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TECHNOLOGICAL AND KINETIC REGULARITIES OF FORMATION OF SUSPENSION AND ITS INTERACTION WITH NITRIC ACID WHILE OBTAINING CALCIUM NITRATE

Розроблено технологію одержання кальцієвої селітри підвищеної концентрації. Встановлено граничні концентрації вапна в розчинах кальцієвої селітри, теоретично розраховано процес гідратації оксиду кальцію в цих розчинах. Досліджено механізм загустіння приготованої суспензії (суспензія Ca(OH)$_2$ в розчині Ca(NO$_3$)$_2$), яка утворюється на виробництвах кальцієвої селітри. Встановлено залежності концентрації Ca(NO$_3$)$_2$ в розчині після нейтралізації від концентрації HNO$_3$ та вмісту вапна в транспортному розчині. Запропоновано технологічну схему одержання кальцієвої селітри збагачену додатковими живильними компонентами

Ключові слова: кальцій нітрат, вапно, гідратація, концентрація, суспензія, нейтралізація, нітратна кислота, технологія

Разработана технология получения кальциевой селитры повышенной концентрации. Установлены предельные концентрации извести в растворах кальциевой селитры, теоретически рассчитан процесс гидратации оксида кальция в этих растворах. Исследован механизм загустения приготовленной суспензии (суспензия Ca(OH)$_2$ в растворе Ca(NO$_3$)$_2$), которая образуется на производствах кальциевой селитры. Установлены зависимости концентрации Ca(NO$_3$)$_2$ в растворе после нейтрализации от концентрации HNO$_3$ и содержания извести в транспортном растворе. Предложена технологическая схема получения кальциевой селитры обогащенной дополнительными питательными компонентами

Ключевые слова: кальций нитрат, известь, гидратация, концентрация, суспензия, нейтрализация, азотная кислота, технология

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1. Introduction

By the scope of application and economic results, mineral fertilizers are one of the important factors of agriculture intensification and increasing the quantity of food products. The volume of production and domestic consumption of mineral fertilizers in Ukraine indicate that only the use of nitrogen fertilizers is approaching the necessary scientifically based amount, whereas phosphate and potassium fertilizers are used less because the raw materials are very expensive.

The scope of using calcium nitrate in other industries, except agriculture, is expanding, in particular, as the basis of anti-ice mixtures, corrosion inhibitors, additives in the construction mixtures, as one of the components of emulsion explosives, accumulative solutions in refrigeration technology, etc.

The chemical industry, including the production of mineral fertilizers, is the industry which requires substantial material and energy consumption and the main trend of its development now is resource saving. Development of energy-saving technologies of the production of calcium nitrate containing

additional nutrients is important nowadays. First of all, the processes of preliminary pretreatment and acid processing of calcium containing raw materials should be improved.

2. The scientific literature analysis and the problem statement

In addition to putting main nutrient components to the soil (MNC), application of calcium containing compounds is also important [1, 2]. The use of solutions of calcium nitrate as a component of emulsion explosives reaches 15÷30 % of their total mass [2]. A broad scope of application leads to a series of requirements for this product: reduction of the content of insoluble substances, enrichment of calcium nitrate solutions and the granulated product with the additional nutrients for using such fertilizers in greenhouses and the national economy without salinization of soil [3].

For the development of technology and the expansion of fertilizers assortment, the authors study kinetics of dissolving and processing borate flour into calcium and magnesium nitrates by nitrate acid [4]. The received nitrates are the side products and the results cannot be used in the production of calcium nitrate. In the paper [5], to reduce the losses of nitrogen and to prevent ammonium nitrate from caking, the authors proposed processing with the substances based on calcium and silica acids. In the case of the calcium nitrate production, it is necessary to receive waterless salt, which can be stored without caking for a long time. Obtaining calcium nitrate with a low content of insoluble impurities is possible through processing with the flocculent [6]. This method allows receiving a high quality solution of calcium nitrate but the flotation process and the use of the flocculent leads to the complication of technology and the cost rise of the product. In the production of lime-ammonium nitrate, acidic condensate forms, which is necessary to neutralize and process that leads to additional costs and technological equipment [7].

The data on obtaining a liquid fertilizer on the basis of calcium nitrate were published [8]. In this case, calcium carbonate is used as calcium containing raw material, however, there are no data concerning the kinetics of dissolving and the nature of the interaction. It is proposed to obtain calcium nitrate enriched with microelements by adding them before granulating [9]. However, the concentration of total nitrogen does not exceed 15 %, in other words, the added microelements do not convert it into corresponding nitrates, thereby making their digestibility worse. The process of granulating calcium nitrate is sufficiently explored, in particular [10].

In modern production of calcium nitrate, different kinds of calcium containing raw materials are processed by aqueous solutions of nitrate acid in the suspended reaction system. Quicklime is used with the formation of various intermediate calcium containing compounds that will affect, and at critical concentrations will lead to suspension thickening.

In the existing schemes of production, solutions with a low content of calcium nitrate of about 40 % of $Ca(NO_3)_2$ are obtained. The next stage is the stage of evaporation of the received solution, after which the evaporated solution (fusion) is granulated.

The chemical industry, including the production of mineral fertilizers, applies the processes that require considerable fuel and energy costs. In the production of calcium nitrate, it is connected primarily with the evaporation of solutions after neutralization. The existing technologies of obtaining calcium nitrate were developed in the 40–50-s of the last century, nowadays they are inefficient and need updating. The processes are studied insufficiently, and there are no data on forming transporting calcium hydroxide suspensions and their neutralization by nitrate acid in the production of calcium nitrate. They are fundamental in this production and all the subsequent stages depend on them.

3. The aim and the tasks of the study

The aim of the study is the study of the processes of forming transporting calcium hydroxide suspensions, their neutralization by nitrate acid and development of technological scheme of obtaining calcium nitrate.

To achieve the aim of the research, the following tasks were solved:

– to substantiate the process of the calcium oxide hydration in calcium nitrate;

solutions and to identify the causes of suspension thickening during preparation of transporting solution (suspension of Cao in the solution $Ca(NO_3)_2$;

– to establish kinetic regularities of the degree of converting CaO in the solution of calcium nitrate.

4. Methods and materials of study of CaO hydration in the solution of calcium nitrate, the degree of converting, neutralizing the suspension by nitrate acid and the properties of the obtained product

4. 1. The studied materials and equipment used in the experiments

In this work, we used technical calcium oxide (quicklime) DSTU BV. 2.7-90-99, the solutions of calcium nitrate at the concentrations of 15, 20, 25, 30, 35 and 40 % $Ca(NO_3)_2$. The content of lime in the solution changed during the preparation (in conversion to CaO) from $150\ g/dm^3$ (to maximum possible). To neutralize the calcium containing suspensions, technical non-concentrated nitrate acid (HNO_3, TU: TUU 24.1-33968601-001:2008) and technical concentrated nitrate acid (HNO_3, GOST 701-89) were used. The laboratory testing was carried out at the installation, which consists of thermo-isolated reactor (working volume $1.75\ dm^3$), made of stainless steel 12X18H10T, electric engine with a lobed mixer and the capacity to regulate the number of rotations, fixed on a tripod, electric furnace to maintain the temperature in the reactor.

The titrometric methods were used for determining the concentrations of salt components. The temperature recording was carried out by using mercury thermometers with the scale division of 0.5 °C. The pH value of the solutions was determined using electronic pH-meter (pH-150MI).

The study of the phase composition and the structure of received salts was carried out using the X-ray phase analysis (diffractometer DRON-2). The differential thermal analysis (thermographic studies) of the samples was performed at the derivatograph "MOM" Q-1500D of the system by F. Paulik, I. Paulik, L. Erdey.

4. 2. The methodology of studying hydration and the degree of CaO conversion

The study was carried out at the laboratory installation (Fig. 1) in the following way. 1 dm^3 of the solution of calci-

um nitrate of the concentration 15, 20, 25, 30, 35 and 40 % $Ca(NO_3)_2$ calcium nitrate was loaded to the reactor 2. Each of these solutions was saturated with lime to the maximum possible concentration at 40 °C.
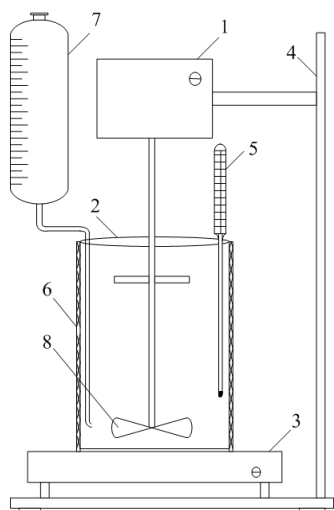

Fig. 1. Scheme of the laboratory installation for preparing hydroxide suspensions: 1 — electric engine; 2 — reactor; 3 — electric stove; 4 — tripod; 5 — thermometer; 6 —thermal insulation; 7 — graded vessel for nitrate acid; 8 — mixer

The solutions (suspensions) that did not lose their mobility (transportability) for 12 hours were considered suitable for using in the following experiments and technologies of obtaining calcium nitrate. The obtained suspensions were neutralized with nitrate acid to receive calcium nitrate solution.

5. Results of the study of hydration and the degree of CaO conversion in calcium nitrate solutions with the subsequent neutralization by nitrate acid

The results of the experiments (Fig. 2) show that with the increase in the concentration in the solution in the range of 15÷40 % $Ca(NO_3)_2$, the amount of lime, which may be introduced to this solution without losing transportability, decreases. For the 15 %-solution of calcium nitrate, the largest possible lime concentration on conversion to CaO is 350 g/dm³, for the 20 %-solution it is 320 g/dm³, for the 25 %-solution – 295 g/dm³, for the 30 %-solution it is 275 g/dm³, for the 35 %-solution – 240 g/dm³ and for the 40 %-solution it is 200 g/dm³, respectively.

Further increase in the above-given lime amount in the solutions of the indicated concentration leads to its thickening and the loss of mobility (transportability). A viscous gel-like mass, which cannot be transported by the pipelines, is formed. It was experimentally found that the dynamic viscosity of the received suspensions should not exceed 1.0–1.1 Pa·s. The increase in viscosity of the suspensions leads to certain difficulties and in some cases it makes their pumping and transportation by pipelines impossible.

In further studies, the 35 %-solution of $Ca(NO_3)_2$ was used and the degree of conversion (hydration) of CaO in it was defined. The time of the reagents interaction, which determines the degree of CaO slaking, productivity and the dimensions of the equipment, are especially important for the

stage of preparing the suspension in experimental research. The intensity of mixing considerably influences the CaO conversion degree. Dependency of the conversion degree (the Reynolds criterion) Re on the interaction time is shown in (Fig. 3).

The thickening of suspension, formed by adding CaO to the solution of $Ca(NO_3)_2$ with variable concentration, occurs at different amount of CaO in the solution.

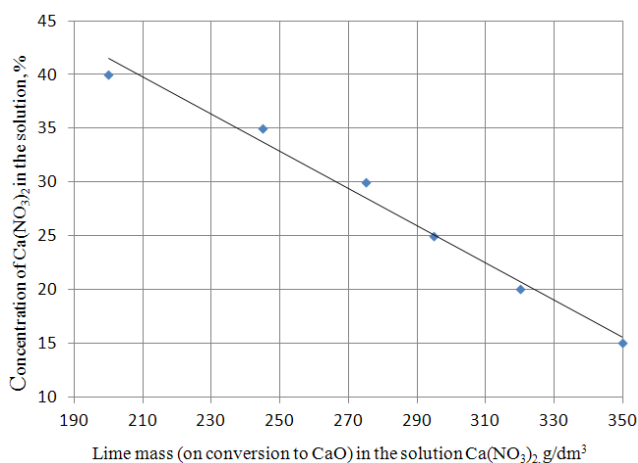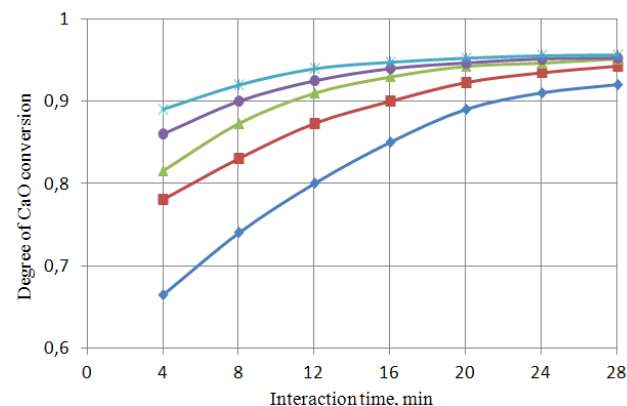Fig. 2. Dependency of the lime concentration in transportation solution on the concentrations of $Ca(NO_3)_2$

Fig. 3. Dependency of the degree of CaO conversion on the mixing intensity and the time of interaction; 1 ◆ — Re=1000; 2 ■ — Re=4000; 3 ▲ — Re=7000; 4 ● — Re=10000; 5 × — Re=13000

In this situation, an increase in the concentration of $Ca(NO_3)_2$ solution leads to a decrease in the CaO amount, at which the thickening of suspension occurs. The experimental results are shown in Table 1.

The results of Table 1 show that the mass of water necessary for full hydration of CaO by the reactions

$$CaO+H_2O=Ca(OH)_2 \qquad (1)$$

or

$$CaO+Ca^{2+}+H_2O=2CaOH^+, \qquad (2)$$
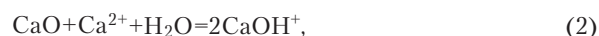
is considerably less than the mass of the water, present in the suspension. So, it is impossible to explain the process of thickening by water consumption in the reactions (1) and (2). In this case, other processes occur, which possibly pass according to the following scheme:

$$Ca(OH)_2 \xleftrightarrow{K_2} CaOH^+ + OH^- \xleftarrow{K_1} Ca^{2+} + 2OH^-, (3)$$
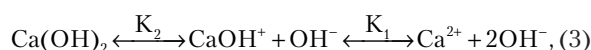
$$K_2 = \frac{[CaOH^+] \cdot [OH^-]}{[Ca(OH)_2]} = 1 \text{ (strong alkali)}, \qquad (4)$$

$$K_1 = \frac{[Ca^{2+}] \cdot [OH^-]}{[CaOH^+]} \approx 5 \cdot 10^{-2}. \qquad (5)$$

According to the given scheme, material balance for calcium containing compounds may be represented by designating C as their general concentration in the solution as follows:

$$C = [Ca(OH)_2] + [CaOH^+] + [Ca^{2+}].$$

We will use the expressions K_1 and K_2, assuming that $K_2 = 1$, to calculate the equilibrium concentration of $[CaOH^+]$ in the solution. Then $[Ca(OH)_2]$ and $[Ca^{2+}]$ may be expressed through $[CaOH^+]$ and material balance will take the following form:

$$C = \frac{[CaOH^+] \cdot [OH^-]}{K_2} + [CaOH^+] + \frac{K_1[CaOH^+]}{[OH^-]}. \qquad (6)$$

After solving equations for $[CaOH^+]$, we will receive the expression

$$\frac{[CaOH^+]}{S} = \frac{K_1[OH^-]}{[OH^-]^2 + K_1[OH^-] + K_1K_2}, \qquad (7)$$

where S is the value of solubility.

The expression (7) allows calculating in the units of the part the relative concentration of $[CaOH^+]$ at the change in the concentration of $[OH^-]$ (i. e., relative to the pH medium).

Similarly, the equation for calculating the equilibrium concentration of $[Ca(OH)_2]$ and $[Ca^{2+}]$ may be represented in the following form:

$$\frac{[Ca(OH)_2]}{S} = \frac{[OH^-]^2}{[OH^-]^2 + K_1[OH^-] + K_1K_2}, \qquad (8)$$

$$\frac{[Ca^{2+}]}{S} = \frac{K_1K_2}{[OH^-]^2 + K_1[OH^-] + K_1K_2}. \qquad (9)$$

The distribution of the existing forms of calcium containing compounds is presented in Fig. 4.
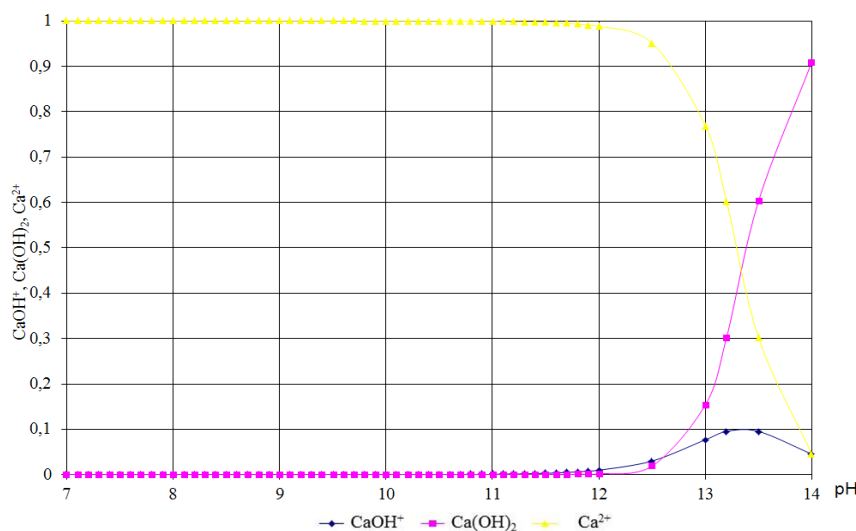

Fig. 4. Distribution of forms of calcium containing compounds on the pH solution at achieving thickening

As can be seen from Fig. 4, CaO hydration occurs partly by the reaction:

$$CaO + Ca^{2+} + H_2O = 2CaOH^+. \qquad (10)$$

In this case, the ion $CaOH^+$, in which oxygen is in the state of unfilled orbitals, is formed. This should contribute to the formation of hydrogen bonds and the emergence of clusters (Fig. 5) that capsulate the solution, resulting in the thickening of suspension.
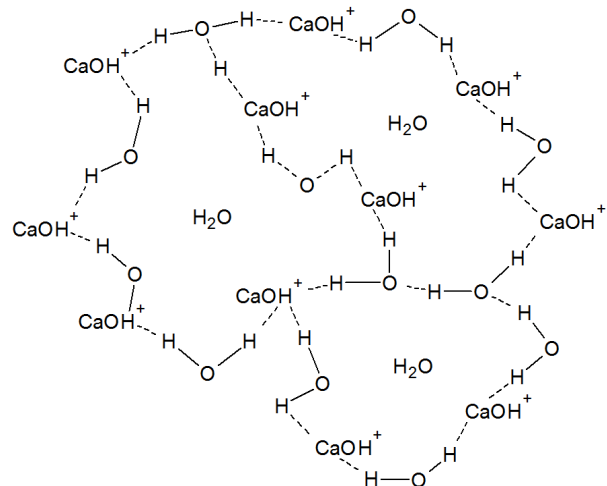

Fig. 5. Formation of clusters with the help of hydrogen bonds

The alkalinities were not taken into account while calculating the values of the coefficients because at high values of the ionic strength, for the rough approximation one may accept their constant value.

The value of solubility (S), necessary for the calculations, is defined by using the solubility product SP $[Ca(OH)_2] = 5,47 \cdot 10^{-6}$. The calculation is performed without taking into account the CaO hydration degree and the activity coefficients, taking the additional concentration (C) as the molar concentration of $Ca(NO_3)_2$ in the solution.

$$SP = [Ca^{2+}] \cdot [OH^-]^2 = 5,47 \cdot 10^{-6}. \qquad (11)$$

The material balance of dissolution $Ca(OH)_2$:

$$Ca(OH)_2 \leftrightarrow Ca^{2+} + 2OH^-, \qquad (12)$$
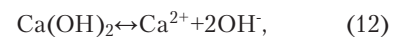
$$[OH^-] = 2S; \quad [Ca^{2+}] = S + C, \qquad (13)$$

$$SP = (S + C) \cdot (2S)^2. \qquad (14)$$

Using the value of C, given in Table 1, we will calculate the value S, which is suitable for determining relative concentration by using the equations (10)–(12).

The calculations showed that with the presence of calcium nitrate, i. e. calcium ions, i. e., the solubility of $Ca(OH)_2$ decreases by approximately an order, which may form the solid phase of $Ca(OH)_2$ on the CaO particle surface, which may also form hydrogen bonds with the solution components.

But $Ca(OH)_2$ can be formed on the CaO particle surface by the value of solubility of $(Ca(OH)_2)$ in the presence of Ca^{2+}. Since there is high possibility of forming hydrogen bonds in the solution, there is a probability of the formation of clusters of the type shown in Fig. 6.

Table 1

Properties of the suspension with critical CaO concentration for the thickening of suspension

Components and certain suspension indicators	Values of magnitudes					
Concentration of the original solution of $Ca(NO_3)_2$, %	15,0	20,0	25,0	30,0	35,0	40
Concentration of the original solution of $Ca(NO_3)_2$, mol/dm³	0,998	1,418	1,845	2,302	2,796	3,330
Density of the original solution of $Ca(NO_3)_2$, g/dm³	1119,3	1163,6	1211,0	1259,0	1311,0	1366,0
Critical content of lime on conversion to CaO with suspension thickening, g/dm³	350,0	300,0	295,0	275,0	243,0	200,0
Critical content of lime on conversion to CaO with suspension thickening, mol/dm³	6,24	5,35	5,26	4,90	4,33	3,57
Mass of water in the original solution of $Ca(NO_3)_2$, g	951,4	930,9	908,3	881,3	852,2	819,6
The mass of H_2O necessary for full hydration of CaO to $Ca(OH)_2$, g	112,5	96,4	94,8	88,4	78,1	64,3
The mass of water that remained after hydration of CaO, g	838,9	834,5	813,5	792,9	774,1	755,3
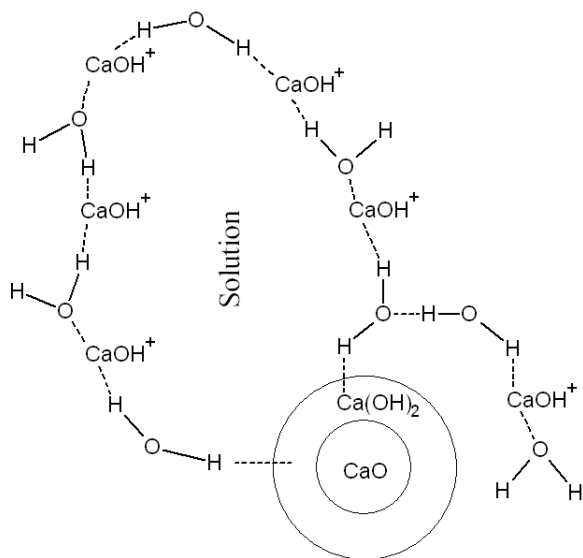
Fig. 6. Formation of the shell $Ca(OH)_2$ around the grain CaO and the clusters by hydrogen bonds

The results of exploring dependency of the $Ca(NO_3)_2$ concentration in the solution after neutralization on the HNO_3 concentration and the lime content in the transportation solution (Fig. 7).
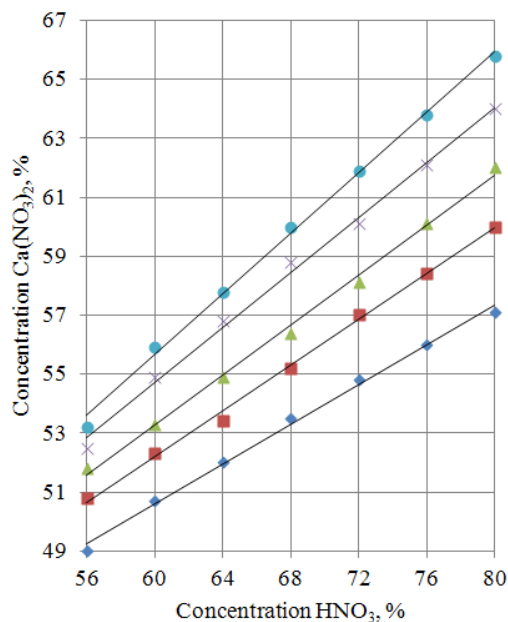
Fig. 7. Dependency of the $Ca(NO_3)$ concentration in the solution after neutralization on the HNO_3 concentration and the lime content in the solution, g/dm³: ● — 450; × — 400; ▲ — 350; ■ — 317; ◆ — 250

The composition of the obtained solutions with the use of circulating 35 % solution of calcium nitrate and various lime concentrations in accordance with the introduced additives after the nitrate acid neutralization was determined by using titrometric analysis. The data of Tables 2, 3 show that the received fertilizer using ammonium nitrate and potassium carbonate additives has a higher concentration of the main component compared with the calcium nitrate solution, received at a working industry enterprise.

Table 2

Composition of the obtained solutions with the use of NH_4NO_3

Sample №	Concentration of calcium nitrate $Ca(NO_3)_2$, %	Concentration of NH_4NO_3, %	Insoluble impurities, g/dm³
1	39,3	3,1	0,089
2	49,72	12,4	0,011
3	49,84	12,7	0,010

Table 3

Composition of the obtained solutions with the use of K_2CO_3

Sample №	Concentration of calcium nitrate $Ca(NO_3)_2$, %	Concentration of KNO_3, %	Insoluble impurities, g/dm³
1	39,3	missing	0,089
2	49,72	13,1	0,011
3	49,84	13,4	0,010

Tables 2, 3 display: 1 is the 39.3 %-solution of CN from PrAT «Himdivizion» (Dniprodzerzhynsk, Ukraine) after filtration; 2, 3 are the samples obtained after filtration.

To develop the technology of obtaining the solutions of the modified CN, ammonium nitrate and potassium carbonate were selected as the substances that not only increase the lime content in a suspension but also enrich the product with additional nutritious components.

Using K_2CO_3 as an additive with the aim of increasing the lime content in TR (transport solution) distinguishes it among other additives. As a result of neutralization of the acid in the suspension containing K_2CO_3, all of it fully transfers to KNO_3, which allows increasing the lime content in the TR to 380 g/dm^3 and obtaining more nutritious ingredients in the production solution. Besides, the regulated content of insoluble substances of 0.02 g/kg is not exceeded.

For the confirmation of phase composition of the received fertilizers, the X-ray structural analysis was performed, which allowed establishing which components each of the received samples consists of. The results of the X-ray structural studies are shown in Fig. 8.

The presence of calcium nitrate and potassium nitrate was proved in the received samples. The resulting mixture of salts is not inferior to its analogue, calcium nitrate produced by PrAT «Himdivizion» (Dniprodzerzhynsk, Ukraine) and is distinguished by the presence of potassium nitrate.

The conducted derivatographic analysis of the sample of the obtained fertilizer in comparison with its analogues is shown in Fig. 9. It was established that the received fertilizer is not inferior to the products of PrAT «Himdivizion» (Dniprodzerzhynsk) and is better than the foreign product of Buysk factory (Russia), in which all the calcium nitrate is in the form of tetrahydrate.

Based on the experimental data and theoretical calculations, a technological scheme of obtaining calcium nitrate from unslaked lime and nitrate acid was developed. It is presented in Fig. 10.

The given technology is recommended under condition of using K_2CO_3, NH_4NO_3, $NaHCO_3$, KCI, KNO_3, $NaNO_3$ as additives, taking into account specific features of each additive.

The part of the solution, as the circulating one from gathering tank 12, enters tank 16 by a pipeline for accumulation and then enters unit 1. The water is also supplied here at the rate of obtaining 35 %-solution of $Ca(NO_3)_2$.

Quicklime is loaded by the belt conveyor to the feeding bunker 2, from which it is supplied in the appropriate amount to the crusher (ball mill) 4. Then the circulating 35 %-solution of CN from the unit 1 is simultaneously supplied to lime slaker 5, as well as shredded quicklime. Lime slaking occurs in unit 5 with the formation of its suspension in the 35 %-solution of CN.
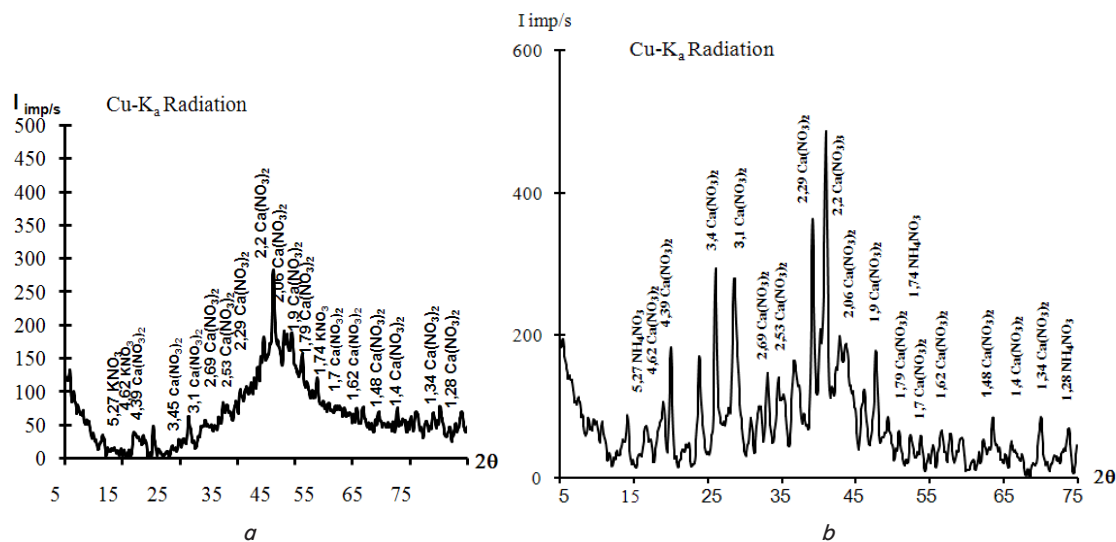

Fig. 8. Phase composition of fertilizers: a — CN modified $Ca(NO_3)_2$ — 94.5 %; KNO_3 — 5,2 %; b — CN granulated by PrAT "Himdivizion" $Ca(NO_3)_2$ — 96 %; NH_4NO_3 — 3,1 %
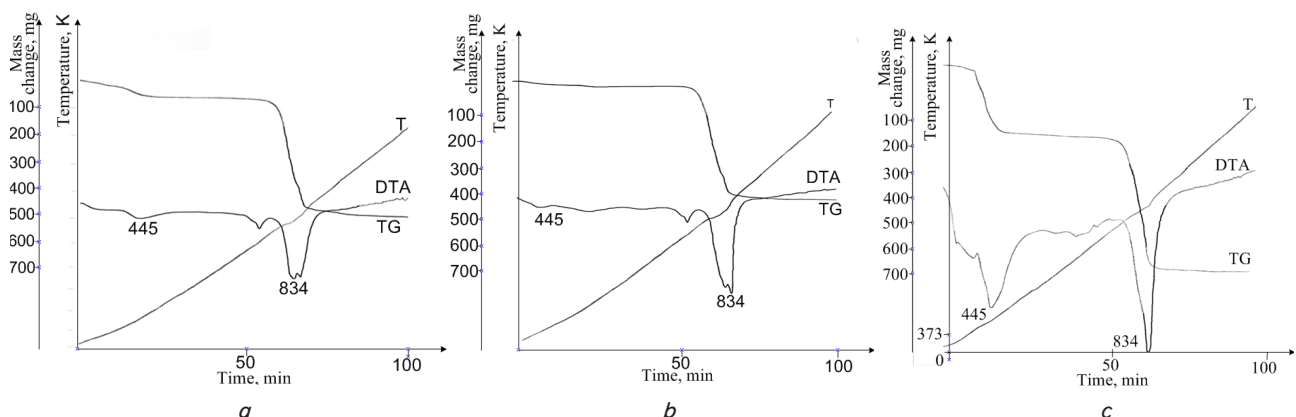

Fig. 9. Thermograms: a — of the received fertilizer; b — of calcium nitrate produced by PrAT "Himdivizion"; c — of calcium nitrate produced by Buysk factory (Russia)
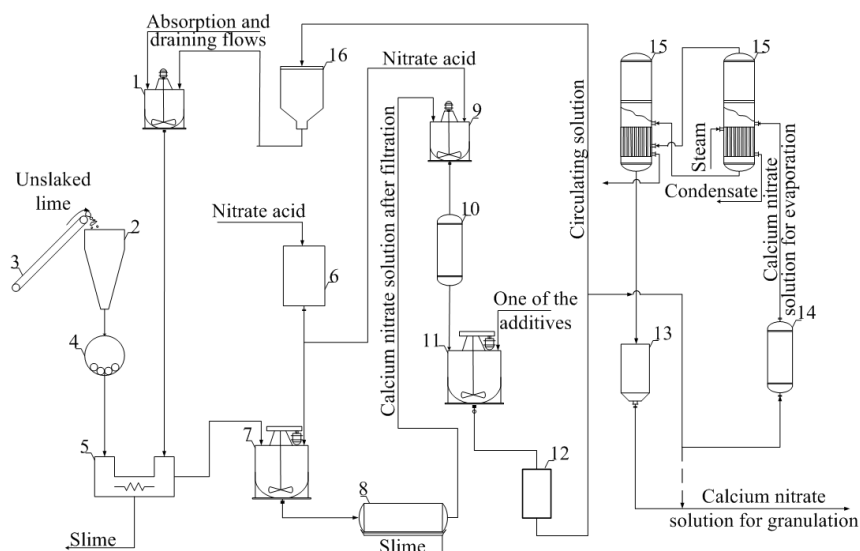
Fig. 10. Fundamental technological scheme of calcium nitrate production

The neutralized solution is accumulated in the collector 12, after which one part of it is sent to start the process of preparing transportation solution, and the other part is dispatched as the finished product. If there is a necessity, the solution is vaporized to the required concentration at the evaporation plant.

6. Conclusions

1. The process of calcium oxide hydration in the calcium nitrate solutions is substantiated. A mechanism of suspension thickening (suspension of $Ca(OH)_2$ in the solution of $Ca(NO_3)_2$), based on the formation of hydrogen bonds due to the presence of oxygen with unfilled orbitals was suggested.

Nitrate acid with mass fraction not less than 54.6–56 % is supplied to the pressurized container 6, from where it goes by the current to neutralizer 7, to which the transportation solution is also supplied. In the neutralizer, the interaction of nitrate acid with suspendized lime in a transportation solution takes place with the increase in the temperature of reaction mixture to 102–108 °C. At filter press 8, the solution is filtered from insoluble and mechanical impurities. After the filtration, the calcium nitrate solution is supplied to unit 9, where the introduction of nitrate acid occurs that provides the final CaO neutralization. Further, the acidified solution is accumulated in collector 10 and is sent to reactor 11, where the free acid is neutralized by the introduction of the additive to pH 6.5–7.0.

2. The degree of CaO conversion (kinetics of hydration) was defined from time and the intensity of mixing in 35 %-solution of calcium nitrate, which increases from 0.67 to 0.89 o.n. with an increase in the mixing intensity Re=1000÷13000. The limit lime content for different $Ca(NO_3)_2$ concentrations was established; for 15 %-solution of calcium nitrate, the highest possible lime concentration on conversion to CaO is $350 \, g/dm^3$, for 20 %-solution, it is $320 \, g/dm^3$, for 25 %-solution – $295 \, g/dm^3$, for 30 %-solution, it is $275 \, g/dm^3$, for 35 %-solution – $240 \, g/dm^3$ and for 40 %-solution, it is $200 \, g/dm^3$, respectively.

3. A technological scheme for obtaining calcium nitrate was developed; its characteristic feature is obtaining the calcium nitrate solutions of increased concentration of the content of additional nutrients.

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