PRODUCTION OF PHOSPHORUS-HUMUS FERTILIZERS BASED ON THE PROCESSING OF PHOSPHATE RAW MATERIALS WITH SULFURIC ACID AND OXIDIZED MEAL

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Annotatsiya. Maqolada fosforli xomashyolarni monokalsiyfosfat hosil bo‘lishi uchun stexiometrik 40-80% me’yorida 92% konsentratsiyali sulfat kislotasi bilan parchalash va kislotali fosforit massasiga qizilmiya shrotini sirka kislotasi ishtirokida vodorod peroksid bilan oksidlash (massa nisbatida: xomashyosining organik qismiga: H_2O_2: CH_3COOH = 100: 10: 1) natijasida olingan oksidlangan qizilmiya shroti massasini qo‘shish orqali donador fosfor-gumusli o‘g‘itlar olish jarayonlarini o‘rganish, Fosfor-gumusli o‘g‘itlar olishning maqbul sharoitlarini aniqlash natijalari keltirilgan.

Kalit so‘zlar: shrot, vodorod peroksid, fosforit, ekstraktiv moddalar, sulfat kislota, oksidlanish, gumin kislotalar, fosfor, azot, kalsiy, oltingugurt.

Аннотация. В статье представлены результаты изучения процессов получения гранулированных фосфорно-гумусовых удобрений путем разложения фосфорсодержащего сырья серной кислотой с концентрацией 92% при норме 40-80% стехиометрии для образования монокальцийфосфата и окисления солодкового шрота перекисью водорода в присутствии уксусной кислоты (в массовом соотношении: к органической части сырья: H_2O_2: CH_3COOH = 100: 10: 1) путем добавления массы окисленного солодкового

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шрота к кислой суперфосфатной массе, а также определения оптимальных условий получения фосфорно-гумусовых удобрений.

Ключевые слова: шрот, пероксид водорода, фосфорит, экстрактивные вещества, серная кислота, окисление, гуминовые кислоты, фосфор, азот, кальций, сера.

Abstract: The article presents the results of studying the processes of obtaining granulated phosphorus-humus fertilizers by decomposing phosphorus-containing raw materials with sulfuric acid with a concentration of 92% at a stechometric norm of 40-80% to form monocalcium phosphate and oxidizing licorice meal with hydrogen peroxide in the presence of acetic acid (in a mass ratio: to the organic part of the raw material: H_2O_2: CH_3COOH = 100: 10: 1) by adding the mass of oxidized licorice meal to the acid superphosphate mass, as well as determining the optimal conditions for obtaining phosphorus-humus fertilizers.

Keywords: meal, hydrogen peroxide, phosphorite, extractive substances, sulfuric acid, oxidation,humic acids, phosphorus, nitrogen, calcium, sulfur.

Introduction.

World experience in the sustainable development of agriculture and agrochemical tests have shown that the application of organic and organomineral fertilizers is the main factor in preserving soil fertility, increasing the beneficial effects of mineral fertilizers, and obtaining high and quality yields of agricultural crops. Therefore, obtaining and applying organic and organomineral fertilizers based on organic plant resources, phosphate raw materials, and agricultural ores containing all the nutrients necessary for the normal growth and development of plants is a criterion for increasing agricultural productivity. In this regard, the development and implementation of a technology for obtaining organic and organomineral fertilizers based on plant-based organic resources, phosphate raw materials, and agricultural ores is of great importance.

In global agricultural practice, soil fertility is typically assessed based on three main types of indicators: agrophysical, biological, and agrochemical. These soil fertility indicators are closely interrelated. Agrophysical indicators of soil fertility include structure, fractional and mineralogical composition, porosity, air and moisture capacity, and water permeability. The agrophysical indicators of soil usually remain stable for long periods, and when they do change, restoration is extremely difficult. The agrochemical indicators of soil fertility include the content of nitrogen, phosphorus, potassium, and other macro- and microelements, as well as their availability to plants. These agrochemical indicators determine the supply of essential nutrients for plant growth and development. The biological indicator of soil fertility is determined by the quantity, composition, and properties of organic matter, as well as its biological activity and phytosanitary condition. It

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should be noted that in most cases, the primary indicator of soil fertility is the amount of organic matter and its qualitative state. This is because organic substances have the strongest influence on the most crucial soil properties: agrophysical, biological, and agrochemical states. The reserves of organic or humic substances in the soil are the main indicator of soil fertility. Soil organic matter accumulates carbon, nitrogen, potassium, phosphorus, and other macro- and microelements, ensures the formation of optimal conditions for plant development in the soil, and mitigates the effects of toxic substances [1].

Plant residues in soil undergo humification and mineralization under the influence of microflora, simultaneously releasing nutrients. The increase in humus content in the upper soil horizon is related to the nature of input, distribution, and decomposition of plant residues. The role of crops in humus accumulation in soils is determined by their yield and crop rotation structure. The annual approximate replenishment of soil carbon after plant residue humification ranges from 0.71 to 1.34 t/ha. Plant residues contain a large amount of nutrients available to cultivated plants. The quantity of nitrogen, phosphorus, and potassium entering the soil depends on the type of crop rotation, crop yield, and the level of mineral and organic fertilizer application. Plant residues contribute 27.2-49.0 kg/ha of nitrogen, 13.6-24.5 kg/ha of phosphorus, and 27.2-49.0 kg/ha of potassium to the soil. On average, 90.9 kg/ha of nitrogen, phosphorus, and potassium combined are returned to the soil with agricultural crop residues [2].

In the work [3], it was shown that the application of organomineral fertilizers was positive both for the total weight of the bunch and for the elements of the crop structure. The highest grain, straw, and bunch yields were obtained in the variant with a manure-lignin mixture at a rate of 60 t/ha - 20.04%; 23.60 and 43.89 g/vessel, respectively, which is 65%-79% higher than in the control group. Relative grain yields of oats were obtained when applying semi-rotted manure at a rate of 60 and 80 t/ha and manure-lignin mixture at a rate of 40 t/ha - from 44 to 46 g/container. The action of the manure-lignin mixture at a rate of 80 t/ha and the lignin-melt mixture at a rate of 40 t/ha showed a tendency towards a decrease in the grain of oats, while the mass of straw and hay increased by 58 and 28%; 32% and 62% respectively.

The use of humic substances (HS) in combination with mineral fertilizers improves the agrochemical properties of soils and maintains their fertility. Humic acids form organomineral complex particles with soil mineral particles, capable of absorbing moisture and dissolved substances. HS bind the mineral particles of the soil and contribute to the formation of a water-resistant loose crumb-granular structure, enhancing the moisture-absorbing and agrochemical properties of soils.

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The nutrients present in such soils are not chemically bound to soil minerals, are not washed away by water, and remain in a form accessible to plants [4].

In work 5, the possibility of obtaining phosphorus-containing bicomposite fertilizers with increased resistance to water washing by impregnating porous substrates made of birch bark and bark with a K_2HPO_4 aqueous solution was shown. The conditions for obtaining bicomposite fertilizers with the highest resistance to phosphate leaching were determined: isothermal holding of the impregnated samples at 100°C for 2 hours; drying at 200°C and subsequent treatment with a 0.1 N HNO_3 solution. From fertilizers obtained under these conditions and containing 3.5-4 wt.% phosphorus, about 35% of phosphates are washed away by water within 72 hours, which ensures the effect of their prolonged action. It has been shown that to obtain fertilizers with high resistance to phosphate leaching, the amount of phosphorus applied to the substrate should not exceed 4.0 wt.%. It has been established that biocomposite fertilizers based on lump and bark substrates surpass industrial granulated fertilizers in their resistance to phosphate leaching.

The problem of phosphorus in agriculture has been of interest since the formation of agrochemistry as a science. This is due to the following factors. Firstly, the total content of this element in the vast majority of soils is lower than in other nutrient elements. Secondly, due to the element's chemical nature, along with its low content, it is characterized by very low mobility in the soil, i.e., poor availability for plants. Thirdly, the reserves of phosphate raw materials for fertilizer production are very limited, and some of them are practically unsuitable for industrial processing, for obtaining water-soluble phosphorus fertilizers. To maintain food production for the growing population of the planet, it is necessary to combine phosphorus management approaches not only to extend the service life of the remaining non-renewable phosphate reserves, but also to improve the efficiency and sustainable phosphorus cycle. Solutions include improving the efficiency of fertilizer application to agricultural lands along with better understanding of phosphorus cycling in soil-plant systems and the interaction between soil physics, chemistry, and biology in conjunction with plant characteristics [6].

The initial raw materials for the production of phosphorus fertilizers and other phosphorus-containing products are natural mineral phosphate ores - apatites and phosphorites. Phosphate ores differ in their physical and chemical properties depending on their mineralogical composition, structure, and impurity content. Phosphate ore reserves are mainly represented by phosphorites, the amount of apatite does not exceed 6% of reliable reserves, and its share is about 15%. The useful mineral in both types of raw materials is calcium fluorapatite, the

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composition of which corresponds to the formula $Ca_5(PO_4)_3F$. The most common in nature are calcium fluorapatite $3Ca_3 (PO_4)_2CaF_2$ and hydroxyapatite $3Ca_3(PO_4)2 \cdot Ca(OH)_2$. The richest industrial apatite-nepheline ore deposit in terms of concentration and reserves is located in the Kola Peninsula [7,8].

The identified phosphate ore reserves are accounted for in more than 76 countries and are estimated at 70587.4 million tons of P_2O_5, including 65328.4 million tons of phosphorite and 5259 million tons of apatite ores. In ten countries (Morocco, USA, China, Russia, Mexico, Kazakhstan, Peru, South Africa, Western Sahara, and Tunisia), 61015.4 million tons of P_2O_5 are concentrated, representing 87% of global reserves. Significant reserves of phosphate rocks have been identified at the bottom of seas and oceans, mainly on shelves [9].

Phosphorite deposits are found in many regions of Uzbekistan. A promising deposit for industrial development is the Central Kyzylkum region. To date, four phosphorite deposits have been identified: Jeroy-Sardarinsky, Jetymtau, Tashkurinsky, and Karakatinsky. Of these, the most studied is the Jeroy-Sardara deposit, where three areas have been explored: Jeroy Yuzhny, Kurukkuduk, and Tashkura, with total reserves estimated at 384,413 thousand tons of ore or 739,916 thousand tons of P_2O_5 [10,11].

The demand for phosphorus fertilizers in the agriculture of the Republic of Uzbekistan averages 660 thousand tons of 100% P_2O_5 per year. However, chemical enterprises produce only 150-160 thousand tons of 100% P_2O_5 per year, which is about 23% of the total demand. This means that the amount of phosphorus fertilizer applied to the soil in terms of P_2O_5 is 4.3 times less than the annual requirement. The main reason for this situation is the shortage of high-quality phosphate raw materials.

The limited production of phosphorite concentrate in the Central Kyzylkum and the lack of significant prospects for its growth necessitate, under the current conditions of soil phosphorus depletion, the search for alternative sources of mineral raw materials for phosphorus fertilizer production and increasing its efficiency.

Currently, the most common phosphorus-containing fertilizer worldwide is simple superphosphate. This is mainly water-soluble calcium monophosphate $Ca(H_2PO_4)_2$. It is obtained by decomposing phosphate raw materials with sulfuric acid. When applied to neutral, bases-saturated soils, it relatively quickly transforms into $CaHPO_4$ and $Ca_3(PO_4)_2$.

$$Ca(H_2PO_4)_2+Ca(HCO_3)_2 = 2CaHPO_4 \times 2H_2O+2CO_2$$

$$Ca(H_2PO_4)_2+2Ca(HCO_3)_2 = Ca_3(PO_4)_2 +4H2O + 4CO_2Ca(H_2PO_4)_2$$

In such conditions, hydroxyapatite or fluorapatite, not assimilated by plants, may appear in the soils. In acidic soils rich in one and a half oxides, poorly soluble,

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difficult-to-absorb phosphorus compounds can form. For this reason, phosphate consumption generally does not exceed 25%. Consequently, the consumption of water-soluble phosphate fertilizers is much higher than the actual required amount of phosphorus [12; pp. 2260-265, 13; pp. 85-94].

The works [14-17] detail the significance and mechanism of action of organomineral fertilizers when used in agricultural production. The humic substances contained in fertilizers contribute to the better assimilation of essential nutrients by plants. They prevent the retrogradation of digestible phosphates, contain microelements, physiological and growth-active substances, form a loose structure, create favorable conditions for the life of microorganisms, stimulate the growth and development of plants.

Raw material sources for obtaining organic or organomineral fertilizers are manure, peat, lignin, sapropel, brown coals, and other organic substances of plant origin.

Licorice meal can serve as a good raw material for obtaining humic fertilizers. It should be noted that in Uzbekistan, more than thirty enterprises and companies of various forms of ownership are engaged in the procurement and processing of licorice root in various regions. It grows in the northwestern part of Uzbekistan - Khorezm, Bukhara regions, as well as in the Republic of Karakalpakstan [18].

Licorice is a herbaceous plant belonging to the legume family. Licorice leaves are used for medicinal infusions and decoctions, in addition, licorice hay is rich in proteins and is a good fodder for livestock, but the main medicinal properties are possessed by the plant's root. The chemical composition of the root includes malic, citric, and succinic acids, beta-carotene, a large number of vitamins, as well as mineral substances necessary for the human body: potassium, calcium, iron, phosphorus, magnesium, and others. The main biologically active substances of licorice root are triterpenoid compounds, mainly glycyrrhizic acid and flavonoids, the content of which is up to 25%. It should be noted that after processing the licorice root, i.e., after the extraction of glycyrrhizic acid and other biologically active substances, a significant amount of meal remains, more than 80% of the initial raw material (over 100 thousand tons per year in Karakalpakstan), which is a production waste, as well as a liquid solution of ammonium sulfate (0.5-1%), about 400 thousand tons, containing a certain amount of physiologically active substances [19-21].

From the above, it can be seen that to date, there is no method for converting the insoluble part of licorice meal into beneficial products such as humic acids, fulvic acids, or humino-like substances necessary for increasing and maintaining soil fertility. It should be noted that such studies have not been conducted on

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licorice root meal - a waste product of pharmaceutical production of medicines based on licorice root.

The purpose of the research is to study the processes of oxidation of licorice meal with hydrogen peroxide in the presence of acetic acid and to process the resulting oxidation product from the decomposition of phosphate raw materials with sulfuric acid into phosphorus-humus fertilizers.

Licorice root meal was used as the initial raw material, which was dried to air-dry state, then ground to a particle size of 0.25 mm. After drying and grinding, an average representative sample of more than 10 kg of meal was formed for analysis and research, from which weighed samples were taken to determine moisture content, ash content, extractive substances with water and alkaline solution. The obtained results of the initial meal analysis are presented in Table 1.

Table 1.

Chemical composition of the initial licorice root meal

Moisture, %	Ash content, %	The content of extractive substances extracted by a 1% NaOH solution, %	Content of extractive substances extracted by water, %	Insoluble organic, %
5.41	4.66	5.87	15.78	68.28

Table 2 presents the results of mass spectrometric analysis (ICP-MS) of licorice meal ash. The table demonstrates that licorice meal contains a wide range of microelements essential for plant growth and development.

Table 2.

Results of mass spectrometric analysis of licorice meal ash

Name and content of elements, in g/t									
Li 59	Be 1,80	B 16	Na 12000	Mg 14000	Al 80000	P 770	K 21000	Ca 65000	Cr 55
Mn 1200	Fe 34000	Co 16	Ni 40	Cu 75	Zn 100	Mo 3,30	Ag 0,490	Ba 440	Ti 3600

Mineralized mass of phosphate raw material and Slime, namely, mineralized mass of phosphate raw material, having the composition,%: P_2O_5 - 15.18_{total}; $P_2O_{5sol.\ for\ citric\ acid}$ - 0.72; $P_2O_{5sol.\ for\ Tr\text{-}B}$ - 2.11; CaO_{total} - 45.49; MgO - 1.19; Al_2O_3 - 1.10; Fe_2O_3 - 0.89; F - 2.2; CO_2 - 15.23; SO_3 - 2.82; $P_2O_{5sol.\ for\ citric\ acid}$ / P_2O_{5total} - 4.77; $P_2O_{5sol.\ for\ Tr\text{-}B}$ / P_2O_{5total} - 13.89 and Phosphate raw material Slag with the

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composition, %: P_2O_{5total} - 9.74; $P_2O_{5sol.\ for\ citric\ acid}$ - 0.58; $P_2O_{5sol.\ for\ Tr\text{-}B}$ - 2.00; CaO_{total} - 42.45; MgO - 0.37; Al_2O_3 - 1.17; Fe_2O_3 - 1.19; F - 1.71; CO_2 - 22.36; SO_3 - 0.10; $P_2O_{5sol.\ for\ citric\ acid}$ / P_2O_{5total} - 5.89; $P_2O_{5sol.\ by\ Tr\text{-}B}$ / P_2O_{5total} - 20.53.

At the beginning of the work, the oxidation processes of the ground licorice meal to a size less than 0.1 mm were studied by a water solution of hydrogen peroxide in the presence of acetic acid at a mass ratio of the organic part of the licorice meal: H_2O_2: CH_3COOH = 100: (10-20): (0.1: 1) The experiments were carried out in a glass cylindrical reactor equipped with a thermostating jacket and a stirrer. An oxidizer solution was poured into the reactor, the specified temperature was set, the mixer was turned on, and a sample of ground licorice meal was loaded. At the end of the process, the reaction mass was dried to air-dry state and its ash content, moisture content, organic matter, and the yield of extractive substances with a 1% sodium hydroxide solution were determined, and analyses were conducted according to the methods described in the works [22,23].

Under optimal conditions, the oxidation state of the meal was 70.94%. The resulting oxidation product contains 87.78% organic matter, 35.88% humic acids, 26.39% fulvic acid, and 29.06% residual meal. We used this moist, thick mass of oxidized meal as a starting component for processing the decomposition product of phosphate raw materials.

In the next stage of the work, the processes of obtaining phosphorus-humus fertilizers by decomposing the phosphate raw material, the mineralized mass, and the slime of the above composition with sulfuric acid were studied. Sulfuric acid with a concentration of 92% was used to activate the phosphate raw material.

In the first stage of research on the process of obtaining phosphorus-humus fertilizers, phosphate raw materials were decomposed with sulfuric acid to convert the undigested form of P_2O_5 into the raw material into a form readily available to plants. The sulfuric acid norm was taken in amounts of 40, 50, 60, 70, and 80% of the stoichiometry for the formation of monocalcium phosphate according to the reaction:

$$CaO_{\text{ in phosphorus}} + 2H_2SO_4 \rightarrow Ca(H_2PO_4)_2 \cdot H_2O$$

Treatment of the phosphate raw material with sulfuric acid was carried out for 60 min. After the decomposition of the phosphate raw material with sulfuric acid was completed, oxidized meal was introduced into the mixture. It was taken in weight ratios of phosphorite: meal (organic part of oxidized meal) = 1: (0.20 - 1). Then, the resulting mixture was stirred for 30 minutes and neutralized with 25% aqueous ammonia to a pH of 4-4.5. Drying was carried out at 80°C, and granulation was carried out by the rolling method during the ammonization and drying process. The chemical composition and strength of the fertilizer granules were determined. The strength of 2-3 mm granules was determined using the IPG-1M granule

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strength gauge, with an average value of 2.1-2.5 MPa. The determination of all forms of P_2O_5 was carried out by the weight method by precipitating the phosphate ion with a magnesium-ammonium phosphate mixture, followed by calcination of the precipitate at 1000-1050 ºC according to GOST 20851.2-75. Nitrogen was determined according to GOST 26715-85. SO_3 was determined by precipitation in the form of barium sulfate, and the CaO content was determined by titration with a 0.05 N Trilon B solution in the presence of a fluorescent indicator. The analysis results are presented in Tables 3-4.

Table 3.

Composition of phosphorus-humus fertilizers obtained on the basis of hydrogen peroxide-oxidized meal and phosphate raw materials, mineralized mass

Ratio Phosphorite: Meal	P_2O_5 total, %	P_2O_5 sol. for citric acid, %	P_2O_5 sol. by Tr-B, %	CaO total, %	$\frac{P_2O_{5усв.}}{P_2O_{5общ.}}$, %	SO_3 total, %	N total, %	OS, %	ES, %
The norm of H_2SO_4 from stoichiometry for the formation of $Ca(H_2PO_4)_2$, 40%									
1 : 0	13,02	5,15	3,74	37,18	39,56	29,31	0,56	0	0
1 : 0,2	11,35	4,74	3,25	32,34	41,77	25,69	0,81	14,46	10,25
1 : 0,4	9,88	4,37	2,90	28,81	44,28	23,06	0,93	24,93	18,88
1 : 0,6	8,62	3,92	2,42	25,93	45,56	20,27	1,12	32,84	23,80
1 : 0,8	7,91	3,66	1,98	22,79	46,33	18,33	1,31	38,72	27,46
1 : 1,0	7,38	3,41	1,78	20,25	47,18	16,22	1,44	43,51	30,86
The norm of H_2SO_4 from stoichiometry for the formation of $Ca(H_2PO_4)_2$, 50%									
1 : 0	12,57	5,57	4,66	35,73	44,31	28,98	1,11	0	0
1 : 0,2	10,98	4,99	4,31	31,32	45,46	25,32	1,28	14,11	9.98
1 : 0,4	9,51	4,42	3,77	27,90	46,52	22,63	1,47	24,43	18,11

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1 : 0,6	8,33	3,99	3,14	25,06	47,87	19,86	1,67	32,35	23,04
1 : 0,8	7,68	3,72	2,71	22,19	48,55	18,12	1,88	38,12	27,04
1 : 1,0	6,92	3,42	2,21	19,85	49,47	15,78	2,15	42,97	30,48
The norm of H_2SO_4 from stoichiometry for the formation of $Ca(H_2PO_4)_2$, 60%									
1 : 0	11,93	5,75	4,84	33,78	48,23	28,37	1,43	0	0
1 : 0,2	10,52	5,16	4,57	30,16	49,07	24,66	1,67	13,76	9,76
1 : 0,4	9,17	4,60	3,93	27,21	50,18	22,21	1,91	23,84	17,13
1 : 0,6	7,98	4,08	3,68	24,16	51,22	19,16	2,15	31,85	22,41
1 : 0,8	7,45	3,90	2,99	21,52	52,35	17,54	2,38	37,66	26,71
1 : 1,0	6,80	3,62	2,56	19,66	53,26	15,22	2,55	42,51	30,16
The norm of H_2SO_4 from stoichiometry for the formation of $Ca(H_2PO_4)_2$, 70%									
1 : 0	11,76	5,98	4,97	31,77	50,93	27,87	2,01	0	0
1 : 0,2	10,25	5,35	4,76	29,09	52,21	23,91	2,33	13,42	9,52
1 : 0,4	8,80	4,70	4,23	26,34	53,40	21,32	2,57	23,45	16,45
1 : 0,6	7,76	4,24	3,87	23,29	54,66	18,78	2,78	31,33	21,78
1 : 0,8	6,96	3,88	3,41	21,12	55,82	17,10	3,10	37,11	26,32
1 : 1,0	6,24	3,54	2,92	19,42	56,78	14,83	3,36	42,14	29,89
The norm of H_2SO_4 from stoichiometry for the formation of $Ca(H_2PO_4)_2$, 80%									
1 : 0	11,38	6,22	5,26	30,22	54,64	27,11	2,53	0	0
1 : 0,2	9,89	5,53	4,92	28,15	55,96	23,50	2,76	12,98	9,21

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1 : 0,4	8,50	4,86	4,67	25,47	57,17	20,83	3,13	23,11	15,88
1 : 0,6	7,54	4,48	4,28	22,59	59,45	18,39	3,61	30,89	21,14
1 : 0,8	6,49	3,90	3,85	20,24	60,15	16,78	3,92	36,77	26,08
1 : 1,0	5,76	3,55	3,42	19,20	61,58	14,41	4,30	41,73	29,60

Table 4.

Composition of phosphorus-humus fertilizers obtained on the basis of hydrogen peroxide-oxidized meal and phosphate raw material Slime

Ratio Phosphorite: Meal	P_2O_5 total, %	P_2O_5 sol. for citric acid, %	P_2O_5 sol. by Tr-B, %	CaO total, %	$\frac{P_2O_{5усв.}}{P_2O_{5общ.}}$, %	SO_3 total, %	N total, %	OS, %	ES, %
The norm of H_2SO_4 from stoichiometry for the formation of $Ca(H_2PO_4)_2$, 40%									
1 : 0	8,87	3,51	2,66	38,55	39,53	30,75	0,86	0	0
1 : 0,2	7,12	2,99	2,09	30,08	41,96	28,32	1,16	14,81	10,51
1 : 0,4	6,35	2,83	1,92	26,75	44,58	26,54	1,33	25,21	17,88
1 : 0,6	5,61	2,65	1,70	25,36	47,32	22,98	1,62	33,15	23,51
1 : 0,8	5,03	2,45	1.54	23,17	48,76	20,24	1,87	39,06	27,70
1 : 1,0	4,76	2,38	1,31	21,13	50,12	18,40	2,11	43,89	31,13
The norm of H_2SO_4 from stoichiometry for the formation of $Ca(H_2PO_4)_2$, 50%									
1 : 0	8,65	4,22	3,12	37,12	48,85	32,14	1,18	0	0
1 : 0,2	6,94	3,50	2,88	29,42	50,43	29,70	1,42	14,53	10,29
1 : 0,4	6,16	3,21	2,57	26,31	52,12	27,86	1,67	24,88	17,64

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1 : 0,6	5,45	3,03	2,33	24,67	55,67	24,32	1,85	32,75	23,23
1 : 0,8	4,88	2,82	2,18	22,65	57,84	22,23	2,13	38,71	27,46
1 : 1,0	4,32	2,58	1,95	20,56	59,66	20,06	2,31	43,52	30,87
The norm of H_2SO_4 from stoichiometry for the formation of $Ca(H_2PO_4)_2$, 60%									
1 : 0	8,42	4,72	3,65	35,67	56,07	33,45	1,41	0	0
1 : 0,2	6,75	3,93	3,44	28,89	58,21	31,11	1,68	14,36	10,18
1 : 0,4	5,97	3,60	3,21	25,94	60,33	29,25	1,96	24,41	17,31
1 : 0,6	5,28	3,35	3,03	24,15	63,51	25,66	2,27	32,06	22,74
1 : 0,8	4,62	3,03	2,88	22,09	65,71	23,57	2,55	38,45	27,27
1 : 1,0	4,05	2,75	2,57	19,93	67,90	21,79	2,87	43,22	30,66
The norm of H_2SO_4 from stoichiometry for the formation of $Ca(H_2PO_4)_2$, 70%									
1 : 0	8,26	5,31	4,12	34,11	64,25	34,72	1,89	0	0
1 : 0,2	6,55	4,36	3,85	28,25	66.60	32,45	2,35	14,05	9,96
1 : 0,4	5,83	3,97	3,61	25,43	68,13	30,67	2,66	23,96	17,00
1 : 0,6	5,13	3,66	3,43	23,76	71,47	26,96	2,84	31,61	22,42
1 : 0,8	4,47	3,27	3,20	21,34	73,18	24,83	3,19	38,10	27,03
1 : 1,0	3,91	2,95	3,01	19,41	75,54	22,90	3,57	42,91	30,44
The norm of H_2SO_4 from stoichiometry for the formation of $Ca(H_2PO_4)_2$, 80%									
1 : 0	8,11	5,89	4,65	32,65	72,62	35,86	2,25	0	0
1 : 0,2	6,39	4,75	4,08	27,43	74,43	33,75	2,81	13,68	9,70

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1 : 0,4	5,75	4,38	3,83	25,05	76,27	31,90	3,36	23,60	16,75
1 : 0,6	5,06	3,97	3,68	23,07	78,51	28,11	3,92	31,20	22,13
1 : 0,8	4,31	3,43	3,43	20,86	79,76	26,18	4,46	37,70	26,74
1 : 1,0	3,76	3,05	3,21	18,80	81,13	24,27	4,93	42,54	30,18

The results for both types of phosphate raw materials are similar. The higher the norm of sulfuric acid and the less phosphate raw material is taken, the lower the P_2O_{5total} content in the product, but the higher the relative content of the assimilable form P_2O_5. As can be seen from Table 4, at a meal: phosphorite ratio of 1:0.2 and a sulfuric acid norm of 40% of the stoichiometry for the formation of monocalcium phosphate, a phosphorus-humus fertilizer with the composition (wt. %): $P_2O_{5tot.}$ - 11.35; $P_2O_{5sol.\ for\ citric\ acid}$ - 4.74; $P_2O_{5sol.\ by\ Trilon\text{-}B}$ - 3.25; organic substances - 14.46; extractive substances - 10.25; nitrogen - 0.81; $CaO_{tot.}$ - 32.34; relative content of $P_2O_{5abc.\ for\ citric\ acid}$ - 41.77. With the same ratio of meal to phosphorite, but with a rate of 80% of the stoichiometry for the formation of monocalcium phosphate, a fertilizer with a composition (wt. %): P_2O_{5tot}t. - 9.89; $P_2O_{5sol.\ for\ citric\ acid}$ - 5.53; $P_2O_{5sol.\ by\ Trilon\text{-}B}$ - 4.92; organic substances - 12.98; extractive substances - 9.21; nitrogen - 2.76; $CaO_{tot.}$ - 28.15; the relative content of P_2O_5 absorbed by citric acid is 55.96.

The table also shows that with an increase in the amount of oxidized meal, the relative content of the assimilable form P_2O_5 increases. For example, at a phosphorite: meal ratio of 1:0 and a sulfuric acid norm of 40% of the stoichiometry for the formation of monocalcium phosphate, the relative content of the assimilable form of P_2O_5 is 39.56%, at the same sulfuric acid norm for the formation of monocalcium phosphate, but at a phosphorite: meal ratio of 1:1, the relative content of the assimilable form of P_2O_5 is 47.18%.

Similar fertilizers are obtained when processing phosphorus raw materials. (table 5). Thus, when using Slime phosphate raw material at a meal: phosphorite ratio of 1:0.4 and a sulfuric acid norm of 70% of the stoichiometry for the formation of monocalcium phosphate, a phosphorus-humus fertilizers with a composition (wt. %): $P_2O_{5tot.}$ - 5.83; $P_2O_{5sol.\ for\ citric\ acid}$ - 3.97; $P_2O_{5sol.\ by\ Trilon\text{-}B}$ - 3.61; organic substances - 23.96; EA - 17.00; nitrogen - 2.66; CaOtot. - 25.43; relative content of P2O5ass. for citric acid - 68.13. And at an acid norm of 80%, with the same ratio of meal: phosphorite, the fertilizer contains P2O5total. - 5.75; P2O5sol. for citric acid - 4.38; P2O5sol. by trilon B - 3.83; organic substances - 23.60; extractive substances - 16.75; nitrogen - 3.36; CaO_{tot}t. - 25.05; relative content of $P_2O_{5ass.\ for\ citric\ acid}$ - 76.27.

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Figures 1-4 show the X-ray diffraction patterns of the initial phosphate raw material Mineralized mass and Sludge, as well as phosphorus-humus fertilizers obtained at a phosphorite: meal ratio of 1:0,4 and a sulfuric acid norm of 70% of the stoichiometry for the formation of monocalcium phosphate. X-ray diffraction analysis was performed on an XRD-6100 apparatus with a controlled computer. Phase identification was performed using domestic catalogs and ASTM.

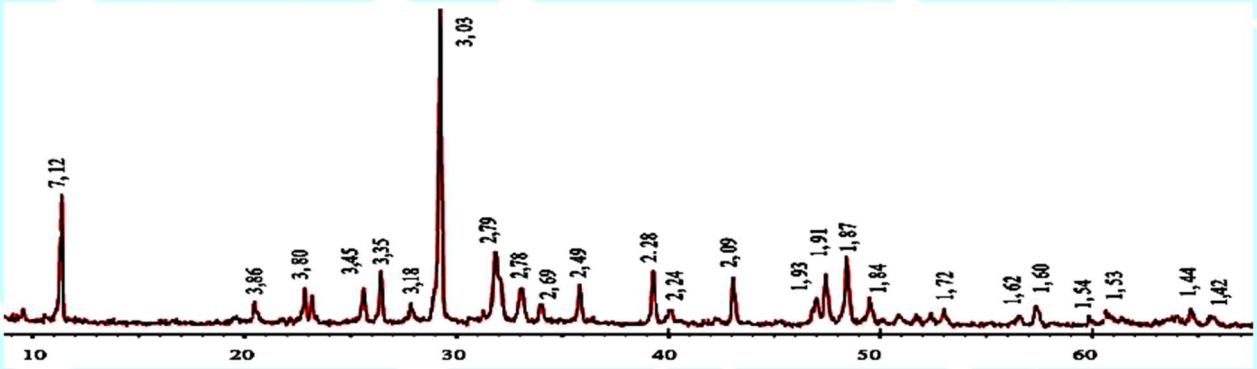


Fig. 1. X-ray diffraction pattern of phosphate raw material of mineralized mass

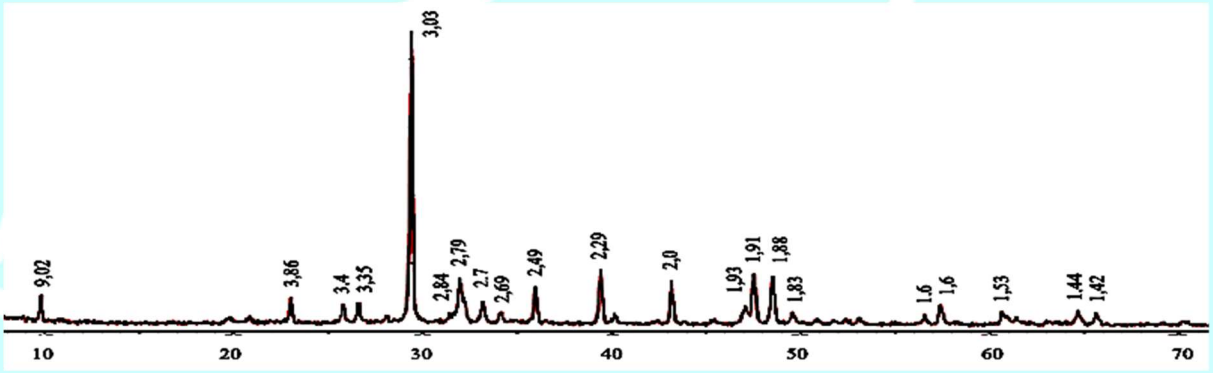


Figure 3 - X-ray diffraction pattern of the sludge phosphorite.

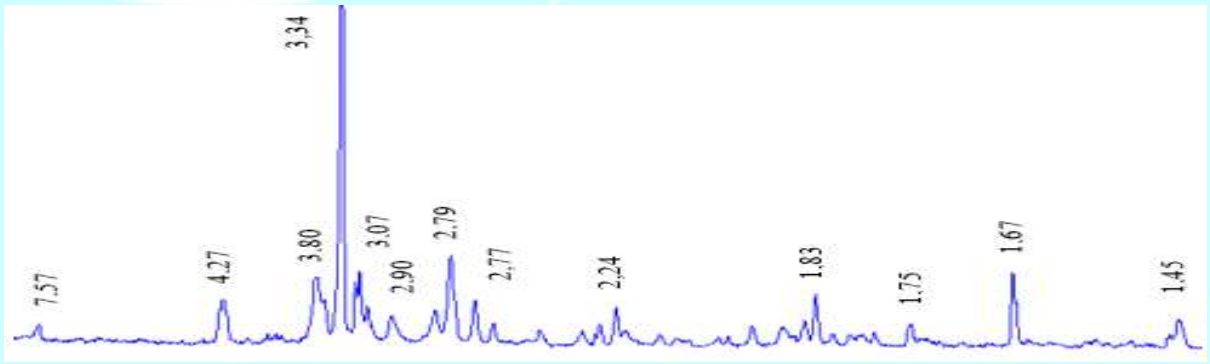


Fig. 3. X-ray diffraction pattern of phosphorus-humus fertilizer obtained on the basis of phosphate raw materials of mineralized mass and oxidized meal

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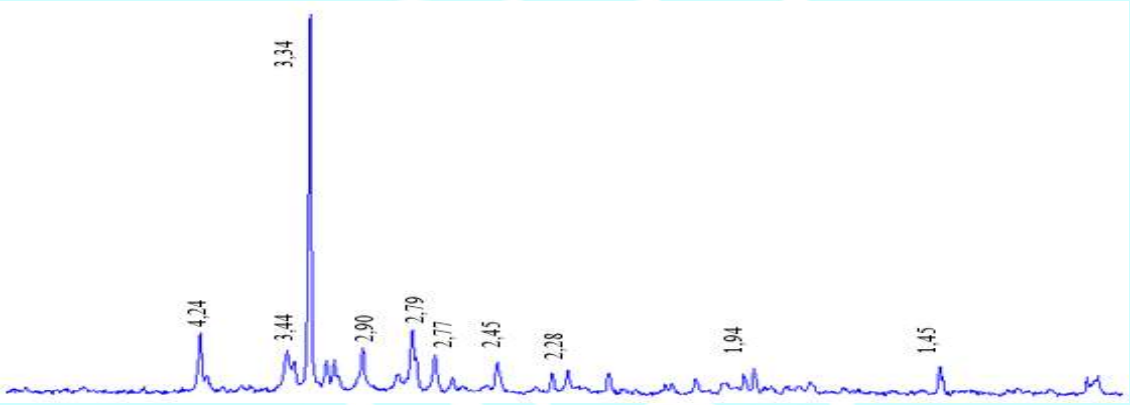


Fig. 3. X-ray diffraction pattern of phosphorus-humus fertilizer obtained on the basis of phosphate raw materials of sludge and oxidized meal

On the X-ray diffraction pattern of the mineralized mass (Fig. 1), the diffraction bands are 1.72; 1.84; 1.93; 2.24; 2.69; 2.78; 2.79; 3.18; 3.45 Å belong to fluorocarbonate apatite. The presence of calcite is confirmed by the interplanar distances of 1.87; 2.28 Å, dolomite -1.42; 1.44; 1.53 Å. The most intensive peaks were 1.91; 2.09; 2.49; 3.35; 3.80 Å indicate the presence of a large amount of silicon oxide. The 1.37 and 1.93 Å bands relate to calcium fluoride, and 2.09; 2.49; 3,03 and 3.35 Å can be attributed to $CaSiO_3$.

On the X-ray diffraction pattern of the sludge (Fig. 2), the diffraction bands are 1.83; 1.93; 2.29; 2.69; 2.77; 2.79; 3.44 Å belong to fluorocarbonate apatite. The presence of calcite is confirmed by the interplanar distances of 1.88; 2.28; 3.05 Å, dolomite -1.42; 1.44; 1.53 Å. The most intensive peaks were 1.83; 1.98; 2.45; 3.35 Å indicate the presence of a large amount of silicon oxide. The 1.37 and 1.93 Å bands relate to calcium fluoride, and 2.45; 3.35 and 3.03 Å can be attributed to $CaSiO_3$.

On the X-ray diffraction pattern of the phosphorus-humus fertilizer (Fig. 3), obtained by decomposing the phosphate raw material into a mineralized mass with sulfuric acid and adding oxidized meal, diffraction maxima are observed: monocalcium phosphate - 3.80; 2.79; 2.90 Å; dicalcium phosphate - 3.50; 2.77; 2,24 Å, tricalcium phosphate 3.44 Å, ammonium sulfate 2.32 Å, gypsum 1.45 Å.

On the X-ray diffraction pattern of the phosphorus-humus fertilizer (Fig. 4), obtained by decomposing the phosphate raw material into a sludge with sulfuric acid and adding oxidized meal, diffraction maxima are observed: monocalcium phosphate - 3.80; 2.79; 2.90 Å; dicalcium phosphate - 3.50; 2.77 Å, tricalcium phosphate 3.44 Å, ammonium sulfate 2.32 Å, gypsum 1.45 Å.

It should be noted that in the production of phosphorus fertilizers, the assimilable form of P_2O_5 decreases due to the retrogradation of phosphorus during ammonization and drying. And the combination of oxidized meal with phosphate raw materials in the production of phosphorus fertilizers leads to a significant increase in the relative content of the assimilable form P_2O_5. Obviously, when

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oxidized meal is added to the acidic superphosphate mass, organic acids, due to interaction with monocalcium phosphate and other phosphates, prevent the retrogradation process, due to which the assimilable form of phosphorus does not decrease, but, on the contrary, significantly increases during the ammonization of the superphosphate mass.

According to modern agricultural requirements, it is desirable that the relative content of assimilable forms of phosphorus compounds in complex fertilizers be at least 50%. Therefore, for processing the phosphate raw material into a mineralized mass, we consider the optimal sulfuric acid rate to be 70% of the stoichiometric norm for the formation of monocalcium phosphate, and the phosphorite-to-oxidized meal weight ratio to be 1:0.4. Under optimal conditions, fertilizer (wt. %): $P_2O_{5tot.}$ - 8.80; $P_2O_{5sol.\ for\ citric\ acid}$ - 4.70; organic substances - 23.45; humic acids - 16.45; nitrogen - 2.57; $CaOt_{otal}$ - 26.34; relative content of $P_2O_{5sol.\ for\ citric\ acid}$ - 53.40; moisture - 5.46; SO_{3total} -21.32, granule strength 2.1 MPa.

For processing the phosphate raw material sludge, we consider the optimal sulfuric acid norm to be 80% of the stoichiometric norm for the formation of monocalcium phosphate, and the phosphorite-to-oxidized meal weight ratio to be 1:0.4. Under optimal conditions, fertilizer (wt.%) $P_2O_{5total.}$ - 5.75; $P_2O_{5sol.\ for\ citric\ acid}$ - 4.38; organic substances - 23.60; humic acids - 16.75; nitrogen - 3.36; CaO_{total} - 25.05; relative content of $P_2O_{5sol.\ for\ citric\ acid}$ - 76.27; moisture - 5.62; SO_{3total} -31.90 with a granule strength of 2.3 MPa.

The optimal technological regime for obtaining phosphorus-humic fertilizer is: grinding of licorice meal to particle size less than 0.25 mm; hydrogen peroxide concentration 10%; weight ratio of the organic part of licorice meal to H_2O_2 and acetic acid 100: 1: 0.1; sulfuric acid rate for decomposition of phosphate raw material Mineralized mass to $Ca(H_2PO_4)$ from stoichiometry 70%; sulfuric acid rate for decomposition of phosphate raw material Sludge to $Ca(H_2PO_4)$ from stoichiometry 80%; weight ratio of the organic part of meal to phosphorite 1: 0.4; oxidation temperature 60°C; oxidation duration 60 min; phosphorite decomposition duration 30 min; pulp neutralization with ammonia to pH 4.5; neutralization duration 20 min; product drying temperature 80-100°C.

Conclusion. Thus, to increase the content of humic substances and organic acids in licorice meal, the process of hydrogen peroxide oxidation in the presence of acetic acid was studied depending on the oxidizer concentration, temperature, and the weight ratio of the organic part of the meal to the anhydrous part of hydrogen peroxide. The content of humic substances and functional groups in the oxidation products of meal was determined, and a technology for obtaining phosphorus-humus fertilizer by adding oxidized meal to the acidic superphosphate mass before ammonization and drying was developed. This, on the one hand,

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allows for a significant increase in the relative content of assimilable forms of P2O5, and on the other hand, reduces the sulfuric acid norm for the decomposition of phosphate raw materials. When these fertilizers are applied in agriculture, the humus content in the soil will undoubtedly increase, and the soil structure and physical-mechanical properties will significantly improve. By containing all the necessary nutrients for plants, the possibility of obtaining higher and better yields is created, and the nutritional properties of plants and their resistance to diseases are increased.

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