

## Preparation of a Complex Phosphorus Fertilizer of the Double Superphosphate Type

**Khoidarova Gulsanam Akramjon qizi**

Student, Namangan Institute of Engineering and Technology

### Abstract:

The article found that: in the sulfuric acid processing of Kyzylkum phosphorites, the technological parameters are similar to the processing of Karatau phosphorites with improved crystallization and washing of phosphogypsum. Gypsum number 1.42 water for washing is reduced to 1.3-1.5 depending on the w: t in the extractor and fluorine partially (up to 40%) passes into phosphogypsum  $K_{izv} = 97.6$  and  $K_{vy} = 97.5\%$ .

**Keywords:** phosphorite, Kyzylkum, Karatau, sulfuric acid, phosphoric acid, phosphogypsum, fluorine, thermostated three-necked flask, electric mixer, thermometer, de-fluorination of EFC,  $NH_4NO_3$ , ammonization, redox processes, degree of decomposition, gypsum number 1.42.

Uzbekistan mainly uses ammophos and simple superphosphate as phosphorus fertilizers instead of imported double superphosphate from Russia. During the long-term use of ammophos and simple superphosphate, which does not contain soluble calcium, the soil is depleted, this important element in plant nutrition and in the development of living organisms. Calcium neutralizes acidity in soils, prevents the formation of clay minerals by the interaction of  $Al_2O_3$ ,  $Fe_2O_3$ ,  $SiO_2$ , etc., coming with mineral fertilizers with decomposed plant residues, and improves the accumulation of humus and the activity of bacteria in the soil.

Calcium starvation of the soil leads to a constant decrease in its fertility, crop yields, livestock productivity, etc. It is known that calcium strengthens the stems of cotton and other plants, is part of the bone tissues of living organisms and by improving the composition and structure of the soil contributes to increasing plant yields and improving product quality. In this regard, the question arose about the use of new types of fertilizers that compensate for the lack of soluble calcium in the soil and other nutrients. In addition, phosphorus and nitrogen-phosphorus fertilizers (ammophos, superphosphate) currently obtained contain agrochemical aggressive fluorine (2.5-4.0%), which destroys plant cells by disrupting redox processes. As a result, the yield decreases. In addition, it enters the body of animals and humans through feed, vegetables, fruits, etc. it is washed out and enters drinking water. Fluorine in living organisms, as well as in plants, disrupts redox processes, causes diseases of the kidneys, liver, blood vessels, brain, etc.

Phosphorus fertilizers currently produced do not contain soluble sulfates, so sulfur contributes to the formation (synthesis) of the most important components of the blood, such as albumin, fibrin and casein in the plant body. In addition, 50-70% of the annual norm of ammophos is plowed in autumn. At the same time, ammonia in the composition of fertilizers is nitrified, and the assimilated phosphates undergo retrogradation, i.e. they pass into indigestible forms of iron phosphates, aluminum, etc. So a significant part of the nutrients is lost. As a result, the efficiency of phosphorus fertilizers in the first year is about 25%, and the second year reaches up to 40% due to their slow dissolution in soil solutions when using nitrate components. And calcium phosphates (mono- and

di) are not subjected to retrogradation. Therefore, it is advisable to use double superphosphate as phosphorus fertilizers.

Currently, ammophos is used in the quality of complex phosphorus fertilizers, about 70% of the cost of the product is raw materials (phosphorite, sulfuric acid and ammonia). Secondly, ammophos is introduced in autumn when plowing, in spring when sowing seeds and in the third feeding of cotton. In terms of agrochemical properties, ammophos differs from simple and double superphosphate in that water-soluble phosphates, non-citrate-soluble forms of calcium phosphates (especially in Uzbekistan, high-carbonate soils), iron and aluminum occur during prolonged stay in the soil. Calcium phosphates are absorbed by plants and iron phosphates are not absorbed, and aluminum is unknown. This is how the retrogradation of assimilated phosphates occurs. Ammonium ions are fixed by the soil complex. However, nitrification occurs with the participation of the nitrifying bacteria, and with the participation of the denitrifying bacteria, nitrates pass into elementary nitrogen and are released into the gas phase. This is how the loss of assimilable nitrogen occurs. Therefore, the introduction of ammophos into the soil in late autumn is impractical.

In this type, a simple and double superphosphate has advantages over ammophos. So the retrogradation process is moderate. Only a part of the free phosphoric acid that binds to iron in the soil is amenable to this, since the soil is carbonate, mono- and diphosphates of calcium are formed, which do not respond to retrogradation in soil conditions.

When obtaining double superphosphate, the main part of fluorine, which is agrochemical (biologically) aggressive (destroy cells) in a significant amount in fertilizer, is reduced in the process of EFC steaming (concentration) and in the process of phosphoric acid decomposition of secondary phosphate.

Phosphoric acid decomposition of phosphorites uses the chemical energy of acid, which reduces the consumption of sulfuric acid per unit of product. And in the process of ammonification of the acidic product to pH = 2.3 -2.6 reduces the consumption of ammonia per unit of additional product by 70-75%. Conducting agrochemical studies, we have justified the similar effectiveness of superammophos - K and ammophos [1]. These advantages of double superphosphate over ammophos give grounds to develop such production.

Therefore, in order to obtain a double superphosphate, the decomposition of secondary  $P_2O_5$  phosphate of Kyzylkum was carried out with a fluid concentrated (30-37%  $P_2O_5$ ) obtained by the known method [2-4] by evaporation of magnesium-containing weak EFC of the following composition, mass%:  $P_2O_5$  =21.06; CaO= 0.32, MgO= 1.68;  $SO_3$ =2.05, F=1,37; $R_2O_3$ =0.65, suspensions 0.12, etc.

Indeed, magnesium-containing EFC with an MgO content even up to 0.3%, it thickens when the concentration reaches 37-38%  $P_2O_5$  (approved by American scientists). However, with the introduction of secondary phosphate, it can thicken (of course, if the reactor is accidentally shut down). Secondly, as indicated above, when ammonium nitrate is introduced in a small amount, the solubility of phosphates increases (justified by many scientists).

The concentration of the first hydrogen ions in phosphoric acid after evaporation is 0.35-0.42%, the degree of desfluorination is 17.3-25%, i.e. two times less than the degree of desfluorination of EFC from Karatau phosphorites under these conditions. Since the Karatau EFC contains fluorine in the form of  $H_2SiF_6$  and its salts, and the Kyzylkum EFC contains HF, in the first case HF and  $SiF_4$  enter the gas phase, and in the second HF, whose partial vapor pressure is less than the partial pressure of  $SiF_4$  and less volatilization. And so the load of the fluoride gas absorption system is reduced.

Kyzylkum phosphorite of the following composition was used as a secondary phosphate for phosphoric acid decomposition (mass. %):  $P_2O_5 = 25.62$ ;  $CO_2 = 12.84$ ;  $CaO = 48.56$ ;  $MgO = 1.78$ ;  $Fe_2O_3 = 0.35$ ;  $Al_2O_3 = 0.42$ ;  $SO_3 = 2.94$ ;  $F = 2.78$ ; n.o. = 0.61 and  $H_2O = 0.6$ .

The decomposition process was carried out in a thermostatically controlled three-necked flask with a hydraulic seal equipped with an electric mixer, thermometer and the reverse refrigerator. After reaching the acid temperature to  $60^\circ C$ , phosphorite was injected into the flask. Phosphorite Weight ratio: EFC ( $100\%P_2O_5$ ) = 100:100:150 (1:1÷1,5). The process time is 2 hours with constant stirring.

The stoichiometric amount of EFC ( $P_2O_5$ ) for the formation of calcium, magnesium, iron and aluminum monophosphate according to the well-known equation [2] was 90-135%. The technological parameters of obtaining superphosphate pulp and its chemical composition are given in Table 1.

**Table 1. Technological parameters of production and chemical composition of superphosphate pulp based on Karatau and Kyzylkum phosphorites**

$N_0$	EFK, % $P_2O_5$	(Weight ratio phosphorite) EFK (100% $P_2O_5$ )	J:T	$P_2O_5$ gen.%	$P_2O_5$ .%	$P_2O_5$ v.r.%	$N_{a.m.m.}$ %	$N_{gen}$ %	pH	$H_2O$ ,%	$\frac{P_2O_5}{P_2O_5\ gen} * 100\%$	$\frac{P_2O_5\ v.r}{P_2O_5} * 100\%$	$Q_p$ %.
<b>Based on Karatau phosphorites</b>													
1.	30,18	1:1	3,31: 1	30,3 0	28,0 2	25,8 8	0,3 5	0,7 0	2,1 4	41,4 4	92,47	92,36	62,3 5
2.	30,18	1:1,5	4,97: 1	30,7 9	29,7 7	27,9 8	0,3 8	0,7 6	2,0 8	44,6 4	96,70	94,00	76,9 2
3.	35,60	1:1	2,81: 1	34,8 4	32,9 8	30,9 2	0,3 6	0,7 2	2,1 6	24,4 8	94,66	93,75	73,3 0
4.	35,60	1:1,5	4,21: 1	35,6 2	34,9 5	33,6 3	0,4 0	0,8 0	2,2 0	26,8 3	98,12	96,22	86,8 5
5.	37,20	1:1	2,69: 1	36,1 0	34,0 4	31,7 9	0,3 8	0,7 6	2,1 0	22,0 0	94,29	93,39	71,4 5
6.	37,20	1:1,5	4,03: 1	36,9 4	36,0 7	34,6 0	0,4 2	0,8 4	2,1 5	24,1 3	97,65	94,26	83,5 7
<b>Based on Kyzylkum phosphorites</b>													
1.	30,22	1:1	3,31: 1	30,8 5	28,6 3	26,6 6	0,3 4	0,6 8	2,1 5	40,8 6	92,81	93,12	64,0 5
2.	30,22	1:1,5	4,96: 1	31,2 0	30,2 8	28,6 2	0,3 8	0,7 6	2,0 5	43,8 8	97,05	94,48	79,8 0
3.	35,36	1:1	2,82: 1	35,1 3	33,4 5	31,3 7	0,4 0	0,8 0	2,1 2	27,7 0	95,49	94,78	77,4 5
4.	35,36	1:1,5	4,24: 1	35,4 6	34,9 8	33,6 0	0,4 2	0,8 4	2,0 0	30,5 8	98,66	96,05	90,8 2

5.	37,28	1:1	2,68: 1	36,5 3	34,8 7	32,5 6	0,4 4	0,8 8	2,0 8	24,2 7	95,29	93,54	76,4 5
6	37,28	1:1,5	4,02: 1	36,8 0	36,2 0	34,7 9	0,4 7	0,9 4	2,1 8	26,4 8	93,37	96,10	88,8 4

Previously [3].it was found that the main amount of phosphate decomposes from Karatau phosphorites within 90-120 minutes; with an increase in the duration of the process to 180 minutes at 60 ° C, the degree of decomposition increases by only 1-4%, despite the high content of phosphoric acid in the liquid phase of the pulp. And with an increase in the concentration and proportion of acid, the degree of decomposition increases. The optimal concentration was chosen 35-37% P<sub>2</sub>O<sub>5</sub> and the weight ratio phosphorite: EFC (100%P<sub>2</sub>O<sub>5</sub>) was chosen 1.5, i.e. the amount of acid 130-135% of stoichiometry. Therefore, the experiments were carried out under these optimal conditions.

Based on the works[2], it was interesting to compare the process taking place with Kyzylykum phosphorite with Karatau phosphorite. Since there are more carbonates in Kyzylykum phosphorites, and the insoluble residue is much smaller (almost absent) compared with Karatau phosphorite, composition (mass %): P<sub>2</sub>O<sub>5</sub> = 25.04; CaO = 39.74; MgO = 2.57; F = 2.29; CO<sub>2</sub> = 7.16; I.O. = 15.70, etc.

It can be seen from the results that in acid pulp at an acid concentration of 30.18% P<sub>2</sub>O<sub>5</sub>, the degree of decomposition (Cr) is 62.35% with a ratio of phosphorite: EFC (100%P<sub>2</sub>O<sub>5</sub>) = 1:1. With an increase in the acid concentration to 35.60 - 37.20%, P<sub>2</sub>O<sub>5</sub>Cr increases to 71.45%, respectively. And the increase in the proportion of acid by 1.5 times increases to 76.92%, 86.85% and 83.57%, respectively, acid concentrations.

With an increase in the acid concentration from 35.60% P<sub>2</sub>O<sub>5</sub> to 37.20% P<sub>2</sub>O<sub>5</sub>, Kr decreases slightly (by 3.28%). This is due to an increase in the viscosity of the acid, which somewhat reduces diffusion.

And the interactions of phosphoric acid with Kyzylykum phosphorite are slightly more active than with Karatau phosphorite. Thus, at an acid concentration of 30.22% and a weight ratio of phosphorite: EFC (100% P<sub>2</sub>O<sub>5</sub>) = 1:1, Kr is 64.05% (1.7% higher), and at an acid concentration of 35.36%-37.28%, Kr reaches 77.45-76.45%, respectively (4.15-5.0% higher than in Karatau phosphorites).

In the process of drying the pulp at a temperature of 105 ° C to a moisture content of 1.12-1.85%, the process of decomposition of phosphate continues due to the presence of free acid. At the same time, the Kr when obtaining a product from Karatau phosphorites, depending on the acid concentration (30.18 - 37.20%), is 74.20-81.70%, and from Kyzylykum (30.22-37.28%) are equal to 76.75-83.40% (Table 2).

The degree of decomposition increases with an increase in the proportion and concentration of acid. The maximum degree is achieved with stoichiometry for the formation of calcium monophosphate of 135% and a concentration of the initial acid of about 35% (Cr = 97.60%).

Next, superphosphate pulps from Kyzylykum phosphorites were neutralized with ammonia gas from pH = 2.00-2.18 (Table.2) (acid suspension) to pH = 2.28-3.22 (in an ammoniated suspension). The ammonification was carried out installed in a thermostatically controlled three-necked flask with continuous stirring using an electric mixer. Ammonia gas was supplied through the 2nd throat, and a thermometer was installed in the 3rd throat.

At the same time, the pulp temperature rises from 60 ° C to 70-80 ° C depending on W:T and the concentration of the initial acid. In the process of ammonization to a pH of about 2.5, a slight decomposition occurs, which increases the Cr.

**Table 2. Technological parameters of production and chemical composition of acid fertilizers of the double superphosphate type based on Karatau and Kyzylkum phosphorites**

№	EFK, % P <sub>2</sub> O <sub>5</sub>	Weight ratio phosphorite $\frac{EFK}{EFK (100\% P_2O_5)}$	P <sub>2</sub> O <sub>5</sub> gen. %	P <sub>2</sub> O <sub>5</sub> . %	P <sub>2</sub> O <sub>5</sub> v.r. %	P <sub>2</sub> O <sub>5</sub> fr. %	N <sub>амиак</sub> , %	N <sub>ген</sub> %	H <sub>2</sub> O, %	pH	$\frac{P_2O_5}{P_2O_5\ gen} * 100\%$	$\frac{P_2O_5\ v.r.}{P_2O_5} * 100\%$	Q <sub>p</sub> %.
<b>Based on Karatau phosphorites</b>													
1.	30,18	1:1	43,07	40,85	38,1 7	2,7 6	0,44	0,8 8	1,2 2	2,2 4	94,84	93,90	7 4, 2 0
2.	30,18	1:1,5	44,03	43,16	40,8 5	6,7 2	0,58	1,1 6	1,8 5	2,1 6	98,02	94,65	8 6, 1 5
3.	35,60	1:1	43,24	41,73	39,4 6	2,2 5	0,48	0,9 6	1,2 6	2,2 6	96,50	94,56	8 2, 5 0
4.	35,60	1:1,5	44,74	44,32	42,5 6	6,2 0	0,66	1,3 2	1,4 4	2,2 8	99,06	96,03	9 3, 4 3
5.	37,20	1:1	43,68	42,08	39,6 1	2,2 7	0,46	0,9 2	1,5 6	2,2 6	96,34	94,13	8 1, 7 0
6.	37,20	1:1,5	45,46	44,94	43,1 7	6,2 8	0,56	1,1 2	1,1 2	2,2 2	98,86	96,06	9 2, 0 3
<b>Based on Kyzylkum phosphorites</b>													
1	30,22	1:1	44,49	41,46	39,25	2,54	0,42	0,84	1,24	2,22	95,33	94,67	76,65
2	30,22	1:1,5	44,75	43,92	41,80	6,45	0,52	1,04	1,61	2,08	98,14	95,17	87,26



3	35,36	1:1	44,61	43,15	41,20	2,81	0,44	0,88	1,32	2,15	96,72	95,69	83,60
4	35,36	1:1,5	45,84	45,58	43,87	6,33	0,56	1,52	1,48	2,04	99,65	96,24	97,60
5	37,28	1:1	44,93	43,44	40,77	2,72	0,44	0,88	1,42	2,16	96,68	95,23	83,40
6	37,28	1:1,5	46,18	45,76	44,12	6,68	0,58	1,16	1,18	2,25	99,09	96,41	93,44

At the same time, the assimilable form increases, and the water-soluble one decreases. So the monofarm by the interaction of ammonia passes to the diform with the formation of monoammonium phosphate. With a decrease in monocalcium phosphate in the system, the equilibrium shifts to the right side (apparently also under the action of ammonium monophosphate), the formation of monophosphate, which immediately passes to diphosphate. A further increase in pH to 2.7-3.22 (Namm.=1.7-2.5) leads to a decrease in the digestible  $P_2O_5$  in the product due to the retrogradation of mono- and diphosphates into triphosphates.

The optimal conditions for obtaining ammoniated double superphosphate (or rather superammophos, since the content of monoammonium phosphate is over 20%) are the concentration of the initial EFC of about 35%  $P_2O_5$ , W:T = 4.24:1, the decomposition time of phosphate is 2 hours at a temperature of 60 ° C, the ammonification of the pulp to a pH of about 2.5 at a temperature of 70-80 ° C. At the same time,  $P_2O_5_{usb} / P_2O_5O_6SH$  is 97-98% (Cr = 84.93-88.29%).

When drying the product, the degree of decomposition of phosphate also increases slightly. With the above optimal condition,  $P_2O_5_{usb} / P_2O_5C$  is about 98.5% (pH = 2.6).

The pH of the fertilizer increases slightly due to a decrease in the content of free acid. The free  $P_2O_5$  in this case is 4.44%.

In the product, depending on the proportion of acid in the mixture and the pH of the solution, the free acid in the product is different (0.81 - 5.37%  $P_2O_5COB$ ). Under optimal conditions, a product containing in mass is obtained. %:  $P_2O_5C$  = 44.5;  $P_2O_5_{usb}$  = 44.0;  $P_2O_5b.p.$  = 40.0;  $SO_3$  = 4.5 ; Namm=2.15; Fsc = 3.12; Cr is about 90%.

Thus, it was found that: during the sulfuric acid processing of Kyzylykum phosphorites, the technological parameters are similar to the processing of Karatau phosphorites with improved crystallization and washing of phosphogypsum. The gypsum number is 1.42, the water for washing decreases to 1.3-1.5 depending on the w: t in the extractor and fluorine partially (up to 40%) passes into phosphogypsum  $K_{zv} = 97.6$  and  $K_{vy} = 97.5\%$ . With phosphoric acid decomposition of secondary Kyzylykum phosphate, the optimal conditions are: the weight ratio of EFC (100%  $P_2O_5$ ) and phosphorite about 135%  $P_2O_5$  of stoichiometry (with the introduction of  $NH_4NO_3$ ) for the conversion of calcium to monophosphate and the concentration of EFC 35%, temperature 60 ° C, mixing time 1.5-2.0 hours. The pulp is ammoniated to a pH of 2.0-2.5 at 70-80 ° With and dried at 105 ° C to obtain NP fertilizers, composition by weight %:  $P_2O_5C$  = 44.5-45.5%,  $P_2O_5_{usb}$  = 44-45 %,  $P_2O_5COB$  = 4.5-5%, N = 2-3%,  $H_2O$  = 1.5-2.0%, etc. The savings of sulfuric acid is 15-20%, ammonia 60-70%.

## Literature

1. Shamshidinov I.T. Obtaining fertilizers of the double superphosphate type from Karatau phosphorites. Diss... cand. tech.. - Tashkent, 1994.

2. Shamshidinov I.T. Development of an improved technology for the production of extraction phosphoric acid and the production of concentrated phosphorus-containing fertilizers from phosphorites of Karatau and Central Kyzylkums: Diss. ... doct. technical sciences. – Tashkent: IONKH AN RUz, 2017. – 193s.
3. Gafurov K., Shamshidinov. I.T., Arislanov A.S. De-fluoridation of extraction phosphoric acid during its extraction. "Bulletin of FerPI", Fergana, 2005, No. 1
4. Gafurov K., Arislanov A., Shamshidinov I. Reduction of fluoride compounds in phosphogypsum // Scientific and Technical Journal of FerPI. – Ferghana, 2004. – No. 3. – pp. 63-66.