УДК: 541.64:553.54

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БОРБОРДУК КЫЗЫЛКУМДУН ФОСФОРИТТЕРИНЕН АЛЫНГАН БУУЛАНГАН ЕРАНЫН (40÷56% P_2O_5) ФИЗИКАЛЫК-ХИМИЯЛЫК КАСИЕТТЕРИ

ФИЗИКО-ХИМИЧЕСКИЕ СВОЙСТВА ВЫПАРЕННОЙ ЭФК (40÷56% P_2O_5) ИЗ ФОСФОРИТОВ ЦЕНТРАЛЬНОГО КЫЗЫЛКУМА

PHYSICO-CHEMICAL PROPERTIES OF EVAPORATED EPA (40÷56% P_2O_5) FROM PHOSPHORITES OF THE CENTRAL KYZYLKUM

Аннотация. Бул макалада Борбордук Кызылкум чөлүнүн төмөнкү сорттогу фосфат тектеринен алынган нымдуу процесстеги фосфор кислотасынын (ФКК) концентрациясын жогорулатуу менен жогорку сапаттагы фосфор жер семирткичтерин өндүрүү технологиясы сунушталат. Фосфат кенинен чыккан кошулмалар ФККга өтүп, акыркы продуктта жол берилген деңгээлден ашып кеткендиктен, кислотаны тазалоо жана концентрациялоо талап кылынат. P_2O_5 курамы 25,13–27,5% болгон ФКК алуу үчүн эки баскычтуу буулануу ыкмасы колдонулган. Концентрация учурундагы курамдык өзгөрүүлөрдү көзөмөлдөө үчүн төрт ФКК үлгүсү жана 16 үлгү талданган. Магнийге бай чөкмөнү (40–46% P_2O_5) алып салуу процесстин натыйжалуулугун жогорулатат. Концентрацияланган кислоталар (45–55% P_2O_5) жогорку сапаттагы минералдык жер семирткичтерди өндүрүүгө мүмкүндүк берет.

Негизги сөздөр: Фосфор, фосфорит, нымдуу процесстеги фосфор кислотасы, концентрация, тазалоо, чыпкалоо, жер семирткичтер, кислотанын касиеттери.

Аннотация. Статья представляет технологию получения высококачественных фосфорных удобрений за счёт повышения концентрации экстракционной фосфорной кислоты (ЭФК), полученной из низкосортных фосфоритов Центрального Кызылкума. Поскольку примеси из фосфоритовой руды переходят в ЭФК и превышают допустимые уровни в конечном продукте, требуется очистка и концентрирование кислоты. Для получения ЭФК с содержанием P_2O_5 25,13–27,5% применён двухстадийный метод выпаривания. Были проанализированы четыре образца ЭФК и шестнадцать проб для отслеживания изменений состава в процессе концентрации. Удаление богатого магнием осадка (40–46% P_2O_5) повышает технологичность процесса. Концентрированные кислоты (45–55% P_2O_5) позволяют получать высококачественные минеральные удобрения.

Ключевые слова. Фосфор, фосфорит, экстракционная фосфорная кислота, концентрация, очистка, фильтрация, удобрения, свойства кислоты.

Abstract. The article presents a technology for producing high-quality phosphorus fertilizers by increasing the concentration of extraction phosphoric acid (EPA) obtained from low-grade phosphorites of the Central Kyzylkum Desert. Since impurities from phosphorite ore pass into the EPA and exceed permissible levels in the final product, purification and concentration of the acid are required. A two-stage evaporation method was used to obtain EPA with 25.13–27.5% P_2O_5. Four EPA samples and sixteen subsamples were analyzed to track changes in composition during concentration. Removing a magnesium-rich precipitate (40–46% P_2O_5) improves processability. Concentrated acids (45–55% P_2O_5) enable the production of high-quality mineral fertilizers.

Keywords. Phosphorus, phosphorite, extraction phosphoric acid, concentration, purification, filtration, fertilizers, acid properties.

Introduction. Agriculture heavily depends on fertilizers, and phosphorus is a key nutrient for all crops. It enhances respiration, photosynthesis, and metabolic processes, improving the absorption of potassium, nitrogen, magnesium, and other nutrients. Phosphorus fertilizers increase the effectiveness of other fertilizers, boosting yield and fruit quality. Although the number of phosphorus fertilizer types is smaller than others, phosphorus is present in many complex fertilizers. The main types used by farmers are simple and double superphosphate. Simple superphosphate contains 16–20% phosphorus, easily dissolves in water or acids, and includes nitrogen, magnesium, calcium, and sulfur, with low moisture content to prevent caking.

Both simple and double superphosphates are effective fertilizers, but their efficiency varies with soil type. Simple superphosphate works less effectively on acidic soils, while double superphosphate, containing 42–50% phosphorus, is highly concentrated and suitable for all soil types. Both are beneficial for plants, though double superphosphate and other phosphorus-rich ammonium phosphates are considered more important in practice.

To improve the quality of phosphorus fertilizers, it is important to ensure a high phosphorus content in phosphate rock and the absence of deterioration of its quality indicators by other impurities. It is also technologically possible to process EPA and obtain high-quality EPA from them.

The rapid growth of the Earth's population requires an increase in the quantitative indicators of its food supply. This, of course, requires an increase in the quantity and improvement of the quality of fertilizers, which are the basis for plant development. Based on this, the development of phosphorus-containing fertilizers is considered a priority.

As is known, phosphoric acid is used to produce phosphate fertilizers. There are two types of phosphoric acid: thermal and extraction phosphoric acid. Thermal production of these acids is expensive and, of course, requires the extraction of phosphoric acid. Therefore, various impurities in phosphate rock, especially those that are not needed for fertilizer, cause problems in the fertilizer industry. That is why phosphoric acid is obtained by extraction and used for production.

If we consider the entire world industry of phosphorus fertilizer production, it is convenient to obtain high-quality fertilizer by purification from the initially obtained phosphorite and the EPA obtained from it. It is known that scientists from all over the world have achieved many achievements in this direction. The cost of this is determined by the cost of the reagents used [1].

Therefore, in order to provide agricultural production with high-quality phosphorus and complex nitrogen-phosphorus, and, if necessary, potassium fertilizers, special attention is paid to the following areas: development of effective methods for simplifying the process of purification of EPA using inexpensive and cheap calcium salts and magnesium, including mineral substances as additives. It is important to develop an appropriate technology for obtaining improved quality phosphate ore and complex nitrogen-phosphorus fertilizers.

To date, our republic has achieved significant results in modernizing and improving the chemical industry based on innovation, building enterprises to produce new types of high-quality products, and localizing the raw material base. Large-scale measures have been implemented to develop the chemical industry. Both scientific and practical results have been achieved in the production of new types of import-substituting products [2].

In this regard, the issue of developing a technology for obtaining high-quality phosphorus and complex nitrogen-phosphorus fertilizers free from unnecessary impurities by purifying extracted phosphoric acid (EPA) from fluorides, sulfates, etc. during the extraction process is relevant. It is very important that the technological efficiency of the processes of obtaining EPA, its concentration, obtaining solid and liquid phosphorus fertilizers and feed phosphates largely depends on the physicochemical properties of the solutions used and formed and, it should be noted, on the technology of obtaining their products [3-7].

Such properties of EPA solutions as density, viscosity and electrical conductivity are necessary for assessing the possibility of transporting solutions, analyzing the processes of decomposition of phosphate raw materials and crystallization, selecting flow meters, pumps and other chemical equipment, and carrying out EPA evaporation processes.

An analysis of scientific and technical literature shows that the density ρ, viscosity μ and electrical conductivity *w* of extraction phosphoric acid are mainly determined by its chemical composition, which depends on the type and quality of the phosphate raw material and the content of various impurities in it [8,9,10].

For example, the viscosity of the EPA from Karatau phosphorites, all other things being equal, is 1.5÷3.2 times higher than the viscosity of the acid from the apatite concentrate. Moreover, as the acids evaporate, the difference increases sharply [11,12].

The viscosity of evaporated EPA from Chilisai phosphorite, containing 47.7% P_2O_5 at 70 °C is 3 times higher than the viscosity of acid from Karatau phosphorites [13]. Thus, the type and quality of natural phosphate raw materials has a significant impact on the rheological characteristics of phosphoric acid solutions.

In the literature, we did not find any information about the physicochemical properties of extractive phosphoric acid from phosphorites of the Central Kyzylkum Desert. The latter are characterized by a fairly high content of carbonates, mainly in the form of calcite, a relatively low content of impurities of MgO and R_2O_3, which creates certain prerequisites for obtaining high-quality extraction phosphoric acid and its concentration.

Necessary materials. In this regard, we conducted studies to determine the density, viscosity and electrical conductivity of evaporated EPA from phosphorites of the Central Kyzylkum. Evaporation of the initial EPA of the following composition, wt.% (Table 1):

Table 1. Contents of components in the composition of EPA

EPA at the rate of H_2SO_4 from stoichiometry, %	Content of components, mass%						
	P_2O_5	CaO	MgO	Fe_2O_3	Al_2O_3	Na_2O	K_2O
95	25,13	0,41	0,56	0,57	1,09	0,362	0,014
100	27,53	0,34	0,55	0,58	1,08	0,364	0,015
101	27,39	0,24	0,53	0,58	1,07	0,377	0,015
103	27,42	0,21	0,49	0,59	1,07	0,387	0,016

The procedure was carried out in the same way as described in the previous section, with the concentration of EPA reaching 40÷56,10% P_2O_5. Preliminary experiments have shown that with single-stage evaporation of acid, without intermediate purification of the EPA from impurities, as the P_2O_5 content increases above 57-58% by weight at room temperature, the acid quickly crystallizes and loses fluidity. In this regard, concentration was carried out to a content in the EPA, depending on the sulfuric acid standard, of 54,88 and 56,11% P_2O_5.

Laboratory studies. Samples of evaporated EPA were analyzed for the content of P_2O_5, SO_3, MgO, CaO, Al_2O_3,Fe_2O_3. The chemical composition of evaporated EPA from phosphorites of the Central Kyzyl Kum is given in following composition, wt.% (Table 1):

Table 2. Chemical composition of evaporated EPA from phosphorites of the Central Kyzylkum

No of acid samples	Norm of H_2SO_4 when obtaining EFA, % of stoichiometry	Content of components, mass%					
		P_2O_5	$SO_{3\ freely}$	CaO	MgO	Fe_2O_3	Al_2O_3
1	95	38,0	0,85	0,35	0,77	0,79	1,50
2		45,5	0,98	0,32	0,81	0,91	1,64
3		48,8	1,30	0,34	0,96	1,01	1,80
4		53,9	1,46	0,37	0,11	1,12	1,96
5	100	40,0	1,31	0,25	0,73	0,88	1,60
6		46,1	1,50	0,29	0,84	1,01	1,85
7		49,8	1,71	0,31	0,91	1,09	2,00
8		54,9	1,76	0,34	0,99	1,20	2,20
9	101	41,7	2,20	0,26	0,73	0,90	1,73
10		46,6	2,37	0,29	0,82	1,01	1,94
11		51,2	2,62	0,32	0,90	1,10	2,13
12		56,1	2,91	0,35	0,99	1,21	2,33
13	103	41,9	2,25	0,27	0,76	0,93	1,78
14		46,2	2,47	0,30	0,83	1,04	2,04
15		50,9	2,71	0,38	0,92	1,12	2,19
16		56,7	2,98	0,42	1,09	1,27	2,41

The determination of the density (ρ), viscosity (μ), and electrical conductivity (w) of the evaporated EPA obtained from the phosphorites of the Central Kyzylkum was carried out in the temperature range of 20–120 °C with a thermostatting accuracy of ±0.1 °C, in accordance with standard methods. The results are presented in Tables 3–5. Analysis of the data in Table 3 shows that the density of the evaporated EPA solutions depends significantly on both the acid concentration and the temperature.

An increase in temperature leads to a linear decrease in the acid density. At the same time, the slope tangent of the straight lines is practically constant for all studied concentrations of evaporated EPA from phosphorites of the Central Kyzylkum. This indicates that, at a constant rate of sulfuric acid in the process of obtaining EPA, the density of the evaporated EPA (in the studied concentration range) is directly proportional to the content of P_2O_5.

From the data conducted it can be shown that 100% and 101% sulfuric acid standards coincide almost closely with production. Therefore, the data below shows data on these standards.

Table 3. Density ρ (kg/m^3) of evaporated EPA from the phosphorites of the Central Kyzylkum

№	Temperature, °C							
	20	30	40	50	70	80	100	120
1	1602,9	1596,1	1589,7	1582,9	1567,3	1558,6	1544,6	1529,9
2	1713,6	1706,1	1698,3	1691,9	1675,9	1668,1	1652,7	1637,3
3	1802,8	1793,3	1786,0	1778,4	1763,1	1754,4	1739,2	1725,1
4	1888,8	1879,4	1871,1	1864,4	1849,3	1840,4	1825,6	1810,8
9	1541,7	1535,2	1528,2	1521,3	1506,9	1499,7	1485,8	1471,3
10	1642,1	1634,4	1627,7	1620,4	1604,7	1597,3	1582,1	1567,2
11	1752,6	1745,5	1738,3	1730,9	1715,1	1707,8	1691,8	1676,3
12	1853,2	1746,6	1839,0	1832,2	1816,3	1808,3	1792,4	1777,1

Discussion. Increasing the rate of sulfuric acid in the process of obtaining EPA from 100 to 101% of stoichiometry leads to a significant change in the physicochemical properties of the solutions. With the same content of P_2O_5 in the evaporated EPA, the acid ρ in the second case is 60-70 kg lower than in the first. As the concentration of EFA increases, this difference decreases somewhat, but insignificantly. The concentration of acid and temperature have a very significant effect on the viscosity of the evaporated EPA (Table 4).

Table 4. Viscosity μ, ($mPa \cdot s$) of evaporated EPA from phosphorites of the Central Kyzylkum

№	Temperature, °C					
	20	40	60	80	100	120
1	30,25	27,66	8,28	5,58	4,11	2,84
2	66,15	30,10	14,98	10,23	6,78	3,33
3	202.30	77,26	37,46	21,23	13,16	8,88
4	829,40	254,20	17,40	53,26	30,96	19,66
5	26,52	21,45	7,98	5,25	5,69	2,13
6	61,32	27,87	15,29	9,38	6,19	3,08
7	192,64	73,15	35,56	19,96	12,43	8,28
8	676,40	213,00	89,43	44,97	25,91	16,31

Such a sharp change in viscosity in solutions with increasing concentrations of phosphoric anhydride is caused by a significant decrease in the amount of free water in the system and a corresponding increase in the salt content of the solutions. A decrease in the temperature of concentrated EPA (50–56% P_2O_5) leads to the formation of stable solutions supersaturated with sesquioxide phosphates, which exhibit high viscosity. For example, in EPA containing 40.0% P_2O_5, the viscosity at 20 °C is 30.25 mPa·s, while at 120 °C it is 2.84 mPa·s; thus, the ratio μ_{20}/μ_{120} equals 10.65.

Some reduction in the viscosity of EPA is facilitated by an increase in the content of free sulfuric acid in solutions, achieved by using a slight excess of sulfuric acid in the process of obtaining EPA. Apparently, this is due to an increase in the solubility of salts and an increase in the proportion of a component that is less viscous than phosphoric acid.

Thus, the analysis of the results of the study of the rheological characteristics of evaporated EPA from phosphorites of the Central Kyzylkum shows that it retains sufficient fluidity for technological purposes up to a content of 50-56% P_2O_5. Increasing the temperature of acids to 40-60 °C leads to a sharp decrease in the viscosity of evaporated EPA.

The study of the electrical conductivity of evaporated EFA has established (Table 5) that w depends significantly on the acid concentration and temperature, and fluctuates in the range of $(1,93 \div 22,8) \cdot 10^{-2} Sm/m$. An increase in the P_2O_5 content and a decrease in temperature leads to a decrease in the specific electrical conductivity of the evaporated EPA.

Increasing the temperature from 20 to 120 °C increases the electrical conductivity of concentrated (55÷56% P_2O_5) EPA by 9÷14 times, while in solutions containing 40÷42% P_2O_5 only by 3,2÷3,3 times. Moreover, with an increase in the content of free sulfuric acid in the evaporated EFC, the electrical conductivity of the latter increases (Table 5), which is due to an increase in the concentration of hydrogen ions in the system.

Table 5. Specific electrical conductivity ℵ, (10^{-2} Sm/m) of evaporated EPA from phosphorites of the Central Kyzylkum

№	Temperature, °C					
	20	40	60	80	100	120
1	6,97	10,60	14,44	18,16	20,76	22,77
2	4,04	6,85	9,75	13,32	17,87	19,68
3	2,35	4,32	7,03	11,07	15,10	19,54
4	1,04	2,50	4,71	7,13	11,29	14,86
5	9,49	14,05	18,34	23,24	25,90	30,04
6	6,33	10,34	14,71	17,11	22,41	26,39
7	3,63	6,55	10,19	14,40	17,87	22,23
8	1,93	3,87	6,76	10,12	13,51	17,43

Based on the conducted research, it can be concluded that extraction phosphoric acid from the phosphorites of the Central Kyzylkum can be easily evaporated without preliminary purification from impurities to a concentration of 50–55% P_2O_5. The content of impurities in the evaporated acid is within the following ranges (wt.%): MgO – 0.7–1.0; Fe_2O_3 – 0.9–1.2; Al_2O_3 – 1.6–2.2. The evaporated extraction phosphoric acid exhibits satisfactory rheological characteristics, providing technological prerequisites for its use in the production of liquid complex fertilizers, polyphosphate fertilizers, double superphosphate, and feed phosphates.

Conclusion. To produce high-quality phosphorus fertilizers based on modern technologies for the production of mineral fertilizers, the phosphorus fertilizer obtained from phosphorite, which is its main raw material, must be of high quality. The main problem is that the high content of fluorine, which is an impurity in phosphate rock, relative to the total mass makes it difficult to obtain high-quality fertilizer. Therefore, an important aspect of the process is heating the initially obtained low-concentration EPA in order to concentrate it and remove excess fluorine from it. It has been proven that complex fertilizer and, in addition, livestock feed can be obtained on the basis of the obtained concentrated EPA.

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