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MICROELEMENT-CONTAINING NITROFOS

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Abstract

When the elements nitrogen, phosphorus, potassium, which are considered macronutrients, are replenished by adding mineral fertilizers to plants, it is not possible to meet the demand for plants due to the lack of production of micronutrients. Despite the great importance of micronutrients in the life of plants, micronutrients are almost not produced in the country. The following are the reasons that delay the production of micronutrient fertilizers. Cheap and usable copper, zinc, cobalt, nickel, molybdenum, manganese, barium and other micronutrient raw materials are not fully studied, lack of annual data on the mobile forms of trace elements in the soil, insufficient scientific and technological developments, Insufficient recommendations on the rational application of micronutrients in the soil and information on the status of micronutrients in the production of complex fertilizers. Fertilizers based on Central Kyzylkum phosphorites meet 25-30% of agricultural demand for phosphorus fertilizers. Due to the lack of micronutrients, plants suffer from various diseases. As a result, the absorption of 25-30% of the phosphorus nutrient or other nutrients used by plants is reduced and the nutrients remain in the soil. Therefore, a decrease in productivity is observed in plants. At a time when the demand for phosphorus fertilizers in the country is high, their waste is one of the factors delaying the development of agriculture in our country. Along with nitrogen, phosphorus and potassium fertilizers, the demand for micronutrient fertilizers is growing in the country. At present, micronutrients are used in very small quantities in practice. Various wastes and products of non-ferrous metallurgy, which contain trace elements in the production of mineral fertilizers, the use of sour effluents, depleted catalysts and other types of by-products is one of the solutions for the production of micronutrient fertilizers.

In this article the results of laboratory investigations on obtaining microelement containing nitrogen-phosphorus fertilizers based on introduction nitrogen-phosphate pulp obtained at decomposition Central Kyzylkum's phosphorites at various ratios of nitric acid and of microelement containing wastes have been given.

Key words. Central Kyzylkum's phosphorites, nitric acid, decomposition, microelements, wastes of manufacture, microelement containing nitrophos.

Introduction

The rapid growth of the world's population, the depletion of arable land resources and water resources are exacerbating the problem of new types of fertilizer production worldwide. Therefore, one of the important tasks of the fertilizer industry and agriculture is to fully meet the demand of the population for quality products. Therefore, it is important to implement the production of micronutrient fertilizers, expand their range and reduce the cost of manufactured products.

In our republic, on the basis of local raw materials, the creation and development of technologies for the production of fertilizers containing nitrogen, phosphorus, potassium and other nutrients will be organized at a high level, and a wide range of theoretical and practical measures will be taken to develop economically effective methods of their use in agriculture. results are being achieved. In the third direction of the Action Strategy of the Republic of Uzbekistan for 2017-2021, important tasks such as "... production of high-tech processing sectors of the industry, first of all, on the basis of in-depth processing of local raw materials..." [1]. In

this regard, it is important to create and improve the production technology of new types of micronutrient fertilizers based on local micronutrient salts and industrial micronutrient secondary raw materials.

As you know, agricultural crops receive biogenic nutrients necessary for their development through roots and leaves. For normal development, plants especially need, along with carbon, oxygen, hydrogen, also nitrogen, phosphorus, potassium, calcium, magnesium and sulfur. These elements in plants are contained in significant quantities - up to several percent - and are called macronutrients. Along with this, crops also need micronutrients. Trace element compounds include substances that are required by plants in small quantities - their content in plants is only thousandths or hundred thousandths of a percent. These trace elements include boron, zinc, manganese, molybdenum, iron, cobalt, and other elements [2].

The mineral nutrition of the plant is significantly improved by applying scientifically based fertilizer rates containing the necessary nutrients. It has been established that at least half of the increase in yield is provided by improving nutritional conditions with the use of mineral fertilizers [3].

The agrochemical and physiological role of microelements in plant development is very important and multifaceted. When providing the soil with nitrogen, phosphorus, potassium, calcium, magnesium and sulfur and a lack of trace elements, it is impossible to obtain a high yield [4]. Therefore, to obtain high-quality agricultural products, the balance of all macro- and microelements for plant nutrition during the growing season of their development is of decisive importance [5].

Improving the quality and increasing the agrochemical efficiency of mineral fertilizers is an urgent problem of modern chemical technology. Despite the positive aspects of microfertilizers, they are practically not used in our Republic. The main reasons for this are the low knowledge of the reserves of local microelement-containing raw materials, as well as the lack of scientific foundations and technological developments for the production of microfertilizers.

In Uzbekistan, about 600 thousand hectares of land used for agricultural purposes are deficient in copper, molybdenum and zinc. Deficiency in manganese and boron, respectively, extends to 250-280 thousand and 450 thousand hectares of land. For the effective use of trace elements, they should be added to the composition of complex fertilizers [6].

With a lack of trace elements, plants are exposed to various diseases, which leads to a decrease in yield. Due to the deficiency of microelements in the soil, the introduction of a sufficient amount of nitrogen, phosphorus and potassium fertilizers for agricultural crops does not give positive results, since the assimilation of nutrients by plants is difficult [7]. Only with the combined use of fertilizers with trace elements can good results be achieved. In this regard, the development of technology for the production of microelement-containing complex fertilizers is one of the urgent problems.

The purpose of this work is to obtain a microelement-containing complex fertilizer based on high-carbonate phosphorites of the Central Kyzylkum and industrial waste (IW) from molybdenum production of JSC Uzbek Combine of Refractory and Heat-Resistant Metals (JSC "UCRHRM").

Object and methods of research

The aim of the research is to introduce micro-elemental salts and microelement fertilizers using microelement salts and microelement-containing secondary raw materials of hydrometallurgy to the technologies of obtaining new varieties of phosphorus fertilizers on the basis of incomplete norms of mineral fertilizers and acids or their salty mixtures, which are widely used in agriculture.

Despite the above-mentioned advantages of micro-fertilizers, micro-fertilizers are almost not used in practice in our country. One of the main reasons for this is the lack of research on the availability of cheap and usable local micronutrient raw materials, the lack of science and technology-based micronutrient production technology and developments. In order to theoretically substantiate the production of micronutrients and to develop their

production technology, it is necessary to conduct in-depth physicochemical studies to study the interaction of micronutrients with nitrogen-phosphorus fertilizers, fertilization technology and interactions in the addition of micronutrients to fertilizers.

Research results

To obtain microelement-containing nitrophos in laboratory experiments, unenriched Kyzylkum phosphorite flour of the composition was used, (wt.%): P_2O_5 - 16.38; CaO-45.93; CO_2 - 18.15, 58.50% nitric acid and industrial waste (IW) of the composition; 13.09% NH_4NO_3; 1.37% $(NH_4)_2SO_4$; trace elements (Fe, Mn, Cu, Zn, Ni, Co, Mo) - 0.035%, the rest is water, d=1.01 g/sm^3, pH=2.35. The stoichiometric rate of nitric acid was calculated for the decomposition of phosphate and carbonate minerals of phosphate raw materials to the formation of monocalcium phosphate and calcium nitrate.

In quantitative chemical analysis, the following well-known methods of analytical chemistry were used: nitrogen content was determined by the Keldahl method [8], the content of sulfate ion and P2O5 was determined, respectively, by gravimetric and spectrophotometric methods [9, 10]. Trace elements were determined on a PGS-2 diffraction spectrograph by the method. Calcium was determined by the volumetric complexometric method [11], the pH of the industrial waste of molybdenum production and suspensions obtained by nitric acid decomposition of phosphate rock was measured using a pH meter METTLER TOLEDO.

For the physical and chemical substantiation of obtaining microelement-containing nitrophos, studies were carried out to study the process of activation of high-carbonate phosphate rock with an acidic solution of industrial waste UCRHRM.

The obtained results of chemical activation of phosphate rock (table 1) show that with an increase in the rate of industrial waste, the degree of decomposition (activation) of phosphate raw materials increases. For example, in a suspension obtained at a ratio of IW:FR of 60:40, the degree of decomposition of phosphorite is 46.15%, i.e. out of 6.37% of the total P_2O_5 content, 2.94% is in the form assimilated by plants. The medium of this solution changes from pH 2.35 to 6.57. The degree of decarbonization of phosphate rock is 76.03%.

Table 1

Chemical composition of microelement-containing suspension (MC) obtained by chemical activation of phosphate rock

Mass ratio IW : FR	suspension pH	The content of the mass components %							Decomposition coefficient, %		∑ Micro elements, %
		N	P_2O_5		CaO		CO_2	H_2O	P_2O_5	CaO	
			total	digestible	total	digestible					
100 : 0	2,35	4,87	–	–	–	–	–	–	–	–	0,035
80 : 20	6,11	3,76	3,16	3,06	8,86	7,56	0,11	67,54	96,83	85,33	0,027
60 : 40	6,57	2,84	6,37	2,94	17,86	9,65	4,35	51,11	46,15	54,03	0,020
40 : 60	6,73	1,9	9,65	2,03	27,05	12,68	8,87	34,3	21,04	46,88	0,014

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In order to develop a rational technology for obtaining a microelement-containing complex fertilizer such as nitrophos, phosphorite flour at a temperature of 30-40 °C was processed at an incomplete rate (40-80% of the stoichiometry) of nitric acid. The interaction of phosphorus with acid occurs in the "solid-phase mode" without foaming for 15-20 minutes.

The experiments (table 2) show that with the increase in the norm of nitric acid from stoichiometry, the degree of decomposition of phosphorite increases.

Table 2.

The chemical composition of the products of nitric acid decomposition of phosphorus

Norm HNO_3, %	received product pH	The content of the mass components %							Decomposition coefficient, %	
		N	P_2O_5		CaO		CO_2	H_2O		
			total	digestible	total	digestible			P_2O_5	CaO
40	5.94	4.97	10.65	7.49	29.88	14.64	7.01	17.78	70.33	49.00
60	4.38	6.34	9.07	6.90	25.44	18.11	3.92	22.72	76.07	71.19
80	2.62	7.35	7.89	6.85	22.12	20.11	1.75	26.34	86.82	90.91

At a rate of nitric acid of 40% of the stoichiometry, out of 10.65% of the total content of P_2O_5, 70.33% is in an assimilable form, 49.00% of CaO also passes into a form assimilable by plants. With an increase in the norm of nitric acid from 60% to 80% of the stoichiometry, the content of P_2O_5 assimilated by plants increases from 76.07% to 86.82%. An increase in the norm of nitric acid from stoichiometry also leads to an increase in the degree of decarbonization of phosphate raw materials, while the content of CO_2 decreases from 7.01% to 1.75%. With an increase in the rate of acid from 40% to 80%, the amount of nitrogen in the nitric-phosphoric acid intermediate (nitrophosphate mass) increases from 4.97% to 7.35% and is in the form of calcium nitrate.

For the synthesis of microelement-containing nitrophos, the nitrophosphate mass (NM) was mixed with a suspension (MS) obtained at a ratio of IW:FR 60:40, at a ratio of NM:MS 1: (0.25-1). The resulting mixture was stirred for 15 minutes, dried at a temperature of 90-100 ^{0}C, granulated under laboratory conditions on a plate granulator at a humidity of 10-15% H_2O.

Table-3

Chemical composition of microelement-containing nitrophos, %

Ratio FR:MC	pH 10% product solution	N	P_2O_5		CaO		∑ trace elements	H_2O	degree of decarbonization CO_2, %
			total	dgas tible	total	dgas tible			
Norm HNO_3 40 %									
1:1	6.99	5,84	12,70	8,09	35,63	18,53	0,15	2,15	57,35
1:0,75	6.57	5,88	12,78	8,23	35,84	18,62	0,13	1,54	58,50
1:0,50	6.36	5,84	12,64	8,38	35,44	18,28	0,10	2,59	59,78

1:0,25	6.02	5,90	12,71	8,78	35,69	18,21	0,05	1,88	60,75
Norm HNO_3 60 %									
1:1	6.43	7,06	11,88	7,87	33,31	22,55	0,15	2,95	69,46
1:0,75	6.12	7,22	11,81	8,08	33,12	22,83	0,13	2,82	71,07
1:0,50	5.84	7,49	11,84	8,29	33,20	22,96	0,10	1,72	73,38
1:0,25	5.47	7,75	11,68	8,67	32,77	22,99	0,05	1,92	76,29
Norm HNO_3 80 %									
1:1	5.31	8,10	11,32	8,08	31,73	24,62	0,16	2,75	77,19
1:0,75	5.13	8,34	11,11	8,17	31,23	25,05	0,14	3,00	80,23
1:0,50	4.79	8,73	11,00	8,50	30,90	25,82	0,10	2,39	83,80
1:0,25	4.45	9,21	10,80	8,87	30,39	26,74	0,06	1,86	87,12

As can be seen from the data (Table 3) that with an increase in the norm of nitric acid from 40% to 80% of the stoichiometry, the quantitative content of P_2O_5 and CaO increases, and the content of trace elements decreases. For example, the microelement-containing nitrophos, synthesized by mixing the nitrophosphate mass obtained at a rate of nitric acid of 40%, with a microelement-containing suspension at a ratio of 1: 0.25, contains 5.90% nitrogen, 12.71% of total phosphorus, of which 8.78% or 69.07% are in an assimilable form, out of 35.69% of the total CaO, 51.02% is also in plant-assimilable form and 0.05% of trace elements. With an increase in the acid rate from 60 to 80%, the finished product contains, respectively, 7.75 and 9.21% nitrogen, 74.22% and 82.12% of assimilable phosphorus, and 70.15 and 87.98% of assimilable CaO. This pattern is also observed at other ratios and norms of acid.

Conclusion

Micronutrient phosphate suspension was obtained by activating highly carbonated Central Kyzylkum phosphorite samples (MESRM:FR in the proportions 80:20, 60:40, 40:60) on the basis of secondary raw materials of "Almaliq KMK" JSC. MESRM was used to activate phosphorite samples because the pH medium was acidic. The absorbed state of phosphorus and the percentage of trace elements in the activated suspension were analyzed. Phosphorite activation results in a reduction of acid consumption and a significant saving of enterprise costs from the economic point of view.

Thus, the fundamental possibility of obtaining microelement-containing complex fertilizer based on the rational processing of Kyzylkum phosphate rock and microelement-containing industrial waste from hydrometallurgical production has been shown.

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