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Research of the Crystallization Process of Monocalcium Phosphate and the Multiplicity of Using the Mother Liquor

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ABSTRACT: The results of studies on the crystallization and isolation of crystalline monocalcium phosphate from a concentrated suspension obtained by decomposition of limestone from the Kutarmina deposit with evaporated extraction phosphoric acid from phosphate raw materials of Central Kyzylkums at elevated acid rates are presented. The influence of the norm and concentration of acid, crystallization temperature, the cooling rate of the solution and the multiplicity of the use of the mother liquor on the chemical composition of monocalcium phosphate, the mother liquor, the degree of transition of the components to the solid phase and on the technological parameters of the process was studied.

KEY WORDS: Limestone, Evaporation, Crystallization, Cooling Rate, Drying, Crystalline Monocalcium Phosphate.

I.INTRODUCTION

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 machine-building industries. The main amount of phosphate raw materials is used to obtain mineral fertilizers (about 80%), 12% - to obtain detergents, 5% - to obtain feed phosphates, 3% - to obtain special-purpose products [1-4].

II.LITERATURE SURVEY

The world assortment of basic mineral top dressing has more than 10 names. Phosphorus-containing mineral fertilizers based on calcium, sodium, ammonium phosphates and other chemical components have been widely used in animal husbandry, poultry farming, and fish farming [5, 6].
The most valuable are calcium phosphates [7]. In feeds where there is a significant amount of calcium and not enough phosphorus, phosphoric sodium supplements are used. To compensate for the lack of protein in the diets of cattle and sheep, non–protein nitrogen-containing compounds - ammonium phosphates are used [8].
Modern industrial methods of livestock production are characterized by the widespread use of mineral feed additives, which contribute to increasing productivity, livestock safety and reducing feed costs [9].
Phosphoric salts of higher qualification are obtained by neutralization of deeply purified thermal phosphoric acid to the corresponding grades "p", "pfa", "chp" with corresponding carbonates or metal hydroxides [10]. The chemistry of obtaining monocalcium phosphate, dicalcium phosphate and their mixtures can be represented by the following reaction equations:

$$CaCO_3 + 2H_3PO_4 \rightarrow Ca(H_2PO_4)_2 \cdot H_2O + CO_2$$
$$CaCO_3 + H_3PO_4 \rightarrow CaHPO_4 + CO_2 + H_2O$$

Another way to obtain feed and cleaner calcium phosphates involves the interaction of dicalcium phosphate dihydrate with purified phosphoric acid. The process of obtaining monocalcium phosphate is described by the following equation:

$$CaHPO_4 \cdot 2H_2O + H_3PO_4 \rightarrow Ca(H_2PO_4)_2 \cdot H_2O + H_2O$$

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Depending on the norm of phosphoric acid, a mixture of monocalcium phosphate and dicalcium phosphate with their different ratios can be obtained.

In recent years, studies have been carried out to obtain feed and purer calcium phosphates from extraction phosphoric acid (EPA), the essence of which is to purify the acid from fluorine, sulfates, iron, aluminum from other interfering impurities by introducing alkali metals, partial neutralization with ammonia in the presence of salts calcium, separating precipitated compounds and isolating dicalcium phosphate [11].

In recent years, methods for obtaining monocalcium phosphate by liquid-phase circulation method have become widespread. In the works using solubility diagrams in $CaO-P_2O_5-HCl-H_2O$ and $CaO-P_2O_5-H_2O$ systems, graphical calculations of the process of obtaining monohydrate of monocalcium phosphate from Karatau phosphorites [12, 13] and Central Kyzylkums [14, 15] under conditions of mother liquor recycling at a temperature of 40°C.

In this regard, our research was aimed at obtaining fluorinated monocalcium phosphate with feed and higher purity from EPA based on Central Kyzylkums phosphorites, which is heavily contaminated with one-and-a-half oxides and fluorine [16, 17].

III.RESEARCH METHODS

In order to establish the optimal technological parameters and indicators of the process of crystallization and filtration, as well as to increase the maximum yield of P_2O_5 in the final product and reuse the mother liquor to create a cyclic method, the process of crystallization and filtration of a monocalcium phosphate suspension obtained by decomposition of calcium carbonate of defluorinated and desulphated EPA from phosphorites was studied. Central Kyzylkums, previously evaporated to a content of 40-55% P_2O_5 at its rate of 300-500% of the stoichiometry for the formation of monocalcium phosphate.

EPA was preliminarily purified from sulfates and fluorine using phosphate concentrate and sodium salts – carbonate and metasilicate [8–11]. The purified acid had the composition (wt %): P_2O_5 - 17.02; SO_4 - 0.23; CaO - 1.58; MgO - 0.49; Fe_2O_3 - 0.25; Al_2O_3 - 0.38; F - 0.30. As a calcium-containing raw material, natural limestone of the Kutarma deposit was used, containing (wt.%): CaO - 54.88; MgO - 0.47; SiO_2 - 0.49; Fe_2O_3 - 0.10; Al_2O_3 - 0.21.

The study of the process was carried out on 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 3 hours. After reaching the specified time, the phosphate mass was filtered at the test temperature to separate the insoluble residue, the filtrate was cooled to a temperature of 60-70°C and crystalline monocalcium phosphate was separated, washed with water and dried at a temperature of 100-110°C.

The analysis of the initial, intermediate and final products was carried out by known methods of chemical and physico–chemical analysis [12-14].

IV.EXPERIMENTAL RESULTS

Crystallization of monocalcium phosphate was carried out at a temperature of 70-80°C, suspension concentrations of 50-55% P_2O_5 and the cooling rate was adjusted every 5°C (from 15, 10 and 5°C). The results are shown in Tables 1 and 2.

It can be seen from the obtained results that the main factor affecting the filtration rate of crystalline monocalcium phosphate is the cooling rate of solutions. Decreasing the solution cooling rate from 15 to 5.0°C/hour at a solution concentration of 50% and a process temperature of 70°C, the filtration time decreases from 1.63 min to 0.53 min. The decrease in the rate of cooling of the monocalcium phosphate solution from 15 to 5.0°C/hour increases the sludge removal from 450 to 820 kg/m3·hour for a solution concentration of 50%.

Changes in the concentration and temperature of the solution within 50-55% and 70-80°C do not have a noticeable effect on the nature of the change in the filtration time and sediment removal. The slow cooling rate contributes to the precipitation of less impurities in the sediment. As the cooling rate decreases, the amount of SO_3, MgO, Al_2O_3, Fe_2O_3 and F impurities in the product decreases by about a factor of two. An increase in the concentration of solutions over 50% leads to a slow increase in the content of impurities in the finished product.

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Table 1. Influence of the concentration of solutions, temperature and cooling rate on the technological parameters of crystallization and the chemical composition of monocalcium phosphate

$C_{susp.}$ P_2O_5,%	$t_{cristal.}$, °C	Cooling rate, °C/hour	L:S	Filtration time, min	Sediment removal, kg/m^2•h	Chemical composition, wt. %						
						P_2O_5	SO_3	CaO	MgO	Al_2O_3	Fe_2O_3	F
Initial suspension						50,01	0,768	4,366	1,709	1,332	0,860	0,171
50	70	15,0	7,72	1,63	450	54,20	0,190	18,70	0,067	0,096	0,085	0,014
		10,0	7,81	0,95	680	54,46	0,185	18,81	0,062	0,087	0,078	0,012
		5,0	7,86	0,53	820	54,52	0,182	18,84	0,060	0,081	0,074	0,009
	80	15,0	8,91	0,45	680	54,41	0,192	18,35	0,069	0,097	0,088	0,014
		10,0	9,05	0,40	770	54,62	0,183	18,27	0,064	0,089	0,081	0,011
		5,0	9,11	0,36	860	54,65	0,181	18,21	0,062	0,083	0,077	0,009
Initial suspension						55,00	0,845	4,80	1,880	1,465	0,946	0,160
55	70	15,0	6,60	1,10	580	54,53	0,189	18,22	0,067	0,094	0,083	0,013
		10,0	6,68	0,67	710	54,71	0,181	18,10	0,062	0,086	0,078	0,011
		5,0	6,71	0,40	890	54,73	0,180	18,08	0,060	0,081	0,075	0,009
	80	15,0	7,61	0,30	760	54,88	0,187	18,15	0,065	0,092	0,080	0,012
		10,0	7,70	0,28	830	55,03	0,180	18,03	0,061	0,084	0,075	0,010
		5,0	7,74	0,26	980	55,06	0,179	17,99	0,059	0,080	0,074	0,008

Table 2. The degree of transition of the components of the solutions into the product and the chemical composition of the mother liquor after the crystallization of monocalcium phosphate

$C_{susp.}$ P_2O_5, %	$t_{cristal.}$, °C	Cooling rate, °C/hour	The degree of transition of components into the product, %							The chemical composition of the mother liquor, wt. %						
			P_2O_5	SO_3	CaO	MgO	Al_2O_3	Fe_2O_3	F	P_2O_5	SO_3	CaO	MgO	Al_2O_3	Fe_2O_3	F
50	70	15,0	18,24	4,76	67,64	0,80	0,16	1,96	0,87	31,61	0,498	1,166	1,105	0,87	0,56	0,707
		10,0	18,19	4,72	67,53	0,79	0,15	1,94	0,85	31,56	0,501	1,162	1,108	0,89	0,58	0,709
		5,0	18,17	4,71	67,51	0,78	0,14	1,93	0,82	31,54	0,502	1,159	1,110	0,90	0,59	0,712
	80	15,0	18,78	4,88	68,35	0,83	0,17	2,00	0,91	31,34	0,491	1,147	1,162	0,92	0,61	0,715
		10,0	18,71	4,84	68,21	0,82	0,16	1,98	0,89	31,28	0,494	1,142	1,167	0,95	0,63	0,717
		5,0	18,68	4,83	68,15	0,81	0,15	1,97	0,86	31,25	0,495	1,140	1,169	0,96	0,64	0,719
55	70	15,0	19,23	4,96	69,60	0,86	0,22	2,09	0,96	32,13	0,479	1,184	1,182	0,98	0,67	0,725
		10,0	19,17	4,93	69,47	0,83	0,21	2,04	0,94	32,18	0,474	1,181	1,187	1,00	0,70	0,729
		5,0	19,15	4,92	69,43	0,82	0,20	2,02	0,91	32,20	0,471	1,180	1,189	1,01	0,71	0,731
	80	15,0	19,86	5,04	70,25	0,91	0,27	2,15	0,99	32,02	0,473	1,178	1,179	1,04	0,73	0,733
		10,0	19,79	5,02	70,13	0,89	0,23	2,12	0,96	32,08	0,468	1,175	1,174	1,07	0,75	0,737
		5,0	19,77	5,01	70,12	0,88	0,21	2,11	0,94	32,10	0,465	1,174	1,172	1,08	0,76	0,740

The research results show that the optimal parameters of the crystallization process and the separation of crystalline monocalcium phosphate are the suspension concentration of at least 50%, suspension cooling at a rate of not more than 5.0°C/hour to a temperature of 70-80°C. At the same time, the resulting mother liquor after separation of crystalline monocalcium phosphate can be reused, after concentration, for the crystallization of monocalcium phosphate.

In order 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 repeated use of the mother liquor on the composition of the resulting crystalline monocalcium phosphate of feed and higher purity was studied. At the same time, the mother liquor after crystallization of the product from the previous stage was subjected to evaporation to a given concentration (tables 3 and 4).

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The process of the cyclic method for obtaining crystalline monocalcium phosphate using a mother liquor was carried out as follows: solutions obtained by decomposition of calcium carbonate of one stripped off EPA from phosphorites of the Central Kyzylkums in the presence of one stripped off mother liquor at a rate of 400% of the stoichiometry for the formation of monocalcium phosphate with a temperature of 90°C were poured into a reactor with a water jacket cooled by water. After cooling to 60-80°C, with constant stirring of the solution, the coolant supply was reduced, cooling at a rate of 5.0°C/hour. Upon reaching a temperature of 60–80°C, cooling was stopped, and the suspension was separated on a Buchner funnel (filter surface 0.005 m^2).

Next, the crystals on the filter were squeezed out by sucking in air for 2 minutes. Washed with acetone and dried at 100°C for 1 hour. Then, according to standard methods, chemical analyzes of the initial, mother solutions and crystals of monocalcium phosphate were carried out, and the indicators of technological parameters (ratio L:S, time and filtration rate) and the degree of transition of the components were determined, the results of which are shown in tables 3 and 4.

Table 3. The effect of repeated use of the mother liquor on the composition of the resulting product

Stage	Sample	Chemical composition, wt. %						
		P_2O_5	SO_3	CaO	MgO	Al_2O_3	Fe_2O_3	F
Initial EPA		17,0	0,230	1,58	0,490	0,38	0,25	0,310
1	Initial	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
	Mother liquor	31,61	0,498	1,166	1,105	0,870	0,560	0,673
2	Initial	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
	Mother liquor	31,64	0,570	0,955	1,313	1,028	0,655	0,788
3	Initial	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
	Mother liquor	31,66	0,057	0,956	1,523	1,191	0,750	0,903
4	Initial	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
	Mother liquor	31,755	0,679	1,09	1,732	1,34	0,844	1,013

Table 4. The effect of repeated use of the mother liquor on the technological parameters of the process

Stage	Ratio L:S	Filtration time, min.	Sediment removal, $kg/m^2 \cdot h$	The degree of transition to the product, mass. %						
				P_2O_5	SO_3	CaO	MgO	Al_2O_3	Fe_2O_3	F
1	7,61	0,30	760	18,17	4,71	67,51	0,78	0,14	1,93	1,33
2	7,61	0,30	755	18,16	4,15	71,72	0,66	0,12	1,65	1,14
3	7,60	0,32	755	18,15	3,71	71,70	0,57	0,10	1,45	1,00
4	7,59	0,38	740	17,99	7,58	69,64	0,60	1,07	1,57	1,39

From the experimental data (tables 3 and 4) it can be seen that with threefold reuse of the mother liquor, the increase in the degree of transition of impurities into product crystals is relatively low and amounts, %: for SO_3 - 4.19; MgO - 0.67; Al_2O_3 - 0.12; Fe_2O_3 - 1.68 and F - 0.82. This is due to the fact that during the reuse of the mother liquor, the content of impurities in the product gradually increases. The yield of P_2O_5 in qualified feed monocalcium phosphate is 67.51%.

As a result of the research, it was determined that the three-fold reuse of the circulating mother liquor can be considered optimal, which ensures the production of feed monocalcium phosphate, and for further use of the mother liquor, preliminary purification from some interfering impurities is necessary.

V.CONCLUSION

Thus, the conducted studies have shown the fundamental possibility of isolating monocalcium phosphate crystalline hydrate from stripped off solutions obtained on the basis of EPA from phosphate raw materials of Central Kyzylkums by preliminary purification from fluorine ions, sulfates, and other associated components and sequential neutralization with calcium carbonate. The optimal technological parameters and indicators of the crystallization process and reuse of

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the mother liquor for the maximum yield of crystalline monocalcium phosphate and its chemical composition have been established. The resulting products fully comply with the requirements of GOST 23999-80 for feed phosphates.

REFERENCES

[1] Arifdjanova K.S., Mirzakulov Kh.Ch., Khujamberdiev Sh.M., Melikulova G.E. Synthesis of sodium ammonium tetrahydrate and sodium dihydrophosphate based on extraction phosphoric acid from phosphorites of Central Kyzylkums // Journal "Chemistry and Chemical Technology", – Tashkent, 2021. No.1. pp. 19-25.
[2] Arifdjanova K.S., Mirzakulov Kh.Ch., Melikulova G.E., Khujamkulov S.Z., Usmanov I.I. Research of the process of desulfurization of extraction phosphoric acid from phosphorites of Central Kyzylkums // Journal "Chemical Industry". Sankt-Petersburg, Russia. 2017. No.5. pp. 18-25.
[3] Khujamberdiev Sh., Mirzakulov Kh., Arifdjanova K. Research of the process thermal dehydration of orthophosphate is sodium phosphate from Central Kyzylkum // International Journal of Chemical Petrochemical Technology // USA. 2019, ISSN(P): 2277-4807; ISSN(E): 2319-4464. (Impact Factor (JCC): 5.5342) Vol. 9, Issue 1, Dec 2019, pp. 1-8.
[4] Melikulova G.E., Mirzakulov Kh.Ch., Usmanov I.I., Isakov A.F. Research of the process of obtaining feed dicalcium phosphate from phosphorites of Central Kyzylkums // Universum: technical sciences: electron. scientific. journal. 2018. No.6(51). URL: https://7universum.com/ru/tech/archive/item/6037.
[5] Gorlov I.F., Randelin D.A., Struk A.N., Struk V.N., Struk M.V., Struk N.V. Innovative technologies for the development and use of new feed and biologically active additives in the production of meat of farm animals and poultry. Volgograd, Russia. 2012. 236 p.
[6] Vinogradov V.N., Duborezov V.M., Kirilov M.P. Feeding and feed production in dairy cattle breeding // Journal "Achievements of science and technology in agriculture". Moscow, Russia. 2009. No.8. pp. 33-35.
[7] Ryabov N.I., Levakhin V.I., Zelepukhin A.G., Korolev L., Popov V.V. Improving the efficiency of feeding young cattle. Moscow, Russia. 2005. 109 p.
[8] Arifdjanova K.S., Mirzakulov Kh.Ch., Melikulova G.E., Khujamkulov S.Z., Usmanov I.I. Research of the process of desulfurization of extraction phosphoric acid from phosphorites of Central Kyzylkums // Journal "Chemical Industry". Sankt-Petersburg, Russia. 2017. No.5. pp. 18-25.
[9] Litusova N.M. Technology of obtaining feed calcium phosphates in granular form based on chalk and extraction phosphoric acid. Diss. ... cand. of techn. sciences. Moscow, Russia. 2004. – 97 p.
[10] Bushuev N.N. Physico-chemical bases of the influence of impurities of phosphate raw materials in the technology of phosphorus-containing mineral fertilizers and pure substances. Diss. ... doct. of techn. sciences. Moscow, Russia. 2000. 412 p.
[11] Melikulova G.E. Development of technology of feed ammonium and calcium phosphates from phosphorites of Central Kyzylkums. Diss. ... PhD – Tashkent, 2018. 107 p.
[12] Myrzakhmetov B.B., Besterekov U.B., Petropavlovsky I.A., Pochitalkina I.A., Kiselev B.G. Kinetic regularities of the decomposition of low-grade phosphorites by the liquid-phase method under the conditions of mother liquor recycling. // Journal "Chemical industry today". - Moscow, 2012. No.5, pp. 6-9.
[13] Moldabekov K.T., Jantasov J.K., Janmoldaeva J.M., Balabekov O. Kinetics of decomposition of low-quality phosphoric acid phosphorites and production of double superphosphate by cyclic method. // Journal "Modern high-tech technologies". – Moscow, Russia. 2013. No.11, pp. 107-112.
[14] Alimov U.K., Namazov Sh.S., Reimov A.M., Kaimakova D.A. Flow-circulation method for obtaining double superphosphate based on phosphorites of Central Kyzylkums // Journal "Chemical industry". – Sankt-Petersburg, 2015. Vol. 92. No.3. pp. 109-118.
[15] Alimov U.K., Rasulov A.A., Namazov Sh.S., Kaymakova D.A. The use of mineralized mass of phosphorites of Central Kyzylkums in the process of obtaining double superphosphate by cyclic method // Journal "Chemical Industry". – Sankt-Petersburg, 2017. - Vol. 94. No.1. pp. 1-10.
[16] Shaymardanova M.A., Melikulova G.E., Usmanov I.I., Mirzakulov Kh.Ch. Monocalcium phosphate from phosphorites of Central Kyzylkums // Journal "Chemistry and Chemical Technology" - Tashkent, 2019. No.2. pp. 12-15.
[17] Shaymardanova M.A., Khujamberdiev Sh.M., Melikulova G.E., Mirzakulov Kh.Ch. Technology of obtaining feed monocalcium phosphate from phosphorites of Central Kyzylkums // Universum: technical sciences: electron. scientific. journal. 2021. 10(91). URL:https://7universum.com/ru/tech/archive/item/12471.