STUDY OF THE PROCESS OF DECOMPOSITION OF TRICALCIUM PHOSPHATE BY PHOSPHORIC ACID WITH PARTIAL REPLACEMENT OF P2O5 BY SULFURIC ACID IN THE PRESENCE OF AMMONIUM NITRATE

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Annotation

In the article, the study of the decomposition process of tricalcium phosphate with a mixture of thermal phosphoric acid with partial replacement of phosphoric acid with sulfuric acid in the presence of ammonium nitrate and their joint presence, the study of the conversion of calcium sulfate to ammonium sulfate.

Keywords: Uzbekistan, tricalcium phosphate, decomposition of tricalcium phosphate, thermal phosphoric acid, sulfuric acid, agrochemical complex, macronutrient, nitrogen, phosphorus, potassium, calcium, magnesium, sulfur, decomposition coefficient, SO_3 extraction rate into aqueous solution, water-soluble form, ammonium nitrate, rheological properties.

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INTRODUCTION.

The agrochemical complex is a key component of the economic development of the Republic, on the development of which the well-being of the population depends. In this regard, providing the agro-industrial complex with the necessary plant protection products, plant growth and development stimulants, mineral and organo-mineral fertilizers in a wide range, with different ratios of the main macronutrients - nitrogen, phosphorus, potassium, calcium, magnesium, sulfur is an important direction in increasing productivity. crops.

Increasing the rate of application of mineral fertilizers no longer contributes to an increase in yield. In addition to nitrogen, phosphorus and potassium, plants need calcium, magnesium, sulfur and trace elements. The presence in the Republic of a powerful industrial base for the production of mineral fertilizers, including single phosphate fertilizers, effective for application under autumn plowing, is directly related to the introduction of scientific achievements in the processing of phosphate raw materials into production, with the expansion of their range and the content of macro and microelements.

In Uzbekistan, as concentrated phosphorus fertilizers, at present, mainly ammophos is used, obtained from phosphorites of the Central Kyzylkum. As a result of the use of ammophos, the amount of soluble and assimilated by plants calcium, magnesium and sulfur compounds introduced into the soil

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annually decreases, which in turn leads to a deficiency of these elements in the body of animals and plants.

In this aspect, an important task is to substantiate scientific and technical solutions for the development of technologies for single and concentrated phosphate fertilizers with a water-soluble form of sulfates.

MATERIALS AND METHODS. For the theoretical justification of the processing of phosphorites into single phosphate fertilizers with phosphoric acid, with partial replacement of P_2O_5 phosphoric acid with sulfuric acid, studies were carried out on the decomposition of tricalcium phosphate by thermal phosphoric acid containing 20% P_2O_5 with the replacement of 10, 20 and 30% P_2O_5 with sulfuric acid at a total stoichiometric the norm of acids, at a temperature of 80^{o}C and a process duration of 2 hours.

The study of the decomposition process of tricalcium phosphate was also carried out with a more concentrated thermal phosphoric acid, and the replacement of 10, 20 and 30% P_2O_5 with H_2SO_4 with a concentration of 91.8% in a laboratory installation under periodic conditions. To do this, a certain amount of phosphoric acid was introduced into a thermostatically controlled reactor equipped with a paddle stirrer, and after reaching a predetermined temperature, the calculated amount of tricalcium phosphate was dosed. After a certain period of time, pulp samples were taken for analysis to determine the content of various forms of P_2O_5, CaO, SO_3 and to calculate the coefficient of decomposition of tricalcium phosphate, the coefficients of extraction of CaO and SO_3 into the liquid phase.

DISCUSSION. To reveal the role of sulfuric acid in the partial replacement of P_2O_5 thermal phosphoric acid by sulfuric acid, the decomposition of tricalcium phosphate by a mixture of acids was studied when 10, 20, and 30% P_2O_5 were replaced by sulfuric acid.

Chemical analysis of the pulp for the content of the main components showed that when tricalcium phosphate is decomposed by thermal phosphoric acid with an initial concentration of 18.25% P_2O_5 and containing 1.14% SO_3, the content of P_2O_{5total} is 23.25%, $P_2O_{5assimilable}$ 21.69%, $P_2O_{5water\text{-}soluble}$ 19.83% . With an increase in the amount of replacement of P_2O_5 with sulfuric acid, the content of P_2O_{5total} in the product decreases to 21.83% and 20.39%, respectively, when replacing 20 and 30% P_2O_5 with sulfuric acid. The decomposition ratio of tricalcium phosphate increases from 81.21% to 87.50% and 94.58%. The results obtained are presented in table 1.

Table 1.

Influence of partial replacement of phosphoric acid by sulfuric acid on the chemical composition of the pulp.

№	Performance	The content of components in the pulp, wt. %								
		when replacing H_3PO_4 with H_2SO_4, %								
		10	20	30	10	20	30	10	20	30
1.	Initial concentration of P_2O_5 in WPPA, %	18,25	16,45	14,60	27,38	24,68	21,90	36,50	32,90	29,20
2.	Initial concentration of SO_3 in WPPA, %	1,14	2,32	3,53	1,71	3,48	5,30	2,28	4,64	7,06
3.	Content in the pulp:									
	P_2O_5 (total), %	23,25	21,83	20,39	31,97	30,00	27,99	39,36	36,90	34,40
	P_2O_5 (assimilable), %	21,69	20,78	19,85	30,15	28,62	27,04	38,53	36,38	34,02
	P_2O_5 (water-soluble), %	19,83	19,25	18,43	26,95	26,82	25,64	34,99	33,80	32,10

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	SO_3(total), %	0,93	1,89	2,86	1,28	2,60	3,95	1,58	3,20	4,85
	SO_3 (water-soluble), %	0,37	0,59	0,69	0,52	0,82	0,94	0,65	0,97	1,16
	CaO (total), %	9,82	9,94	10,09	13,51	13,65	13,80	16,63	16,79	16,96
	CaO (total), %	2,78	2,66	2,27	4,01	3,70	2,83	5,01	4,28	3,59
	влага, %	56,96	57,60	58,29	40,78	41,75	42,72	27,18	28,35	29,63
4.	($P_2O_{5assimilable}$:P_2O_{5total})×100, %	93,29	95,19	97,35	94,30	95,40	96,60	97,90	98,60	98,90
5.	($P_2O_{5water\text{-}soluble}$:$P_2O_{5total}$)×100, %	85,29	88,18	90,39	84,30	89,40	91,60	88,90	91,60	93,31
6.	$K_s$of $P_2O_{5assimilable}$, %	81,21	87,50	94,58	84,04	88,05	93,05	94,12	96,36	97,75
7.	K_{ext} for CaO in aqueous solution, %	28,31	26,76	22,50	29,68	27,10	20,51	30,13	25,49	21,17
8.	Degree of extraction of SO_3 into aqueous solution (Degree of conversion of calcium sulfate), %	39,79	31,22	24,13	40,62	31,54	23,80	41,14	30,31	23,92

When using more concentrated phosphoric acid, the content of the total form of SO_3 is 1.28-4.85% and water 0.52-1.16%. The recovery factor of SO_3 into the liquid phase, with an increase in the proportion of H_2SO_4, decreases and amounts to 39.79-24.13% when replacing 10% P_2O_5 with H_2SO_4, 40.63-23.80% when replacing 20% and 41.14-23, 92% with 30% replacement. This indicates that with an increase in the content of H_2SO_4 in phosphoric acid, the proportion of the water-soluble form of SO_3 in the pulp decreases.

Table 2 shows the results of the process of drying the decomposition products of tricalcium phosphate with 20% thermal phosphoric acid when replacing 10%, 20% and 30% P_2O_5 with sulfuric acid.

The use of more concentrated phosphoric acid with the replacement of 10, 20 and 30% P_2O_5 with sulfuric acid makes it possible to obtain a product with a higher degree of decomposition.

Table 2.

Influence of partial replacement of phosphoric acid by sulfuric acid on the chemical composition of the product

№	Performance	Content of components, wt. %								
		when replacing H_3PO_4 with H_2SO_4, %								
		10	20	30	10	20	30	10	20	30
1.	Initial concentration of P_2O_5 in WPPA, %	18,25	16,45	14,60	27,38	24,68	21,90	36,50	32,90	29,20
2.	Initial concentration of SO_3 in WPPA, %	1,14	2,32	3,53	1,71	3,48	5,30	2,28	4,64	7,06
3.	Content in the product:									
	P_2O_5 (total), %	53,44	50,36	48,51	53,00	50,14	50,07	53,14	49,86	48,02
	P_2O_5 (assimilable), %	50,22	48,37	47,66	50,53	48,08	48,61	52,26	49,46	47,92

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	P_2O_5 (water-soluble), %	46,12	44,89	44,26	45,17	45,15	46,19	47,42	46,19	45,09
	SO_3(total), %	2,14	4,36	6,80	2,20	4,35	6,73	2,13	4,32	6,77
	SO_3 (water-soluble), %	0,86	1,42	1,82	0,94	1,42	1,67	0,90	1,36	1,75
	CaO (total), %	22,57	22,93	24,00	22,40	22,81	24,69	22,45	22,69	23,67
	CaO (total), %	6,62	6,24	5,58	6,78	6,48	5,38	6,99	6,02	5,28
	влага, %	1,08	2,18	0,77	1,83	2,64	2,41	1,69	3,18	1,77
4.	($P_2O_{5assimilable}$:P_2O_{5total})× 100, %	93,97	96,05	98,25	95,34	95,89	97,08	98,35	99,20	99,80
5.	($P_2O_{5water-soluble}$:P_2O_{5total})×100, %	86,30	89,13	91,24	85,23	90,05	92,25	89,25	92,64	93,90
6.	$K_s$of $P_2O_{5\ assimilable}$, %	83,12	89,74	96,42	86,95	89,32	94,03	95,38	97,92	99,51
7.	K_{ext} for CaO in aqueous solution, %	29,33	27,21	23,25	30,27	28,41	21,79	31,13	26,53	22,31
8.	Degree of extraction of SO_3 into aqueous solution (Degree of conversion of calcium sulfate), %	40,19	32,57	26,76	42,73	32,64	24,81	42,25	31,48	25,85

The highest results of the decomposition coefficient were obtained when phosphoric acid was evaporated to a content of 32.90% P_2O_5 and 4.64% SO_3, as well as up to 29.20% P_2O_5 and 7.06% SO_3, respectively, 97.92% and 99.51% .

In the works of K. Gafurov, I.T. Shamshidinov, the possibility of evaporating WPPA from phosphorites of Karatau and Central Kyzylkum to a content of 40-45% P_2O_5 and obtaining an acid with acceptable physico-chemical characteristics by introducing ammonium nitrate into the initial acid was shown.

The introduction of ammonium nitrate into the composition of WPPA not only improves the rheological properties of stripped off acids, but also promotes the activation of phosphoric acid, which is reflected in the intensification of the process of decomposition of phosphate raw materials. Taking this into account, the effect of partial replacement of P2O5 with thermal phosphoric acid containing 1% ammonium nitrate on sulfuric acid was studied. The conditions are the same as in the absence of ammonium nitrate. The results of the decomposition of tricalcium phosphate with thermal acid containing 1% ammonium nitrate and the replacement of 10%, 20% and 30% P_2O_5 with sulfuric acid are shown in Table 3.

Table 3

The effect of partial replacement of phosphoric acid containing ammonium nitrate with sulfuric acid on the chemical composition of the pulp

№	Performance	Content of components, wt. %								
		when replacing H_3PO_4 with H_2SO_4, %								
		10	20	30	10	20	30	10	20	30
1.	Initial concentration of P_2O_5 in WPPA, %	18,07	16,29	14,45	27,11	24,44	21,68	36,14	32,57	28,91
2.	Initial concentration of	1,13	2,30	3,50	1,69	3,45	5,25	2,26	4,59	6,99

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	SO_3 in WPPA, %									
3.	Content in the product:									
	P_2O_5 (total), %	23,06	21,66	20,22	31,73	29,79	27,78	39,09	36,64	34,16
	P_2O_5 (assimilable), %	21,75	20,73	19,81	30,24	28,63	27,06	38,62	36,31	33,90
	P_2O_5 (water-soluble), %	20,04	19,44	18,53	27,65	26,88	25,54	35,44	33,88	32,49
	SO_3(total), %	0,93	1,88	2,86	1,27	2,59	3,92	1,57	3,17	4,82
	SO_3 (water-soluble), %	0,39	0,66	0,81	0,54	0,92	1,09	0,68	1,13	1,34
	CaO (total), %	9,74	9,86	9,97	13,40	13,55	13,70	16,52	16,68	16,84
	CaO (total), %	3,11	2,93	2,53	4,26	4,05	3,08	5,36	4,59	3,91
	влага, %	56,48	57,12	57,80	40,48	41,41	42,41	26,92	28,16	29,42
4.	($P_2O_{5assimilable}$:P_2O_{5total})× 100, %	94,32	95,70	97,97	95,30	96,10	97,40	98,80	99,10	99,24
5.	($P_2O_{5water\text{-}soluble}$:$P_2O_{5total}$)×100, %	86,90	89,75	91,64	87,14	90,23	91,94	90,66	92,47	95,11
6.	$K_s$of $P_2O_{5\ assimilable}$, %	84,10	88,83	95,85	86,84	89,87	94,69	96,64	97,66	98,45
7.	K_{ext} for CaO in aqueous solution, %	31,93	29,72	25,38	31,79	29,89	22,48	32,45	27,52	23,22
8.	Degree of extraction of SO_3 into aqueous solution (Degree of conversion of calcium sulfate), %	41,94	35,11	28,32	42,52	35,52	27,81	43,31	35,65	27,80

The introduction of 1% ammonium nitrate into the original phosphoric acid with a content of 20% P_2O_5 and the replacement of 10% P_2O_5 with sulfuric acid leads to a decrease in P_2O_5 to 18.07%, which contains 1.13% SO_3.

Chemical analysis of the pulp for the content of the main components showed that when tricalcium phosphate is decomposed by thermal phosphoric acid with an initial concentration of 18.07% P_2O_5 and containing 1.13% SO_3, the content of P_2O_{5total} is 23.06%, $P_2O_{5assimilable}$ 21.75%, $P_2O_{5water\text{-}soluble}$ 20, 04%.

With an increase in the amount of replacement of P_2O_5 with sulfuric acid, the content of P_2O_{5total} decreases to 21.66% and 20.22%, respectively, when 20 and 30% of P_2O_5 are replaced with sulfuric acid. The decomposition coefficient of tricalcium phosphate increases from 84.10% to 88.83% and 95.85%.

With an increase in the content of H_2SO_4 in phosphoric acid, the proportion of the water-soluble form of SO_3 in the pulp decreases.

Table 4 shows the results of the process of drying the decomposition products of tricalcium phosphate with 20% thermal phosphoric acid when replacing 10%, 20% and 30% P_2O_5 with sulfuric acid.

The table shows that the decomposition coefficient is 85.72%, 89.87% and 96.10% when replacing 10%, 20% and 30% P_2O_5 with sulfuric acid.

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Table 4

Effect of partial replacement of phosphoric acid containing ammonium nitrate with sulfuric acid on the chemical composition of the product

№	Performance	Content of components, wt. %								
		when replacing H_3PO_4 with H_2SO_4, %								
		10	20	30	10	20	30	10	20	30
1.	Initial concentration of P_2O_5 in WPPA, %	18,07	16,29	14,45	27,11	24,44	21,68	36,14	32,57	28,91
2.	Initial concentration of SO_3 in WPPA, %	1,13	2,30	3,50	1,69	3,45	5,25	2,26	4,59	6,99
3.	Content in the product:									
	P_2O_5 (total), %	52,15	49,21	47,06	52,27	49,35	46,83	52,76	49,91	47,92
	P_2O_5 (assimilable), %	49,49	47,29	46,16	50,07	47,79	46,01	52,36	49,66	47,80
	P_2O_5 (water-soluble), %	45,42	44,26	43,41	45,99	45,03	43,19	48,04	46,63	46,07
	SO_3(total), %	2,10	4,27	6,66	2,09	4,29	6,61	2,12	4,32	6,76
	SO_3 (water-soluble), %	0,94	1,52	1,95	0,91	1,57	1,90	0,94	1,58	1,94
	CaO (total), %	22,03	22,40	23,20	22,07	22,45	23,10	22,30	23,73	23,63
	CaO (total), %	7,20	6,77	6,10	7,23	6,94	5,31	7,42	6,76	5,72
	влага, %	1,57	2,58	1,79	1,95	2,94	2,91	1,37	2,15	0,98
4.	$(P_2O_{5assimilable}:P_2O_{5total})\times100$, %	94,90	96,10	98,09	95,79	96,84	98,25	99,24	99,50	99,75
5.	$(P_2O_{5water\text{-}soluble}:P_2O_{5total})\times100$, %	87,11	89,94	92,24	87,99	91,25	92,23	91,05	93,43	96,14
6.	$K_s$of $P_2O_{5\ assimilable}$, %	85,72	89,87	96,10	88,21	91,79	96,42	97,87	98,80	99,45
7.	K_{ext} for CaO in aqueous solution, %	32,68	30,22	26,29	32,76	30,91	22,99	33,27	28,50	24,21
8.	Degree of extraction of SO_3 into aqueous solution (Degree of conversion of calcium sulfate), %	44,76	35,60	29,28	43,54	36,60	28,74	44,34	36,57	28,70

The use of more concentrated phosphoric acid with the replacement of 10.20 and 30% P2O5 with sulfuric acid makes it possible to obtain a product with a higher degree of decomposition. With an increase in the proportion of sulfuric acid to 20%, the degree of decomposition increases to 91.79% and to 96.42% when 30% P_2O_5 is replaced by sulfuric acid. The highest results of the decomposition coefficient were obtained when phosphoric acid was evaporated to a content of 32.57% P_2O_5 and 4.59% SO_3, as well as up to 28.91% P_2O_5 and 6.99% SO_3, respectively, 98.80% and 99.45%.

CONCLUSION.

The use of more concentrated phosphoric acid with the replacement of 10, 20 and 30% P_2O_5 with sulfuric acid makes it possible to obtain a product with a higher degree of decomposition. The highest results of the decomposition coefficient were obtained when phosphoric acid was evaporated to a content of 32.90% P2O5 and 4.64% SO_3, as well as up to 29.20% P_2O_5 and 7.06% SO_3, respectively, 97.92% and 99.51%.

Decomposition of tricalcium phosphate with thermal acid containing 1% ammonium nitrate and replacement of 10%, 20% and 30% P_2O_5 with sulfuric acid. The highest results of the decomposition coefficient were obtained

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when phosphoric acid was evaporated to a content of 32.57% P_2O_5 and 4.59% SO_3, as well as up to 28.91% P_2O_5 and 6.99% SO_3, respectively, 98.80% and 99.45% .

The use of more concentrated phosphoric acid with the replacement of 10, 20 and 30% P_2O_5 with sulfuric acid makes it possible to obtain a product with a higher degree of decomposition. The best indicators of the degree of transition of SO_3 into a water-soluble form are observed when using a mixture of acids containing ammonium nitrate.

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