

EXISTING METHODS FOR PRODUCING PHOSPHORUS-CONTAINING FERTILIZERS

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Abstract. *Phosphate salts of calcium, ammonium, magnesium, etc., obtained by processing natural phosphate raw materials, are usually used as phosphorus-containing fertilizers. Known are single-component fertilizers based on calcium phosphate salts (simple, enriched and double superphosphates, thermal phosphates) and complex fertilizers based on ammonium and calcium phosphates.*

Keywords: *EPA, Karatau phosphorites, Central Kyzylkum, ammaphos, P₂O₅, superphosphate.*

Introduction. In the countries of Central Asia, nitrogen-phosphorus fertilizers (ammophos and ammophosphate) were mainly produced based on Karatau phosphorites. Note that it is impossible to obtain double superphosphate from them, since its production requires extraction phosphoric acid (EPA) with a concentration of 30-54% P₂O₅.

EPA obtained from phosphorites of Karatau, Kingissep, Maardu and Central Kizilkum due to the content of higher amounts (than apatite) of impurities of magnesium and other elements is partially neutralized and the degree of decomposition of secondary phosphate in EPA, containing 21-30% P₂O₅, is very low. In addition, developed methods for concentrating EPA [1-4] were not used to produce concentrated single phosphorus fertilizers. Therefore, more than 50% of the total volume of phosphorus fertilizers consisted of ammophos and ammophosphate.

Ammophos is a nitrogen-phosphorus fertilizer [5-8], mainly consisting of monoammonium phosphate, diammonium phosphate, ammonium sulfate, iron and aluminum phosphates and other components. In terms of the content of active ingredients, ammophos is one of the most concentrated fertilizers. For its production, the following types of technological schemes are used [9-11]:

-based on the neutralization of unevaporated (20-30% P₂O₅) extraction phosphoric acids with subsequent dehydration of the suspension in dryers (spray, drum or fluidized bed);

-based on the neutralization of unevaporated (20-30% P₂O₅) phosphoric acid, followed by evaporation of the ammophosphate suspension, granulation and drying of the product in drum granulator-dryers (DGD);

-based on the neutralization of concentrated (48-54% P₂O₅) evaporated extraction phosphoric acid. Moreover, neutralization is carried out in two stages, first at atmospheric pressure in reactors, and then in drum ammoniator-granulators (AG). There is also a known method for carrying out neutralization in one stage - at elevated pressure, followed by drying the suspension by spraying in towers (or in DGD apparatuses).

You can give comparative characteristics of production. Thus, the consumption coefficients per 1 ton of production ammophos from apatite (51% P₂O₅, 12% N) and

Karatau phosphorites (47% P_2O_5 , 11% N) are approximately the following: extraction phosphoric acid (100% P_2O_5) - 0.54 and 0.50 t; NH_3 – 0.15 and 0.14 t; natural gas ($34.8 MJ/m^3$) – $28 m^3$; electricity 111 kWh; water $22 m^3$; compressed air – $60 m^3$. The degree of utilization of P_2O_5 reaches 96%, NH_3 – 97%.

It is easy to notice that in the production of ammophos, the cost of raw materials is about 70% of the cost of the product. In addition, it is necessary to keep in mind the fact that 70% of phosphorus-containing fertilizers in agricultural production are usually applied in the fall during plowing. At the same time, the nitrogen contained in the raw material (about 10%) is lost in nitrification processes, washed out by precipitation and melt water before spring sowing [12-14]. UzNIIH has established that with long-term use of ammophos, the soil structure and quality of agricultural products deteriorate due to a lack of calcium compounds [15]. According to experts, along with nitrogen-phosphorus fertilizers, it is also necessary to use calcium-containing phosphorus fertilizers.

However, EPA obtained from magnesium-containing raw materials Karatau is low-active and thickens when it is concentrated to 37-38% P_2O_5 [16]. As a result, it was considered unsuitable for phosphoric acid decomposition of phosphate raw materials.

In EPA solutions obtained during the processing of phosphorites, along with magnesium compounds, there are impurities of compounds and other metals, which also have a significant impact on the rheological characteristics of solutions and crystallization of solid phases during evaporation [17].

The process of evaporating phosphoric acid is often complicated by equipment corrosion and the release of impurities. Precipitates released during the evaporation process clog the equipment. Therefore, to obtain concentrated acid (40-60% P_2O_5) from magnesium-containing ores, it is necessary either to purify the acid from magnesium and fluorine ions before evaporation, or to achieve easy filterability of the resulting crystalline precipitates [18].

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In EPA solutions obtained during the processing of phosphorites, along with magnesium compounds, there are impurities of compounds and other metals, which also have a significant impact on the rheological characteristics of solutions and crystallization of solid phases during evaporation [20].

The process of evaporating phosphoric acid is often complicated by equipment corrosion and the release of impurities. Precipitates released during the evaporation process clog the equipment. Therefore, to obtain concentrated acid (40-60% P_2O_5) from magnesium-containing ores, it is necessary either to purify the acid from magnesium and fluorine ions before evaporation, or to achieve easy filterability of the resulting crystalline precipitates [21].

It should also be noted the works in which the rheological properties of magnesium-containing EPA from Karatau phosphorites were studied and for the first time the technological regimes of the process of concentration (up to 50-55% P_2O_5) and defluorination (0.1-0.5% F) were developed by introducing activating additives into the EPA, as well as the production of defluorinated ammonium phosphates in industrial conditions [1]. The achieved results made it possible to significantly expand the scope of use of concentrated EPA in the processes of producing

not only defluorinated ammonium phosphates using an accelerated scheme, but also to obtain concentrated fertilizers such as double superphosphate [22].

Double superphosphate, a product obtained by decomposing natural phosphate with phosphoric acid, is a more concentrated phosphorus fertilizer than simple superphosphate. The main component of double superphosphate is monocalcium phosphate $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$. It contains 42-55% P_2O_5 , including about 90% phosphorus in water-soluble form [23].

The production of double superphosphate is carried out by several methods [24]:

- Chamber method. According to this (semi-continuous) method, phosphate is decomposed with concentrated (evaporated or thermal) phosphoric acid (50-55% P_2O_5) with intense stirring. Chamber double superphosphate undergoes long-term (25 days) warehouse processing, after which it is granulated and dried. The technological scheme of this production method is similar to the production of simple superphosphate.

The chamber-flow method differs from the chamber method in the absence of a stage of additional decomposition of the product. In this regard, to achieve a high degree of phosphate decomposition, easily degradable finely ground phosphorites are usually used.

The multi-return method for producing double superphosphate eliminates the process of drying the pulp in a spray dryer and the evaporation of all introduced water occurs in the granulator, as well as in the drying drum. Repeated circulation of the retur and application of pulp to its surface makes it possible to obtain dense flaky granules. The disadvantage of this method is the presence of a larger mass of the retur, which entails an unproductive increase in the dimensions of the equipment, the need to use powerful transport mechanisms and excessively high energy consumption metals.

Cost-effective processing of technogenic raw materials is possible by conducting preliminary waste mapping and developing technologies for processing individual fractions of raw materials in accordance with the needs of the economy based on the use of new modern methods and equipment, with the production of high-quality commercial products.

Waste-free and low-waste technology is a modern direction for the development of industrial production. The main goal of this direction is to reduce the harmful effects of industrial waste on the environment. Non-waste technologies provide the opportunity for complex processing of raw materials, and the development of such technological processes helps. As a result of the development of these technologies, it is possible to use natural resources more efficiently, recycle industrial waste, reduce the amount of waste and reduce its negative impact on the environment [25].

Results and discussion.

The involvement of poor high-magnesium phosphorite ores of Karatau in the production of mineral fertilizers, due to the depletion of richer sources, raises a serious problem of processing them into phosphoric acid, mineral fertilizers, etc.

An increase in the content of magnesium compounds, sesquioxides, insoluble residue, etc. in the ore leads to a sharp deterioration in the technological parameters of the phosphoric acid extraction process.

Quantitative change in components depending on the quality of raw materials [26] and the degree of phosphorite grinding determines some technological conditions for acid processing of raw materials.

Therefore, we have studied the chemical and salt composition of phosphate raw materials of varying degrees of grinding. For this purpose, two samples of phosphorites from the Kokdzhon deposit were selected. Sample No. 1 complies with the standards of ST TOO 38515646-003-2007, and sample No. 2 does not comply with ST TOO and the content of particles larger than 160 microns is 20%. Sieving and chemical analysis of these samples were carried out.

Chemical analysis of the samples and each fraction was carried out using known methods [27-29], in 3-4 fold repetitions, in order to obtain reliable results. The obtained data are presented in table. 3.1. and 3.2.

By studying the chemical composition (Table 2), it was established that the content of components in various fractions of the studied samples varies depending on the size class according to a certain pattern. The largest amount of insoluble residue and fluorine is characteristic of the fraction of phosphate raw materials, the particle sizes of which are 160-200 and more than 200 microns. With an increase in the degree of fragmentation (grinding), the insoluble residue and fluorine are quantitatively reduced in the raw material, which indicates the high strength of the crystals and their compounds, characterized by high energy of the crystal lattice, which has a high specific surface energy.

Table 1

***Chemical composition of Karatau phosphate raw materials and content
 Particles of varying degrees of grinding***

Name of samples	Particle sizes (μm) and their content (%)							
	More 200 mkm	160-200 mkm	100-160 mkm	70-100 mkm	0-70 mkm			
Sample №1 “normal” (standard) grinding	6,0	4,5	21,0	10,5	58,0			
Sample №2 non-standard grinding	15,0	5,0	26,0	11,5	42,0			
Chemical composition								
	Components, in%							
	P ₂ O ₅	CaO	MgO	R ₂ O ₃	Fe ₂ O ₃	CO ₂	F	Undist. remn.
Sample №1	24,75	41,57	3,40	2,04	0,82	9,04	2,65	11,65
Sample №2	24,53	41,76	3,50	1,92	0,86	9,23	3,75	10,46

From the above, it can be established that small grains have a larger total surface area and the reaction proceeds at a high speed. Large grains, with a relatively small total surface area, react slowly.

The decomposition of phosphorite larger than 200 microns occurs slowly, fewer crystallization centers are formed, as a result of which crystal growth occurs.

The fraction with grain sizes of 160-200 microns decomposes a little faster and crystals of smaller sizes are formed.

Due to the polydispersity of phosphorite, in all cases the rate of decomposition decreases towards the end of the reaction.

Table 2

Chemical composition of Karatau phosphate raw materials by size class

Particle sizes, microns	Components, in%								
	P ₂ O ₅	CaO	MgO	R ₂ O ₃	Fe ₂ O ₃	CO ₂	F	SiO ₂	H ₂ O
Sampe № 1									
More 200	27,05	41,25	2,95	1,24	0,75	6,71	3,27	9,00	12,0
160-200	25,26	41,22	3,15	1,34	0,83	8,53	2,95	8,57	11,0
100-160	25,22	41,25	3,42	1,40	0,40	9,45	2,57	8,15	10,0
70-100	24,84	41,24	3,85	1,85	0,91	9,85	2,5	8,76	10,0
0-70	26,05	41,22	5,53	1,88	1,01	9,00	2,42	8,39	9,6
Sample №2									
More 200	27,21	41,85	3,10	1,10	0,76	6,96	3,26	7,88	10,86
160-200	25,40	41,20	3,37	1,24	0,80	9,06	2,82	8,87	10,72
100-160	26,07	41,43	3,37	1,28	0,85	9,82	2,57	8,34	10,42
70-100	26,11	41,42	3,75	1,56	0,89	10,14	2,51	5,92	9,96
0-70	26,18	41,42	3,60	1,76	1,04	9,86	2,51	4,99	9,16

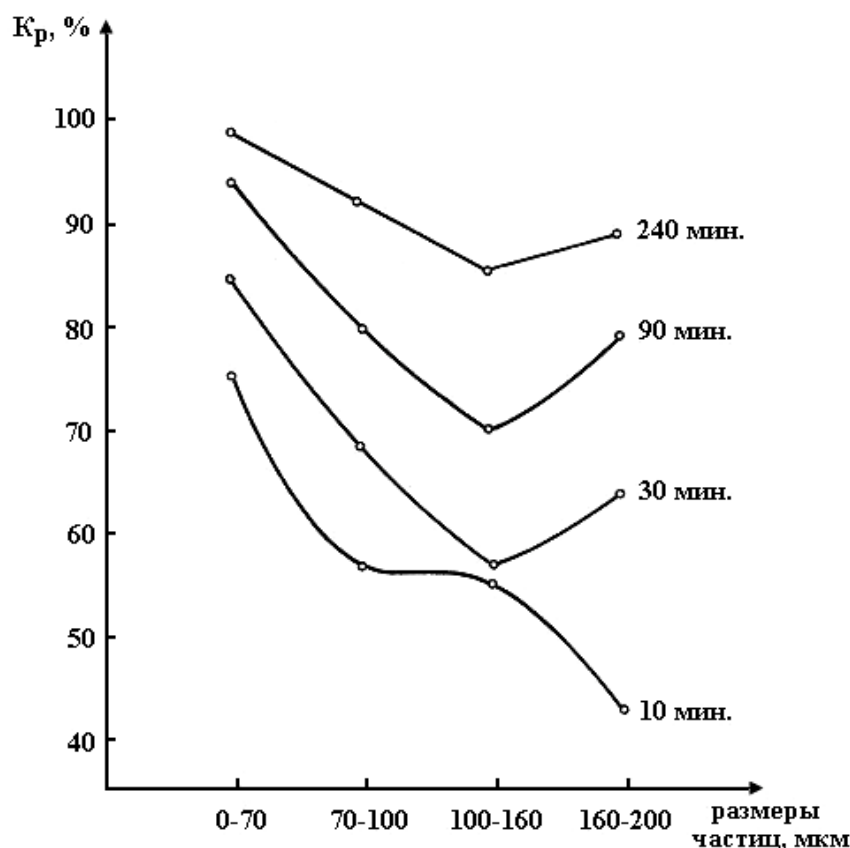


Fig 1. Change in the degree of phosphorite decomposition depending on the particle size over time.

CONCLUSION

The main practical results obtained during this work are:

1. By studying the physical and physicochemical properties in the systems H₃PO₄ – H₂O, H₃PO₄ – MgSO₄ – H₂O, H₃PO₄ – MgSO₄ – NH₄NO₃ – H₂O, the mechanism of the influence of

magnesium sulfate and ammonium nitrate on the properties of magnesium-containing phosphoric acids during concentration was established. It has been shown that in the presence of ammonium nitrate, the number of dissociated first hydrogen ions increases and the pH of the environment of phosphoric acid solutions decreases, which is reflected in a decrease in the heat of vaporization, an increase in vapor pressure and electrical conductivity, confirming the destruction of magnesium sulfate hydrates and changes in the physicochemical and rheological properties of EPA upon concentration.

REFERENCES

1. G'afurov Q., Shamshidinov I. Technology of mineral fertilizers and salts.– T.: Science and technology, 2007. – 352 p.
2. Angelov A.I., Denisov P.L. Phosphate raw materials for the production of mineral fertilizers. // Overview information. Series “Mineral fertilizers and sulfuric acid”. – M.: NIITEKHIM, 1987. – 52 p.
3. The Florida phosphate industry in transition // Phosph. a. Potas. 1985. – No. 140. – P. 25-27.
4. The Florida phosphate industry//Phosph. a. Potas. 1983. – No. 126. – P.23-28.
5. North Carolina phosphates // Phosph. a. Potas. 1986. – No. 141. – P. 22-24.
6. Morocco develops its P₂O₅ supply capability // Phosph. a. Potas. 1985. – No. 136. – P. 22-28.
7. Gock E., Jacob K.-H. Methods of processing pyrite-bearing phosphorite. Abu Tartur, Egypt // Prospect. Areas Desert Terrain. Int. Conf., Rabat, 14-17 Apr. 1985. – London. 1985. – P. 217-232.
8. World Phosphate Rock Statistics // Phosph. a. Potas. 1984. – No. 129. – P. 39-40: 1984. – No. 132. – P. 37-40: 1986. – No. 141. P. 39-40. – No. 142. P. 4-5.
9. Baudet G., Delubac G. Identification des facteurs importants dans la flotation du phosphate des anclens rejets de digues a aterite de Taibe (Senegal)//15 Congres international de meneralurgie, Cannes, 2-9 Juin 1985. St.-Etienne . 1985. – T. 3. – P. 367-379.
10. Timakova E.P. Development of the phosphate mining industry in Jordan. - Bicky. 12/22/1984. No. 152 (5729). – P. 6.
11. Angelov A.I., Borisov V.M. Phosphorus-containing raw materials for the fertilizer industry. // Tr. NIUIF. 1984. – Issue. 245. – pp. 7-24.
12. Klassen V.I. Enrichment of ores (chemical raw materials). – M: Nedra, 1979. – 239 p.
13. Klassen P.V., Samigullina L.I., Kharitonov A.B., Zadko N.I., Kuznetsova G.G. Enrichment and processing of phosphorites from the Chilisay deposit // Review. inf. ser. “Mineral fertilizers and sulfuric acid. – M.: NIITEKHIM, 1988. – 39 p.
14. Baskakova M.I. Productive forces of Southern Kazakhstan. – T. 3. – Alma-Ata.: Science, 1966. – 176 p.
15. Mukhtarov M.A., Urgaliev Sh.Sh., Tyutebaev S.T., Koliev B.V. Problems of complex use of phosphate raw materials Karatau // Chemical industry. Moscow, 1982. – No. 9. – P. 535-539.
16. Krasnov A.A., Nalivkina A.I., Klasson V.P., Romanov V.L., Proshlyakova N.G. The influence of the material composition of phosphorite ores and enrichment products of deposits in the Karatau basin on the technological properties of commercial raw materials. // Industry for the production of mineral fertilizers. Series "Mining and chemical industry". Overview information. – M.: NIITEKHIM, 1985. – P. 3-6.

17. Ratobylskaya L.D., Boyko N.N., Kozhevnikov A.O. Enrichment of phosphate ores. – M.: Nedra, 1979. – 261 p.
18. Sagunov V.G., Virt G.R., Nesipbaev A.N. Phosphate ores of Kazakhstan. Project 156: phosphorites. – Alma-Ata: Science, 1990. – 200 p.
19. Geology and minerals of the Republic of Uzbekistan / T. N. Dolimov, T. Sh. Shayakubov, etc.: Editorial team: T. Sh. Shayakubov (chief editor) and others - T.: University, 1998. - 724 pp.
20. Resolution of the President of the Republic of Uzbekistan No. PP-677 dated July 27, 2007 “On the program of modernization, technical and technological re-equipment of chemical industry enterprises for the period 2007-2011.” – 7 s.
21. Shayakubov T.Sh., Ilyashenko V.Ya., Boyko V.S., Kudryashev N.S., Turanov U.T. Paleogene phosphorites of Uzbekistan // Soviet Geology. – 1982. – No. 7. – P. 3-12.
22. Pokryshkin V.I., Boyko V.S., Ilyashenko V.Ya. Patterns of distribution of granular phosphorites in the Arabian-African province and Central Asia // Lithology and minerals. – 1978. – No. 6. – P. 102-119.
23. Popov V.S., Konov L.P. Phosphorite-bearing basins of Central Asia // Tr. Central Az. Research Institute of Geology and Mineral Resources. – Tashkent, 1981, Issue 3. -WITH. 49-60.
24. Shayakubov T.Sh., Malmatin G.I., Yuldashev A.Z., Ilyashenko V.Ya., Boyko V.S., Fatkhullaev G.F. Phosphorite deposits of the Mesozoic and Cenozoic of Uzbekistan // Geological problems of phosphorite accumulation. – M.: Nauka, 1987. – P. 10-16.
25. Shayakubov T.Sh., Mikhailov A.S., Boyko V.S., Kudryashev N.S., Zhuravlev Yu.P. Central Kyzylkum phosphorite-bearing region and its prospects // Geol. methods of prospecting and exploration of non-metal deposits. useful fossils. Review / All-Russian Scientific Research Institute of Economics miner raw materials and geol. - reconnaissance works VIEMS. – M.: 1983. – 28 p.
26. Boyko V.S., Shabanina N.V. Mineralogical features of granular phosphorite ores of the Kyzylkum and the study of their dressing // Uzbek Geological Journal. – 1979. – No. 3. – P. 84-86.
27. Bliskovsky V.Z., Mager V.O. Features of the material composition of phosphorite ores of the Dzheroy-Sardarinsky deposit, influencing the technology of their enrichment // Technological mineralogy of phosphate ores: Abstracts. report All-Union meeting November 17-18, 1987 - Cherkassy, 1987. - P. 42-43.
28. Shinkorenko S.F., Khryashchev S.V., Mikhailova T.G., Levkina T.T. Enrichment of phosphorites of the Kyzylkum deposit using roasting // Chemical industry. – 1989. – No. 3. – P. 187-189.
29. Kuzovlev A.K., Maltseva I.I., Pugach A.N. Technology of enrichment of granular-detrital phosphate ores of the Dzheroi and Sardarin deposits. – In the book: Tekhnol