



PURIFICATION OF PHOSPHORIC ACID BASED ON PHOSPHORITES OF CENTRAL KYZYL KUM IN THE PROCESS OF EXTRACTION WITH CALCIUM CARBONATE AND OBTAINING FROM A SINGLE PHOSPHORUS FERTILIZER

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ABSTRACT

The work describes the processes of purification of phosphoric acid based on phosphorites of the Central Kyzylkum from impurities of fluorine and sulfates in the process of extraction with calcium carbonate and the production of single phosphorus fertilizer by neutralizing the purified acid with calcium carbonate.

INTRODUCTION. Fluorine compounds have a great harmful effect on the surrounding environment. Studies show that fluorine not only has a negative effect on plants but also causes various serious diseases in humans and other living organisms [1, 2].

Many plants have the ability to absorb large amounts of fluoride. For example, 57 to 1370 mg of fluorine is absorbed in 1 kg of tea and up to 4500 mg in cotton [2, 55 p.]. In this case, fluorine accumulates in the cotton seed, and most of it passes into the cottonseed oil. Studies show that when fluorine falls on the soil, including mineral fertilizers, the amount of fluorine in the crop also increases [3, S. 10–18]. In the presence of nitrogen-phosphorus-potassium fertilizers, the amount of fluorine absorbed by plants increases [4, S. 131–136].

MAIN PART.

Phosphorous fertilizers are the main source of fluorine entering the soil. For example, apatite and phosphorites contain an average of 3.0 and 2.7% fluorine, respectively. Extractable phosphoric acid (WPPA) produced on the basis of Central Kyzylkum phosphorites contains about 1.2% fluorine. The method of deposition from acid using alkali metals in the

form of silicon fluorides is not very effective, because the amount of silicon compounds soluble in acid in EFK is practically very small [5, S. 34-40].

During the processing of natural phosphates, the fluorine contained in them is distributed between gas, liquid (WPPA) and solid (phosphogypsum) phases. 80-85% of the raw materials (apatite and phosphorite) are converted into hydrofluoric acid during the production of phosphoric acid according to the dihydric scheme, and during its further processing, it becomes part of fertilizers.

In order to fully satisfy the demand for fertilizers in agriculture, the increase in the production of phosphorus, especially complex fertilizers, creates a risk of fluorine saturation of soil, plants and water bodies [6, P. 55]. The negative effects of fluorine compounds that fall into the atmosphere and open water bodies and accumulate in living organisms and flora have been sufficiently studied [3, S. 10-18; 4, S. 131-136; 7, S.42-47].

Sodium and potassium sulfates, chlorides, phosphates, carbonates, and hydroxides are used to precipitate fluorine from WPPA in the form of silicon fluoride compounds of poorly soluble alkali metals [8, S.191-206]. These methods are based on the chemical interaction of the above salts with the fluorinated acid contained in WPPA. The level of fluoride removal reaches 90%. According to this method, the level of fluorine removal in WPPA obtained from Central Kyzylykum phosphorites does not exceed 38-40%.

The process of purifying WPPA based on Central Kyzylykum phosphorites with alkali metal salts is sufficiently presented in literature sources. It is suggested to clean WPPA first from sulfates and then from fluorine [9, S.2-4]. The process of defluorination of WPPA based on Central Kyzylykum phosphorites with sodium sulfate, dihydrophosphate, metasilicate was thoroughly studied by the authors and it was shown that the level of fluorination can be increased from 38-40% to 80-85%, and the technology of WPPA defluorination was created [10; S. 16-19, 11; S. 8-11; 12; P.41-45].

Fluorinated WPPA can be made from unenriched raw materials of Central Kyzylykum [13, B.32-39], calcium carbonate and oxide, washed enriched phosphorites [14; 156 p., 15-18] with desulfation materials are also available. A patent was obtained for the method of obtaining a nutrient precipitate by purifying WPPA from fluorine compounds and sulfates [19]. However, there are no materials for simultaneous purification of the extraction slurry from fluorine and sulfates in obtaining WPPA from Central Kyzylykum phosphorites.

Currently, the demand for phosphate raw materials in the world is 190 million tons or 43 million tons of P_2O_5 per year. The demand for phosphate raw materials is expected to grow by 1.3 million tons by 2020 and by 2 million tons by 2030. By 2050, the demand for raw materials will reach 220 million t of phosphate raw materials or 70 million t of P_2O_5 [20].

As a result of the increase in the demand for phosphorous fertilizers in agriculture and the decrease of their stock from year to year as a result of the processing of phosphate raw materials into phosphorous fertilizers, it is one of the urgent tasks of the present time to include other types of raw materials in the production of phosphorous fertilizers along with phosphate raw materials. Neutralization of extractable phosphoric acid (WPPA) produced during the production of phosphorous fertilizers with natural carbonate raw materials gives the opportunity to increase the volume of the product by 4-5%.

In addition, manufactured phosphorus fertilizers contain a large amount (up to 4%) of fluorine. This has a negative impact on the ecological efficiency of fertilizers. In this regard, a

number of studies have been conducted on the treatment of fluorine from the received WPPA. Defluorination of WPPA is carried out by three different methods [8, 19]: defluorination by acid evaporation; conversion of fluorine compounds in acid into water-insoluble compounds and separation of these compounds from WPPA; separation of fluorine compounds in acid using organic reagents. Purification of WPPA by these methods requires additional reagents and bulky equipment, as well as significant capital costs.

That's why research aimed at researching the methods of simultaneously cleaning WPPA from fluorine and sulfates is of great importance.

The purpose of this research work is to reduce the amount of fluorine and sulfates in the extracted phosphoric acid by cleaning the extractive porridge (EB) with the help of calcium raw materials - calcium carbonate before filtering, and to obtain high-quality phosphoric fertilizers containing calcium and magnesium based on it.

For this, in the composition, og. in %: $P_2O_5 = 26,85$; $CO_2 = 3,14$; $CaO = 52,64$; $MgO = 1,03$; $R_2O_3 = 1,16$; $SO_3 = 2,31$; $F = 3,09$; e.g. (insoluble residue) = 1,89 incinerated phosphate concentrate was used.

Precipitation of fluorine and sulfates from extraction porridge was carried out with calcium carbonate (c.t.) at the rate of 60-150% compared to the rate of formation of calcium fluoride from calcium oxide and 80-100% compared to the rate of binding of SO_3 in the form of calcium sulfate. The process of extraction of phosphoric acid with sulfuric acid was carried out in the dihydrate mode, before filtering the resulting extraction slurry, fluorine and free sulfuric acid were precipitated with calcium carbonate (k.t.).

The experiments were carried out in a continuous laboratory unit consisting of a two-section extractor made of EI-943 steel, shielded and equipped with an electric heater layer. Acid and phosphorite enter the device through the moderators. The working volume of the device is 2.5 liters, and its productivity is 150 g of phosphate raw materials.

Phosphorite digestion was carried out in the dihydrate mode with sulfate and circulating phosphoric acid. Before starting the work, both sections of the extractor were filled with the extraction porridge obtained in advance from the standard raw materials under the conditions of the dihydrate regime. The mixing speed was 120-140 rpm in the first section of the reactor, and 80-100 rpm in the second section, and the duration of the process was 3 hours. The ratio of liquid and solid phases was 2.5, the excess amount of sulfate ions in the liquid phase was 3.3-3.5 g/100 ml based on SO_3 . Filtration of porridge in a Buchner funnel through a filter cloth 400 mm sim.set. carried out under vacuum conditions. The time of the extraction porridge in the first section of the reactor is 3 hours, and in the second section it is 30 minutes, because in the second section of the reactor, fluorine and sulfate additives in the extraction porridge are precipitated with the help of calcium carbonate.

Chemical analyzes of raw materials, intermediates and finished products were performed according to known methods [21-24].

The obtained results are presented in Tables 1 and 2.

Table 1

The effect of calcium carbonate (c.t.) rate on the chemical composition of WPPA, the rate of fluorine transfer to the gas phase and phosphogypsum

Naming of indicators	Ratio of calcium carbonate to calcium oxide to bind free fluorine relative to stoichiometry, %						
	-	60	80	100	120	140	150
Rate of calcium carbonate to bind free H ₂ SO ₄ relative to stoichiometry, %	-	80	100	100	100	100	100
Chemical composition of WPPA in weight %							
P ₂ O ₅	17,23	17,28	17,25	17,19	17,10	16,98	16,90
CaO	0,32	0,39	0,54	0,88	1,40	2,21	2,73
MgO	0,66	0,72	0,71	0,68	0,68	0,67	0,67
SO ₃	1,21	0,47	0,28	0,26	0,25	0,25	0,24
R ₂ O ₃	0,71	0,70	0,68	0,67	0,67	0,65	0,65
F	1,18	0,62	0,46	0,29	0,24	0,23	0,22
suspended particle	0,29	0,31	0,27	0,24	0,21	0,18	0,15
Fluoride pass rate, in %							
To phosphogypsum	41,3	69,1	74,5	81,8	84,9	85,2	85,4
and gaseous phase	5,1	5,1	4,9	4,4	4,2	4,1	4,0
Ҳаммаси	46,4	74,2	79,4	86,2	89,1	89,3	89,4
Degree of fluoridation of WPPA	-	47,6	61,1	75,4	79,5	80,2	81,0
The degree of desulfation of WPPA	-	61,3	76,9	78,5	79,2	79,2	79,3

It can be seen from Table 1 that when WPPA is obtained without adding calcium carbonate, 5.1% of the total fluorine in phosphorite goes to the gas phase, 41.3% to phosphogypsum, and 53.6% of fluorine remains in WPPA. The following reactions may occur when calcium carbonate is added to the extraction slurry:

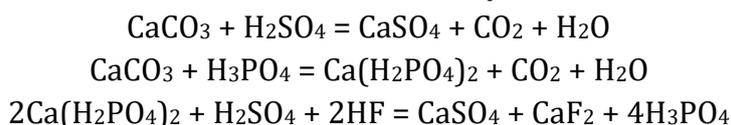


Table 2

Technological indicators of production of fluorinated and desulfurized extractive phosphoric acid

Naming of indicators	Total ratio of calcium carbonate to bind fluorine and free H ₂ SO ₄ relative to stoichiometry, %						
	-	140	180	200	220	240	250
Kparch., %	99,1	99,0	98,9	98,9	98,9	98,8	98,8
Kajr., %	96,3	96,2	96,2	96,1	96,1	96,1	96,1
Cuvil., %	99,0	99,1	99,1	99,2	99,2	99,2	99,2
Day, %	95,3	95,3	95,3	95,3	95,3	95,3	95,3
Porridge density (r), g/cm ³ , at 25°C	1,24	1,24	1,24	1,24	1,25	1,25	1,25
Porridge viscosity (η), spz, at 25°C	3,10	3,42	3,52	3,61	3,68	3,72	3,73
Filtering rate of extractive porridge, kg/m ² ·s	815,4	812,6	811,7	810,6	809,5	808,3	807,6
The size of crystalline phosphogypsum, μm	100x24, 120x20, 220x20, many 560x80, 400x80, 360x28 and partially 100x16, 80x60, 60x20						

The amount of magnesium in WPPA remains unchanged, its amount is 0.66-0.72% in purified acids (Table 1). When calcium carbonate is added and calcium fluoride is formed, the amount of fluorine released into the gas phase decreases from 5.1 to 4.0%, indicating that the main amount is released early in the process. When 100-150% of CaCO₃ is introduced into the decomposition process, the total rate of fluorine transfer to the gas phase and phosphogypsum is 86.2-89.4%. In this case, the amount of fluorine in WPPA is 0.22-0.29%, which is 4.1-5.3 times less than when calcium carbonate is not added. The degree of fluorination of the extractable phosphoric acid product produced by fluoridation of extractive porridge with the help of 100-150% stoichiometric calcium carbonate is 75.4-81.0%.

During the extraction of phosphoric acid and the precipitation of fluorine and sulfates in the resulting extraction slurry with calcium carbonate, when the rate of CaO in the form of CaCO₃ is 100-120%, the degree of fluorine transition to phosphogypsum is 81.8-84.9%, and the degree of transition to the gas phase is 4.4-4.2%. , the degree of fluorination of the product WPPA is 75.4-79.5%, and the degree of sulfation is 78.5-79.2%. When adding more than 120% normal calcium carbonate compared to the amount of fluorine and sulfates present in the acid, fluoridation and desulfation change to a very low degree, that is, to 80.2-81.0% and 79.2-79.3%, respectively. The amount of fluorine remaining in WPPA is 11.3-14.7% compared to the total amount of fluorine in the initial phosphorite. When the ratio of calcium carbonate to available fluorine in phosphorite varies from 60 to 100%, it is observed that the additional transfer of fluorine to phosphogypsum is 27.8-40.5%. When the rate of calcium carbonate is increased by 120-150%, it increases the transfer of fluorine to the solid phase by only 3.1-3.6%. The excess calcium carbonate during the precipitation of fluorine in EB is spent on the formation of calcium sulfate due to the presence of excess sulfuric acid, and due to its reaction with phosphoric acid, monocalcium phosphate is formed.

From the data in Table 1, it can be seen that the amount of SO₃ decreases from 1.21% to 0.24-0.26%, while the amount of calcium oxide increases from 0.32% to 2.73%. In this case, the decomposition, separation, leaching and productivity coefficients are from 60 to 150% to bind fluorine, from 80 to 100% to neutralize excess sulfuric acid, corresponding to 98.8-99.1%, 96.1-96.3% for standard calcium carbonate. , is 99.0-99.2% and 95.3% (Table 2). Due to the formation of crystals of phosphogypsum 100x24, 120x20, 220x20, most 560x80, 400x80, 360x28 and partially 100x16, 80x60, 60x20, the filtration rate is relatively high and is 807.6-812.6 kg/m²•s based on dry residue. is enough.

The conducted studies showed that simultaneous defluoridation and desulfurization of WPPA based on Central Kyzylkum phosphorites by adding calcium carbonate (k.t.) to the extraction slurry is possible in principle. The optimal rate of calcium carbonate is 100-120% of CaO for the formation of calcium fluoride and 100% of CaO for the formation of calcium sulfate. In this case, the amount of sulfates decreases from 1.21% to 0.25-0.26%, fluorine from 1.18% to 0.24-0.29%, the rate of fluorine transition to the gas phase during extraction increases from 5.1% to 4.2- decreases to 4.4%, and the rate of conversion to phosphogypsum increases from 41.3% to 81.8-84.9%. The degree of fluorination of WPPA obtained as a product is 75.4-79.5%, and the degree of sulfation is 78.5-79.2%.

In order to obtain a high-quality defluorinated phosphorous fertilizer containing calcium and magnesium phosphates, the WPPA product purified from fluorine and sulfates using calcium carbonate during the extraction process and the process of neutralization of the concentrated acid obtained from its evaporation with calcium carbonate (c.t.) were studied.

During the extraction of phosphoric acid, the product acid purified from fluorine and sulfate additives and the concentrated acid obtained by evaporating it were neutralized with stoichiometric CaCO₃ to pH = 2.8-3.5, corresponding to the formation of calcium and magnesium monophosphates. The resulting slurry was evaporated to 30-35% H₂O (when unconcentrated WPPA was used) and dried at 100-105°C.

The technological parameters of the neutralization process, the chemical composition of the obtained intermediate and finished products are presented in Tables 3 and 4.

At the stage of phosphoric acid extraction, the amount of sulfates (SO₃) in the phosphate slurry obtained as a result of the neutralization of WPPA, which is not purified from fluorine and sulfates with calcium carbonate, is 1.15%, the amount of fluorine is 1.06%, and the level of defluoridation is 43.70% compared to the initial phosphorite raw material. is enough.

Table 3

Technological indicators of neutralization of WPPA with calcium carbonate (k.t) raw materials and the chemical composition of the obtained intermediate and finished products

T/ p	Indicators	Chemical composition, %					
		Phosphate porridges			Dried calcium-magnesium phosphate fertilizers		
1.	Stoichiometric rate of CaCO ₃ by CaO, %:						
	on F during the extraction step	-	100	120	-	100	120
	on SO ₃ during the extraction step	-	100	100	-	100	100
	for WPPA in the neutralization phase	100	100	100	100	100	100
2.	P ₂ O ₅ general	16,35	17,18	17,24	48,56	52,94	53,41
3.	P ₂ O ₅ absorbed	16,26	16,94	17,20	48,29	52,73	53,26
4.	P ₂ O ₅ water soluble	14,82	15,89	16,15	44,06	49,03	50,08
5.	CaO general	7,77	6,18	6,11	23,08	19,04	18,93
6.	MgO general	0,63	0,68	0,69	1,87	2,09	2,14
7.	R ₂ O ₃ general	0,67	0,67	0,68	1,99	2,06	2,11
8.	SO ₃ general	1,15	0,27	0,25	3,42	0,82	0,77
9.	F general	1,06	0,28	0,24	2,99	0,85	0,74
10.	H ₂ O	66,97	68,65	68,76	1,89	3,39	3,21
11.	$(P_{2O_{5own.}}:P_{2O_{5total.}}) \times 100, \%$	99,45	98,60	99,77	99,44	99,60	99,72
12.	$(P_{2O_{5s.e.}}:P_{2O_{5total.}}) \times 100, \%$	90,64	92,49	93,68	90,73	92,61	93,77

Table 4

Concentrated WPPA is carbonated raw materials - c.t. Technological parameters of the neutralization process with CaCO₃ and the chemical composition of the obtained intermediate and finished products

T/p	Indicators	Chemical composition, %	
		Phosphate porridge	Dried calcium-magnesium phosphate fertilizer
1.	P ₂ O ₅ general	32,94	53,90
2.	P ₂ O ₅ absorbed	32,88	53,81
3.	P ₂ O ₅ water soluble	30,98	50,74
4.	CaO general	11,24	18,39
5.	MgO general	1,30	2,13
6.	R ₂ O ₃ general	1,29	2,11
7.	SO ₃ general	0,48	0,79
8.	F general	0,15	0,23
9.	H ₂ O	40,20	2,15
10.	(P ₂ O _{5own.} :P ₂ O _{5total.})x100, %	99,82	99,83
11.	(P ₂ O _{5s.e.} :P ₂ O _{5total.})x100, %	94,05	94,14
12.	Degree of defluoridation, %	96,06	96,34

The amount of SO₃ in the porridge formed when the extractive porridge is neutralized with 100% and 120% stoichiometric calcium carbonate to form monocalcium and monomagnesium phosphates with 100% and 120% stoichiometric calcium carbonate is 0.25% and 0.27, respectively. %, and the amount of F is 0.28% and 0.24% (Table 3). The ratio of (P₂O_{5own.}:P₂O_{5total.})x100 in porridge is 98.60-99.77%, and the ratio of (P₂O_{5s.e.}:P₂O_{5total.})x100 is 92.49-93.68%.

The pulps were steamed until 30-35% H₂O remained, granulated and dried at 100-105°C, compared to the product obtained from untreated WPPA, the amount of sulfates was from 3.42% to 0.77-0.82%, and the amount of fluorine was from 1.06% to 0.74 Total P₂O₅ in products obtained on the basis of WPPA purified from fluorine and sulfates due to reduction to -0.85%. amount from 48.56% to 52.94-53.41%, P₂O₅ own. amount from 48.23% to 52.73-53.26%, amount of P₂O_{5s.e.} increases from 44.06% to 49.03-50.08%. As a result, the degree of defluoridation of the product reaches 73.9-77.5%. The amount of calcium in the obtained products is 18.93-19.04%, and the amount of magnesium is 2.09-2.14%, (P₂O_{5own.}:P₂O_{5total.})x100 ratio is 92.61-93.77%. The degree of fluoridation of calcium and magnesium phosphate products compared to phosphate raw materials used in the extraction stage is 86.1-87.9%.

In order to further reduce the amount of fluorine in the products, to reduce the thermal energy costs of evaporating the solutions and suspensions generated during production, carbonated raw materials are purified from fluorine and sulfate additives in an optimal ratio (to bind fluorine - 120%, to bind free H₂SO₄) and contain (fat .%): P₂O₅ = 17,10; CaO = 1,40; MgO = 0,68; SO₃ = 0,25; R₂O₃ = 0,67; F = 0,24 by evaporating the acid contained in it (ugh.%): P₂O₅ = 35,25; CaO = 2,25; MgO = 1,39; SO₃ = 0,51; R₂O₃ = 1,38; F = 0,17 concentrated WPPA was formed. In this case, the degree of defluoridation of extractable phosphoric acid reaches 93.0%.

When concentrated WPPA is neutralized with 100% stoichiometric raw calcium carbonate to form monocalcium and monomagnesium phosphates, the amount of SO₃ in the porridge is 0.48%, and the amount of F is 0.15% (Table 4). The ratio of (P₂O₅_{own.}:P₂O₅_{total.})x100 in porridge is 99.82%, and the ratio of (P₂O₅_{s.e.}: P₂O₅_{total.})x100 is 94.05%.

P₂O₅_{general} in the product when the porridge is granulated and dried at a temperature of 100-105°C. amount up to 53.90%, P₂O₅ own. amount up to 53.81%, P₂O₅_{s.e.} amount up to 50.74%. As a result, the degree of defluoridation of the obtained calcium and magnesium phosphate products compared to the phosphate raw materials used in the extraction stage is 96.34%. The amount of calcium in the obtained products is 18.39%, and the amount of magnesium is 2.13%, (P₂O₅_{own.}:P₂O₅_{general.})x100 ratio 99,83% the, (P₂O₅_{s.e.}:P₂O₅_{general.})x100 and the ratio is 94.14%. Evaporation of extracted phosphoric acid to 35% P₂O₅ before neutralization with carbonate raw materials, processing of evaporated acid into phosphorus fertilizers containing calcium and magnesium phosphates, firstly, saves energy resources compared to suspension evaporation costs, and secondly, reduces the amount of fluorine in the product.

Figure 1 shows the material flow block diagram for the production of high-quality phosphorus fertilizer from Central Kyzylkum's washed-burnt phosphate concentrate (WCPC).

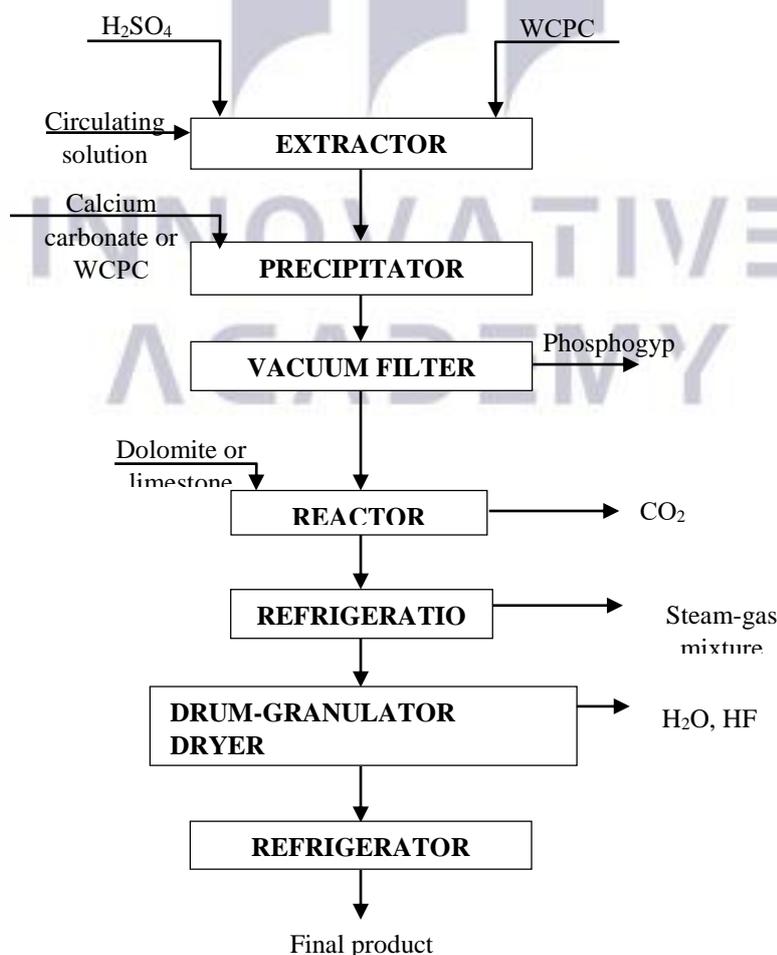


Figure 1. Material flow block diagram for the production of high-quality phosphorus fertilizer from the washed-burned phosphate concentrate (WCPC) of Central Kyzylkum.

CONCLUSION.

Thus, during the extraction process of phosphoric acid, by adding a reagent (calcium carbonate) containing 100% calcium for sulfates and 120% for fluorine to the sulfate-phosphate slurry in the stoichiometric ratio, simultaneous defluoridation and desulfation of extractable phosphoric acid based on Central Kyzylkum phosphorites showed that it is possible. By neutralization with 100% stoichiometric calcium carbonate (c.t.) raw materials to form WPPA monocalcium and monomagnesium phosphates, purified from fluorine and sulfates, it is possible to obtain high-quality concentrated phosphorous simple fertilizers, the composition of which is similar to double superphosphate. Evaporation of extracted phosphoric acid to 35% P_2O_5 before neutralization with carbonated raw materials and processing of evaporated acid into phosphorus fertilizers containing calcium and magnesium phosphates, firstly, saves energy resources compared to suspension evaporation costs, and secondly, reduces the amount of fluorine in the product.

References:

1. Национальный доклад о состоянии окружающей среды и использовании природных ресурсов в Республике Узбекистан (1988-2007). – Ташкент, 2008. – 298 с.
2. Степень и экономические последствия фторидного загрязнения. Обзорная информация. – Обнинск, 1983. – Вып.1. – 55 с.
3. Васяев Г.В., Шевченко Т.П. О содержании фтора в урожае // Записки Ленинградского с-х. ин-та. – Л.: Изд-во ЛСХИ, 1974. – Т. 218. – С.10-18.
4. Халитов А.Х., Розин В.И. О необходимости исключения фтора из состава минеральных удобрений / В кн. Интенсификация сельскохозяйственного производства и проблемы защиты окружающей среды. – М.: Наука, 1980. – 296 с.
5. Хужамкулов С.З., Меликулова Г.Э., Мирмусаева К.С., Мирсаидов М.Х., Мирзакулов Х.Ч. Исследование процессов получения кремнефторида натрия из экстракционной фосфорной кислоты на основе фосфоритов Центральных Кызылкумов // Химическая технология. Контроль и управление. – Ташкент: ТГТУ, 2016. – № 1(67). – С. 34-40.
6. World Fertilizer trends and Outlook to 2018. Food and Agriculture Organization of the Unated Nations. Rome, FAO, 2015, 55 p.
7. Зайцев В.А., Родин В.И. Влияние фтора на организм животных // Журн. ВХО им. Д.И. Менделеева, 1979. – Т. 24. – № 1. – С.42-47.
8. Кочетков С.П., Смирнов Н.Н., Ильин А.И. Концентрирование и очистка экстракционной фосфорной кислоты / ГОУВПО Иван. гос. хим.-технол. ун-т. – Иваново, 2007. – 308 с.
9. Усербаева Д., Тоиров З.К., Эркаев А.У., Каипбергенов А.Т. Обессульфачивание и очистка от примесей экстракционной фосфорной кислоты из фосфоритов Центральных Кызылкумов // Химия и химическая технология. – Ташкент: ТХТИ, 2010. – № 2. – С.2-4.

10. Хужамкулов С.З., Асамов Д.Д., Бардин С.В., Мирзакулов Х.Ч. Обесфторивание экстракционной фосфорной кислоты солями натрия // Кимё ва кимё технологияси. 2008. № 2. С. 16-19
11. Shamshidinov I. T., Mirzakulov Kh.Ch., Mamurov B. A. Processing of magnesium-containing phosphorites for extraction phosphoric acid // Universum: Technical Sciences: electronic scientific journal, 2017. № 2(35). – Pp. 84-88.
12. Shamshidinov I. T., Mamurov B. A., Usmanov I. I., Kodirova G. K. Investigation of the process of neutralization of extractive phosphoric acid with chalk / / Universum: Technical Sciences: electronic scientific journal, 2019. – № 2(57). – Pp. 21-26
13. Арифджанова К.С., Хужамкулов С.З., Нормуродов Б.А., Шамаев Б.Э., Мирзакулов Х.Ч. Обесульфачивание экстракционной фосфорной кислоты из фосфоритов Центральных Кызылкумов небогащенным фосфатным сырьем. Журнал «Кимёвий технология. Назорат ва бошқарув». ТГТУ, 2016. №3. С. 32-39
14. Мирмусаева К.С. Разработка технологии производства ортофосфатов натрия на основе экстракционной фосфорной кислоты Центральных Кызылкумов. Дисс. ... канд. техн. наук. – Ташкент. 2011. – 157 с.
15. Қодирова Г.Қ., Шамшидинов И.Т., Тураев З., Нажмиддинов Р.Ю. Исследование процесса получения высококачественных фосфатов аммония из экстрактной фосфатной кислоты на основе фосфоритов Центрального Кызылкума // Universum: Технические науки: электрон. научн. журн. 2020. – № 12(81). – С. 71-75.
16. Шамшидинов И.Т. Переработка фосфоритов Каратау и Центральных Кызылкумов на экстракционную фосфорную кислоту и концентрированные фосфорсодержащие удобрения. – М.: Издательство Lambert Academic Publishing, 2021. – 225 с.
17. Gulnoza Kodirova, Voxodir Sultonov, Rikxsitilla Najmiddinov, Bakhodir Mamurov. Investigation of the Process of Purification of Wet-Process Phosphoric Acid and Production of Concentrated Phosphoric Fertilizers Based on it // Chemical Science International Journal. 30(1): 1-10, 2021; Article no.CSIJ.66045
18. Гафуров К., Арисланов А.С. Сернокислотная переработка фосфоритов Каратау и сложных удобрений на их основе. – М.: Издательство Lambert Academic Publishing, 2020. – 140 с.
19. Патент № IAP 05054 UZ. МКИ C05 B3/00, C05 B11/00. Способ получения кормового преципитата. / Х.Ч.Мирзакулов, И.И.Усманов, Б.Б.Садыков, Н.В.Волынскова, Г.Э.Меликулова, Ш.И.Умаров, Опубл. 31.07.2015. Бюл. № 7.
20. Ангелов А.И. Мировое производство и потребление фосфатного сырья / А.И. Ангелов, Б.В. Левин, П.В. Классен // Горный журнал. – Москва, 2003. – № 4-5. – С. 6-11.
21. Винник М.М., Ербанова Л.Н. и др. Методы анализа фосфатного сырья, фосфорных и комплексных удобрений, кормовых фосфатов. – М.: Химия, 1975. – 218 с.
22. ГОСТ 24596.4-81. Фосфаты кормовые: Методы определения кальция. – М.: ИПК Издательство стандартов, 2004. – 3 с.
23. ГОСТ 20851.2.75. Удобрения минеральные: Методы определения содержания фосфора. – М.: Издательство стандартов, 1983. – 22 с.
24. Крашенинников С.А. Технический анализ и контроль в производстве неорганических веществ. – М.: Высшая школа, 1986. – 280 с.