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CONCENTRATED COMPLEX FERTILIZERS BASED ON LOCAL RAW MATERIALS

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Abstract:
Phosphoric acid decomposition of phosphate raw materials underlies the production of a single phosphorus fertilizer - double superphosphate, both in-line and in a chamber method. This type of fertilizer is one of the cheapest concentrated phosphate fertilizers, suitable for use on any soil and for all crops. But for its production, high-quality phosphate raw materials are needed, such as, for example, the Khibiny apatite concentrate, and concentrated phosphoric acid. Extractive phosphoric acid from poor phosphorites, such as from Karatau phosphorites (21 % P2O5), is not suitable for the production of double superphosphate.
The desire to reduce the cost of phosphorus-containing fertilizers and involve poor phosphate raw materials in their production led to the development of a new technology based on phosphoric acid activation of phosphorites. In this case, the processing of raw materials is carried out with phosphoric acid, but in quantities significantly less than is required by stoichiometry for the complete decomposition of phosphorites to obtain monocalcium phosphate. In this case, the so-called undecomposed or partially decomposed phosphates are formed. In this case, partial decomposition and granulation occurs.

Keywords: Phosphorites, mineral fertilizer, mineralization, decomposition, activation, digestibility.

Uzbekistan is an agro-industrial country. It has more than 25 million 736 thousand hectares of agricultural land, including over 3.73 million hectares of irrigated land. It is on irrigated lands that over 97 % of all agricultural products of the republic are obtained. Uzbekistan ranks fifth in the world in cotton production. It secured its grain independence by harvesting in recent years over 6 million tons of grain from ear crops. The population of Uzbekistan today is 26.4 million people. The annual growth is at the level of 2.5 %. And irrigated arable land does not increase due to the acute shortage of water resources. In per capita terms, it even falls. So, in 1970, there were 0.22 hectares of irrigated land per person, and now this figure has dropped to 0.14 hectares.

We should not forget about the low utilization of nutrients from mineral fertilizers by plants. Of nitrogen and potassium fertilizers, an average of 60-70% of nitrogen and potassium is used, and of phosphorus fertilizers in the year of application - only about 20-25% and for the next 2-3 years about 40% of phosphorus. Poor use of phosphorus fertilizers in the year of application is caused by the fact that phosphorus compounds are in a stationary or extremely inactive state in the soil and therefore cannot be completely absorbed by the roots of plants. Therefore, phosphorus fertilizers must be applied in an amount 4-5 times higher than the removal of phosphorus by the increase in yield (of a particular crop) that they want to receive.

All this suggests that in Uzbekistan it is necessary to increase the production of mineral fertilizers, especially those containing phosphorus.

Phosphorites of Central KyzylKum have become the main phosphate raw material for factories in Uzbekistan that produce phosphorus-containing mineral fertilizers. Phosphorite occurrences are found in many regions of Uzbekistan. Phosphoric acid decomposition of phosphate raw materials underlies the production of a single

phosphorus fertilizer - double superphosphate, both in-line and in a chamber method. This type of fertilizer is one of the cheapest concentrated phosphate fertilizers, suitable for use on any soil and for all crops. But for its production, high-quality phosphate raw materials are needed, such as, for example, the Khibiny apatite concentrate, and concentrated phosphoric acid. Extractive phosphoric acid from poor phosphorites, such as from Karatau phosphorites (21 % P_2O_5), is not suitable for the production of double superphosphate. Due to the high content of impurities, especially magnesium, it was impossible to concentrate it by the vacuum evaporation method to a P_2O_5 concentration of over 38 %. At the same time, she lost her fluidity.

The desire to reduce the cost of phosphorus-containing fertilizers and involve poor phosphate raw materials in their production led to the development of a new technology based on phosphoric acid activation of phosphorites. In this case, the processing of raw materials is carried out with phosphoric acid, but in quantities significantly less than is required by stoichiometry for the complete decomposition of phosphorites to obtain monocalcium phosphate. In this case, the so-called undecomposed or partially decomposed phosphates are formed. So, in the patents it is proposed to process natural phosphate with a particle size of less than 1 mm in an elongated mixer with blades or with a screw with phosphoric acid, taken in an amount of 15-50 % of that required for complete decomposition of phosphate, with the addition at the end of the process of 3-25 % of water by weight the whole mixture. In this case, partial decomposition and granulation occurs. Additional granulation is carried out in a tray granulator, coating the fine granules with phosphorite flour with the addition of a binder or melting urea or ammonium nitrate with or without the addition of potassium salt.

Phosphoric acid activation of phosphate raw materials involves the processing of this raw material with a lower rate of phosphoric acid compared to the rate required for the complete decomposition of phosphorite with the formation of monocalcium phosphate by the reaction:

$Ca_5F(PO_4)_3 + 7H_3PO_4 + 5H_2O\ 5Ca(H_2PO_4)\ 2 \bullet H_2O + HF$

we calculated the stoichiometric rate of extraction phosphoric acid (18.69 % P_2O_5) for the decomposition of each of the five types of phosphorites of the Central KyzylKum desert using the equation:

CaO in raw material + P_2O_5 in acid $Ca(H_2PO_4)_2$

For phosphate rock, the 100 % rate of extraction phosphoric acid (stoichiometric rate for monocalcium phosphate) is 1 g of P_2O_5 in phosphate flour 6.82 g of P_2O_5 in acid, or P_2O_{5EPM}: P_2O_{5PRM} = 1: 0.147.

In laboratory conditions, phosphate raw materials were treated with phosphoric acid in the range of weight ratios P_2O_5 in raw materials to P_2O_5 in acid from 1: 1 to 1: 3.33 (P_2O_5EPM: P_2O_5PRM = from 1: 1 to 1: 0.3) at a temperature of 75 ° C and an interaction time of 30 minutes. Table 1 shows the actual rates of extraction phosphoric acid (18.69% P_2O_5) as a percentage of the stoichiometric rate for each type of phosphate raw material and for various ratios of P_2O_5EPM: P_2O_5PRM.

Table 1 Actual rates of phosphoric acid for processing phosphate raw materials

Types of phosphorites	EPA norm (in% of stoichiometry) at ratios P_2O_5 EPA: P_2O_5prm						
	1 : 0,3	1 : 0,4	1 : 0,5	1 : 0,6	1 : 0,7	1 : 0,8	1 : 1
Private	48,9	36,7	29,3	24,5	21,0	18,3	14,7
phosphate	54,5	40,9	32,7	27,3	23,4	20,4	16,3
Dusty fraction	47,3	35,5	28,4	23,7	20,3	17,7	14,2
Mineralized mass	68,2	51,1	40,9	34,2	29,3	25,6	20,5
Washed	67,2	50,4	40,3	33,7	28,8	25,2	20,2

After the treatment of phosphorites with acid, the pulps were dried and the products were analyzed. The results are shown in table. 2. The general picture of the results of the interaction of various types of phosphate raw materials with extraction phosphoric acid is similar. Only the absolute values of the content of components in the products differ from each other. First of all, the decomposition of carbonates occurs:

$CaCO_3 + 2H_3PO_4\ Ca(H_2PO_4)\ 2 \bullet H_2O + CO_2$

Even with a normal acidity of only 14 to 20 % of the stoichiometry, the degree of decarbonization of phosphorites ranges from 61 to 73 %. And at rates of acid from 47 to 68 % of stoichiometry, it ranges from 91 to 98 %, depending on the type of raw material.

At the same time, but to a lesser extent, the phosphate mineral is also decomposed:

$Ca\ 5F(PO_4)\ 3 + 7H_3PO_4 + 5H_2O\ 5Ca(H_2PO_4)\ 2 \bullet H_2O + HF$

The more acid is taken, the more complete the decomposition. So, for ordinary phosphorite flour with the ratio P_2O_5epa: P_2O_5prm = 1: 1 (acid rate 14.7% of stoichiometry), we have in the product (wt %): P_2O_5 total. 30.13; P_2O_5 ass. by l. to. 18.27; P_2O_5 water 1.08; . 40.49; Ca. 16.92; CaO water. 0.83 and the degree of decarbonization 66.8 %. The aqueous forms of P_2O_5 and CaO indicate the presence of monocalcium phosphate in the product, but there is very little of it. The difference between the assimilable forms of P_2O_5 and CaO and their aqueous forms gives us the content in the product of dicalcium phosphate and the activated form of the phosphate mineral. And the difference between the common forms of P_2O_5 and CaO and their assimilable forms suggests that both the phosphate mineral and calcium carbonate remained undecomposed in the product.

With a weight ratio P_2O_5 epa: P_2O_5 prm = 1: 0.3 (acid rate 48.9 % of stoichiometry), the product already contains (wt %): P_2O_5 total. 42.22; P_2O_5 ass. by l. to. 38.73; P_2O_5 water 27.23; CaO bsch. 25.37; SaOusv. 18.62;

SaOvodn. 11.00, and its degree of decarbonization was 95.5%. That is, calcium carbonate remained in it about 4.5%. The product is mainly composed of monocalcium phosphate, dicalcium phosphate and an activated form of the phosphate mineral. It has a high content of the general form P_2O_5 and assimilable forms P_2O_5 and CaO in relation to their general forms (P_2O_5 ass.: P_2O_5 total = 91.73% by lim. To-those and 74.06 % by tril. B, P_2O_5 water: P_2O_5total . = 64.49%; CaO rev.: CaO total = 73.39% and CaO water.: CaO total = 43.36%). In terms of composition, such a product meets the requirements of agriculture for single phosphorus-containing fertilizers.

Table 2
Composition of single phosphate fertilizers obtained from ordinary phosphorite flour
Central Kyzylkum

Mass ratio P_2O_5 EPA: P_2O_5 PRM	Humidity pulp after decomposition, %	The chemical composition of the dried product, %							P_2O_5 digestibility P_2O_5 general in 2% lim. acid%	P_2O_5 digestibility P_2O_5 general 0.2 M tril. B%	P_2O_5 water P_2O_5 general %	CaO digestibility CaO general %	CaO water CaO general %
		P_2O_5 general	P_2O_5 digestibility in 2% lim. acid	P_2O_5 digestibility 0.2 M tril. B	P_2O_5 water	CaO general	CaO digestibility in 2% lim. acid	CaO water					
1:0,3	46,86	42,22	38,73	31,27	27,23	25,37	18,62	11,00	91,73	74,06	64,49	73,39	43,36
1:0,4	40,35	38,03	33,04	25,67	21,06	28,85	19,28	8,94	86,88	67,50	55,38	66,83	30,99
1:0,5	39,37	36,60	28,10	21,88	14,36	32,79	18,93	6,66	76,78	59,78	39,23	57,73	20,31
1:0,6	37,21	35,02	25,85	19,82	4,35	34,89	19,02	3,41	73,81	56,62	12,42	54,51	9,77
1:0,7	35,20	33,30	23,60	17,85	2,63	36,83	19,85	1,54	70,87	53,60	7,9	51,22	4,18
1:0,8	33,88	32,03	21,47	16,11	1,81	38,28	18,34	1,08	67,03	50,30	5,65	47,91	2,82
1:1	31,06	30,13	18,27	13,37	1,08	40,49	16,92	0,83	60,64	44,37	3,58	41,78	2,05

With a weight ratio P_2O_5 epa: P_2O_5 prm = 1: 0.3 (acid rate 48.9 % of stoichiometry), the product already contains (wt %): P_2O_5 total. 42.22; P_2O_5 ass. by l. to. 38.73; P_2O_5 water 27.23; CaO bsch. 25.37; SaOusv. 18.62; SaOvodn. 11.00, and its degree of decarbonization was 95.5%. That is, calcium carbonate remained in it about 4.5%. The product is mainly composed of monocalcium phosphate, dicalcium phosphate and an activated form of the phosphate mineral. It has a high content of the general form P_2O_5 and assimilable forms P_2O_5 and CaO in relation to their general forms (P_2O_5 ass.: P_2O_5 total = 91.73 % by lim. To-those and 74.06 % by tril. B, P_2O_5 water: P_2O_5 total . = 64.49 %; CaO rev.: CaO total = 73.39 % and CaO water.: CaO total = 43.36 %). In terms of composition, such a product meets the requirements of agriculture for single phosphorus-containing fertilizers.

When the ratio P_2O_5 epa: P_2O_5 prm = 1: 0.5 (acid rate 29.3 % of stoichiometry), carbonates decomposed by 87.8 %, and the product contained (wt %): P_2O_5 total. 36.60; P_2O_5 ass. by l. to. 28.10; P_2O_5 ass. by trill. B 21.88; P_2O_5 water 14.36; CaO gen. 32.79 %; $CaO_{igestibility}$. 18.93; CaOwater. 6.66; P_2O_5 ass. : P_2O_5 total. = 76.78; P_2O_5water: P_2O_5 total. = 39.23. The high content of total and assimilable P_2O_5 makes it also suitable for use in agriculture.

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