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Studying of The Process of Obtaining Monocalcium Phosphate based on Extraction Phosphoric Acid from Phosphorites of Central Kyzylkum

***Mokhichekhra Shaymardanova*[1], *Kholtura Mirzakulov*[2], *Gavkhar Melikulova*[2], *Sakhomiddin.Khodjamkulov*[1], *Abror Nomozov**[1], *OybekToshmamatov*[1]**

[1]Department of Chemical Technology, Termez Institute of Engineering and Technology, Termez 190100, Uzbekistan.
[2]Department of Chemical Technology, Faculty of Chemical Technology, Tashkent Institute of Chemical Technology, Tashkent, 100011, Uzbekistan.
*Corresponding Author.

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Abstract

In this paper, a study of monocalcium phosphate production based on extractable phosphoric acid obtained from Central Kyzyl-Kum phosphorites was conducted. Effects of various parameters (density, temperature, and viscosity of starting materials) on the process of defluoridation and desulfation of extraction phosphoric acid and production of monocalcium phosphate based on calcium carbonate were studied. The experiments were mainly conducted on two samples, and the composition of the substances before and after the process was studied. According to the results, the contents of other components also increase proportionally (sample 1). Thus, the content of calcium oxide increases from 1.58% to 5.54% with a content of 60% P_2O_5, magnesium from 0.49% to 1.15%, iron oxide from 0.25% to 0.85%, aluminum oxide from 0.38% to 1.24%, sulfate ions from 0.23% to 0.76%, the content of calcium oxide increases from 2.09% to 7.40% with a content of 60% P_2O_5, magnesium from 0.80% to 2.83%, iron oxide from 0.25% to 0.90%, aluminum oxide from 0.38% to 1.34%, sulfate ions from 0.23% to 0.82%. The fluorine content decreases from 0.32% to 0.17% depending on the EPA concentration (sample 2). Some factors, such as the rate and concentration of phosphoric acid and high-speed separation of phosphoric acid, were also studied in the process of obtaining monocalcium phosphate and its chemical composition and properties. The results obtained based on both samples were studied and analyzed using X-ray, IR spectrum, scanning electron microscopic, and elemental analysis.

Keywords: Central Kyzylkum phosphorites, Extraction of phosphoric acid, IR spectrum, Monocalcium phosphate, Scanning electron microscopic, X-ray.

Introduction

In the life activity of all living organisms and flora, along with carbon, hydrogen, and oxygen, an important role belongs to phosphorus and its compounds. Phosphorus occupies a special place among chemical elements[1]. It is part of many minerals, primarily calcium phosphates. In living nature, it forms organophosphorus compounds, which serve as carriers of high-energy reactions that ensure the vital activity of living organisms. The role of phosphorus in living nature is unique[2]. A lack of phosphorus in the diets of farm animals reduces meat and dairy productivity and leads to the occurrence of bone diseases and impaired reproductive function. To eliminate phosphorus deficiency in the body of animals, mineral feed additives are used, which are introduced to improve the quality of feed rations[3].

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The global range of basic mineral supplements includes more than 10 items. Phosphorus-containing mineral fertilizers based on calcium, sodium, ammonium phosphates, and other chemical components are widely used in animal husbandry, poultry farming, and fish farming[4]. The average annual growth in consumption of feed phosphates in the world is 6%, which is approximately 2.5 times higher than for phosphorus-containing fertilizers[5]. The following scientific work describes nitrogen-phosphoric fertilizers produced by introduction into ammonium nitrate melt of ordinary phosphorite powder, dust fraction, and mineralized mass of Central Kyzylkum phosphorites[6]. Phosphoric acid and its salts are widely used in the production of mineral fertilizers, in the food industry, medicine, pharmaceuticals, electronics, chemical, textile, glass, aviation, and engineering industries. The main amount of phosphate raw materials are used for the production of mineral fertilizers (about 80%), 12% - for the production of detergents, 5% - for the production of feed phosphates, and 3% - for the production of special-purpose products[7]. In this regard, calcium phosphates are a universal mineral supplement for farm animals of all types with a lack of phosphorus and calcium in their diets[8]. Monocalcium phosphate is a monosubstituted calcium salt of orthophosphoric acid. Pure monocalcium phosphate in anhydrous form $Ca(H_2PO_4)_2$ contains 60.65% P_2O_5 and 23.96% CaO, and monohydrate $Ca(H_2PO_4)_2{\cdot}H_2O$ – 56.31% P_2O_5 and 22.25% CaO. According to GOST 23999-80, feed monocalcium phosphate of the first and the second grades must contain, respectively, at least 55 and 50% P_2O_5 soluble in a 0.4% solution of hydrochloric acid[9]. The product of both grades must contain no more than 18% calcium, 0.2% fluorine, 0.006% arsenic, 0.002% lead, and 4.0% water. The pH of a 0.01 M aqueous solution must be at least 3. Mono- and dicalcium phosphates dissolve incongruently in water[10,11]. There is a known method for producing a complex fertilizer by reacting a solution of ammonium phosphate with a concentration of 16-20% P_2O_5, obtained by leaching amorphous with water at a temperature of 20-60°C and potassium chloride at a ratio of K^+: NH_4^+=(0.75-1):1[12,13]. Double superphosphate is a concentrated phosphorus fertilizer, the main component of which is monocalcium phosphate. Double superphosphate is obtained by treating natural phosphates with concentrated phosphoric acid[14,15].

The current work is the study of the process of obtaining monocalcium phosphate based on the extraction of phosphoric acid from Central Kyzylkum of phosphorites. The main aims of the present work are the obtaining of extraction of phosphoric acid from central Kyzylkum phosphorite by evaporation and analysis of its composition and the study of physicochemical parameters of obtaining monocalcium phosphate based on extracted phosphoric acid. Also, the crystallization of monocalcium phosphate was obtained, as isolation of crystallized monocalcium phosphate, and study of its chemical composition.

Materials and Methods

To carry out experimental work, we used EPA previously defluorinated with metasilicate and sodium carbonate and desulphated with washed, calcined phosphorus concentrate (MOFC), sodium metasilicate, sodium and calcium carbonates (limestone), calcium oxide, potassium chloride, potassium phosphate, gaseous and aqueous ammonia. Some chemical reagents were purchased and supplied by Merit Chemicals, and raw materials were based on Central Kyzylkum of Phosphorites. The chemical composition of the raw materials used is given in Table 1.

Table 1. Chemical composition of the raw materials used in the work.

Reagent	Chemical composition, mass. %							
	P_2O_5	SO_3	CaO	MgO	Al_2O_3	Fe_2O_3	F	CO_2
EFC (ref.)	18,31	2,32	0,31	1,12	1,36	0,93	1,25	-
Clear EFC (sample 1)	17,02	0,23	1,58	0,49	0,38	0,25	0,30	-
Clear EFC (sample 2)	16,98	0,20	2,09	0,80	0,38	0,25	0,32	-
MOFC	27,50	3,31	54,46	0,99	1,87	0,70	2,70	-
Limestone	-	-	54,88	0,47	0,21	0,10	-	43,76

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EFC was used according to TSh 6.6-21:2018 produced by Ammofos-Maxam JSC, and MOPC produced by the Kyzylkum Phosphorite Plant according to O'zDSt 2825:2018. Purified EPA from fluorine anions and sulfates using known methods. Defluoridation and desulfation of the original EPA was carried out at a MOPC rate of 125% (purified EPA sample 1) and 150% (purified EPA sample 2) CaO for the precipitation of sulfates in the form of gypsum and fluorine in the form of CaF_2.

To characterize the intermediate and final products, some of their physicochemical properties were studied: density, viscosity, and pH. The density of solutions and pulps was determined using a PZh-2 pycnometer. The kinematic viscosity of solutions and pulps was measured with glass capillary viscometers VPZh-1 and VPZh-2, and the pH of solutions and suspensions was determined by the electromechanical method.

IR and X-ray analysis

Identification of the composition and properties of initial and intermediate substances, intermediates, and products was carried out, in addition to chemical analysis and determination of physical properties; by X-ray diffraction patterns of the samples were taken using a computer-controlled XRD-6100 apparatus (Shimadzu, Japan) and IR spectroscopic methods.

SEM analysis

Surface morphology and microstructure studies of the samples were carried out using a scanning electron microscope SEM - EVO MA 10 (Carl Zeiss, made in Germany) with an Aztec Energy Advanced X-Act – Oxford Instruments X-ray spectrometer. This device is designed for microscopic analysis of structure and defects, including the determination of local elemental composition using energy-dispersive spectroscopy.

Studying the evaporation process of defluorinated and desulphated extraction phosphoric acid

Studies on the production of defluorinated monocalcium phosphate were carried out in a glass reactor equipped with a mechanical stirrer and installed in a thermostat. The main raw material for the production of feed phosphates at Ammofos-Maxam JSC is EPA. EPA was preliminarily purified from sulfates and fluorine (samples 1 and 2) using MOPA and sodium salts – carbonate and metasilicate. Subsequently, EPA was concentrated in a vacuum evaporation unit. The presence of a high content of calcium, magnesium, aluminum, and iron in EPA can negatively affect the defluoridation of EPA, binding fluorine into complex or poorly soluble compounds, over which the vapor pressure of hydrofluorosilicic acid is significantly reduced. The compositions of concentrated EPA containing 17-60% P_2O_5 are presented in Table 2. The table shows that with an increase in the content of P_2O_5 in evaporated acids, the contents of other components also increase proportionally (sample 1). Thus, the content of calcium oxide increases from 1.58% to 5.54% with a content of 60% P_2O_5, magnesium from 0.49% to 1.15%, iron oxide from 0.25% to 0.85%, aluminum oxide from 0.38% to 1.24%, sulfate ions from 0.23% to 0.76%. The fluorine content decreases from 0.30% to 0.14% depending on the concentration of EPA[16].

Table 2. Chemical composition of evaporated extraction phosphoric acids from phosphorites of the Central Kyzylkum.

№	Chemical composition, mass. %						
	P_2O_5	CaO	MgO	Fe_2O_3	Al_2O_3	SO_4^{2-}	F
Purified EPA (sample 1)							
1	17,02	1,58	0,49	0,25	0,38	0,23	0,30
2	25,0	2,33	0,72	0,37	0,56	0,34	0,24
3	35,04	3,25	1,01	0,52	0,78	0,48	0,22
4	40,10	3,72	1,44	0,60	0,91	0,55	0,19
5	45,02	4,19	1,62	0,67	1,01	0,61	0,18
6	50,09	4,64	1,80	0,73	1,08	0,66	0,17
7	55,01	5,09	1,98	0,78	1,14	0,70	0,15
8	60,05	5,54	1,15	0,85	1,24	0,76	0,14
Purified EPA (sample 2)							
9	16,98	2,09	0,80	0,25	0,38	0,23	0,32

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10	25,03	2,93	1,17	0,37	0,56	0,34	0,23
11	35,08	4,31	1,64	0,52	0,78	0,48	0,22
12	40,05	4,93	1,88	0,60	0,90	0,54	0,21
13	45,01	5,54	2,11	0,67	1,01	0,61	0,20
14	50,04	6,16	2,36	0,75	1,12	0,68	0,18
15	55,02	6,78	2,59	0,82	1,23	0,75	0,18
16	60,01	7,40	2,83	0,90	1,34	0,82	0,17

The content of calcium oxide increases from 2.09% to 7.40% with a content of 60% P_2O_5, magnesium from 0.80% to 2.83%, iron oxide from 0.25% to 0.90%, aluminum oxide from 0. 38% to 1.34%, sulfate ions from 0.23% to 0.82%. The fluorine content decreases from 0.32% to 0.17% depending on the EPA concentration (sample 2). With an increase in the P_2O_5 content in evaporated EPA, the density and viscosity increase, and with increasing temperature they decrease Table 3. If the initial 17.02% P_2O_5 defluorinated and desulfated EPA (sample 1) has a density of 1.138 g/cm^3 at 20°C, then the acid containing 50% P_2O_5 has a density of 1.622 g/cm^3. An increase in temperature from 20 ºC to 100 ºC leads to a decrease in the density of acid containing 50% P_2O_5 from 1.622 g/cm^3 to 1.583 g/cm^3. Changes in the viscosity of evaporated acids are similar to changes in density. The viscosity of an acid containing 17.02% P_2O_5 is 2.155 mPa·s, and with a content of 50% P_2O_5, it is 41.460 mPa·s at a temperature of 20 ºC and decreases to 0.928 mPa·s and 15.734 mPa·s, respectively, at a temperature of 100 ºC[17].

Table 3. The influence of concentration and temperature on the density and viscosity of evaporated phosphoric acids.

№	Consen Tration EPA	Density, g/cm^3					Viscosity, mPa·s				
		20 °C	40 °C	60 °C	80 °C	100 °C	20 °C	40 °C	60 °C	80 °C	100 °C
Purification EFC (sample 1)											
1	17,02	1,138	1,128	1,121	1,118	1,110	2,155	1,426	1,087	1,021	0,928
2	25,0	1,269	1,258	1,251	1,247	1,239	3,821	2,527	1,757	1,405	1,194
3	35,04	1,379	1,366	1,358	1,355	1,347	9,101	6,021	4,187	3,346	2,811
4	40,10	1,468	1,455	1,446	1,442	1,434	17,882	11,832	8,227	6,575	5,457
5	45,02	1,551	1,536	1,527	1,523	1,514	29,772	19,698	13,697	10,946	8,866
6	50,09	1,622	1,607	1,597	1,593	1,583	41,640	28,953	23,138	18,510	15,734
Purification EFC (sample 2)											
7	16,98	1,184	1,173	1,166	1,163	1,156	2,252	1,490	1,136	1,037	0,931
8	25,03	1,320	1,308	1,300	1,297	1,291	3,992	2,641	1,836	1,468	1,248
9	35,08	1,434	1,421	1,412	1,409	1,403	9,510	6,292	4,375	3,497	2,937
10	40,05	1,527	1,513	1,504	1,500	1,493	18,687	12,364	8,597	6,871	5,772
11	45,01	1,613	1,598	1,588	1,584	1,577	31,112	20,585	14,313	11,439	9,380
12	50,04	1,687	1,671	1,661	1,657	1,650	43,514	30,256	24,181	19,345	16,442

If the initial 16.98% P_2O_5 defluorinated and desulfated EPA (sample 2) has a density of 1.184 g/cm^3 at 20°C, then the acid containing 50% P_2O_5 has a density of 1.687 g/cm^3. An increase in temperature from 20 ºC to 100 ºC leads to a decrease in the density of acid containing 50% P_2O_5 from 1.687 g/cm^3 to 1.650 g/cm^3. The viscosity of an acid containing 16.98% P_2O_5 is 2.252 mPa·s, and with a content of 50% P_2O_5, it is 43.514 mPa·s at a temperature of 20 ºC and decreases to 0.931 mPa·s and 16.442 mPa·s, respectively, at a temperature of 100 ºC.

Studying the influence of parameters on the process of obtaining monocalcium phosphate based on defluorinated and desulfated extraction phosphoric acid and calcium carbonate

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To obtain feed monocalcium phosphate from limestone and defluorinated, desulfated EPA, the effect of temperature and process duration on the degree of limestone decomposition was studied at an acid rate of 100% and a concentration of 17-50% Table 4.

Increasing the temperature of the decomposition process from 20 to 80 °C significantly increases the degree of decomposition of limestone for all values of the process duration. With an increase in the duration of the decomposition process from 10 to 100 minutes, the degree of decomposition from 18.17-19.46% at a temperature of 20 °C increases to 77.67-82.64%, and at a temperature of 80 °C these figures are 54.60- 58.53% and 93.54-98.04%, respectively. Increasing the concentration of EPA from 17% P_2O_5 to 50% P_2O_5 leads to a decrease in the degree of decomposition from 82.64-98.04% to 77.67-92.14% for a temperature of 20-80°C and a process duration of 100 minutes. Tables 4 and 5. show the effect of limestone particle size depending on the concentration of EPA and the duration of the process at an acid rate of 100%. Reducing the particle diameter from 5.0 to 0.1 mm of limestone leads to an increase in the degree of decomposition at a temperature of 60 °C from 49.33% to 69.11% for 30% for P_2O_5 EPA and from 47.36% to 65.20% for EPA 45% P_2O_5[18].

Table 4. The influence of temperature, concentration of extraction phosphoric acid and process duration on the degree of decomposition of limestone.

№	t, °C	Decomposition degree, %						
		10 min	**20 min**	**30 min**	**40 min**	**60 min**	**80 min**	**100 min**
EPA concentration 17% P_2O_5								
1	20	19,46	43,72	63,31	74,86	80,26	81,05	82,64
2	40	33,53	59,57	76,35	84,88	87,12	87,94	89,45
3	60	48,17	70,24	87,02	90,28	92,49	93,79	94,59
4	80	58,53	78,81	94,95	96,87	97,25	97,74	98,04
EPA concentration 20 % P_2O_5								
5	20	19,27	43,29	62,68	74,12	79,47	80,24	81,82
6	40	33,20	58,98	75,59	84,04	86,29	87,07	88,56
7	60	47,69	69,55	86,15	89,39	91,57	92,86	93,65
8	80	57,95	78,03	94,01	95,91	96,29	96,77	97,07
EPA concentration 25 % P_2O_5								
9	20	19,08	42,86	62,05	73,38	78,68	79,44	81,01
10	40	32,87	58,39	74,83	83,20	85,43	86,20	87,68
11	60	47,21	68,85	85,29	88,49	90,65	91,93	92,71
12	80	57,37	77,25	93,07	94,95	95,33	95,80	96,10
EPA concentration 30 % P_2O_5								
13	20	18,99	42,65	61,74	73,01	78,29	79,04	80,60
14	40	32,71	58,10	74,46	82,78	85,01	85,77	87,24
15	60	46,97	68,51	84,86	88,05	90,20	91,47	92,25
16	80	57,08	76,86	92,60	94,47	94,85	95,32	95,62
EPA concentration 35 % P_2O_5								
17	20	18,88	42,39	61,37	72,57	77,82	78,56	80,12
18	40	32,51	57,75	74,01	82,28	84,50	85,26	86,81
19	60	46,69	68,10	84,35	87,57	89,66	90,92	91,70
20	80	56,74	78,39	92,04	93,90	94,28	94,75	95,05
EPA concentration 40 % P_2O_5								
21	20	18,73	42,05	60,88	71,99	77,20	77,93	79,48
22	40	32,25	57,29	73,42	81,62	83,82	84,58	86,12

23	60	46,32	67,56	83,68	86,87	88,94	90,19	90,97
24	80	56,27	77,76	91,30	93,15	93,53	93,99	94,29
EPA concentration 45 % P_2O_5								
25	20	18,45	41,42	60,39	71,41	76,58	77,30	78,85
26	40	31,77	56,43	72,83	80,97	83,15	83,90	85,43
27	60	45,63	66,55	83,01	86,17	88,29	89,47	90,24
28	80	55,43	76,59	90,57	92,40	92,78	93,24	93,54
EPA concentration 50 % P_2O_5								
29	20	18,17	40,80	59,49	70,34	75,44	76,15	77,67
30	40	31,29	55,87	71,74	79,76	81,91	82,65	84,15
31	60	44,95	65,54	81,77	84,88	86,97	88,13	88,89
32	80	54,60	75,45	89,22	91,02	91,39	91,85	92,14

The best results of the degree of limestone decomposition are observed with a particle diameter of less than 1.0 mm and amount to 94.38-97.05% for an EPA concentration of 30% P_2O_5 and process duration of 100 minutes and 93.05-94.12% for an acid concentration of 45% P_2O_5. Thus, the optimal technological parameters for limestone decomposition have been established: decomposition temperature 80-100 °C, process duration 30-60 minutes, particle size 0.1-1.0 mm, Table 5. Increasing the duration of the decomposition process, increasing the temperature, and reducing the diameter of the limestone particles also contribute to an increase in the degree of decomposition[19].

Table 5. The influence of the diameter of limestone particles, the concentration of extraction phosphoric acid and the duration of the process on the degree of decomposition of limestone at a rate of 100% EPA.

№	Particle diameter, mm	Decomposition degree, %						
		10 min	20 min	30 min	40 min	60 min	80 min	100 min
EPA concentration 20% P_2O_5								
1	5,0	49,97	68,51	84,86	89,05	90,59	91,47	92,25
2	3,0	55,01	72,69	88,73	91,86	92,93	93,40	93,94
3	1,0	59,08	76,86	91,6	94,15	94,85	95,32	95,62
4	0,5	62,67	79,79	93,78	95,71	96,22	96,55	96,74
5	0,18	66,05	82,17	95,17	97,08	97,56	97,84	98,03
6	0,1	70,01	87,10	97,07	97,66	98,15	98,33	98,52
EPA concentration 30% P_2O_5								
7	5,0	49,33	67,62	83,76	87,89	89,41	90,28	91,05
8	3,0	54,29	71,75	87,58	90,67	91,72	92,19	92,72
9	1,0	58,31	75,86	90,41	92,93	93,62	94,08	94,38
10	0,5	61,86	78,75	92,56	94,47	94,97	95,29	95,48
11	0,18	65,19	81,10	93,93	95,82	96,29	96,57	96,76
12	0,1	69,11	85,97	96,75	96,11	96,77	97,05	97,05
EPA concentration 45% P_2O_5								
13	5,0	47,36	64,91	80,41	84,38	85,84	86,67	87,41
14	3,0	52,21	67,69	83,41	89,37	90,05	91,13	91,89
15	1,0	55,01	72,61	88,12	90,21	91,95	92,32	93,05
16	0,5	58,91	74,29	90,03	91,71	92,21	92,73	93,32
17	0,18	61,49	77,23	90,32	91,39	91,87	93,33	93,92
18	0,1	65,20	81,11	91,27	92,35	92,79	93,81	94,12

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The influence of the norm and concentration of phosphoric acid on the process of obtaining monocalcium phosphate

For the decomposition of limestone, defluorinated, desulfated, and evaporated acids were used to contain 16.98-45% P_2O_5. The influence of the concentration and norm of EPA on the chemical composition of pulp and defluorinated monocalcium phosphate was studied. The influence of the EPA norm with a concentration of 16.98-45% P_2O_5 on the composition of monocalcium phosphate pulps is given in Table 6.

Table 6. The influence of the rate and concentration of extraction phosphoric acid on the chemical composition of monocalcium phosphate pulp (sample 2).

№	Acid rate, %	Conc. EPA, % P_2O_5	Chemical composition, mass. %						
			P_2O_5	CaO	MgO	Fe_2O_3	Al_2O_3	SO_4^{2-}	F
1	95	17	15,76	8,48	0,94	0,23	0,35	0,21	0,30
	100		15,88	8,22	0,94	0,24	0,36	0,22	0,30
	105		15,93	7,94	0,93	0,24	0,37	0,22	0,30
	110		15,98	7,65	0,93	0,24	0,38	0,22	0,30
2	95	25	22,45	11,95	1,35	0,34	0,50	0,31	0,20
	100		22,69	11,60	1,35	0,34	0,51	0,31	0,21
	105		22,79	11,74	1,34	0,34	0,51	0,31	0,21
	110		22,88	10,88	1,33	0,34	0,51	0,31	0,21
3	95	35	30,19	16,25	1,82	0,45	0,68	0,41	0,18
	100		30,64	15,85	1,82	0,46	0,69	0,42	0,19
	105		30,85	15,42	1,81	0,46	0,70	0,42	0,19
	110		31,06	14,96	1,81	0,46	0,70	0,42	0,19
4	95	40	34,16	18,39	2,05	0,51	0,77	0,46	0,17
	100		34,67	17,94	2,04	0,52	0,78	0,47	0,18
	105		34,91	17,45	2,03	0,52	0,79	0,47	0,18
	110		35,15	16,93	2,03	0,52	0,79	0,47	0,18

With an increase in the acid rate from 95% to 110%, the contents of P_2O_5 and CaO slightly increase, and the contents of impurity components increase by tenths of a percent, regardless of the concentration of EPA. With an acid concentration of 25% P_2O_5, the P_2O_5 content increases from 22.45% at a norm of 95% to 22.88% at a norm of 110% for the formation of monocalcium phosphate. After drying, the P_2O_5 content in monocalcium phosphate changes from 51.97% to 54.99% Tables 6 and 7. At the same time, the CaO content is 25.63-28.24%, fluorine 0.24-1.02%[20].

Table 7. The influence of the norm and concentration of extraction phosphoric acid on the chemical composition of monocalcium phosphate (sample 2).

№	Acid rate %	Conc. EPA, % P_2O_5	Chemical composition of monocalcium phosphate, wt. %						
			P_2O_5	CaO	MgO	Fe_2O_3	Al_2O_3	SO_4^{2-}	F
1	95	17	52,32	28,16	3,14	0,78	1,17	0,71	0,98
	100		53,23	27,55	3,16	0,79	1,19	0,72	1,00
	105		53,88	26,91	3,17	0,80	1,20	0,73	1,01
	110		54,53	26,27	3,18	0,82	1,22	0,74	1,02
2	95	25	52,18	27,77	3,13	0,78	1,17	0,71	0,47
	100		53,01	27,11	3,15	0,79	1,18	0,72	0,47
	105		53,45	26,37	3,16	0,80	1,19	0,72	0,48
	110		53,88	25,63	3,18	0,81	1,20	0,73	0,48
3	95	35	51,97	27,98	3,12	0,77	1,16	0,70	0,31

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	100		53,02	27,44	3,15	0,79	1,18	0,72	0,32
	105		53,98	26,95	3,18	0,81	1,20	0,73	0,32
	110		54,94	26,46	3,20	0,82	1,22	0,74	0,33
4	95	40	52,22	28,11	3,14	0,78	1,16	0,71	0,27
	100		53,04	27,45	3,16	0,79	1,18	0,72	0,27
	105		53,95	26,94	3,18	0,80	1,20	0,73	0,28
	110		54,86	26,43	3,20	0,82	1,22	0,74	0,28
5	95	45	52,47	28,24	3,15	0,78	1,17	0,71	0,24
	100		53,01	27,43	3,16	0,79	1,19	0,72	0,25
	105		54,02	26,96	3,18	0,80	1,21	0,73	0,25
	110		54,99	26,49	3,20	0,82	1,23	0,74	0,26

The conducted studies showed the possibility of obtaining defluorinated, fertilizing monocalcium phosphate based on defluorinated and desulfated EPA from phosphorites. Monocalcium phosphate obtained at an EPA concentration of 25-40% P_2O_5 contains 51.97-54.99% P_2O_5, 25.63-28.24% CaO. Fluorine content is 0.24-1.02%. The higher the concentration of the original EPA, the lower the fluorine content in monocalcium phosphate. Increasing the concentration of EPA to 40% P_2O_5 helps to reduce the fluorine content in the resulting monocalcium phosphate.

For the decomposition of limestone, defluorinated, desulphated, and evaporated acid contents of 45 to 60% P_2O_5 were used. The influence of the concentration and rate of phosphoric acid on the chemical composition of pulp and defluorinated monocalcium phosphate was studied. The influence of the EPA norm with a concentration of 45-60% P_2O_5 on the composition of monocalcium phosphate pulps is given in Table 8. With an increase in the acid rate from 95% to 110%, the contents of P_2O_5 and CaO slightly increase, and the contents of impurity components increase by tenths of a percent, regardless of the concentration of EPA. At an acid concentration of 45% P_2O_5, the P_2O_5 content increases from 38.46% at a norm of 95% to 39.59% at a norm of 110%; at an acid concentration of 50% P_2O_5, the P_2O_5 content increases from 42.31% at a norm of 95% to 43.56 % at a norm of 110%, at an acid concentration of 55% P_2O_5, the P_2O_5 content increases from 46.54% at a norm of 95% to 47.92% at a norm of 110%, and at an acid concentration of 60% P_2O_5, the P_2O_5 content increases from 50.77% at a norm 95% to 52.27% with a norm of 110% for the formation of monocalcium phosphate[21].

Table 8. The influence of the rate and concentration of extraction phosphoric acid on the chemical composition of monocalcium phosphate before drying (sample 1).

№	Acid level,%	Chemical composition, mass. %							
		P_2O_5	CaO	MgO	Fe_2O_3	Al_2O_3	SO_4^{2-}	F	H_2O
EPA concentration - 45% P_2O_5									
1	95	38,46	20,69	1,19	0,85	1,26	0,63	0,131	24,67
2	100	39,09	20,23	1,20	0,86	1,27	0,64	0,136	25,32
3	105	39,35	19,65	1,21	0,87	1,28	0,65	0,142	26,43
4	110	39,59	19,06	1,22	0,88	1,29	0,66	0,149	27,49
EPA concentration - 50% P_2O_5									
5	95	42,31	22,77	1,31	0,94	1,39	0,69	0,140	18,14
6	100	43,01	22,25	1,32	0,95	1,40	0,70	0,146	18,65
7	105	43,29	21,61	1,33	0,96	1,42	0,71	0,153	19,47
8	110	43,56	20,97	1,34	0,97	1,43	0,72	0,160	20,25
EPA concentration - 55% P_2O_5									
9	95	46,54	24,50	1,55	1,03	1,53	0,76	0,132	11,09
10	100	47,31	24,47	1,56	1,05	1,54	0,77	0,138	11,56
11	105	47,62	23,77	1,57	1,06	1,56	0,78	0,145	12,48

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12	110	47,92	23,07	1,59	1,07	1,57	0,79	0,152	13,25
EPA concentration - 60% P_2O_5									
13	95	50,77	27,32	1,80	1,13	1,67	0,83	0,123	4,86
14	100	51,61	26,70	1,81	1,14	1,68	0,84	0,129	5,23
15	105	51,95	25,93	1,82	1,15	1,70	0,85	0,135	5,98
16	110	52,27	25,16	1,84	1,16	1,72	0,86	0,141	6,31

After drying, the P_2O_5 content in monocalcium phosphate changes from 52.58% to 55.26% Table 9 In this case, the CaO content is 26.59-28.30%, fluorine 0.127-0.181%. Increasing the concentration of EPA helps to reduce the fluorine content in the finished product of feed grade[22].

Table 9. Influence of acid rate and concentration on the chemical composition of monocalcium phosphate after drying (sample 1).

№	Acid rate, %	Chemical composition, mass. %						
		P_2O_5	CaO	MgO	Fe_2O_3	Al_2O_3	SO_4^{2-}	F
EPA concentration – 45 % P_2O_5								
1	95	52,58	28,30	3,17	1,17	1,72	0,85	0,181
2	100	53,12	27,51	3,15	1,18	1,73	0,86	0,187
3	105	54,11	27,02	3,18	1,20	1,78	0,89	0,192
4	110	55,08	26,53	3,22	1,23	1,81	0,91	0,196
EPA concentration - 50% P_2O_5								
5	95	52,65	28,33	3,17	1,17	1,72	0,85	0,174
6	100	53,19	27,52	3,15	1,18	1,73	0,86	0,179
7	105	54,17	27,04	3,18	1,20	1,78	0,89	0,186
8	110	55,14	26,55	3,22	1,23	1,81	0,91	0,191
EPA concentration – 55 % P_2O_5								
9	95	52,73	28,09	3,17	1,17	1,73	0,86	0,144
10	100	53,26	27,55	3,16	1,18	1,74	0,87	0,151
11	105	54,18	27,05	3,16	1,20	1,77	0,89	0,164
12	110	55,21	26,58	3,21	1,23	1,81	0,91	0,173
EPA concentration - 60% P_2O_5								
13	95	52,81	27,95	3,18	1,18	1,73	0,86	0,127
14	100	53,33	27,58	3,16	1,18	1,74	0,87	0,132
15	105	54,24	27,07	3,18	1,20	1,77	0,89	0,140
16	110	55,26	26,59	3,22	1,22	1,81	0,90	0,148

Thus, the conducted studies showed the possibility of obtaining granulated feed monocalcium phosphate based on defluorinated and desulfated EPA from CC phosphorites. Monocalcium phosphate, regardless of the initial acid concentration, contains 52.65-55.26% P_2O_5, 26.55-28.33% CaO. The fluorine content is 0.127-0.191%. The higher the concentration of the original phosphoric acid, the lower the fluorine content in monocalcium phosphate. The resulting samples of feed monocalcium phosphate meet the requirements for feed phosphates GOST - 23999-80.

The influence of the return rate on the chemical composition and properties of monocalcium phosphate.

When producing monocalcium phosphate using evaporated acid containing 45-55% P_2O_5, a thick mass is formed, which sets in 10-15 minutes. The moisture content of the products is 24.67-27.49%, 18.14-20.25%, and 11.09-13.25%, respectively, for acid concentrations of 45, 50, and 55% P_2O_5. Drying monocalcium phosphate with high humidity is not economically justified. Therefore, to reduce the moisture content of products supplied for drying, the influence of the MKF: Return ratio on changes in the chemical composition and moisture content of the product was studied[23]. The results obtained are shown in Table 10.

Table 10. Effect of process retardation and phosphoric acid concentration.

№	IFF: retour	Chemical composition, mass. %							
		P_2O_5	CaO	MgO	Fe_2O_3	Al_2O_3	SO_4^{2-}	F	H_2O
EPA concentration - 45% P_2O_5									
1	1:0,3	42,22	21,85	1,29	0,93	1,37	0,69	0,153	21,70
2	1:0,5	43,61	22,57	1,34	0,96	1,42	0,72	0,156	19,45
3	1:0,8	45,11	23,35	1,39	0,99	1,47	0,74	0,160	16,86
4	1:1,0	45,88	23,74	1,41	1,01	1,49	0,75	0,162	14,41
EPA concentration – 50 % P_2O_5									
5	1:0,3	45,23	23,40	1,39	1,00	1,47	0,74	0,146	17,28
6	1:0,5	46,22	23,91	1,42	1,02	1,50	0,75	0,151	16,08
7	1:0,8	47,30	24,47	1,45	1,04	1,54	0,77	0,155	14,62
8	1:1,0	47,83	24,75	1,47	1,05	1,56	0,78	0,159	13,15
EPA concentration - 55% P_2O_5									
9	1:0,3	48,54	25,11	1,60	1,08	1,58	0,79	0,141	10,97
10	1:0,5	49,09	25,39	1,62	1,09	1,60	0,80	0,143	10,19
11	1:0,8	49,68	25,69	1,64	1,10	1,62	0,81	0,145	9,25
12	1:1,0	49,98	25,85	1,65	1,11	1,63	0,82	0,145	8,75

Increasing the ICF: return ratio from 1:0.3 to 1:1 or increasing the return rate from 0.3 to 1, the P_2O_5 content increases from 42.22% to 45.88%, CaO from 21.85% to 23.74% for acid concentration 45%, from 45.23% to 47.83% P_2O_5, from 23.40% to 24.75% CaO for an acid concentration of 50% P_2O_5 and from 48.54% to 49.68% P_2O_5, from 25, 11% to 25.85% CaO for an acid concentration of 55% P_2O_5. The content of oxides of magnesium, iron, aluminum, sulfates, fluorine changes less significantly and is MgO 1.29-1.65%, Fe_2O_3 0.93-1.11%, Al_2O_3 1.37-1.63%, fluorine 0.141-0.162%, while the moisture content of the products is, depending on the return, 14.41-21.70% with an acid concentration of 45% P_2O_5, 13.15-17.28% with an acid concentration of 50 % P_2O_5 and 8.75-10.97% with an acid concentration of 55% P_2O_5. Research has shown that drying pulp at a temperature of 100-110°C allows one to obtain monocalcium phosphate containing 52.65-55.26% P_2O_5, 26.55-28.33% CaO and 0.127-0.191% fluorine[24].

Studying the process of obtaining crystalline monocalcium phosphate based on the extraction of phosphoric acid at a high rate

To obtain defluorinated monocalcium phosphate in crystalline form, without foreign impurities, we studied the process of decomposition of defluorinated and desulfated EPA limestone from phosphorites, previously evaporated to a content of 40-55% P_2O_5 at a rate of 300-500% of stoichiometry for the formation of monocalcium phosphate. The process was studied in a laboratory setup consisting of a reactor, a mechanical stirrer, and a thermostat at a temperature of 95-100°C and a process duration of three hours. After reaching the specified time, the phosphate mass was filtered at the experimental temperature to separate the insoluble residue, the filtrate was cooled to a temperature of 60-70 °C and the crystalline monocalcium phosphate was separated, washed with water and dried at a temperature of 100-110 °C. The process of obtaining monocalcium phosphate by decomposing limestone with concentrated phosphoric acid follows the well-known Eq. 1:

$$CaCO_3 + 2H_3PO_4 = Ca(H_2PO_4)_2 + H_2O + CO_2 \qquad 1$$

The mother liquor, after the separation of monocalcium phosphate crystals, contains calcium salt dissolved in phosphoric acid, and the insoluble residue also contains undecomposed limestone. Crystalline monocalcium phosphate was obtained at rates of 300-500% evaporated extraction phosphoric acid containing 45, 50, and 55% P_2O_5 Table 11. The phosphoric acid mass of limestone decomposition of

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45% by P_2O_5 with phosphoric acid at rates of 300 and 400% of stoichiometry is practically not filtered. A similar picture is observed at a rate of 55% phosphoric acid and 300%. The best filtration results are observed when using 50% phosphoric acid by P_2O_5 at rates of 300-500% and when using 55% phosphoric acid by P_2O_5 at a rate of 500%. In this case, the removal of monocalcium phosphate sediment is 330-450 kg/m^2·h, and the content of P_2O_5 total is 53.6-54.8%, P_2O_5 11.2 – 14.5%, CaO 16.6 – 17.5%. When neutralizing crystalline monocalcium phosphate obtained using 50% P_2O_5 EPA at a rate of 400% with limestone in an amount of 10 and 15% by weight of monocalcium phosphate, the content of free P_2O_5 decreases from 13.7% to 5.2% upon crystallization of monocalcium phosphate at a temperature of 60°C and from 12.0% to 4.7% upon crystallization of monocalcium phosphate at a temperature of 80°C. The pH of a 10% solution of neutralized, crystalline monocalcium phosphate increases from 2.6 to 3.3 and from 2.5 to 3.525.

Table 11. The influence of calcium carbonate on the acidity and commercial properties of monocalcium phosphate.

Amount of $CaCO_3$,% by weight	Cons. H_3PO_4, % P_2O_5	Norma H_3PO_4, % от стех.	°C	pH	Content % P_2O_5 General	Content % P_2O_5 Free	CaO
0	50	400	60	2,6	53,3	13,7	17,3
10				3,1	55,6	10,3	18,4
15				3,3	54,2	5,2	20,3
0	50	400	80	2,5	54,2	12,0	18,5
10				3,2	56,0	9,8	18,5
15				3,5	54,9	4,7	21,0
0	55	300	60	2,3	54,0	16,1	13,8
10				3,0	52,2	6,6	15,4
15				3,25	51,3	3,1	16,9
0	55	400	60	2,2	56,9	20,0	12,5
10				3,0	55,6	8,7	16,3
15				3,1	53,5	5,4	17,5
20				3,3	52,1	2,5	18,7
0	55	400	80	2,2	56,8	19,8	12,1
10				2,8	54,1	8,6	16,5
15				3,2	53,5	5,3	18,3
20				3,5	52,3	2,6	19,8

When neutralizing crystalline monocalcium phosphate obtained using 55% P_2O_5 phosphoric acid, the content of free P_2O_5 decreases from 16.1% to 3.1% at an acid rate of 300% and a crystallization temperature of 60°C.

When neutralizing crystalline monocalcium phosphate obtained at an acid rate of 400%, the content of P_2O_5 decreases from 20.0% to 2.5% and from 19.8% to 2.6%, respectively, for monocalcium phosphate obtained at crystallization temperatures of 60 and 80 °C. Thus, in laboratory conditions, the possibility of obtaining feed, crystalline monocalcium phosphate was established, and the optimal technological parameters of all stages of the process were determined: EPA concentrations 45-55% P_2O_5, norm 350-500%, temperature - 100 °C, process duration 180-300 minutes[26].

Studying the process of isolation of crystalline monocalcium phosphate

Tests were carried out similarly for the production of monocalcium phosphate (the cooling rate was adjusted starting from 65 °C). The results obtained are shown in Tables 11 and 12. From the results obtained, it is clear that the main factor influencing the filtration rate of monocalcium phosphate is the cooling rate of the solutions. Reducing the solution cooling rate from 15 to 5.0°C/hour at a solution concentration of 55% and a process temperature of 60°C, the filtration time decreases from 1.68 minutes to 0.53 minutes. Reducing the cooling rate of the monocalcium phosphate solution from 15 to 5.0°C/hour, sediment removal increases from 330 to 750 kg/m^3·hour for a solution concentration of 60%. Changing the concentration and temperature of the solution within the range of 55-60% and 60-65 °C does not have a noticeable effect on the nature of the change in filtration time and sediment removal. A slow cooling rate allows fewer impurities to precipitate. With a decrease in the cooling rate, the amount of impurities SO_3, MgO, Al_2O_3, Fe_2O_3, and F in the product decreases approximately by half. Increasing the concentration of solutions above 55% leads to an increase in the content of impurities in the finished product[25-27]. Mother solutions after crystallization of monocalcium phosphate can be reused, after concentration, for crystallization of monocalcium phosphate. Thus, the research results show that the optimal parameters for obtaining feed monocalcium phosphate are the suspension concentration of at least 60%, cooling the suspension at a rate of no more than 5.0 °C/hour to a temperature of 60-65 °C, and the resulting products fully comply with the requirements of GOST 23999 -80 for feed phosphates.

Studying the frequency of use of the mother solution

To increase the yield of P_2O_5 in the product and obtain a product that meets the requirements of regulatory documentation, the effect of reusing the mother liquor on the composition of the resulting crystalline monocalcium phosphate of feed grade and higher purity was studied. In this case, the mother liquor, after crystallization of the product from the previous stage, was subjected to evaporation to a given concentration in Tables 12 and 13. When carrying out the experiments, we used solutions that were concentrated after they were obtained by neutralizing a defluorinated and desulfated solution of EPA from phosphorites with calcium carbonate at a rate of 400% of the stoichiometry to form monocalcium phosphate. In the experiments, 200 g of a 55% solution of monocalcium phosphate at a temperature of 90 °C was poured into a reactor with a water jacket and cooled with water. After cooling to 60 °C, with constant stirring of the solution, the refrigerant supply was reduced, cooling at a rate of 5.0 °C/hour. When the temperature reached 60°C, cooling was stopped, and the suspension was separated on a Buchner funnel (filter surface 0.005 m^2). The crystals on the filter were squeezed out by sucking air for two minutes. Wash with acetone and dry at 100°C for a hour[28,29].

Table 12. The effect of reusing the mother liquor on the composition of the resulting product.

Stage	Sample	Chemical composition, mass. %						
		P_2O_5	SO_3	CaO	MgO	Al_2O_3	Fe_2O_3	F
1	Initial EPA	17,0	0,230	1,58	0,490	0,38	0,25	0,310
	Initiall	50,0	0,676	4,647	1,440	1,118	0,735	0,909
	Crystals	54,20	0,190	18,70	0,067	0,096	0,085	0,009
	Solution	31,61	0,498	1,166	1,105	0,870	0,560	0,673
2	Initiall	27,03	0,415	2,36	0,924	0,720	0,465	0,557
	Crystals	54,14	0,192	18,72	0,070	0,098	0,086	0,010
	Solution	31,64	0,570	0,955	1,313	1,028	0,655	0,788
3	Initiall	27,01	0,464	2,358	1,069	0,830	0,530	0,637
	Crystals	54,11	0,195	18,75	0,073	0,099	0,088	0,012
	Solution	31,66	0,057	0,956	1,523	1,191	0,750	0,903
4	Initiall	26,99	0,510	2,50	1,215	0,940	0,598	0,716
	Crystals	53,81	0,430	19,30	0,081	0,112	0,104	0,014
	Solution	31,755	0,679	1,09	1,732	1,34	0,844	1,013

Table 13. The influence of reusing the mother liquor on the technological performance of the process.

Stage	Ratio L:S	Filtration time, min.	Sludge removal, kg/m² h	Degree of transition to product, mass. %						
				P_2O_5	SO_3	CaO	MgO	Al_2O_3	Fe_2O_3	F
1	7,72	0,78	589	18,17	4,71	67,51	0,78	0,14	1,93	1,33
2	7,72	0,71	561	18,16	4,15	71,72	0,66	0,12	1,65	1,14
3	7,72	0,68	552	18,15	3,71	71,70	0,57	0,10	1,45	1,00
4	7,71	1,25	420	17,99	7,58	69,64	0,60	1,07	1,57	1,39

This is due to the fact that as the mother liquor is reused, the content of impurities in the product gradually increases. The yield of P_2O_5 in qualified feed monocalcium phosphate is 67.51%. Thus, three-fold reuse of the recycled mother liquor can be considered optimal, which ensures the production of feed monocalcium phosphate that meets the requirements of GOST 23999-80.

Studying the rheological properties of crystalline monocalcium phosphate solutions

Studies of the rheological properties of products during the decomposition of calcium carbonate at an increased rate of EPA. The EPA rate was varied from 300 to 450 %, and the temperature from 40 to 100 °C. Experimental data are presented in Table 14. Table 14 shows the rheological properties of the monocalcium phosphate suspension.

Table 14. The influence of the rate of extraction phosphoric acid and temperature on the density and viscosity of the suspension formed during the decomposition of calcium carbonate at an increased rate of acid

№	EFC norms, %	Density, g/cm³					Viscosity, mPa.s				
		40°C	60°C	80°C	90°C	100°C	40°C	60°C	80°C	90°C	100°C
1	450	1,263	1,252	1,244	1,241	1,239	3,234	2,258	1,487	1,256	1,245
2	400	1,320	1,308	1,300	1,297	1,295	3,593	2,509	1,652	1,395	1,379
3	375	1,379	1,367	1,358	1,355	1,352	6,314	4,243	2,904	2,358	1,344
4	350	1,434	1,421	1,412	1,409	1,406	9,035	5,977	4,156	3,322	3,309
5	325	1,480	1,467	1,458	1,455	1,452	12,055	7,975	5,546	4,432	4,415
6	300	1,527	1,513	1,504	1,500	1,497	17,753	11,746	8,167	6,527	6,502

With a decrease in the EPA rate of the suspension, the density and viscosity increase slightly and are 1.263-1.527 g/cm^3 and 3.234-17.753 mPa s at a temperature of 40 °C. Increasing the temperature of the suspension leads to a decrease in the density and viscosity of the suspension. At an EFC rate of 450%, an increase in temperature from 40 to 100 °C decreases the density from 1.263 g/cm^3 to 1.239 g/cm^3, and the viscosity under these conditions decreases from 3.234 mPa s to 1.245 mPa s. This indicates acceptable rheological properties of the monocalcium phosphate suspension. Table 14 shows the rheological properties of mother liquors obtained after filtration of a suspension of crystalline monocalcium phosphate.

Results and Discussion

Physicochemical and commercial properties of the resulting monocalcium phosphate

To conduct research using physicochemical methods of analysis, feed monocalcium phosphate was obtained from calcium carbonate and defluorinated, desulfated, and evaporated to 45-55% P_2O_5 EPA at a standard of 95-100%. To check the purity of the resulting feed monocalcium phosphate, X-ray diffraction patterns, and IR spectra were analyzed Figs. 1 and 2.

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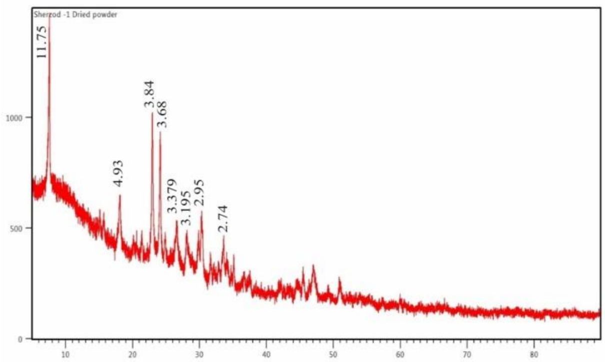

Figure 1. X-ray image of feed monocalcium phosphate.

The X-ray diffraction pattern Fig. 1 contains only diffraction maxima characteristic of monocalcium phosphate with interplanar distances of 11.75, 4.93, 3.379, 3.195, 2.95 Å $Ca(H_2PO_4)_2{\cdot}H_2O$, as well as 3.84 and 3. 68 Å $Mg(H_2PO_2)_2{\cdot}6H_2O$ and $NaH_2PO_4{\cdot}H_2O$.
On the IR spectrum Fig. 2 there are vibration frequencies that characterize vibrations related to PO_4 440.54-1077.68 cm^{-1} and crystalline water - 1647.11-2897.93 cm^{-1}.

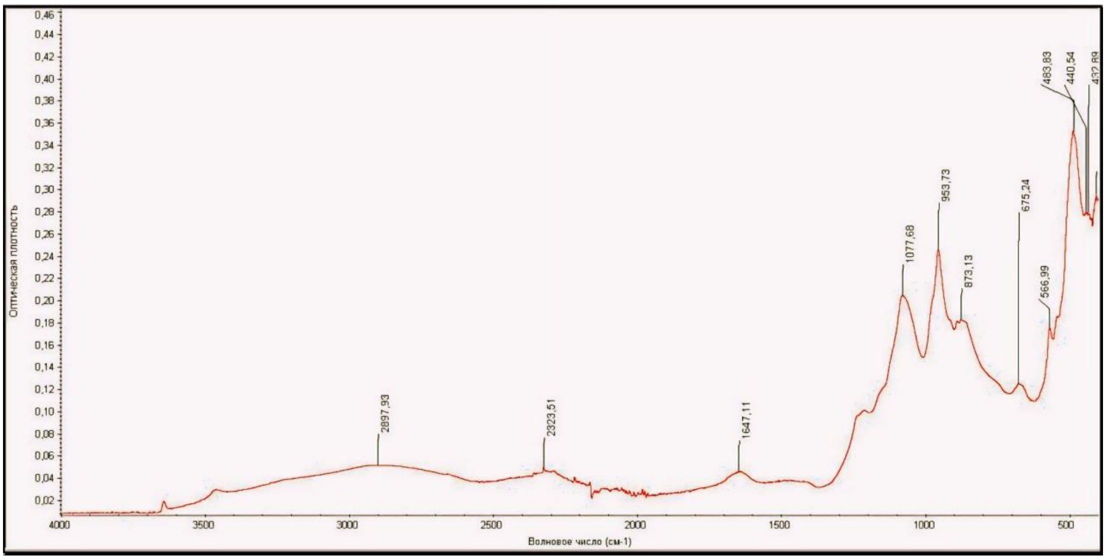

Figure 2. IR spectrum of feed monocalcium phosphate.

Fig. 3 and Table 15. show the main components of the resulting monocalcium phosphate based on defluorinated and desulfated EPA from phosphorites and limestone using the flow method.

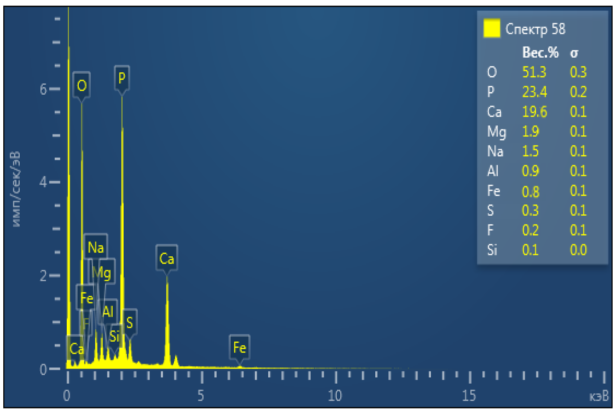

Figure 3. Scanning electron microscopic analysis feed monocalcium phosphate.

Table 15. Chemical composition of monocalcium phosphate.

Element	Weight. %	Sigma, Weight.
O	51.28	0.29
F	0.11	0.06
Na	1.51	0.09
Mg	1.89	0.07
Al	0.92	0.05
Si	0.11	0.03
P	23.38	0.22
S	0.31	0.07
Ca	19.68	0.15
Fe	0.81	0.08
Total:	100.00	

Scanning microscopic analysis of monocalcium phosphate shows the following content of composition elements: O-51.28%, F-0.11%; Na-1.51%; Mg-1.89%; Al-0.92%; Si-0.11%; P-23.38%; Ca-19.68%, S-0.31%, which corresponds to their

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content in feed monocalcium phosphate. Thus, the research has established the possibility of obtaining feed monocalcium phosphate by decomposition of pre-fluorinated, desulphated, and evaporated EPA calcium carbonate under the following optimal conditions: EPA concentration -45-55% P_2O_5, calcium carbonate rate - 95-100%, ratio 1.0:0, 3-1.0, drying temperature no more than 100-110 °C.

Physicochemical studies of the obtained crystalline monocalcium phosphate

To conduct research using physicochemical methods of analysis, crystalline monocalcium phosphate was obtained by decomposing limestone with concentrated EPA at an increased rate. It has been shown that when the concentration of purified EPA is 45-55% P_2O_5 and the norm is 400%, monocalcium phosphate is obtained containing 54-55% P_2O_5 and 0.009-0.02% fluorine. The X-ray diffraction pattern Fig. 4 shows only the diffraction maxima characteristic of monocalcium phosphate with interplanar distances of 11.75, 4.93, 3.007, 2.95 Å.

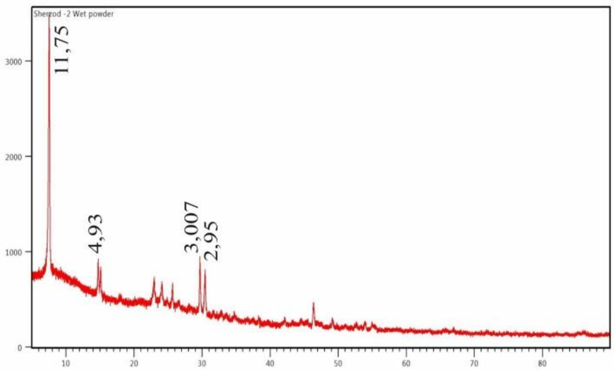

Figure 4. X-ray diffraction pattern of crystalline monocalcium phosphate

On the IR spectrum Fig. 5 there are vibration frequencies that characterize vibrations related to PO_4 440.54-1077.68 cm^{-1} and crystalline water - 1647.11-2897.93 cm^{-1}. An electron microscopic image of monocalcium phosphate crystals obtained after separation from the mother liquor, as well as the results of their elemental chemical analysis, are shown in Fig. 6 and Table 16. Scanning microscopic analysis of crystalline monocalcium phosphate shows the following content of composition elements: O-51.28%, F-0.11%; Na-1.51%; Mg-1.89%; Al-0.92%; Si-0.11%; P-23.38%; S-0.31%, which corresponds to their content in feed monocalcium phosphate.

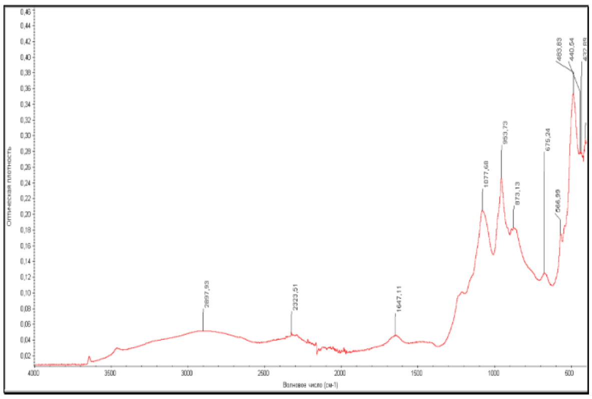

Figure 5. IR spectrum of feed monocalcium phosphate.

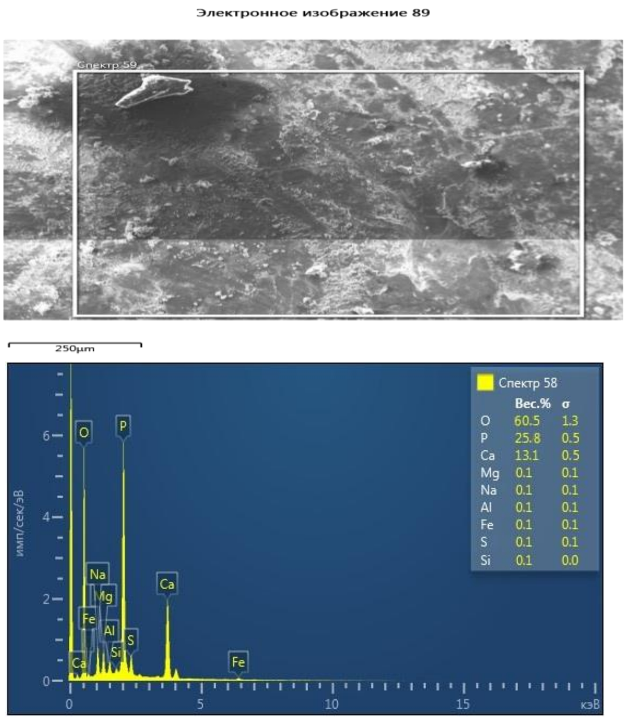

Figure 6. Scanning microscopic analysis of feed monocalcium phosphate

Table 16. Results of elemental chemical analysis of monocalcium phosphate.

Elements	Weight. %	Sigma, Weight. %
O	60.51	1.29
Na	0.09	0.03
Mg	0.06	0.03
Al	0.08	0.04
Si	0.06	0.02
P	25.8	0.22
S	0.09	0.04
Ca	13.08	0.35
Fe	0.07	0.04
Total :	100.00	

Thus, the possibility of obtaining crystalline monocalcium phosphate has been experimentally established, the optimal parameters of all stages of the process have been determined, and its physicochemical and commercial properties have been clarified. Based on systematic experimental studies, two options have been proposed for the taking of defluorinated feed monocalcium phosphate based on EPA from phosphorites.

Taking granulated feed monocalcium phosphate

The technological process for the first option for taking granulated feed monocalcium phosphate based on evaporated EPA from phosphorites includes:

- evaporation of defluorinated and desulfated EPA to a concentration of 45-55% P_2O_5;
- decomposition of calcium carbonate evaporated, partially purified from fluorine and sulfates of EPA;
- granulation and drying in the presence of Retour of defluorinated feed monocalcium phosphate.

The essence of the technology is the decomposition of calcium carbonate by defluorinated, desulphated, and evaporated EPA with a P_2O_5 concentration of 45-55% at a rate of 95-100% of stoichiometry, a temperature of 90-100°C and process duration of 20-40 minutes. In this case, granulation and drying are carried out at a temperature of 105-110 °C using a drum granulator (BG) and a drum dryer (BS) in the presence of a return.

The resulting defluorinated feed granulated monocalcium phosphate has the composition (wt. %): P_2O_5 total. – 52.18; P_2O_5. – 52.01; P_2O_5aq. – 51.78; CaO – 27.14; F – 0.16.

Technical and economic calculations of the feasibility of obtaining feed monocalcium phosphate

The production of feed, granular, and crystalline monocalcium phosphates based on EPA obtained from phosphorites includes the following stages:

Granulated monocalcium phosphate: purification of EPA from fluorine and sulfates, acid evaporation, decomposition of limestone with evaporated phosphoric acid with a concentration of 45-55% P_2O_5 at a stoichiometric rate; granulation in the presence of drying.

Crystalline monocalcium phosphate: purification of EPA from fluorine and sulfates, acid evaporation, decomposition of limestone with evaporated phosphoric acid at high (350-450%) rates; cooling, crystallization, and separation of monocalcium phosphate crystals; return of mother liquors to the initial stage of the process; washing and drying of crystalline monocalcium phosphate.

Conclusion

According to results, obtaining feed monocalcium phosphate from limestone and defluorinated, desulfated EPA, the effect of temperature and process duration on the degree of decomposition of limestone was studied at an acid rate of 100% and a concentration of 17-50% P_2O_5. Also, Monocalcium phosphate obtained at an EPA concentration of up to 40% P_2O_5 contains 51.97-54.99% P_2O_5, 25.63-28.24% CaO. Fluorine content is 0.24-1.02%. The higher the concentration of the original EPA, the lower the fluorine content in monocalcium phosphate. The phosphoric acid mass of limestone decomposition of 45% by P_2O_5 with phosphoric acid at rates of 300 and 400% of stoichiometry is practically not filtered. A similar picture is observed at a rate of 55% phosphoric acid and 300%. The best filtration results are observed when using 50% phosphoric acid by P_2O_5 at rates of 300-500% and when using 55% phosphoric acid by P_2O_5 at a rate of 500%. In this case, the removal of monocalcium phosphate sediment is 330-450 $kg/m^2 \cdot h$, and the content of P_2O_5 total. is 53.6-54.8%, P_2O_5c. 11.2–14.5%, CaO 16.6 – 17.5%. In laboratory conditions, the possibility of obtaining feed, crystalline monocalcium phosphate was established, and the optimal technological parameters of all stages of the process were determined: EPA concentrations 45-55% P_2O_5, norm 350-500%, temperature - 100 ° C, process duration 180-300 minutes.

Overall, extensive research in this study is fºCused on the extraction of monocalcium phosphate based on Central Kyzylkum phosphorites, and it confirms that recognized scientific results have been obtained.

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Authors' Declaration

- Conflicts of Interest: None.
- We hereby confirm that all the Figures and Tables in the manuscript are ours. Furthermore, any Figures and images, that are not ours, have been included with the necessary permission for re-publication, which is attached to the manuscript.
- Ethical Clearance: The project was approved by the local ethical committee at the Termez Institute of Engineering and Technology, and Tashkent Institute of Chemical Technology.
- No animal studies are present in the manuscript.
- No human studies are present in the manuscript.
- No potentially identified images or data are present in the manuscript.

Authors' Contribution Statement

M.S conducted the drafting, K.M; G.M: did the conception, design, drafting, S.K; G.M.: was responsible for the acquisition of data; O.T.: did the interpretation; A.N.: participated in the conception, design, drafting and all the authors took part in revision and proofreading.

References

1. Leonid Lazarevich Ubugunov, Enkhtuyaa B, Maria Merkusheva. The content of available mineral phosphorus compounds in chestnut soils of Northern Mongolia upon application of different forms of phosphorite. Eurasian Soil Sc. 2015; 48: 634–642 https://doi.org/10.1134/S1064229315060113.
2. Shahida Waheed, Sabiha-Javied Skhurram, Naila Siddique, Ribha Shakoor, Muhammad Tufail. Rare earths elements in phosphorite and granulated single super-phosphate fertilizers of Pakistan, a study using instrumental neutron activation analysis. J Radioanal Nucl Chem. 2011; 289: 521–528. https://doi.org/10.1007/s10967-011-1112-0.
3. Zaynitdinova LI, Juraeva RN, Tashpulatov JJ, Kukanova SI, Lazutin NA, Mavjudova AM. Influence of Silver and Copper Nanoparticles on the Enzymatic Activity of Soil-Borne Microorganisms. Baghdad Sci J. 2022; 19(6): 1487. https://doi.org/10.21123/bsj.2022.6532.
4. Baturin G N. Chlorine in phosphorites and bone phosphate from Oceanic and marine deposits. Lith Min Resour 2005; 40: 56–67. https://doi.org/10.1007/s10987-005-0006-z
5. Shamim A Dar, K F Khan, Saif A Khan, Samsuddin Khan, M Masroor Alam. Petro-mineralogical Studies of the Paleoproterozoic Phosphorites in the Sonrai basin, Lalitpur District, Uttar Pradesh, India. Nat Resour Res. 2015; 24: 339–348. https://doi.org/10.1007/s11053-014-9260-x
6. Kurbaniyazov R K, Reimov A M, Dadakhodzhaev A T, Namazov Sh S, Beglov B M. Nitrogen-phosphoric fertilizers produced by introduction of Central Kyzylkum phosphate raw material into ammonium nitrate melt. Russ J Appl Chem 2007; 80: 1984–1988. https://doi.org/10.1134/S1070427207110456
7. Melikulova G E, Mirzakulov Kh Ch, Usmanov I I, Isakov A F. Study of the process of obtaining feed dicalcium phosphate from phosphorites of the Central Kyzylkum. Universum. 2018; 6(51).
8. Valentina K, Krut'ko, Lyubov Maslova, Olga N Musskaya, Safronova T V, Anatoly Kulak. Calcium Phosphate Ceramic Foam Obtained by Firing a Hydroxyapatite – Monocalcium Phosphate Monohydrate Powder Mixture. Glas Ceram. 2022; 11(12): 476-480. https://doi.org/10.1007/s10717-022-00435-y
9. Krut'ko V K, Maslova L Y, Musskaya O N, Safronova T V, Kulak A I. Calcium Phosphate Ceramic Foam Obtained by Firing a Hydroxyapatite – Monocalcium Phosphate Monohydrate Powder Mixture. Glas Ceram. 2022; 78: 476–480. https://doi.org/10.1007/s10717-022-00435-y.
10. Safronova T V, Sadilov I S, Chaikun K V, Shatalova T B, Filippov Ya Yu. Ceramics Based on a Powder Mixture of Calcium Hydroxyapatite, Monocalcium Phosphate Monohydrate, and Sodium Hydrogen Phosphate Homogenized under Mechanical Activation Conditions. Inorg Mater Appl Res. 2020; 11: 879–885. https://doi.org/10.1134/S2075113320040346.
11. Shaymardanova M A, Mirzakulov Kh Ch, Melikulova G, Khodjamkulov S Z, Nomozov A K, Shaymardanova Kh.S. Study of process of obtaining monopotassium phosphate based on monosodium phosphate and potassium chloride. Chemical Problems. 2023; 3 (21): 279-293. https://doi.org/10.32737/2221-8688-2023-3-279-293
12. Saheed SA, aweez SJ, Ahmed SM. Effect of different levels and sizes of walnut seed residues on phosphorus availability and alkaline phosphatase activity in calcareous soil. Baghdad Sci J. 2022; 19(2): 240-245.

https://doi.org/10.21123/bsj.2022.19.2.0240.

13. Safranova T V, Sadilov I S, Chaikun K V, Shatalova T B, Filippov Ya Yu. Synthesis of Monetite from Calcium Hydroxyapatite and Monocalcium Phosphate Monohydrate under Mechanical Activation Conditions. Russ J Inorg Chem. 2019; 64(9): 916-922. https://doi.org/10.1134/S0036023619090171
14. Safronova T V, Korneichuk S A, Shatalova T B, LukinaYu S, Sivkov S P, Filippov, Y A, , et al. $Ca_2P_2O_7$–$Ca(PO_3)_2$ Ceramic Obtained by Firing β-Tricalcium Phosphate and Monocalcium Phosphate Monohydrate Based Cement Stone. Glass Ceram 2020; 77: 165–172. https://doi.org/10.1007/s10717-020-00263-y.
15. Daniel Lemos, Rafael Coelho, Sjo Zwart, Albert Tacon, Albert Tacon.. Performance and digestibility of inorganic phosphates in diets for juvenile shrimp (Litopenaeus vannamei): dicalcium phosphate, monocalcium phosphate, and monoammonium phosphate. AqUac Int. 2021; 29: 681–695. https://doi.org/10.1007/s10499-021-00651-3.
16. Musskaya O N, Krut'ko V K, Kulak A I, Safronova T V, Shatalova T B. Thermal Transformations in Hardening Compositions Based on Hydroxyapatite, Monocalcium Phosphate Monohydrate, and Polymeric Binders. Glass Ceram 2020; 77: 256–262. https://doi.org/10.1007/s10717-020-00283-8.
17. Safronova T V, Shatalova T B, Filippov Y Y, Musskaya Olga, Safronov A S, Toshev O. Ceramics in the $Ca_2P_2O_7$–$Ca(PO_3)_2$ System Obtained by Annealing of the Samples Made from Hardening Mixtures Based on Calcium Citrate Tetrahydrate and Monocalcium Phosphate Monohydrate. Inorg Mater Appl. 2020; 11: 777–786. https://doi.org/10.1134/S2075113320040334.
18. Al-Shahwany A, Greabb B M, Abdul Alohab N K. Effect of saline water and potash fertilizer on proline content and water potental in pisum sativum. Baghdad Sci J. 2021; 4(3): 351-7. https://doi.org/10.21123/bsj.2007.4.3.351-357.
19. AL-SHAHWANY A, OWN A. Effect of Saline water and Potash Fertilizer on some chemical constituents in Pisum sativum L.(Var.Senador Cambados) plant. Baghdad Sci J. 2009; 6(2): 257-64. https://doi.org/10.21123/bsj.2009.6.2.257-264.
20. Fouad H K. Determination of hexavalent and tetravalent uranium in phosphate ores through hydr°Chloric acid selective leaching. J Radioanal Nucl Chem 2010; 285: 193–197. https://doi.org/10.1007/s10967-010-0540-6.
21. Pohreliuk I M, Proskurniak R V, Tkachuk O V, Goral A. Effect of parameters of plasma electrolytic oxidation on formation of calcium-phosphate coatings on titanium. Mater Sci. 2018; 54(6): 36–41. http://jnas.nbuv.gov.ua/article/UJRN-0000958918.
22. Tae-Hyun Yoon, Seunggun Won, Jeong-Dae Lee, Jung-Woo Choi, Changsix Ra, Jeong-Dae Kim. Effect of a new phosphorus source, magnesium hydrogen phosphate (MHP) on growth, utilization of phosphorus, and physiological responses in carp Cyprinus carpio. Fish Aquatic Sci. 2016; 19: 39. https://doi.org/10.1186/s41240-016-0038-4.
23. Abinash Das, Sampad Ghosh, Togam Ringu, Nabakumar Pramanik. A Focus on Biomaterials Based on Calcium Phosphate Nanoparticles: an Indispensable Tool for Emerging Biomedical Applications. Bio Nano Sci. 2023; 13: 795–818. https://doi.org/10.1007/s12668-023-01081-6.
24. Turaeva D Yu, Pochitalkinaa I A. Theoretical and Practical Foundations of the Selective Separation of Phosphate Ions from Phosphate Ores with a High Content of Iron Impurities with the Recirculation Method. Theor Found Chem E. 2022; 56: 252–264. https://doi.org/10.1134/S0040579522020142.
25. Nomozov A K, Beknazarov Kh S, Khodjamkulov S Z, Misirov Z Kh. Salsola Oppositifolia acid extract as a green corrosion inhibitor for carbon steel. Indian J Chem Technol. 2023; 30(6): 872-877. https://doi.org/10.56042/ijct.v30i6.6553
26. Muratov B A, Turaev Kh Kh, Umbarov I A, Kasimov Sh A, Nomozov A K. Studying of Complexes of Zn(II) and Co(II) with Acyclovir (2-amino-9-((2-hydroxyethoxy)methyl)-1,9- dihydro-6H-purine-6-OH), Int J Eng Trends Technol. 2024; 72(1); 202-208. https://doi.org/10.14445/22315381/IJETT-V72I1P120.
27. Sara Chahine, Giovanni Garau, Paola Castaldi, Maria Vittoria Pinna, Sara Melito, Giovanna Seddaiu et al. Stabilising fluoride in contaminated soils with monocalcium phosphate and municipal solid waste compost: microbial, biochemical and plant growth impact. Environ Sci Pollut Res. 2022; 29: 41820–41833. https://doi.org/10.1007/s11356-021-17835-2.
28. Otaboev Kh A, Sherkuziev D S, Badalova O A, Radjabov R, Namazov Sh S, Seytnazarov A R. Mineralogical Composition of Kyzylkum Washed Dry Concentrate and Its Processing into Simple Superphosphate. Russ J Gen Chem. 2022; 92: 505–517. https://doi.org/10.1134/S1070363222030203.
29. Turaev Kh, Shavkatova D, Amanova N, Shadhar MH, Berdimurodov E, Bektenov N, et al. Application of Sulfur-2,4-dinitrophenylhydrazine as Modifier for Producing an Advantageous Concrete. Baghdad Sci J. 2023; 20(6(Suppl)): 2414. https://doi.org/10.21123/bsj.2023.9038.

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دراسة عملية الحصول على فوسفات أحادي الكالسيوم باستخلاص حامض الفوسفوريك من فوسفوريات وسط كيزيلكوم

موخيتشكرا شيماردانوفا [1]، خولتورا ميرزاكولوف [2]، غافكار ميليكولوفا [2]، سخومالدين خوجامكولوف [1]، أبرور نوموزوف [1] ، أويبك توشماماتوف [1]

[1] قسم التكنولوجيا الكيميائية، معهد ترمذ للهندسة والتكنولوجيا، ترمذ 190100، أوزبكستان.

[2] كلية التكنولوجيا الكيميائية، معهد طشقند للتكنولوجيا الكيميائية، طشقند، 100011، أوزبكستان.

الخلاصة

تم في هذا البحث إجراء دراسة لإنتاج فوسفات أحادي الكالسيوم بالاعتماد على حامض الفوسفوريك القابل للاستخلاص والذي تم الحصول عليه من فوسفوريت كيزيل-كوم المركزي. تمت دراسة تأثير العوامل المختلفة (الكثافة ودرجة الحرارة واللزوجة للمواد البادئة) على عملية إزالة الفلور وإزالة الكبريت من استخلاص حامض الفوسفوريك وإنتاج فوسفات أحادي الكالسيوم على أساس كربونات الكالسيوم. أجريت التجارب بشكل رئيسي على عينتين، وتمت دراسة تركيب المواد قبل وبعد العملية. ووفقا للنتائج، فإن محتويات المكونات الأخرى تزيد أيضا بشكل متناسب (عينة 1). وبذلك يرتفع محتوى أكسيد الكالسيوم من 1.58% إلى 5.54% بمحتوى 60% **P2O5**، والمغنيسيوم من 0.49% إلى 1.15%، وأكسيد الحديد من 0.25% إلى 0.85%، وأكسيد الألومنيوم من 0.38% إلى 1.24%، وأيونات الكبريتات. من 0.23% إلى 0.76%، يزيد محتوى أكسيد الكالسيوم من 2.09% إلى 7.40% بمحتوى 60% **P2O5**، والمغنيسيوم من 0.80% إلى 2.83%، وأكسيد الحديد من 0.25% إلى 0.90%، وأكسيد الألومنيوم من 0.38% إلى 1.34%، أيونات الكبريتات من 0.23% إلى 0.82%. ينخفض محتوى الفلور من 0.32% إلى 0.17% اعتماداً على تركيز وكالة حماية البيئة (عينة 2). كما تمت دراسة عدد من العوامل مثل معدل وتركيز حمض الفوسفوريك والفصل عالي السرعة لحمض الفوسفوريك في عملية الحصول على فوسفات أحادي الكالسيوم وتركيبه الكيميائي وخصائصه. تمت دراسة وتحليل النتائج التي تم الحصول عليها على أساس كلا العينتين باستخدام الأشعة السينية وطيف الأشعة تحت الحمراء والمجهر الإلكتروني الماسح وتحليل العناصر.

الكلمات المفتاحية: فوسفورات كيزيلكوم المركزية، استخراج حمض الفوسفوريك، طيف الأشعة تحت الحمراء، فوسفات الكالسيوم، المسح المجهري الإلكتروني، الأشعة السينية.