Original Research Article

FEED MONOCALCIUM PHOSPHATE DERIVED FROM WET-PROCESS PHOSPHORIC ACID AND CALCIUM-BASED RAW MATERIALS

ABSTRACT

In this study, granulated feed-grade monocalcium phosphate was produced using highly purified wet-process phosphoric acid (WPA) and finely milled limestone (99.5% CaCO3). The WPA was desulfated to 0.09–0.14% SO_3, defluorinated to 0.18–0.20% F, and concentrated to 50.55% P_2O_5. Under controlled conditions—achieving a 95% reaction rate and a 15-minute decomposition time—a high-quality product was obtained. The final composition included 50.45% digestible P_2O_5, 38.02% water-soluble P_2O_5, 21.14% total CaO, and 14.39% water-soluble CaO, with a fluoride content of 0.16%. The granules achieved 2.13 MPa in strength, with over 85% in the optimal 2-3 mm size range, meeting GOST 23999-80 standards. This phosphate supplement offers high bioavailability for livestock, poultry, and aquaculture.

Keywords: wet-process phosphoric acid (WPA); raw materials; calcium; decomposition; retur; monocalcium phosphate (MCP); granulation; desulfurization.

1. Introduction

The sector of animal husbandry has key significance for sustainable development of agriculture. It contributes to food security, improved nutrition, poverty reduction and economic growth. According to the State Statistics Committee of the Republic of Uzbekistan, the number of cattle in Uzbekistan has increased by 9.2% over the past four years and reached 13.9 million heads as of October 1, 2023. In particular, in 2018 the growth was 2%, in 2019 – 1.2%, in 2020 – 1.8%, and in 2021 – already 3.1%. At the same time, the number of cattle in private farms (personal subsidiary farms) increased from the beginning of 2018 to the end of 2021 by 6.8% or 12.47 million heads**.** As of 2022, a significant portion of livestock is raised in household settings, comprising 76% of cattle, 78% of goats and sheep, and 53% of poultry. These household operations contribute 93% of the nation's milk production, 88% of meat, and 62% of eggs. Overall, the livestock sector accounts for 40.7% of the country’s agricultural output [1].

Minerals are fundamental to the nutrition of livestock, as they are involved in all metabolic processes within the body. They are essential for skeletal development, and play a critical role in the metabolism of proteins, carbohydrates, and lipids. Mineral elements also regulate the body's water balance and hormonal functions. Adequate mineral intake is necessary for the optimal utilization of feed nutrients, the maintenance of animal health, and the achievement of peak productivity. Among the key macroelements, calcium, phosphorus, potassium, magnesium, sulfur, and sodium hold particular importance [2].

In the body, calcium regulates nervous and muscular activity. In muscles, the role of calcium ions is to counteract the factor that blocks adenosine triphosphate (ATP) of actomyosin [3]. Calcium plays a crucial role in enhancing the body's immune defenses by decreasing membrane permeability to harmful substances and improving leukocyte function. In conjunction with vitamin D, calcium also stimulates the activity of cellulolytic bacteria in the rumen, thereby accelerating fiber breakdown and improving digestive efficiency. This synergistic effect promotes better nutrient absorption and overall health in livestock [4].

Phosphorus deficiency in animals may manifest even when dietary calcium levels are elevated. Consequently, it is essential to consider the phosphorus-to-calcium (P:Ca) ratio when formulating feed rations, which typically averages around 1.5:2.0. Additionally, the normal phosphorus concentration in the blood of cows ranges from 1.45 to 2.0 mmol/l, while the calcium level should fall between 2.5 and 3 mmol/l. The regular incorporation of nutritional phosphates into animal diets plays a crucial role in normalizing mineral metabolism, shortening the duration of obesity, and promoting the health of offspring by reducing morbidity rates. Furthermore, it supports the growth of young animals and helps prevent conditions such as rickets, while simultaneously enhancing the nutritional quality of meat and improving overall farm profitability [5-7].

Crude phosphates cannot be used directly by animals but must be converted into a form that is digestible by animals**.** MCP effectively balances dietary phosphorus while ensuring an optimal calcium-to-phosphorus ratio. Its true phosphorus absorption rate surpasses that of other feed phosphates, making it particularly advantageous. MCP is most conveniently utilized as a component of compound feed, as it exhibits good solubility in the gastrointestinal tract, even under low gastric acidity. Consequently, this phosphate is regarded as a valuable mineral supplement for livestock nutrition [8].

According to GOST 23999-80 standards, the mass fraction of phosphorus (P_2O_5) that is soluble in a 0.4% hydrochloric acid solution for feed MCP should be within 55–56% for grade 1 and 50–51% for grade 2. Additionally, the fluorine content must not exceed 0.2%, and the mass fraction of ash insoluble in HCl should be no more than 10%. The pH value should be no less than 3, and the residue retained on a sieve with 3 mm diameter holes should not surpass 80%. For MCP specifically intended for the compound feed industry, the residue on the sieve should not exceed 10%.

Feed calcium phosphates can be obtained in the following ways:

- - decomposition of finely dispersed limestone or chalk with thermal or purified from fluorine and solid suspensions phosphoric acids;
- hydrochloric acid decomposition of phosphate raw materials;
- defluorination of phosphate raw materials or double superphosphate.

In the work [9], based on the neutralization of carbonate raw materials Kazakhstan (98.8% $CaCO_3$) with 75% orthophosphoric acid (chemically pure grade), the following optimal modes for obtaining MCP were proposed: temperature – 75 °C, pH = 3.8–4, L:S = 2:1 and processing time – 1.5–2 hours, during which a product with a content of 59.29% P_2O_5 was obtained.

In addition to thermal acid, purified WPA free from fluorine and other impurities is utilized in the production process. According to the method described in reference**,** WPA is generated by combining purified WPA with a calcium-containing component, along with a recycle from the product itself. This mixing process occurs in two stages: the initial stage involves introducing WPA with a concentration of 62–65% P_2O_5 at a recycle ratio of 1:(0.3–0.5). The second stage, which integrates granulation, takes place in a high-speed mixer, where water is added to the mixture to achieve a moisture content of 9.5–13%. The mixing speed and duration are adjusted to attain a decomposition level of the calcium-containing raw materials between 0.93 and 0.99. The final product is subsequently dried at a temperature range of 105–115 °C.

2. METHODS AND MATERIALS

In this study, we investigated the process of producing granulated MCP through the neutralization of purified and concentrated WPA with limestone flour (99.5% $CaCO_3$) in the presence of a return product (fine fraction with a size of less than 1 mm). The initial WPA contained 18.95% P_2O_5, 0.45% F, 0.27% CaO, 0.26% MgO, 0.41% Fe_2O_3, 0.56% Al_2O_3, and 2.96% SO_3. For its purification, strontium carbonate of grade "chemical pure" (not less than 98% $SrCO_3$) was used for desulfurization, while sodium carbonate (not less than 98% Na_2CO_3) was employed for defluorination.

Evaporation of purified WPA (from 46.01 to 59.41% P_2O_5) was carried out under vacuum at a pressure of 0.65 mm Hg. The chemical composition of the purified and evaporated WPA samples is given in Table 1.

Table 1. Composition of samples of purified and evaporated wet-process phosphoric acid

Concentration P_2O_5, %	Content of components, wt. %					
	CaO	MgO	Fe_2O_3	Al_2O_3	SO_3	F
46.01	0.03	0.39	0.79	1.04	0.09	0.19
50.55	0.03	0.33	0.91	1.37	0.11	0.18
55.65	0.004	0.52	1.27	1.32	0.14	0.20
59.41	0.026	0.41	0.38	0.14	0.17	0.18

The decomposition of limestone flour was conducted at stoichiometric rates ranging from 90% to 100%. Initially, a fraction of the reture product with granule sizes smaller than 1 mm was prepared for different concentrations of evaporated acid. The use of reture promotes optimal conditions for the limestone's decomposition by acid, while also enhancing the mixing and rolling of the reaction mass. This process yields marketable granules (1-4 mm) with an efficiency of at least 70%. Furthermore, the granules produced by this method exhibit enhanced strength, contributing to the overall profitability of the production process.

In a controlled laboratory setting, the requisite amount of limestone flour was introduced into a porcelain vessel maintained at a constant temperature of 80°C within a thermostat. Concurrently, samples of evaporated WPA were preheated to 80°C and incrementally combined with the limestone flour. The duration of the mixing process for the reaction mass was dependent on the WPA concentration, specifically: 30 minutes for a concentration of 46.01% P_2O_5, 15 minutes for both 50.55% and 55.65% P_2O_5, and 10 minutes for 59.41% P_2O_5. A lower concentration of phosphoric acid necessitated a longer duration to achieve a sufficiently loosened mass, which facilitated subsequent granulation and drying processes. Following this stage, the wet product was dried at 100°C until a constant mass was obtained, after which it was finely ground into powder. Chemical analysis of the recycled products was then conducted to determine the content of various forms of

P_2O_5 and CaO, utilizing established analytical techniques [10]. The assimilable forms of P_2O_5 and CaO were quantified by assessing their solubility in a 0.4% HCl solution. The pH of the medium for 10% product solutions was measured using a METTLER TOLEDO FE20/EL20 device, following the method outlined in [11].

3. RESULTS AND DISCUSSION

The detailed composition of the recycled products is presented in Table 2.

Table 2. Composition of samples of the recycled product (return) monocalcium phosphate depending on the rate and concentration of evaporated extraction phosphoric acid

Norm WPA, %	pH value of 10% solution of the product	W moisture, %	Content of components, wt. %									
			P_2O_{5dig} by 0.4% HCl solution	P_2O_5 wat.	CaO tot.	$CaO_{5dig.}$ by 0.4% HCl solution	CaO wat.	MgO tot.	Fe_2O_3 tot.	Al_2O_3 tot.	SO_3 tot.	F
Concentration of evaporated WPA – 46.01% P_2O_5												
100	2.87	4.55	51.65	43.49	20.48	20.18	16.83	0.42	0.86	1.14	0.09	0.21
95	2.98	4.18	51.57	40.64	21.47	21.12	16.26	0.42	0.87	1.14	0.09	0.19
90	3.01	3.92	50.49	38.24	22.17	21.89	15.89	0.41	0.86	1.11	0.09	0.19
Concentration of evaporated WPA – 50.55% P_2O_5												
100	2.92	3.14	51.29	42.95	21.12	20.74	16.52	0.34	0.96	1.40	0.11	0.19
95	3.08	2.27	51.26	38.53	21.73	21.35	15.48	0.32	0.93	1.45	0.11	0.18
90	3.14	2.67	49.44	36.39	22.16	21.79	15.32	0.31	0.92	1.39	0.11	0.16
Concentration of evaporated WPA – 55.65% P_2O_5												
100	3.28	4.77	50.66	44.00	19.91	19.56	17.99	0.47	1.14	1.19	0.13	0.18
95	3.33	4.81	48.96	42.68	20.25	19.89	17.69	0.45	1.10	1.16	0.12	0.17
90	3.37	4.59	47.89	42.02	20.99	20.66	17.09	0.44	1.08	1.13	0.12	0.15
Concentration of evaporated WPA – 59.41% P_2O_5												
100	3.21	4.19	49.40	44.19	20.11	19.77	18.05	0.35	0.31	0.12	0.14	0.14
95	3.29	4.09	48.71	43.09	20.34	19.92	17.50	0.34	0.30	0.11	0.14	0.14
90	3.40	3.82	47.62	40.48	21.11	20.75	16.76	0.33	0.28	0.10	0.15	0.13

Subsequent experiments involved the production of granulated monocalcium phosphate (MCP) by decomposing a mixture of $CaCO_3$ and recycled waste in varying ratios of Product: Recycled waste, using wet-process phosphoric acid (WPA) heated to 80°C. This approach allowed for the analysis of how different proportions of recycled materials influence the decomposition process and the characteristics of the granulated MCP. In the experiments, the amount of retur used varied from 30 to 70% in relation to the total mass of the finished product.

The duration of the stirring process for the reaction mass varied depending on the concentration of phosphoric acid. For 46.01% P_2O_5, stirring lasted 60 minutes, while for 50.55% P_2O_5, the process took 15 minutes. In the case of 55.65% P_2O_5, stirring was reduced to 10 minutes, and for 59.41% P_2O_5, only 5 minutes were required. Granulation of the wet, loosened reaction mass was achieved through intensive mixing and rolling. The resulting MCP granules were then subjected to drying in a drying cabinet at a controlled temperature of 75–80°C for a duration of 4–6 hours. The result was rounded granules. They were cooled and then sieved by size. The granulometric composition of the product was determined by sieve analysis. Particles of 2–3 mm in size were measured for granule strength on the Spring Testing Machine MIP-1 device using a method developed at the SIFI (The Scientific Institute of Fertilizers and Insectofungicides) [12]. Table 3 shows the fractional composition (The percentage of the fraction smaller than 1 mm is not included in the table 3), and Table 4 shows the strength of the granules of finished product samples.

Table 3. The yield of the granule fraction of monocalcium phosphate samples depending on the rate and concentration of evaporated wet-process phosphoric acid, the recycle rate

Norm H_3PO_4, %	Mass ratio Product : Recycle rate											
	1:0.3				1:0.5				1:0.7			
	Residue on a sieve with holes of diameter (not more than, mm), %											
	+5 мм	+3 мм	+2 мм	+1 мм	+5 мм	+3 мм	+2 мм	+1 мм	+5 мм	+3 мм	+2 мм	+1 мм
Concentration of evaporated WPA – 46.01% P_2O_5												
100	2.16	65.45	18.26	10.74	2.20	66.24	17.98	10.35	2.42	68.55	16.52	9.95

95	1.36	66.44	18.17	10.04	1.84	68.31	17.56	9.25	1.93	69.60	16.12	9.64
90	1.11	67.39	17.88	9.82	1.31	69.29	16.84	8.74	1.44	71.49	15.11	8.45
Concentration of evaporated WPA – 50.55% P_2O_5												
100	1.29	68.12	16.85	9.86	2.02	70.21	15.34	9.06	2.31	70.07	15.11	8.94
95	0.97	70.13	15.65	9.14	1.33	72.17	14.04	8.77	1.55	71.06	14.93	8.72
90	0.85	72.01	14.29	8.23	1.05	73.05	13.78	8.09	1.13	72.13	13.99	8.45
Concentration of evaporated WPA – 55.65% P_2O_5												
100	2.89	67.31	17.78	9.69	3.12	66.14	17.84	10.25	3.16	67.51	17.44	10.02
95	2.47	67.25	17.25	9.46	2.88	68.20	16.79	9.35	2.99	69.24	16.12	9.03
90	2.19	69.32	15.76	9.14	2.34	69.08	16.01	9.17	2.56	72.29	14.08	8.63
Concentration of evaporated WPA – 59.41% P_2O_5												
100	2.26	68.03	16.77	9.51	2.30	68.13	16.71	9.48	2.43	69.34	15.67	9.83
95	1.15	69.15	15.68	9.11	1.22	70.04	15.09	9.14	1.51	70.19	15.03	8.97
90	0.97	70.11	15.26	8.82	1.07	71.19	14.15	8.25	1.23	71.22	13.94	8.11

Table 4. Strength of granules of monocalcium phosphate samples depending on the rate and concentration of wet-process phosphoric acid, the recycle rate

Norm H_3PO_4, %	Granule strength (granule diameter 2–3 mm), MPa		
	Mass ratio Product : Recycle rate		
	1:0.3	1:0.5	1:0.7
Concentration of evaporated WPA – 46.01% P_2O_5			
100	2.07	1.56	2.15
95	2.25	2.14	2.28
90	2.4	2.32	2.35
Concentration of evaporated WPA – 50.55% P_2O_5			
100	1.85	1.9	1.86
95	1.94	2.48	2.13
90	2.06	2.65	2.24
Concentration of evaporated WPA – 55.65% P_2O_5			
100	1.65	1.69	1.66
95	1.82	2.2	2.06
90	1.97	2.31	2.13
Concentration of evaporated WPA – 59.41% P_2O_5			
100	1.5	1.58	1.52
95	1.66	1.79	1.74
90	1.85	1.98	1.86

Table 3 demonstrates that across all concentrations and rates of WPA, as well as varying amounts of supplied recycle, the majority of the commercial fraction (2–3 mm) exceeds 80%, while the fine fraction remains below 10%. The data indicate that both the concentration of WPA and the amount of recycle have minimal impact on the commercial fraction yield. A slight improvement in the commercial fraction yield is observed with a decrease in the phosphoric acid rate, but this effect is marginal.

Relatively high strength of granules is observed when using evaporated WPA with a concentration of 46.01% P_2O_5. The lower the acid rate, the higher the strength of the granules. The highest granule strength, reaching 2.65 MPa, was observed with an acid concentration of 50.55% P_2O_5 and at 90% of stoichiometry, with a product-to-recycle ratio of 1:0.5. Conversely, the lowest granule strength, recorded at 1.5 MPa, occurred with an acid concentration of 59.41% P_2O_5 and 100% of stoichiometry, with a product-to-recycle ratio of 1:0.7 (Table 4). Despite these variations, all granule strengths meet the requirements for agricultural applications.

The compositions of the products for each concentration, rate of evaporated WPA, and mass ratio of product to recycle are presented in Tables 5–8. The degree of formation of $Ca(H_2PO_4)_2$ in the products was calculated using the following formula:

$$\frac{CaO_{water.} : P_2O_{5water.}}{0.39944} \cdot 100\ \%$$

here, CaO_{water}. in finished product, %; $P_2O_{5water.}$ in finished product, %; 0.3944 – CaO : P_2O_5 in monocalcium phosphate.

Table 5. Composition of granulated monocalcium phosphate depending on the rate of evaporated extraction phosphoric acid and the mass ratio Product:Recycle ratio (concentration of H_3PO_4 – 46.01% P_2O_5)

Norm H_3PO_4, %	pH value of 10% solution of the product	W moisture, %	Content of components, wt. %										Degree of formation of $Ca(H_2PO_4)_2$, %
			P_2O_{5dig} by 0.4% HCl solution	P_2O_5 wat.	CaO tot.	CaO_{5dig} by 0.4% HCl solution	CaO wat.	MgO tot.	Fe_2O_3 tot.	Al_2O_3 tot.	SO_3 tot.	F	
At a recycle ratio of 1:0.3													
100	2.88	3.83	50.51	41.88	20.44	20.11	16.29	0.38	0.82	1.06	0.08	0.12	98.62
95	2.96	2.36	49.50	41.39	21.02	20.98	15.93	0.39	0.81	1.06	0.08	0.11	97.59
90	3.04	2.95	48.47	39.44	22.08	21.62	14.88	0.38	0.81	1.06	0.07	0.11	95.66
At a recycle ratio of 1:0.5													
100	2.91	3.51	49.85	41.28	20.36	20.07	15.97	0.37	0.81	1.05	0.08	0.11	98.09
95	3.03	3.26	48.86	41.03	20.86	20.69	15.62	0.38	0.80	1.05	0.08	0.10	96.52
90	3.14	2.96	47.84	39.09	21.75	21.51	14.65	0.37	0.80	1.05	0.07	0.10	95.02
At a recycle ratio of 1:0.7													
100	2.89	3.85	49.39	41.09	20.12	19.94	15.86	0.37	0.80	1.05	0.08	0.10	97.87
95	3.06	3.11	48.41	39.78	20.69	20.57	15.46	0.38	0.80	1.04	0.08	0.09	98.54
90	3.15	2.72	46.43	37.58	21.62	21.36	14.53	0.37	0.79	1.04	0.07	0.09	98.03

Table 6. Composition of granulated monocalcium phosphate depending on the rate of evaporated extraction phosphoric acid and the mass ratio Product: Recycle ratio (concentration of H_3PO_4 – 50.55% P_2O_5)

Norm H_3PO_4, %	pH value of 10% solution of the product	W moisture, %	Content of components, wt. %										Degree of formation of $Ca(H_2PO_4)_2$, %
			P_2O_{5dig} by 0.4% HCl solution	P_2O_5 wat.	CaO tot.	CaO_{5dig} by 0.4% HCl solution	CaO wat.	MgO tot.	Fe_2O_3 tot.	Al_2O_3 tot.	SO_3 tot.	F	
At a recycle ratio of 1:0.3													
100	2.91	1.71	51.11	41.91	20.10	19.99	14.84	0.31	0.93	1.38	0.10	0.18	89.78
95	3.10	1.34	50.63	38.15	21.94	21.27	14.56	0.29	0.92	1.40	0.11	0.17	96.77
90	3.18	1.36	49.36	37.91	21.18	20.81	14.17	0.26	0.91	1.37	0.11	0.17	94.77
At a recycle ratio of 1:0.5													
100	2.93	2.26	50.86	41.08	20.03	19.26	14.68	0.30	0.92	1.37	0.10	0.17	90.61
95	3.16	1.30	50.45	38.02	21.60	21.14	14.39	0.28	0.91	1.39	0.10	0.16	95.96

90	3.29	1.16	49.28	37.66	21.02	20.63	14.03	0.24	0.90	1.38	0.10	0.15	94.46
At a recycle ratio of 1:0.7													
100	2.84	1.33	50.67	40.87	19.86	19.16	14.76	0.28	0.91	1.35	0.10	0.16	91.57
95	2.99	1.09	50.22	37.92	21.13	20.64	14.32	0.27	0.90	1.37	0.10	0.17	95.75
90	3.04	0.86	49.07	37.38	20.77	20.36	14.01	0.25	0.88	1.36	0.10	0.15	95.03

Table 7. Composition of granulated monocalcium phosphate depending on the rate of evaporated extraction phosphoric acid and the mass ratio Product: Recycle ratio (concentration of H_3PO_4 – 55.65% P_2O_5)

Norm H_3PO_4, %	pH value of 10% solution of the product	W moisture, %	Content of components, wt. %										Degree of formation of $Ca(H_2PO_4)_2$, %
			P_2O_{5dig} by 0.4% HCl solution	P_2O_5 wat.	CaO tot.	CaO_{5dig} by 0.4% HCl solution	CaO wat.	MgO tot.	Fe_2O_3 tot.	Al_2O_3 tot.	SO_3 tot.	F	
At a recycle ratio of 1:0.3													
100	3.24	3.13	49.89	43.78	19.76	19.45	16.02	0.40	1.12	1.17	0.11	0.16	92.78
95	3.30	3.08	48.31	41.56	20.11	19.78	15.89	0.39	1.08	1.15	0.12	0.15	96.94
90	3.34	2.90	47.56	40.07	20.65	20.35	15.31	0.35	1.05	1.11	0.12	0.16	96.88
At a recycle ratio of 1:0.5													
100	3.24	2.54	49.84	43.56	19.71	19.34	16.00	0.39	1.11	1.15	0.11	0.15	93.13
95	3.29	2.60	48.17	41.06	20.06	19.65	15.81	0.37	1.06	1.14	0.11	0.15	97.63
90	3.36	2.83	47.12	39.69	20.45	20.32	15.27	0.33	1.03	1.10	0.11	0.15	97.55
At a recycle ratio of 1:0.7													
100	3.29	2.68	49.73	43.46	19.70	19.28	15.98	0.38	1.10	1.14	0.11	0.15	93.23
95	3.37	2.42	48.06	40.86	19.93	19.52	15.77	0.35	1.05	1.13	0.11	0.14	97.86
90	3.36	2.90	46.95	39.45	20.33	20.25	15.16	0.31	1.02	1.08	0.10	0.14	97.44

Table 8. Composition of granulated monocalcium phosphate depending on the rate of evaporated extraction phosphoric acid and the mass ratio Product: Recycle ratio (concentration of H_3PO_4 – 59.41% P_2O_5)

Norm H_3PO_4, %	pH value of 10% solution of the product	W moisture, %	Content of components, wt. %										Degree of formation of $Ca(H_2PO_4)_2$, %
			P_2O_{5dig} by 0.4% HCl solution	P_2O_5 wat.	CaO tot.	CaO_{5dig} by 0.4% HCl solution	CaO wat.	MgO tot.	Fe_2O_3 tot.	Al_2O_3 tot.	SO_3 tot.	F	
At a recycle ratio of 1:0.3													
100	3.19	1.75	50.05	44.48	19.78	19.70	17.11	0.29	0.24	0.11	0.12	0.11	97.53
95	3.26	1.65	48.61	44.36	20.30	20.18	16.93	0.27	0.23	0.12	0.12	0.12	96.77
90	3.38	2.09	47.46	43.22	21.04	20.75	16.49	0.24	0.22	0.10	0.12	0.11	96.74
At a recycle ratio of 1:0.5													
100	3.22	1.75	49.84	43.66	19.72	19.68	16.77	0.24	0.19	0.09	0.09	0.10	97.39
95	3.28	1.77	48.39	44.04	20.23	19.98	16.94	0.23	0.18	0.09	0.10	0.10	97.53
90	3.32	1.91	47.41	43.15	20.97	20.69	16.58	0.20	0.17	0.08	0.09	0.10	97.42
At a recycle ratio of 1:0.7													
100	3.20	2.19	49.55	42.38	19.69	19.63	16.29	0.20	0.18	0.09	0.08	0.10	97.46
95	3.29	1.97	48.27	43.58	20.11	19.95	16.77	0.20	0.18	0.08	0.09	0.09	97.57
90	3.38	2.22	47.09	42.13	20.89	20.63	16.20	0.18	0.17	0.07	0.09	0.09	97.51

Table 5 clearly demonstrates that with a Product : Recycle ratio of 1:0.3 and a WPA concentration of 46.01% P_2O_5, increasing the acid rate from 90% to 100% leads to an increase in the content of the assimilable form of P_2O_5 from 48.47% to 50.51%. At a Product : Recycle ratio of 1:0.5, this value increases from 47.84% to 49.85%, and at 1:0.7, from 46.42% to 49.39%. Similarly, for WPA with a concentration of 50.55% P_2O_5, the corresponding values shift from 49.36% to 51.11%, from 49.28% to 50.86%, and from 49.07% to 50.67%, respectively (Table 6).

As a result, the content of the water-soluble form of P_2O_5 increases progressively from 39.44% to 41.88%, from 39.09% to 41.28%, and from 37.58% to 41.09% for WPA concentrations of 46.01% P_2O_5, with Product : Recycle ratios of 1:0.3, 1:0.5, and 1:0.7, respectively. Similarly, for WPA with a concentration of 50.55% P_2O_5, the values range from 37.91% to 41.91%, from 37.66% to 41.08%, and from 37.38% to 40.87%. Monocalcium phosphate produced under these conditions, with such concentrations of digestible and water-soluble P_2O_5, is considered a high-quality, efficient product. It is suitable for use as a phosphate supplement in the diets of cattle, poultry, and fish.

The interaction patterns of limestone flour with 55.65% and 59.41% WPA solutions, at Product:Recycle ratios of 1:0.3, 1:0.5, and 1:0.7, exhibit similar trends (Tables 7 and 8). The primary distinction lies in the absolute values of the component contents. A greater excess of acid leads to more complete decomposition of $CaCO_3$. The difference between the assimilable and water-soluble forms of P_2O_5 provides an indication of the dicalcium phosphate content in the product.

The resulting products contain substantial amounts of both digestible and water-soluble forms of CaO, a critical element for bone tissue development in all living organisms. Specifically, for the concentration of WPA at 46.01% P_2O_5, the feed products exhibit 19.94–21.62% digestible CaO_{dig}. and 14.53–16.29% water-soluble CaO_{wat}. With an WPA concentration of 50.58% P_2O_5, these values range from 19.16–21.27% digestible $CaO_{dig.}$ and 14.01–14.84% water-soluble CaO_{wat}. For a 59.41% P_2O_5 concentration, the products contain 19.63–20.75% digestible $CaO_{dig.}$ and 16.20–17.11% water-soluble $CaO_{wat.}$.

In a previous study, we explored the process of producing granulated monocalcium phosphate by decomposing limestone flour with thermal phosphoric acid in the presence of a recycled product. The optimal conditions identified were: phosphoric acid concentration at 50.55% P_2O_5, an H_3PO_4 rate of 95%, a decomposition time of 5 minutes, and a recycle ratio of 1:0.5. Under these conditions, the resulting product had the following composition (wt. %): 53.42% $P_2O_{5dig.}$, 52.45% $P_2O_{5wat.}$, 21.85% $CaO_{dig.}$, 20.67% $CaO_{wat.}$, with a pH of 2.93 and a granule strength of 2.70 MPa.

The following The X-ray diffraction (XRD) patterns depict the crystallographic structure of MCP samples, which were selected based on their chemical composition and physical properties. The XRD analysis provides detailed insights into the crystalline phases present in the MCP samples, highlighting the degree of crystallinity, potential impurities, and the overall phase composition (Fig. 1.). Through this analysis, key structural features of the MCP are identified, which are critical for understanding its reactivity, solubility, and effectiveness as a feed additive.

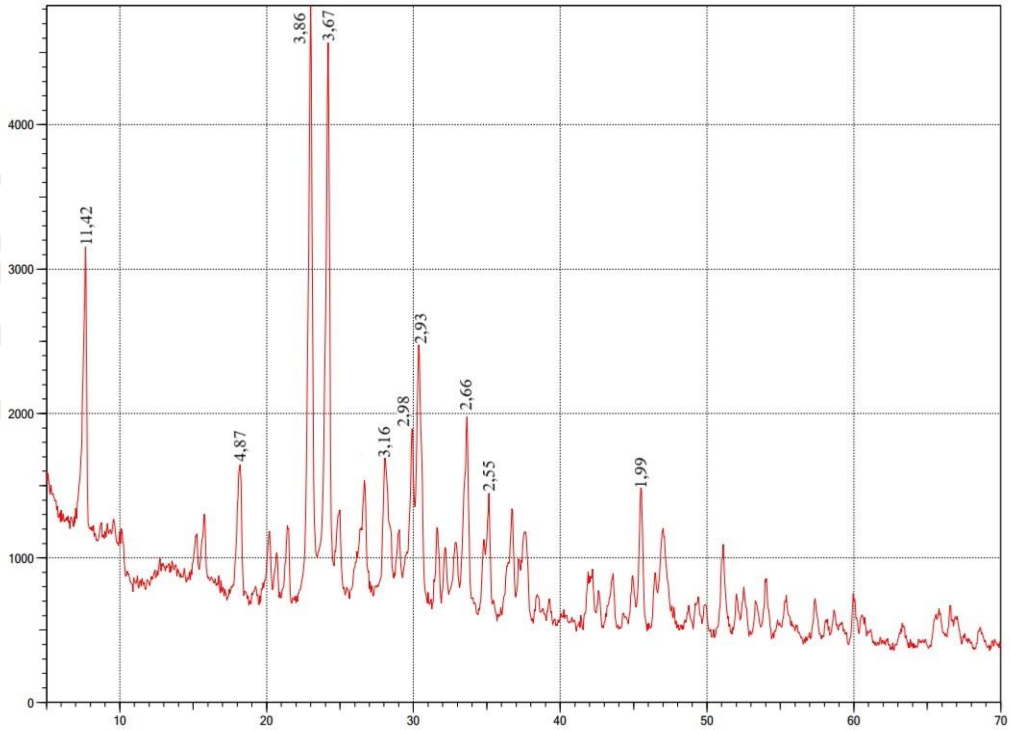

Fig. 1. The XRD patterns of monocalcium phosphate (50.55% P_2O_5, an H_3PO_4 norm of 95%)

The XRD composition of granulated monocalcium phosphate is detailed in Table 9. This table presents the various crystalline phases identified in the calcined bone meal, providing insights into the mineralogical composition post-treatment. Understanding these phase compositions is crucial for optimizing the chemical processes involved in producing monocalcium phosphate, as the crystalline structure directly influences reactivity and the efficiency of the phosphate production process.

Table 9. The XRD composition of granulated monocalcium phosphate (50.55% P_2O_5, an H_3PO_4 norm of 95%)

No.	dÅ	The corresponding substance
1	11,42	$Ca(H_2PO_4)_2 \cdot H_2O$
2	4,87	$Ca_2P_2O_7$
3	3,86	$Ca_3(PO_4)_2 \cdot H_2O$
4	3,67	$Ca(H_2PO_4)_2$
5	3,16	$Ca_3(PO_4)_2 \cdot H_2O$
6	2,93	$Ca(H_2PO_4)_2 \cdot H_2O$
7	2,98	$Ca(H_2PO_4)_2 \cdot H_2O$
8	2,66	$Ca(H_2PO_4)_2 \cdot H_2O$
9	2,55	$Ca_2P_2O_7$
10	1,99	$Ca(H_2PO_4)_2 \cdot H_2O$

As it is seen that MCP obtained from original evaporated WPA has diffraction peaks monocalcium phosphate with maximal 11.42, 3.67 Å and minimal 2.93, 2.98, 2.66 and 1.99 Å. Whereas, diffraction lines with 3.86, 3.16 Å belong to Tricalcium phosphate and 4.87, 2.55 Å belong to calcium pyrophosphate (Fig. 1 and Table 9). XRD analysis confirms that the WPA containing 50.55% P_2O_5 primarily led to the formation of (MCP) in the resulting lime product. This dominant phase suggests successful decomposition of limestone flour and optimal conditions for MCP formation, validating its suitability for use as a feed phosphate additive.

4. CONCLUSION

In our case, using evaporated WPA with a concentration of 50.55% P_2O_5, an H_3PO_4 rate of 95%, a decomposition time of 15 minutes, and a recycle ratio of 1:0.5, we successfully obtained granulated monocalcium phosphate (MCP) with the following composition (wt.%): digestible P_2O_5 - 50.45; water-soluble P_2O_5 - 38.02; digestible CaO - 21.14; water-soluble CaO - 14.39; fluorine (F) - 0.16; pH - 3.16; and a granule strength of 2.13 MPa. The degree of formation of $Ca(H_2PO_4)_2$ was 95.96%, with more than 85% of the product falling into the 2-3 mm commercial fraction. According to GOST 23999-80, the product complies with the second-grade classification.

This study demonstrates the feasibility of producing feed-grade phosphate in the form of granulated MCP through the decomposition of purified limestone flour using evaporated WPA and a recycled product. This process offers a practical and efficient method for producing high-quality phosphate feed additives.

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