American Journal Of Applied Science And Technology
(ISSN – 2771-2745)
VOLUME 04 ISSUE 11 Pages: 47-58
OCLC – 1121105677

Publisher: Oscar Publishing Services

Research Article

IMPROVEMENT OF THE PRODUCT COMPOSITION FROM NITRIC ACID PROCESSING OF KYZYLKUM CARBONATE PHOSPHORITES

Journal Website: https://theusajournals.com/index.php/ajast

Submission Date: November 06, 2024, Accepted Date: November 11, 2024,
Published Date: November 16, 2024
Crossref doi: https://doi.org/10.37547/ajast/Volume04Issue11-08

Ayjamal Allamuratova
Associate Professor, Karakalpak State University, Named After Berdakh, Uzbekistan

Aktam Erkaev
Professor, Tashkent Institute Of Chemical Technology, Uzbekistan

Akhmed Reymov
Professor, Karakalpak State University. Named After Berdakh, Uzbekistan

Kazakhbaev Saparbay
Basic Doctoral Student, Karakalpak State University. Named After Berdakh, Uzbekistan

ABSTRACT

The process of producing NP-fertilizers by nitric-sulfuric acid decomposition of phosphate rock (17.20% P_2O_5) under thickening slurry conditions has been studied. It was shown that the higher the recycle ratio, the lower the moisture content of the final product. Increasing the HNO_3 dosage above 30% and H_2SO_4 above 70% is undesirable, as the product's moisture content exceeds 6.03% and it has increased acidity. To avoid issues during ammoniation, an optimal rate of nitric and sulfuric acid was proposed—73.5-91%, which produced products containing 9.34-10.61% -P_2O_5total; 3.04-4.54% N; P_2O_5 digestive:P_2O_5 total = 73.4-82.3%; pH = 3.3-3.6, and granule strength of 2.1-2.3 MPa. The process of producing NPK-fertilizers was also studied by adding nitrogen components such as K_2SO_4, KCl, and K_2CO_3 to the products of complete nitric acid decomposition of washed and dried concentrate (24.10% P_2O_5) and fine fractions (18.55% P_2O_5). The process includes decarbonization and decomposition of the phosphate raw material (simultaneously in one apparatus), neutralization to a pH not lower than 3.5, evaporation of the slurry to a density of at least 1750 kg/m^3, the addition of potassium salts at N:P_2O_5:K_2O ratios of 1:1:1, 1.5:1:1, and 1:1.5:1, product granulation, drying in the presence of recycle, and cooling.

KEYWORDS

Phosphorites of Central Kyzylkum and Karakalpakstan, inorganic salts, activation, complex NPK fertilizers, physicochemical analysis methods.

INTRODUCTION

Since 2005, a pilot-industrial unit for the production of nitrocalcium phosphate fertilizer (NPF) has been operating at OAO "Samarqandkimyo" [1]. The production process is based on the decomposition of unbeneficiated phosphate rock from the Kyzylkum deposit (mass %): P_2O_5 17.20; CaO 46.22; CaO : P_2O_5 = 2.96; Al_2O_3 1.24; Fe_2O_3 1.05; MgO 1.75; F 2.00; CO_2 16.0; Cl 0.1 with 57% nitric acid (HNO_3) in the range of 55-65% of stoichiometry for binding all the CaO in the phosphate, followed by neutralization of the free acidity of the nitrocalcium phosphate slurry with gaseous ammonia, evaporation, granulation, and drying of the final product [2-5]. With incomplete HNO_3 dosage, the overall reaction is as follows:

$$2Ca_5(PO_4)_3F + 10HNO_3 = Ca(H_2PO_4)_2 + 4CaHPO_4 + 5Ca(NO_3)_2 + 2HF$$

According to this reaction, the final product consists of mono- and dicalcium phosphate salts mixed with calcium nitrate in various degrees of hydration. The latter depends on the crystallization conditions of calcium nitrate from the slurry during ammoniation, evaporation, and drying. The moisture content of the initial slurry is 37% H_2O, while the evaporated slurry has 25% H_2O. The temperature of the initial slurry is 40°C, and the evaporated slurry is at 80°C. The slurry evaporated in contact-type apparatus contains 8-9% P_2O_5, 5-6% N, and has a density of 1.7-1.8 t/m³. Due to the combination of evaporation and neutralization of the residual acidity in the slurry with gaseous ammonia in a single technological unit, the pH of the slurry during evaporation increases and fluctuates between 3.5-4.0. The product obtained from such slurry consists of dicalcium phosphate (20-25%), monocalcium phosphate (10-15%), and calcium nitrate (50-55%) in terms of anhydrous salt forms. Fertilizer of this composition is undoubtedly of great agrochemical interest [6].

Additionally, maintaining such a ratio of water- and citrate-soluble forms of P_2O_5 and CaO in the reaction mixture throughout the entire production cycle allows the processing of nitrophosphate slurry into finished fertilizers without the need to separate calcium nitrate [7]. The granulation and drying of NPF in this case can be carried out using the well-known scheme for producing ammonium phosphate with the use of drum granulator dryer apparatuses [8].

It should be noted that NPF granules have very poor physical properties: they are highly hygroscopic, sticky, disperse poorly, and are unsuitable for mechanized soil

application and fertilizer mixing [9]. Therefore, to improve the physicochemical properties of NPF, we proposed [10-12]: deep drying and instant cooling of the product, the use of a large amount of fine product fraction (granules smaller than 1 mm), and the treatment and coating of granules with sulfate, phosphate, and carbonate salts in the presence or absence of organic substances (surfactants). These proposed methods significantly improve the consumer properties, particle size, and flowability. However, during long-term storage and transportation of the finished product, various secondary physicochemical processes occur: moisture absorption from the air or drying out, recrystallization due to hydration, retrogradation, dehydration, polymorphic transformations, and others.

To improve the properties of products from nitric acid processing of carbonate phosphate raw materials, various methods are used to remove excess calcium or reduce the $CaO:P_2O_5$ ratio in the nitric acid slurry being processed: 1) freezing (crystallization) of calcium nitrate; 2) the introduction of additional amounts of phosphoric acid; 3) precipitation of excess calcium with sulfuric acid or ammonium sulfates; 4) precipitation of excess calcium in the form of $CaCO_3$ with carbon dioxide and ammonia [13].

In the conditions of Uzbekistan, the most promising and accessible method for improving the commercial quality of NPF is the use of sulfuric acid to bind part of the calcium in the nitric acid slurry into gypsum. In this process, a target product can be obtained, containing P_2O_5 partially or fully in water-soluble form. In this case, phosphate raw material is decomposed using nitric and sulfuric acids in a molar ratio.

In some countries, when producing nitrogen-phosphorus fertilizer of the nitroammophosphate type with a mass ratio of $N : P_2O_5 = 1 : 1$ and water-soluble forms of P_2O_5 accounting for no less than 60% of the total phosphorus content, the total consumption of nitric and sulfuric acids is taken at 140% of the stoichiometric amount to bind calcium and remove it from the system as gypsum. In this case, the phosphate is decomposed with nitric acid in the first two reactors, with 60% of the total sulfuric acid being added to the third and fourth reactors, and the remaining amount dosed into the ammoniation reactor. The wet product is then dried and granulated. However, to carry out this process, high-quality phosphate raw material is required, such as apatite concentrate from the Kola Peninsula (39.5% P_2O_5, calcium modulus—i.e., the ratio of CaO to P_2O_5—is 1,32) [13].

In contrast to the above method, we have developed a process in which decarbonization and decomposition of phosphate raw materials are carried out using low-concentration nitric acid at various rates from the stoichiometric amount needed to form calcium nitrate. Both processes are conducted in a single apparatus, with the acid being introduced into the reaction zone

in equal portions over 2-4 minutes with active stirring. Then, sulfuric acid is added to the resulting nitrocalcium phosphate slurry, which facilitates further decomposition of the phosphate raw material and partial drying of the slurry. In this case, the liquid phase content in the reaction slurry is 2-4 times less than that in the developed NPF technology [2, 14]. As a result, the decomposition of carbonate phosphate raw materials does not result in excessive foaming or the release of nitrogen oxides into the gas phase. The resulting thick mass, or its mixture with neutralizing additives (such as ammonia), is fed into a mixer where return material is simultaneously added in the amount needed to maintain a moisture content of 20-25%. Granulation of the slurry is best performed in a screw or pan granulator in the presence of return material.

METHODS

For laboratory studies, three types of phosphate raw materials from the Kyzylkum deposit were used: phosphate flour, washed dried concentrate, and fine fraction. The fine fraction is produced during the crushing and grinding of the ore to produce phosphate flour and is currently not utilized. Given the acute shortage of high-quality phosphate raw materials, we believe that these materials should also be used in agricultural production. The only requirement is to convert the non-available P_2O_5 form into a form that is accessible to plants. Kyzylkum phosphorites are granular phosphorites, whose main mineral is francolite. It has the unit cell parameters $a_0 = 9.33A^\circ$, $c_0 = 6.89A^\circ$, and contains 37% P_2O_5, 3.5% CO_2, and up to 3% SO_3, which isomorphic enters its crystal structure.

The chemical formula of francolite (staffelite) is as follows:

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

At the initial stage, we studied in laboratory conditions the process of producing nitrogen-phosphorus fertilizers through decarbonization and decomposition of phosphate flour, the composition of which is shown in Table 1, first with nitric acid, then sulfuric acid, with a total acid norm ranging from 20.7% to 123% of the stoichiometry for the formation of calcium nitrate.

Table 1

Chemical composition of various types of phosphorites from Central Kyzylkum

Name of Phosphate Raw Materials	Content of components, mass. %						
	P_2O_5	CaO	Al_2O_3	Fe_2O_3	MgO	F	CO_2

Phosphate flour	17,20	46,30	1,23	1,04	1,70	1,98	15,5
Washed dried concentrate	24,10	46,40	0,34	0,47	0,93	2,44	9,5
Dust fraction	18,55	45,01	0,96	0,78	0,90	2,2	15,0

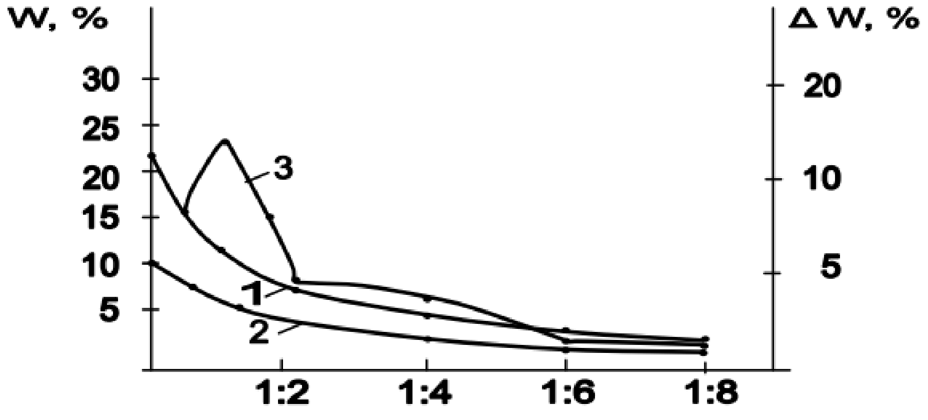
In this process, the amount of HNO_3 ($NHNO_3$) varied from 5% to 31%, and H_2SO_4 (NH_2SO_4) varied from 7.6% to 93% of the stoichiometry required to bind the CaO in the phosphate raw material. The concentration of the first acid was ($CHNO_3$) 50% and 54%, and of the second (CH_2SO_4) 65% and 92%. The interaction time between the phosphate raw material and nitric acid was 15 minutes, and the reaction time of the nitrocalcium phosphate slurry with sulfuric acid was also 15-20 minutes at a temperature of 75-80°C. After completing the mixing process, the acidic reaction mixtures were neutralized with gaseous ammonia until the pH was no lower than 3.0. They were then dried at 90-100°C. The mass of the product was measured, and the moisture content of the slurry was determined. Granulation of the wet phosphate masses was performed during the drying process using intensive mixing and granulation in the presence of return material. The final samples were then cooled, crushed, and chemically analyzed for various forms of P_2O_5 and CaO, as well as nitrogen and CO_2 content according to known methods [15]. The degree of decarbonization of the phosphate raw material was calculated by changes in CO_2 content. The pH of the product was determined after shaking a 10% aqueous suspension for one hour. The strength of the fertilizer granules was determined using the MIP-10-1 device [15].

DISCUSSION

Experimental data showed that the higher the amount of return material, the lower the moisture content of the final product. For example, with an increase in the amount of return material to 8 parts by mass in relation to 1 part by mass of the initial product, the moisture content decreased from the initial 22% to 1.5% in the final product (see figure, curve-1), meaning that the granulation process can be carried out using a pan or screw granulator. Table 2 presents the composition of products obtained from nitric-sulfuric acid processing of phosphate flour, depending on the amount of nitric and sulfuric acids used with a return ratio of 1:6.

Table 2.
Composition of products from nitric-sulfuric acid processing of ordinary phosphate flour from Central Kyzylkum

№ experience	Concentration and norm HNO_3, %		Concentration and norm H_2SO_4, %		Sum N_{HNO3}+N_{H2SO4}, %	Content nitrogen, wt.%			Content P_2O_5, wt. %		P_2O_5 total/ P_2O_5 digestive	degree of decarbonization of phosphorus raw materials %
	C_{HNO_3}	N_{HNO_3}	$C_{H_2SO_4}$	$N_{H_2SO_4}$		$N_{nitrate}$	$N_{ammonia}$	N_{total}	P_2O_5 total	P_2O_5 digestive		
1	54	11	92	23	33	1,97	-	1,97	13,50	5,4	40,1	75,00
2	54	11	92	70	80	1,57	1,50	3,04	10,54	8,22	78,2	95,00
3	54	11	92	93	103	1,37	2,90	4,27	9,36	8,55	91,3	97,50
4	54	21	92	23	45	3,75	1,05	4,80	12,80	6,40	50,4	86,00
5	54	21	92	70	91	2,73	1,81	4,54	9,34	7,66	82,3	96,00
6	54	21	92	93	114	2,46	3,01	5,47	8,43	7,76	92,1	98,00
7	54	31	92	23	53	5,05	1,21	5,9	11,54	6,92	60,1	90,00
8	54	31	92	70	100	3,89	2,02	6,26	8,89	8,0	90,1	97,00
9	54	31	92	93	123	3,56	3,51	7,07	8,14	7,73	95,1	98,00
10	54	15	92	11,7	20,7	3,03	-	3,03	14,82	5,04	34,1	68,00
11	54	15	92	32,7	47,7	2,73	1,15	3,88	13,31	6,79	51,1	86,50
12	54	15	92	58,5	73,5	2,17	2,03	4,20	10,61	7,75	73,4	89,00
13	54	16	65	7,6	23,7	3,24	-	3,24	14,68	4,55	31,1	65,00
14	54	16	65	15,2	31,2	3,03	-	3,03	13,82	5,25	38,2	71,00
15	54	16	65	22,8	38,8	2,83	1,03	3,86	12,94	5,69	44,3	77,00
16	50	15	65	7,6	22,6	2,78	-	2,78	13,70	4,11	30,4	60,00
17	50	10	65	15,2	25,2	1,88	-	1,88	13,93	4,60	33,4	67,10
18	50	5	65	22,8	27,8	0,94	-	0,94	13,93	4,88	35,2	70,02



Return Ratio

Figure-1. Changes in product moisture depending on the return ratio.

(1 – powdery fraction; 2 – phosphate flour; 3 – washed dried concentrate)

It can be observed that with identical concentrations of nitric and sulfuric acids (54% HNO_3 and 92% H_2SO_4) and a constant norm of HNO_3 at 11% and 21%, increasing the amount of H_2SO_4 from 23% to 93% results in a decrease in total P_2O_5 content in the products from 13.50% to 9.36% and from 12.80% to 8.43%, respectively. Conversely, the total nitrogen content (Ntotal) increases from 1.97% to 4.27% and from 4.80% to 5.47%, respectively. In this case, the ratio P_2O_5 digestive: P_2O_5total increases from 40.1% to 91.3% and from 50.4% to 92.1%, with the degree of decarbonization of phosphate raw materials (Kdecarb.) rising from 75.0% to 97.5% and from 86% to 98%. It is worth noting that under these conditions, the total norms of nitric and sulfuric acids fluctuate within 33-103% and 45-114% of stoichiometry, respectively.

With the same changes in H_2SO_4 norms and a relatively high norm of HNO_3 at 31% (with a total acid norm of 53-123%), the total P_2O_5 content in the products decreases, albeit slightly (from 11.54% to 8.14%), while the Ntotal content remains sufficiently high (5.47%-7.07%). At this point, the phosphate raw materials are fully decarbonized (90%-98%), and the products have a soluble P_2O_5 to total P_2O_5 ratio ranging from 60% to 95%.

However, increasing the norm of HNO_3 beyond 30% and H_2SO_4 beyond 70% is undesirable, as the product moisture exceeds 6.03% and exhibits increased acidity, necessitating deeper ammonization of the reaction mass. This leads to a reduction in the content of nutrients and retrogradation of P_2O_5, which is the transition of water-soluble monocalcium phosphate to citrate-soluble dicalcium phosphate according to the reaction:

$$Ca(H_2PO_4)_2 + NH_3 = CaHPO_4 + NH_4H_2PO_4$$

Further reduction of soluble forms of P_2O_5 during ammonization can be attributed to subsequent retrogradation of P_2O_5 according to the reaction:

$$2CaHPO_4 + CaSO_4 + 2NH_3 = Ca_3(PO_4)_2 + (NH_4)_2SO_4$$

To avoid additional ammonization processes that lead to the negative phenomena mentioned above, we selected the optimal total norms of nitric and sulfuric acids as 73.5%, 80%, and 91%, respectively, with HNO_3 at

15%, 11%, and 21%, and H_2SO_4 at 58.5%, 70%, and 70%. In these cases, the obtained nitrogen-phosphorus fertilizers contain (weight %): in the first case - P_2O_5 total – 10.61; Ntotal – 4.20; P_2O_5 digestive:P_2O_5total = 73.4; degree of decarbonization Kdecarb– 89; granule strength – 2.3 MPa; pH = 3.5; in the second case - P_2O_5total – 10.54; Ntotal – 3.04; P_2O_5 digestive: P_2O_5total = 78.2; Kdecarb. – 95; granule strength – 2.1 MPa; pH = 3.6; and in the third case - P_2O_5total – 9.34; Ntotal – 4.54; P_2O_5 digestive: P_2O_5total = 82.3; Kdecarb. – 96; granule strength – 2.2 MPa; pH = 3.3. With this content of available phosphorus, the products obtained are effective nitrogen-phosphorus fertilizers.

Next, the process of obtaining complex NPK fertilizers was studied. For this, potassium components were added to the products of nitric acid processing of washed dried concentrate and powdery fractions, the compositions of which are presented in Table 1.

The process includes the simultaneous decarbonization and decomposition of phosphate raw materials (in one apparatus), neutralization to a pH of no less than 3.5, evaporation of the pulp to a density of at least 1750 kg/m³, addition of potassium salts in a mass ratio of $N:P_2O_5:K_2O$ equal to 1:1:1, 1.5:1:1, and 1:1.5:1, granulation of the product, and drying in the presence of return and cooling. The amounts of nitric acid and potassium salts per 100 kg of phosphate rock, given the specified mass ratio of $N:P_2O_5:K_2O$, are calculated using the following formulas:

$$A_{HNO_3} = (C_{P_2O_5}*63/14)*(100 / C_{HNO_3})*(П_N / П_{P_2O_5});$$

$$A_{p/r} = 100 * П_{P_2O_5};$$

$$A_{к.salt} = 0{,}5(C_{P_2O_5}* M_{к.salt} / C_{K_2O})*(П_{K_2O} / П_{P_2O_5});$$

Where, A_{HNO_3}, $A_{p/r}$, $A_{K.salt}$, are the amounts of nitric acid, phosphate raw material, and potassium salts, respectively; $C_{P_2O_5}$, C_{K_2O} are the contents of P_2O_5 and K_2O in the phosphate raw material and potassium salt, respectively; C_{HNO_3} is the concentration of nitric acid;

$M_{K.salt}$ is the molecular weight of potassium salts;

and $П_N$, $П_{P_2O_5}$, $П_{K_2O}$ are the numerical values of the specified mass ratios of N, P_2O_5, and K_2O, respectively.

As potassium components, we used sulfate, chloride, and carbonate salts, whose hygroscopicity (on a 10-point scale) is presented below (table-3):

Table-3

№	Components	Points (α)	Qualitative assessment of hygroscopicity
1	K_2SO_4	>1	Almost non-hygroscopic
2	K_2CO_3	>1	Almost non-hygroscopic
3	KCl	(3,62) 3-5	Hygroscopic

Potassium salts are added to the mixer, where the evaporated melt is simultaneously introduced in an amount necessary to maintain the mass ratio of N:P2O5:K2O equal to 1:1:1, 1.5:1:1, and 1:1.5:1. Visual observations indicate that the granulation process in the presence of return must be conducted while maintaining the moisture content in the mass at no more than 7-8%. It is important to note that reducing the density of the melt to less than 1750 kg/m^3 complicates the granulation process and deteriorates the properties of the resulting fertilizers due to increased moisture content.

Table 3 presents the compositions of the complex fertilizers. It is evident that based on the product of nitric acid decomposition of washed dried concentrate and potassium components, with the mass ratio of N:P2O5:K2O varying from 1:1:1 to 1.5:1:1 and 1:1.5:1, the composition of granulated NPK fertilizers appears as follows: for K2SO4 – 7.2-10.89% N; 7.26-10.76% P2O5 with a total of nutrients – 25.5-26.5%; 7.2-8.84% K2O; for KCl – 7.7-11.6% N; 7.72-11.43% P2O5; 7.7-9.53% K2O with a total of nutrients – 27-28.5%; for K2CO3 – 7.9-9.84% N; 7.92-11.9% P2O5; 7.9-9.84% K2O with a total of nutrients – 27.7-29.5%.

A similar pattern is observed for NPK fertilizers based on powdery fractions and potassium components, but with a relatively low content of nutrients. In any case, all samples of the products meet all the requirements of agriculture in terms of physical-chemical and commercial properties, making them suitable for bulk storage, transportation, and application.

Thus, as a result of implementing the proposed option, all the advantages of existing methods are preserved: the drying stage is reduced, and the technology allows for the regulation of the compositions of complex fertilizers within a wide range of nutrient component ratios and their physical-chemical properties. The obtained complex fertilizers possess good agrochemical properties and are suitable for all types of agricultural crops.

Table 3. Composition of complex fertilizers obtained from the products of nitric-sulfuric acid processing of phosphorites from Central Kyzylkums and potassium components.

Table-4

Mass ratio. N:P_2O_5:K_2O	Type of phosphorites	Type of potassium salts	Mass ratio original components A_{HNO_3}: $A_{ф/с}$: $A_{к.соль}$	Contents of components %			Amount of nutrients components,%
				N	P_2O_5	K_2O	
1:1:1	Washed dried. concentrate	K_2SO_4	192,9:100:77,59	8,84	8,83	8,84	26,5
1,5:1:1			298,3:100:77,59	10,89	7,26	7,3	25,5
1:1,5:1			192,9:150:77,59	7,2	10,76	7,2	25,5
1:1:1	-	KCl	192,9:100:56,86	9,53	9,53	9,53	28,5
1,5:1:1			298,3:100:56,86	11,6	7,72	7,7	27,0
1:1,5:1			192,9:150:56,86	7,7	11,43	7,7	27,0
1:1:1	-	K_2CO_3	192,9:100:48,86	9,84	9,84	9,84	29,5
1,5:1:1			298,3:100:48,86	11,9	7,92	7,92	27,7
1:1,5:1			192,9:150:48,86	7,9	11,9	7,9	27,7
1:1:1	Dust fraction	K_2SO_4	148,8:100:59,74	7,62	7,62	7,62	22,86
1,5:1:1			223,47:100:59,74	9,76	6,51	6,51	22,78
1:1,5:1			1489,48:150:59,74	6,33	9,49	6,33	22,78
1:1:1		KCl	148,8:100:43,78	8,2	8,16	8,2	24,6
1,5:1:1			223,47:100: 43,78	10,3	6,9	6,89	24,1
1:1,5:1			1489,48:150:43,78	6,9	10,3	6,9	24,1

Technical and economic calculations indicate the profitability of the proposed method. Savings are achieved through improved product quality and the use of inexpensive highly carbonized phosphorites (unbeneficiated phosphorite, washed dried concentrate, and powdery fraction).

CONCLUSION

Based on the conducted research on the improvement of the composition of products from the nitric acid decomposition of carbonate phosphorites: methods for enhancing the quality of products from the nitric acid processing of carbonate phosphate raw materials have been analyzed; the process of obtaining NP fertilizers through the nitric-sulfuric acid decomposition of phosphate rock in the conditions of thickening pulp has been studied, which excludes the stage of ammonization of the decomposition products; and the process of obtaining NPK fertilizers by adding nitrogen components such as K_2SO_4, KCl, and K_2CO_3 to the products of complete nitric acid decomposition of washed dried concentrate and powdery fractions has been studied. It has been established that when using washed dried concentrate, products with a relatively low content of nutrients are obtained.

REFERENCES

1. Rajabov R.R. Experimental-industrial installation for the production of nitrocalcium phosphate fertilizer // Chemical Technology. Control and Management. – 2006, No. 3, pp. 5-11.
2. Reymov A.M. Development of technology for the production of nitrocalcium phosphate and nitrocalcium sulfophosphate fertilizers based on the decomposition of Kyzylkum phosphorites with a reduced norm of nitric acid: Author's abstract of the dissertation for the degree of candidate of technical sciences. – Tashkent, IONKh AN RUz. – 2004. - 23 p.
3. Preliminary patent RUz IDP 05291. MKI 7S 05B 13/06. Method for producing a complex fertilizer. / Erkaev A.U., Yusupbekov N.R., Artikov G.O., et al. // Inventions Official Bulletin. 2002, No. 4.
4. Patent RUz No. IAP 05335. Method for processing highly carbonized phosphorites / Erkaev A.U., Yakubov R.Ya., Allamuratova A., Toirov Z.K. // Published 04.01.2017. – Bulletin No. 2.
5. Method for producing a complex fertilizer. Pat. RUz No. IAP 04239, S 05 B 13/00 / Namazov Sh.S., Rajabov R., Yakubov R., Salikhov Sh.I., Reymov A.M., Beglov B.M., Zakirov B.S., Tajiyev S.M. // Published 16.09.2010. – Bulletin of Inventions No. 10.
6. Calcium nitrate. Its properties, production, and application in agriculture / B.M. Beglov, Sh.S. Namazov, A.T. Dadahodzhaev, Sh.Kh. Yuldashev, G.I. Ibragimov. – Tashkent: Mekhnat, 2001, 280 p.
7. Rajabov R.R., Namazov Sh.S. Granulation and drying of nitrophosphate fertilizers. Relevant issues of chemical processing of phosphorites from Central Kyzylkums. // Materials of the conference Tashkent, 2006, pp. 32-36.
8. Dokholova A.N., Karmyshev V.F., Sidorina L.V. Production and application of ammonium phosphates. – Moscow: Chemistry, 1986, 256 p.
9. A.M. Reymov, D.Sh. Sherkuziyev, Sh.S. Namazov, R.R. Rajabov, B.M. Beglov. Liquid nitrocalcium

fertilizers based on nitric acid extraction of phosphates and urea. // Chemical Industry. – St. Petersburg, vol. 87, No. 5, 2010. – pp. 228-234.

10. Erkaev A.U., Ibragimov K.G., Toirov Z.K., Yakubov R.Ya. Conditioning of nitrocalcium phosphate fertilizer with inorganic additives. // Chemistry and Chemical Technology. - 2010, No. 2, pp. 7-12.
11. Yakubov R.Ya., Ibragimov K.G., Erkaev A.U., et al. Research on ways to improve the physicochemical properties of nitrocalcium phosphate fertilizers // Theses of reports of the international scientific conference: Volgograd. – 2009. – p. 31.
12. Yakubov R.Ya., Erkaev A.U., Ibragimov K.G., Toirov Z.K. Determination of the effectiveness of the influence of modifying mineral salts on the hygroscopicity of complex fertilizers. // Chemical Technology. Control and Management. - 2010, No. 3, pp. 5-11.
13. Research of the process of obtaining potassium dihydrophosphate using diethylamine Bobokulov, A., Erkaev, A., Toirov, Z., Axmadova, M., Eshmetova, D. E3S Web of Conferences 2023, 458, 02035 (2023)
14. Reymov A.M., Erkaev A.U., Namazov Sh.S., Beglov B.M. Nitrogen-phosphorus-calcium fertilizers based on the decomposition of common and phosphorite flour from Central Kyzylkums with an incomplete norm of nitric acid. // Reports of the Academy of Sciences of RUz, No. 5, pp. 50-52.
15. Allamuratova, A., Erkaev, A., Reymov, A., Tairov, Z., Alimov, U. COMBINED TECHNOLOGY FOR PRODUCING COMPOUND FERTILIZERS FROM LOW- GRADE PHOSPHORITES FROM CENTRAL KYZYLKUM European Chemical Bulletin, 2022, 11(6), pp. 7–1416. GOST 21560.2-82. Mineral fertilizers. Test methods. – Moscow: State Standard, 1982. - 30 p.