 μm are agglomerated, during the movement of the material, for example, during its rotation on a rotating drum, these particles combine to form small spheres and washes. This is due to the electrostatic charge of the particles. They can get this load as a result of crushing and friction during movement. This load only affects the agglomeration process and does not increase the strength in the formed wash, as it soon balances. The main reason for maintaining the mechanical stability of the granules in the process of granulation of dust particles is the formation of liquid or solid bridges between the particles. Bond - as a bridge material, it can be the granular substance itself and its additives. In order to increase the durability of the granules, a solution containing natural zeolite and NH_4OH was used as additives and moisturizing liquid.

Moisturizing the powdered superphosphate with the above solution ensures the plasticity of the material and agglomeration of particles during granulation. It has been found that in small amounts of liquid, bridges are formed between the individual particles. However, at optimal humidity, the solution can fill all the pores. In both cases, agglomeration, that is, the formation of granules and the increase in durability, are affected by the combined capillary forces and surface tension forces. Completely covers the liquid phase granules at high humidity. It resembles a drop of liquid densely filled with solid particles under the influence of surface tension. The resulting granular mass becomes extremely sticky or uneven.

Thus, in the process of granulation of moisturizing, liquid and powdery superphosphate, in addition to liquid dams, solid dams are also formed. The formation of solid bonds between the particles of granulated material occurs during the crystallization of $Ca(H_2PO_4)_2$, $Mg(H_2PO_4)_2$, $NH_4H_2PO_4$, that is the drying of granules from the liquid phase and the chemical reaction between free phosphate acid in powder superphosphate and ammonia water in the moisturizing liquid. These give the granules the stability they need. Natural zeolite contains a certain amount of SiO_2, Fe_2O_3, Al_2O_3, K_2O. They bring higher mechanical strength by filling the pores of the granules during the granulation process. Free phosphoric acid in powdered superphosphate reacts with calcite and dolomite minerals, partly in natural zeolite, and with ammonia water in the moisturizing liquid.

It was found that the friction of the formed granules on the wall of the inner surface of the cylindrical apparatus, as well as the contact and friction of the granules with each other significantly affect the size of the granules. A general description of the forces acting on the granule is given in Figure 2. According to this scheme, the final vector of forces acting on the surface of the granule is expressed as follows:

$$\vec{F} = \sigma_D \vec{n} S_p - \vec{\tau}_w S_p \qquad (1.1)$$

The projection of the vector of the force acting on the granule on the axis of the direction of motion $(\vec{F})$ at the moment of its rotation is as follows.

$$\vec{F} = \sigma_D \cos(\vec{n}, x) S_p - \tau_w \cos(\vec{\tau}_w, x) S_p$$

In particular, if we take into account the expressions $cos(\vec{n}, x) = 0$ and $\cos(\vec{\tau}_w, x) = -1$ in this equation, we can get a simpler form of the equation:

$$\vec{F} = \tau_w S_p \qquad (1.2)$$

where $\tau_w = \sigma_D tang(\varphi_1) + C_1$, $\mu = \tan g(\varphi_1) -$ is the friction modulus, its value is in the range of $0.3 \le \mu \le 0.6$

Considering these expressions in equation (1.2), the following expression is obtained:

$$\vec{F} = \sigma_D \mu S_p$$

According to the scheme, we determine the strength of the granules as follows,

$$\frac{d\Delta}{dt} = C_m \vec{F} V = \gamma \sigma_D a^2 V \qquad (1.3)$$

where $\gamma = C_m \gamma \pi \psi$, $C_m -$ is the coefficient depending on the properties of the surface of the granular material and the inner wall of the apparatus, and $S_p = \psi \pi a^2$. $\psi -$ is the coefficient characterizing the layering of the powder material on the surface of the granule.

As can be seen from equation (1.3), the wear rate of the granules is proportional to the square of the size of the granule and its velocity. Therefore, in order for the granules to be large, the system inside the apparatus must be large.

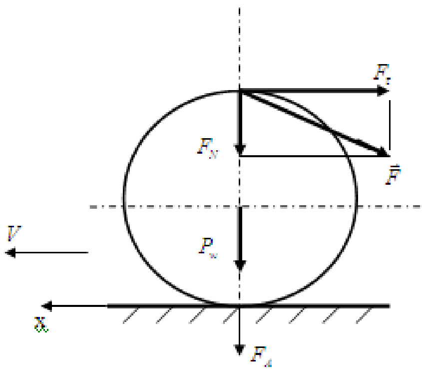


Figure 2. Schematic description of the forces acting on the formed granules

Thus, the resulting granulated superphosphate is enriched with additional nutrients such as nitrogen, potassium and magnesium. The formation of granules is due to the condensation of agglomerates as a result of the adhesion of individual particles of the granulated material to each other under the influence of dynamic loads.

Therefore, a mixture of natural zeolite with ammonium hydroxide was used as a supplement to reduce porosity and increase durability, resulting in the enrichment of superphosphate granules with additional nutrients such as nitrogen, potassium and magnesium.

The effect of additives on the physicochemical and mechanical properties of granulated superphosphate was studied in experimental studies conducted in a laboratory granulator. In this regard, the effect of a mixture of natural zeolite with ammonium hydroxide (NH_4OH) on the composition, physicochemical and mechanical properties of granulated superphosphate was studied in the laboratory, the results of which are given in Table 1.

Table 1

Dependence of physical-chemical, mechanical parameters and composition of the finished product on the amount and composition of the additive (mass,%)(natural zeolite solution – 35-38; solution of *NH_4OH*- 14-15; *H_2O* – 47-51).

The ratio of superphosphate and binder	P_2O_5 (assimilable)	P_2O_5 (free)	N	K_2O	MgO	H_2O	Δ, MPa	Yield Q, %
1:0,10	18,21	3,52	0,25	0,12	0,14	0,87	0,8	57,6
1:0,15	18,53	2,95	0,44	0,15	0,18	0,93	0,9	58,8
1:0,20	18,85	2,58	0,63	0,18	0,26	1,01	1,0	60,2
1:0,25	19,02	1,75	0,96	0,24	0,30	1,09	1,1	63,7
1:0,30	20,03	0,28	1,56	0,34	0,40	1,12	2,6	84,6
1:0,35	20,26	0,24	1,72	0,37	0,43	1,25	2,7	85,1
1:0,40	20,45	0,18	2,01	0,42	0,45	1,36	2,8	86,2
1:0,45	19,31	0,12	2,13	0,46	0,48	1,39	1,2	65,4
1:0,50	18,75	0,10	2,35	0,50	0,52	1,45	1,0	58,5

As can be seen from the table, the highest strength of the granules is obtained in the ratio of powdered superphosphate and binder 1: (0.30 - 0.40). Thus, limestone is not completely consumed, and the free phosphate acid in superphosphate is partially neutralized by ammonia water in the moisturizing liquid, as well as by the minerals calcite and dolomite in natural zeolite.

The reason for the increase in the durability of the granules is due to the fact that during the formation of SiO_2, Fe_2O_3, Al_2O_3, K_2O granules, which are part of natural zeolite, they bind superphosphate particles more closely, fill the pores and ensure their fuller rolling. Ammonia water in the moisturizing liquid and calcite and dolomite minerals in natural zeolite interact with free phosphoric acid in powdered superphosphate. As a result, the resulting calcium hydrophosphate, ammonium dihydrogen phosphate and magnesium dihydrogen phosphate crystallize. The crystalline structure of these salts is accompanied by the formation of point defects, as they, in turn, have a favorable effect on the mechanism of formation of granules.

Thus, the obtained granular superphosphate is enriched with nitrogen, potassium and magnesium. The reactions that take place in this process can be represented by the following equations:

$$2H_3PO_4 + CaCO_3 \rightarrow Ca\,(H_2PO_4)_2 + 2H_2O + CO_2$$

$$2H_3PO_4 + MgCO_3 \rightarrow Mg(H_2PO_4)_2 + 2H_2O + CO_2$$

$$H_3PO_4 + NH_4OH \rightarrow NH_4H_2PO_4 + H_2O$$

When the granulation process is carried out at the optimal inretval ratios of powdered superphosphate and moisturizing liquid, ie 1: (0.30-0.40), the mechanical strength of the granules is up to 2.6-2.8 MPa, the yield of the commodity fraction of granulated superphosphate is up to 84,6-86,2% %. It is possible to improve the quality of the final product by enriching it with nutrients such as nitrogen, potassium and magnesium. In order to study the evolution of the growth of granules, the granular mass along the length of the cylindrical granulator was analyzed by sieving. Samples were taken along the length of the granulator and at distances L10, 20,40,60,80 cm, the weight of each sample -200 gr. Each sample was dried at t = 100^0C for 1 hour, sifted through sieves (13 pieces - dimensions 0.1-6.0 mm), and fractions of the appropriate measurement intervals were weighed. Table 2 shows the experimental results of the sorting analysis of each fraction measured. As can be seen from Table 2, the proportion of small fractions is higher in the initial part of the drum apparatus (L = 10 cm and L = 20 cm), and the proportion of large fractions is lower.

However, the mass fraction of 1.0-5.0 mm fractions in L = 40 cm, L = 60 cm and L = 80 cm sections is very high.

Thus, the use of a mixture of natural zeolite with ammonia water as a modified additive, on the one hand, improves the formation of granules, on the other hand, improves the physical and chemical properties of the granules formed by filling their pores, as well as the obtained granulated superphosphate is also enriched with additional nutrients such as nitrogen, potassium, and magnesium, ie the process of neutralization of free phosphoric acid in powdered superphosphate occurs due to the crystallization of the corresponding salts of these elements.

Table 2.

Experimental data on the length distribution of the apparatus according to the size of the granules

Fraction size, mm	L=10cm		L=20cm		L=40cm		L=60cm		L=80cm	
	Amount,gr	Mass share	Amount,gr	Mass share	Amount,gr	Mass share	Amount,gr	Mass share	Amount,gr	Mass share
0,1-0,2	15,4	0,077	10,02	0,050	3,98	0,020	5,97	0,03	3,02	0,015
0,2-0,4	19,3	0,097	11,75	0,059	6,87	0,034	9,02	0,04	4,58	0,023
0,4-0,6	22,5	0,113	14,98	0,075	11,0	0,055	10,9	0,05	7,04	0,035
0,6-0,8	26,9	0,135	16,87	0,084	12,9	0,065	13,6	0,06	9,03	0,045
0,8-1,0	28,8	0,144	18,93	0,095	14,6	0,073	15,3	0,07	10,5	0,053
1,0-1,2	26,9	0,135	22,41	0,112	16,9	0,085	17,8	0,08	15,0	0,075
1,2-1,5	23,6	0,118	25,84	0,129	19,7	0,099	19,9	0,10	17,9	0,090
1,5-2,0	18,3	0,092	24,58	0,123	22,0	0,110	22,1	0,11	20,1	0,101
2,0-2,5	11,0	0,055	20,96	0,105	24,8	0,124	25,0	0,12	21,0	0,105
2,5-3,0	5,17	0,026	16,73	0,084	23,9	0,120	25,9	0,13	29,0	0,145
3,0-4,0	1,05	0,005	10,05	0,050	21,0	0,105	17,8	0,08	29,9	0,150
4,0-5,0	0,52	0,003	6,18	0,031	14,9	0,075	11,6	0,05	23,1	0,116
5,0-6,0	0,00	0,00	0,62	0,003	7,03	0,035	4,56	0,02	8,67	0,043

1.2. Some kinetic regularities of the process of granulation of powdered materials in a cylindrical apparatus

In the chemical industry, the use of a binder solution in the granulation process of powdered substances increases the efficiency of the technology. Different types of granulators are used in these processes. It is known from the scientific literature that cylindrical devices are widely used on an industrial scale and have great prospects. In granulation processes, the formation and growth of granules occurs as a result of hydration of dust particles. This causes granules to form due to agglomeration and coagulation when the particles collide with each other. Therefore, the growth and formation of granules in the first stage of granulation leads to the formation of larger granules due to the adhesion of small particles and agglomerates. The effect of the liquid phase on the granulation process is very large. Thus, due to it, adhesion, capillary and surface tension forces are created, which keep the particles on the surface of the granules. The mixing frequency (rotational speed of the apparatus), the degree of filling of the apparatus and the angle of inclination, the ratio of liquid and solid phases also have a significant effect on the formation of granules as a result of agglomeration of dust particles. These criteria determine the quality (density, hardness, fluidity, coefficient of internal friction) and quantity (productivity) of the product.

As a result of the growth of granules in the process of formation occurs under the influence of external stresses - compaction, deformation of the form and wear of the surface, which determine the shape and size of the granules. Thus, the mechanism of granule formation is complex, multi-stage, and the events in the process are stochastic. The agglomeration and aggregation of dust particles into a single system (granules) in the presence of a binder is determined by the laws of physics. However, the interaction of particles (collision, adhesion, shredding) is stochastic. While the formation of granules in the initial stage of nucleation and granulation occurs by surface tension and capillary forces, the dust particles adhere to the nucleus, while the further growth of the granules is accompanied by the accumulation and compaction of dust particles on the surface of the granules.

Figure 1 shows the experimental indicators of the moisture dependence of medium-sized granules, granulation formation. The equation for the change in size for spherical granules is expressed as follows:

$$\frac{da}{dt} = K_0(w)a \tag{1.4}$$

where K_0 (w) is the coefficient of granulation.

Equation (1.1) under $t = 0,\ a = a_0$ is as follows:

$$a(t) = a_0 \exp(K_0(w)t) \tag{1.5}$$

where $a_0 = a_0$ (w) is the initial size of the granulation nucleus, depending on the amount of solution or droplet size of the binder. Figure 1 shows the experimental evidence and the granule size increase and size distribution curves based on Equation (1.5). When using the experimental results, the unknown coefficients can be estimated in equation (1.5) as follows:

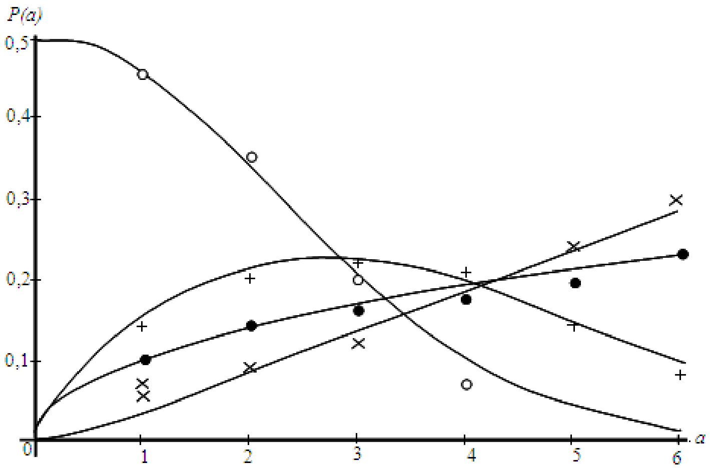
$$K_0(w) = 0.00353w^2 - 0.10355w + 1.0743$$

$$a_0(w) = -0.00175w^2 + 0.0849w - 0.786$$

Coefficients for the first and second equations, respectively: $r^2 = 0.9999$ and $r^2 = 0.9975$.

In practice, in most cases, the granules are characterized by a non-spherical shape. In general, ensuring the perfect formation of granules can be achieved more precisely by the symmetry of two factors, ie by the interaction of the dynamics of movement of the granules during the rolling process and the anisophropic properties of the granules (softness, hardness).

The forced convective transfer of the binder in the pores solved the problem of the effect of external stresses during the compaction of the granules and determined the type of function for the Sherwood number (1.6). As a result of experimental studies of the effect of moisture on the formation of granules, it was determined that the dimensions are divided into fractions based on moisture.



Graph 1. Distribution of granules by size depending on moisture content:1 – 0,14 (o); 2 – 0,18 (+); 3 – 0,22(x); 4 -0,26(•).

The size distribution of the granules over time is described as follows from the solution of the Fokker-Planck equation.

$$P(a) = B(w)a^{m(w)} \exp\left(-n(w)a^2\right) \qquad (1.6)$$

where P (a) is the size distribution function of the granules; B (w), m (w), n (w) are scattering coefficients depending on the moisture content of the granules:

$$B(w) = -736.98\times10^{-6}w^3 + 485.468\times10^{-4}w^2 + 10.69w + 7.90$$

$$m(w) = 1549.48\times10^{-6}w^3 - 928.90\times10^{-4}w + 19.0w - 12.0$$

$$n(w) = 106.77\times10^{-6}w^3 - 55.78\times10^{-4}w^2 + 0.830w - 0.2628$$

These coefficients are the calculated values of the scattering function calculated by formula (1.3).

Thereby, the formation of granules of powdered superphosphate is associated with the alternation of layering and compaction processes. During lamination, the size of the granules increases, and during compaction - decreases. Completion of the granule form is determined by the distribution of the binder concentration in the granule volume. The optimum moisture content of the grain in the granulator is 17-18%.

Table 3.

Dependence of mass fractions of granule fractions on material moisture

Average size of granules, a, mm	Composition, mass, w, %			
	14	18	22	28
≤ 1.0	0.45	0.21	0.115	0.055
1.0-2.0	0.35	0.20	0.140	0.090
2.0-3.0	0.20	0.22	0.160	0.180
3.0-4.0	0.07	0.21	0.170	0.200
4.0-5.0	-	0.14	0.195	0.240
5.0-6.0	-	0.08	0.230	0.300

It was found that each of the dust particles in the granule collides with other particles, and the binder is stored in the circular capillaries formed between the particles. As a result of agglomeration of particles into a single system, different coordination number (Nk) structures can be formed; this means the number of collisions of one particle with another, which determines the porosity of the granule as a whole. The dependence of the formed granules on the coordination number can be determined by the following formula:

$$\theta = 0.693 - 0.0372\ Nk \qquad (1.7)$$

where θ is the porosity of the granule; Nk - coordination number.

As can be seen from formula (1.7), the porosity is θ = 0.476 when the coordination number of the soft granule (Nk = 6) and məs = 0.259 when it is denser - (Nk = 12). An increase in the coordination number or a decrease in the porosity of the granule is determined by its compaction mechanism, one of which is the rearrangement of the granules in the layer due to the relocation of solid granular dust particles in the granule under the influence of external stresses. The nature of the external stresses acting on the granule or particle in the granule is determined by the presence of centrifugal forces due to the rotation of the drum, mass forces based on the weight of the above layers, as well as forces between the granules and the wall of the apparatus.

2. Obtaining modified granular superphosphate

It is known that in the process of granulation of powdered superphosphate by the classical method, limestone is used to neutralize free phosphoric acid, which is prone to high labor intensity and is associated with the operation of complex technological equipment. Therefore, limestone is not used at all in the proposed method. A suspension containing natural zeolite and ammonia water is used to neutralize free phosphoric acid. In general, different forces act on the particles during the growth and formation of granules in a drum-type granulator. These forces include capillary and surface active forces at the boundary between solid and liquid phases, gravitational forces between solid particles — these include Van der Waals monomolecular forces and electrostatic gravitational forces. It is also possible to show the contact forces resulting from the formation of material bubbles as a result of drying, chemical reaction, solidification of the binding reagent and crystallization of the solute. Therefore, it is necessary to conduct appropriate experimental studies to increase the efficiency of these forces in the process of granulation of dusty materials. It should be noted that in order for granules to form from the initial particles of powdered materials, they must be brought closer together. It should be noted that the interaction forces are effective at optimal measurements of the distance between the particles. When the liquid phase, ie the connecting fluid, is not used, granulation is carried out by compression or pressing, in which case the Van der Vaals and electrostatic contact forces are mainly affected. When granulation is carried out by the rolling method, the forces between the particles, which are based on capillary forces, are more effective. This is possible due to the bridges formed by the crystallization of substances formed as a result of a chemical reaction between the binder supplied through the liquid phase and the components of the powdery material. Defects in the crystal lattice, which occur during the crystallization of substances, also lead to an increase in the bond between the particles in the formation of granules and an increase in their mechanical strength.

2.1. New method of obtaining granular superphosphate enriched with nitrogen, potassium and magnesium

In this case, the production of newly modified granular superphosphate in the laboratory is carried out in the following sequence.

In the process of granulation, the free phosphate acid contained in the powdered superphosphate is neutralized by the calcite and dolomite minerals contained in zeolite, and part of the phosphoric acid is neutralized by ammonium hydroxide in the suspension. Thus, the obtained granular superphosphate is enriched with nitrogen, potassium and magnesium. The zeolite used in the experiments is clinoptilolite type zeolite obtained from Aydag deposits of Tovuz region of the Republic of Azerbaijan. The results of the study are given in Table 1.1. As can be seen from the table, when the mass ratio of the suspension with superphosphate is in the range (1: 0.30-1: 0.40), the total amount of nutrients in the obtained granular superphosphate is (22.13-22.62)%, which is due to the enrichment of the product with additional nutrients nitrogen, potassium and magnesium. In this case, the mechanical strength of the granules is (2.6-2.8) MPa, and the yield of the commodity fraction is (84.6-86.2)%, which in the process of granulation, the pores of the granular superphosphate are captured by SiO_2, Fe_2O and Al_2O_3 in zeolite. the mechanical strength of the obtained granules and the yield of the commodity fraction are high.

2.2. Production of modified granular superphosphate new technology

The production of granular superphosphate on the basis of classical technology is based on the formation, sieving and cooling of the charge by neutralizing the free phosphoric acid contained in the initial simple powdered superphosphate with limestone. There is a need to use an additional complex technological device for grinding and feeding limestone. This is a complex technological process that requires a significant amount of manpower and resources, along with additional material and energy costs. The proposed technology does not use limestone at all, but is based on the hydration and granulation of free phosphate acid in the form of powdered superphosphate obtained from the decomposition of fluoroapatite with sulfuric acid with a suspension of natural zeolite and ammonia water. Modified granular superphosphate supplements obtained with the developed new technology are enriched with nitrogen, potassium and magnesium. The technological process is carried out in the following sequence (Figure 3).

Apatite concentrate with standard composition is passed from the bunker (1) to the mixer (4) through the conveyor (3) through the dispenser (2), where it is also supplied with (67-68)% sulfuric acid. To prepare sulfuric acid at the required concentration, 75% sulfuric acid is passed from the pressure tank (5) to the acid tank (9) through the flow meter (7), where water from the other tank (6) enters the acid tank (9) through the flow rate (8). The 68% sulfuric acid obtained by mixing 75% sulfuric acid with the required amount of water is heated to 105-1100C and fed directly to the mixer (4). The speed of rotation of the feathers in the mixer is in the range of 530-550 $min^{-1.}$ The mixing time of apatite concentrate and sulfuric acid in the mixer is 7 minutes, during which time the solidification-oriented chorus is obtained for the normal continuation of the reaction. The resulting mixture is then transferred to the superphosphate chamber (10). The reaction in the chamber lasts for 1.5 hours at a temperature of 110-115^{0}C. The obtained superphosphate is fed to the spreader (12) through a belt conveyor (11) and from there to the warehouse (13) by scattering. Powdered superphosphate is mixed several times in the warehouse and given to granulation after the "ripening" process for 10-12 days. The powdered fertilizer is fed to the hopper (15) by means of a grab crane (14), then by a belt feeder (16) to the crusher (17) and then to the hopper (19) fed by a belt conveyor (18), and then to the granulator (21) by a belt feeder (20). The feed fraction (19) is also fed a fine fraction (retour) returned from the system.

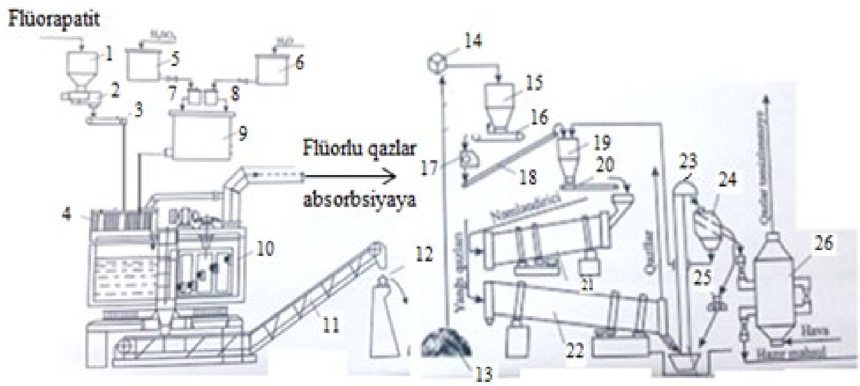


Figure 3. 1,15-bunkers; 2-dispenser; 3,11-belt conveyors; 4-mixer; 5-pressure jaw; 6-water tank; 7,8-consumers; 9-acid tank; 10-superphosphate chambers; 12-scatter; 13-powdered superphosphate; 14-grapple crane; 16-band dispenser; 17-crushing; 18-belt conveyor; 19-feeder bunker; 20-band feeder; 21-cylindrical type granulator; 22-drying apparatus; 23-elevator; 24 sieves; 25-shredder; 26- "Hot layer" type refrigerator.

The granulator is equipped with 4 injectors. Powdered superphosphate mixed with retur is hydrated and neutralized by suspension. The rotation time of the charge in the granulator is 10-12 minutes. The wet charge then enters the dryer (22), where it is dried in the same direction as the hot flue gases. The moisture content of the charge from the granulator is 17-18%, the moisture content of the charge after drying in the dryer should not exceed 3%. The dried charge is transferred to the sieves (24) by elevator (23), from where the fraction of 1-4 mm is transferred to the "hot layer" type refrigerator (26) and from there to the warehouse as a finished product. The large fraction is crushed in a shredder (25) and sent back to the sieves, and the fine fraction is sent back to the granulator. During the industrial test studies, the optimal values of the main parameters of the technological regime corresponded to the values determined in the laboratory studies. The main quality indicators of the modified granular superphosphate obtained by the industrial test method were analyzed by standard methods and the obtained results confirmed the results of laboratory researches.

RESULTS

1. Theoretical and experimental research of the process of granulation of powdered materials in cylindrical type apparatus with the participation of intensifying components was carried out and optimal values of the main parameters of the standard product were determined. [1,2].
2. In the process of granulation of powdered superphosphate, the process of obtaining granular mineral fertilizer modified with additional nutrients was studied using a suspension containing manganese oxide, aluminum oxide and ammonium hydroxide as a moisturizing, binding, and neutralizing reagent and the yield of the commodity fraction in the product obtained in the laboratory was 85.8 - 86.7%. [5].
3. The study of the mechanism and regularities of formation and condensation of granules as a result of the agglomeration of particles around the nucleus in the process of granulation of powdered substances with the addition of intensifying additives revealed that the formation of granules depends on their stratification and compaction and is characterized by a gradual change in size. [3,4,7].
4. By studying the theoretical and experimental regularities of the formation of granules, as well as the modes of application of the moisturizing, binding, and neutralizing solution, a mathematical expression was obtained that determines the optimal values of the frequency and amplitude of the oscillation regime that the wetting regime in the granulation process on the basis of the proposed expression leads to an increase in the yield of completed standard granules [8,9].
5. Systematic analysis of the granulation process of powdered substances with the participation of intensifying additives revealed that in order to determine the patterns characterizing the formation of granules as a result of the agglomeration of particles around the nucleus in the granulation process and for establishing

a deterministic-stochastic model of the process, in addition to stochastic modeling methods, transfer events described by phenomenological models must also be applied and stochastic modeling with hierarchical regularity, the process of determination should be described as a phenomenological dependence, and randomness as a function of evolution in the distribution of granules according to their size. [10].

6. In contrast to the classical method, the use of limestone as a neutralizing reagent in the granulation process of powdered superphosphate was completely eliminated, and the proposed method used a suspension containing intensifying components as a neutralizing, moisturizing, and binding reagent, which enriched the product with additional nutrients, increased the economic and environmental efficiency of the technological process [6, 22].
7. As a result of complex researches enriched with nitrogen, potassium and magnesium, new universal technology of granular superphosphate was developed, physical-chemical and mechanical properties of the obtained product were determined and the results of laboratory researches were confirmed by industrial-experimental experiments in the industrial facility. [22, Əlavə 1].

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