



Researching of the Processes of Obtaining NP and NPK Fertilizers by Processing Phosphorite of Central Kyzylkum with the Participation of Sulfuric and Nitric Acids

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ABSTRACT: In this article, research was carried out to obtain NP and NPK fertilizers from the nitrogen-phosphorus liquid fraction by chemically enriching the calcium module of the Central Kyzylkum washed and calcined phosphate concentrate with weak nitric acid in order to reduce the CaO/P₂O₅, and by disintegrating it in the ratio of nitric and sulfuric acids: HNO₃:H₂SO₄ 35:70 and 25:80 with a solid-liquid phase ratio of S:L from 1:3.0 to 1:4.0

I. INTRODUCTION

The production of mineral fertilizers is a large and steadily developing branch of the chemical complex of Uzbekistan. The production of nitrogen, phosphorus and potassium fertilizers has become one of the main directions of our country's economy, and these products have become an important export commodity. The organization of the production of complex fertilizers is an urgent task for the chemical industry of the republic. The large amount of phosphogypsum released in the production of extractive phosphoric acid, which is considered the main product in the production of complex fertilizers, has created problems in its processing and reduction. To this end, our scientific research will allow us to reduce the amount of phosphogypsum in the production of mineral fertilizers.

II. LITERATURE SURVEY

The most common method is the sulfuric acid treatment of natural phosphates. Phosphate raw materials are treated with sulfuric acid in an amount sufficient to produce monocalcium phosphate, resulting in simple superphosphate. The main disadvantage of this fertilizer is that due to the high content of phosphogypsum in the product, the content of phosphorus pentoxide in superphosphate does not exceed 12-19.5%, depending on the quality of the phosphorite [1-5].

Technological variables affecting the process of processing the washed burned phosphate concentrate (WBPC) from the Central Kyzylkum (CK) with sulfuric acid to obtain extraction phosphoric acid (EPA), such as process temperature, S:L ratio, and time, have been studied in the scientific literature [6].

Several scientific studies have been conducted on methods for producing single and complex fertilizers by decomposing CK phosphorites with nitric acid [7-9]. In addition, scientific work has been carried out on the chemical enrichment of WBPC CK and the reduction of the calcium modulus [10]. We also previously studied the kinetics of decomposition of various types of CK phosphorites - unenriched phosphate raw materials and WBPC - in the presence of HNO₃:H₂SO₄ acids in different ratios, at 100-105% standards, at a temperature of 40-50°C and a process duration of 60 minutes, and the processes of obtaining NPCa and NPK fertilizers with different nutrient contents by directly neutralizing the resulting acidic slurry with gaseous ammonia to pH 3-3.5 without filtering [11, 12].

Due to the large calcium module ($\text{CaO}/\text{P}_2\text{O}_5$ ratio) of WBPC CK, when processing them with acid, the consumption of acid is much higher. In addition, the processing of these phosphorites with nitric acid produces a large amount of calcium nitrate. It is known that calcium nitrate salt is a very strong hygroscopic substance and absorbs moisture to a high degree.

Hence, the more calcium nitrate remains in a sample of phosphorus fertilizer, the more it negatively affects the commercial properties of the mixed fertilizers obtained on its basis. Therefore, it is necessary to separate and remove this salt from phosphorus fertilizer samples as much as possible.

In our scientific research, in order to reduce acid consumption and reduce the amount of phosphogypsum, it was scientifically proven that when the WBPC is initially calculated relative to the amount of free CaO at a low concentration of nitric acid, the calcium modulus in the enriched phosphorus concentrate decreases. The effect of technological parameters (concentration and rates of nitric acid) on the processes of processing WBPC at a low rate of nitric acid was studied.

III. RESEARCH METHODOLOGY

The chemical composition of the WBPC CK, selected as the object of study, is presented in the table below.

Table 1. Chemical composition of phosphorite samples, %

№	Raw materials	Chemical composition wt. %								
		P_2O_5	CaO	MgO	Al_2O_3	Fe_2O_3	F	CO_2	SO_3	H.O.
1	WBPC №1	27,61	55,83	0,98	0,49	0,44	2,78	2,57	2,65	4,77
2	WBPC №2	26,25	51,64	0,64	0,84	0,61	2,65	11,46	2,36	1,18

At the beginning of the experiments, in order to reduce the $\text{CaO}/\text{P}_2\text{O}_5$ ratio in the composition of the WBPC, it was chemically enriched with a low rate and concentration of nitric acid relative to CaO, using unconcentrated nitric acid (TSh 00203068-08:2013).

A solution containing $\text{Ca}(\text{NO}_3)_2$ as the liquid phase was isolated. The chemically enriched phosphate concentrate was decomposed with nitric and sulfuric acids. The experiments were conducted with sulfuric and nitric acids in the ratios of 70:35 and 80:25 to CaO in the phosphorite, in the presence of circulating solutions at a temperature of 50°C .

In the presence of a circulating solution of porridge containing the resulting phosphatic acid, calcium nitrate and calcium sulfate, the precipitate method was used in the case of calcium sulfate which is phosphogips ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), contained in the subcutaneous suspension. It is known that the process of filtering phosphites in the acid decomposition of nitrate and sulfate is one of the main limiting factors in technology. Cases where the solid and liquid phases in the filtering time were equal to the ratio $S:L=1-3.0\div 4.0$ were studied. The resulting suspensions were filtered through the Büchner vacuum funnel and separated into phosphogips (solid phase) and nitrogen-phosphorus solution (liquid phase).

IV. EXPERIMENTAL RESULTS

For the initial decomposition of the WBPC with nitric acid, 12 and 15% nitric acid was added to the reactor equipped with a mechanical mixer at a rate of $24\div 30\%$ relative to the total CaO in the WBPC, and the liquid phase was separated by filtration. The solid phase (chemically enriched phosphate concentrate-ChEPC) formed during filtration and the liquid phase were analyzed for P_2O_5 , N, and CaO (Table 2).

Table 2. Effect of acid standards on the process of enrichment of fosconcentrate with nitric acid

№	HNO ₃ standart, %	C _{HNO₃} , %	S:L	Composition of solid phases, wt. %		CaO/P ₂ O ₅	Composition of liquid phase, wt. %		
				CaO	P ₂ O ₅		CaO	N	P ₂ O ₅
1	24	12	1:2,5	35,23	22,82	1,544	5,79	2,90	0,00
2	25	12	1:2,6	34,91	22,73	1,536	5,764	2,88	0,09
3	27	12	1:2,8	34,19	22,51	1,519	5,69	2,84	0,23
4	30	15	1:2,5	31,44	21,02	1,488	7,41	3,69	0,624

The table shows that the calcium modulus in the solid phase isolated from the initial decomposition of the WBPC decreases from 1.488 to 1.544 as a result of the reaction of free CaO in the phosphate concentrate with nitric acid at a low concentration and rate after the initial decomposition.

One of the most important characteristics of the process of producing nitrogen-phosphorus solutions by breaking down phosphorites in the presence of nitric and sulfuric acids was analyzed: its chemical composition, filtration rate, the effect of the circulating phosphorus solution, and other indicators. The decomposition of ChEPC in the presence of nitric and sulfuric acids and a circulating nitrogen-phosphorus solution was carried out at temperatures of 45, 50 and 55°C, in the ratios of S:L=1:3.0÷4.0. In the process of obtaining nitrogen-phosphorus solutions by decomposition of ChEPC in the presence of sulfuric and nitric acids, solutions containing 4.7 and 5.1% P₂O₅ were used (Table 2).

According to the results obtained H₂SO₄ : HNO₃ = 70 : 35, a concentration of P₂O₅ in the circulating solution of 5.1%, and a ratio of S:L = 1:3.0-1:4, it was found that at temperatures of 45, 50 and 55°C, P₂O₅ changed from 12.90% to 9.00%, and the amounts of N and CaO changed from 3.52 to 2.42% and 5.52-3.87% respectively.

It was observed that with increasing nitrogen content of the liquid to solid phase (phosphogypsum) ratio (1:3.5 and 1:4) during the fragmentation process, the amount of components in the phosphorus solution decreased based on the concentration. The filtration rate was 1731-1903 kg/m².h.

H₂SO₄ : HNO₃ = 80 : 25, a circulating solution with a P₂O₅ concentration of 4.7% was used in the cyclic processing process. At a solid-liquid ratio of 1:3, the P₂O₅ content was 10.35-10.38%, nitrogen 2.03-2.06% and CaO - 3.56-3.58% respectively. At a S:L ratio of 1:3.5, at a temperature of 45-55°C, P₂O₅ - 8.61-8.66%; N - 1.68-1.73%; CaO - 2.97-3.01%, and at a S:L ratio of 1:4, P₂O₅ - 7.39-7.42%; N - 1.45-1.49%; CaO - 2.53-2.57% respectively and the filtration rate is 1750-1953 kg/m².h. The decrease in the concentration of phosphorus oxide in the nitrogen-phosphorus solution is directly explained by the increase in the amount of phosphogypsum with an increase in the standard proportion of sulfuric acid during the decomposition process and the increase in the amount of circulating solution to calculate the S:L ratio. It was also found that with a decrease in the proportion of nitric acid, the amount of N and CaO in the filtrate decreases accordingly.

Table 3. The effect of various technological parameters on the processes of decomposition of ChEPC in the presence of sulfuric and nitric acids

№	S:L	°C	Chemical composition of nitrogen-phosphorus solution, wt. %							Filtration rate relative to pulp, kg/m ² .h
			P ₂ O ₅	N	CaO	MgO	Al ₂ O ₃	Fe ₂ O ₃	F	
H ₂ SO ₄ : HNO ₃ = 70 : 35, circulating solution 5,1% P ₂ O ₅										
1	1:3	45	12,90	3,52	5,52	0,33	0,13	0,12	0,50	1731
2		50	12,94	3,50	5,54	0,35	0,15	0,13	0,53	1749
3		55	12,96	3,49	5,55	0,36	0,16	0,14	0,52	1758

4	1:3,5	45	10,58	2,89	4,53	0,29	0,12	0,10	0,47	1802
5		50	10,62	2,87	4,55	0,30	0,14	0,11	0,46	1816
6		55	10,64	2,86	4,56	0,30	0,15	0,11	0,44	1827
7	1:4	45	8,95	2,45	3,82	0,24	0,11	0,07	0,41	1880
8		50	8,99	2,43	3,85	0,26	0,13	0,09	0,39	1895
9		55	9,00	2,42	3,87	0,27	0,13	0,09	0,38	1903
H ₂ SO ₄ : HNO ₃ = 80 : 25, circulating solution 4,7% P ₂ O ₅										
10	1:3	45	10,35	2,06	3,56	0,29	0,12	0,09	0,49	1750
12		50	10,37	2,04	3,58	0,31	0,14	0,10	0,47	1782
13		55	10,38	2,03	3,58	0,32	0,14	0,11	0,46	1795
14	1:3,5	45	8,61	1,73	2,97	0,26	0,10	0,08	0,43	1821
15		50	8,64	1,70	2,99	0,27	0,12	0,09	0,41	1855
16		55	8,66	1,68	3,01	0,27	0,12	0,09	0,40	1878
22	1:4	45	7,39	1,49	2,53	0,22	0,10	0,07	0,36	1911
23		50	7,41	1,46	2,56	0,23	0,11	0,07	0,34	1937
24		55	7,42	1,45	2,57	0,23	0,11	0,07	0,33	1953

It should be noted that the obtained technological parameters correspond to the chemical composition of the obtained nitrogen-phosphorus solutions. In addition, the technological parameters of the processing of enriched phosphorus concentrate with the participation of sulfuric and nitric acids are more effective than the processes for obtaining nitrogen-phosphorus solutions from the primary WBPC. The low amount of phosphogypsum produced and the high content of nutrient components in the obtained solutions are also significant. Thus, studies have shown that the optimal technological parameters that allow obtaining nitrogen-phosphorus solutions of maximum concentration from primary chemically enriched phosphorus concentrate with the participation of nitric acid are: H₂SO₄ : HNO₃ = 70 : 35, circulating solution 5.1% P₂O₅, temperature - 50-55°C, S:L ratio 1:3.

The research work conducted studies on the production of NP and NPK-type mixed fertilizers from solutions obtained as a result of processing of ChEPC with the participation of sulfuric and nitric acids according to various technological parameters.

Research on NP fertilizer production processes

In the production of NP-type complex fertilizers, ammonium-based suspensions were obtained by neutralizing nitrogen-phosphorus-calcium solutions processed with sulfuric and nitric acids at various technological parameters with gaseous ammonia to various pH values (Table 4).

Table 4. Chemical composition of ammonisation nitrogen-phosphorus-calcium pulp

№	pH	Chemical composition of nitrogen-phosphorus solution, wt. %						
		P ₂ O ₅	N	CaO	MgO	Al ₂ O ₃	Fe ₂ O ₃	F
HNO ₃ :H ₂ SO ₄ 35:70		12,94	3,50	5,54	0,35	0,15	0,13	0,53
1	3,14	12,58	5,32	5,39	0,34	0,15	0,13	0,52
2	3,52	12,43	5,69	5,33	0,33	0,14	0,12	0,51
HNO ₃ :H ₂ SO ₄ 25:80		10,37	2,04	3,58	0,31	0,14	0,10	0,47
3	3,28	10,21	4,68	3,53	0,31	0,14	0,10	0,46
4	3,46	10,15	4,97	3,50	0,30	0,13	0,09	0,44

H₂SO₄ : HNO₃ = 70 : 35 standard ratio of ChEPC at 50°C, circulating solution - 5.1% P₂O₅, S:L=1:3 neutralized solution at pH values of 3.14 and 3.52 the composition of the suspensions is as follows, wt. % : P₂O₅ - 12,43-12,58; N - 5,32-5,69;

CaO - 5,33-5,39 as well as $H_2SO_4 : HNO_3 = 80 : 25$, circulating solution-4.7% P_2O_5 , S:L=1:3 neutralized solution to pH values of 3.28 and 3.46, the composition is wt. %: P_2O_5 - 10,15-10,21 respectively; N - 4,68-4,97; CaO - 3,50-3,53 respectively.

Nitrophos fertilizers with nitrogen-phosphorus-calcium were obtained by drying the resulting ammonification porridges (Table 5).

Table 5. The composition of nitrophosphate fertilizers obtained by processing WBPC with sulfuric and nitric acids

№	P_2O_5			N	CaO	$P_2O_{5assim.}$, %	$P_2O_{5water.}$, %
	gener.	assim.	water.				
1	27,32	26,16	23,24	11,27	11,71	95,75	85,06
2	26,79	25,54	21,74	12,06	11,47	95,33	81,14
3	30,86	29,63	26,35	12,57	10,67	96,02	85,37
4	30,14	28,77	24,80	12,92	10,39	95,47	82,29

The composition of the nitrofos fertilizer obtained by neutralizing the resulting solution to pH=3.14 and 3.52 by heating the ChEPC at a temperature of 50°C with a standard ratio of acids $H_2SO_4 : HNO_3 = 70 : 35$, circulating solution - 5.1% P_2O_5 , S:L=1:3 ratio, is as follows, wt. %: P_2O_5 - 27.32, 26.79; N - 11.27, 12.06; CaO - 11.71, 11.47; of which, P_2O_{5ass} is 95.75, 95.33; $P_2O_{5wat.}$ - 85.06, 81.14 and $H_2SO_4 : HNO_3 = 80 : 25$, circulating solution - 4.7% P_2O_5 , the resulting solution was neutralized to pH = 3.28 and 3.46 in the ratio S:L = 1:3, and the composition of the nitrofos fertilizer was as follows, wt. %: P_2O_5 - 30.86, 30.14; N - 12.57, 12.92; CaO - 10.67, 10.39; of which, $P_2O_{5ass.}$ - 96.02, 95.47; $P_2O_{5wat.}$ - 85.37, 82.29 respectively.

Research on NPK fertilizer production processes

In subsequent laboratory studies, the ammoniated slurry samples presented in Table 3 (No. 2 and No. 4) were used to obtain NPK-type mixed fertilizers. For this, K_2SO_4 was added, calculated as N: P_2O_5 : K_2O relative to the P_2O_5 content of the slurry (Table 6).

Table 6. Chemical composition of NPK fertilizers

№	N: P_2O_5 : K_2O	Chemical composition, wt. %						$P_2O_{5assim.}$, %	$P_2O_{5water.}$, %
		N				CaO			
			gener.	assim.	water.				
1	0,5:1:07	9,08	19,84	18,70	16,24	13,89	8,49	94,27	81,83
2	05:1:1	8,40	18,35	17,66	15,80	18,48	7,85	96,24	86,10
3	05:1:0,8	9,85	20,12	18,89	16,53	15,86	6,94	93,89	82,16
4	0,5:1:1	9,60	19,50	18,78	16,85	19,21	6,73	96,31	86,42

The NPK fertilizer obtained by decomposing the ChEPC at a temperature of 50°C with a standard ratio of acids $H_2SO_4 : HNO_3 = 70 : 35$, circulating solution - 3.24% P_2O_5 , S:L=1:3.5, N: P_2O_5 : K_2O =0.5:1:08 and K_2SO_4 in the ratios of 0.5:1:1 respectively. The composition of the NPK fertilizer obtained was as follows, wt. %: N - 7.78, 7.60; P_2O_5 - 17.55, 17.10; K_2O - 14.04, 17.00; CaO - 8.29, 8.01; of which, $P_2O_{5assim.}$ - 94.35, 95.03; P_2O_{5water} - 82.34, 85.50 respectively.

The standard ratio of $H_2SO_4 : HNO_3 = 70 : 35$, circulating solution - 5.1% P_2O_5 , S:L = 1:3, the composition of the NPK fertilizer obtained by adding N: P_2O_5 : K_2O = 0.5:1:07 and K_2SO_4 in the ratios 05:1:1 to the ammoniated slurry of the resulting solution is as follows, wt. %: N - 9.08, 8.40 respectively; P_2O_5 - 19.84, 18.35; K_2O - 13.89, 18.48 respectively; CaO - 8.49, 7.85; of which, P_2O_{5ass} - 94.27, 96.24; $P_2O_{5wat.}$ - 81.83, 86.10 respectively and $H_2SO_4 : HNO_3 = 80 : 25$, circulating solution - 4.7% P_2O_5 , S:L=1:3, the resulting solution was added to the ammoniated slurry with the addition



of $N:P_2O_5:K_2O=0.5:1:0.8$ and K_2SO_4 in the ratios $0.5:1:1$, the composition of the NPK fertilizer is as follows, wt. %: N - 9.85, 9.60; P_2O_5 - 20.12, 19.50; K_2O - 15.86, 19.21; CaO - 6.94, 6.73; of which, $P_2O_{5\text{assim}}$ - 93.89, 96.31; $P_2O_{5\text{water}}$ - 82.16, 86.42 respectively.

V. CONCLUSION

The main conditions affecting the filtration rate of mixtures of decomposition of WBPC with nitrate and sulfate: the ratio of acids, concentration, temperature and duration of the process, have been determined, which allows achieving a filtration rate of 1751-1953 kg/m²·h of slurry. It was shown that the process of acid processing of WBPC with sulfate and nitrate leads to a relatively low production of phosphogypsum waste, which in turn leads to a decrease in acid consumption. The use of the calcium nitrate solution formed during the enrichment process as a by-product allows achieving not only technological but also economic efficiency. Nitrogen-phosphorus fertilizers containing 38.59-43.43% of nutrients with a ratio of N:P₂O₅ from 0.412:1 to 0.407:1 and a ratio of CaO:P₂O₅ from 0.345:1 to 0.428:1 were obtained. Nitrogen-phosphorus-potassium fertilizers containing 42.81-48.31% of nutrients with a ratio of N:P₂O₅:K₂O from 0.5:1:0.7 to 0.5:1:1 were also obtained. The content of soluble and water-soluble forms of P₂O₅ in the obtained NP and NPK fertilizers was also 94-96 and 82-86%.

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