Technology of obtaining micronutrient fertilizers based on micronutrient secondary raw materials of the industry

Dilmurod Uktamov*, and *Mukhayyo* Aliyeva

Namangan Institute of Engineering and Technology, Namangan, 160115, Uzbekistan

Abstract. The article presents the research results of obtaining nitrogen-phosphorus-calcium-microelement fertilizers by adding suspensions obtained by activating phosphorite with microelement industrial waste in different proportions to the superphosphate mass formed by decomposition of Central Kyzylkum phosphorite flour at different rates of sulfuric acid in laboratory conditions. Experiments were carried out with low-quality phosphorite flour, non-enriched phosphorite flour and washed-burned (thermoconcentrate) phosphorite concentrates (UzDSt 2825:2014) obtained on the basis of phosphorites of the Central Kyzylkum. Also, in order to obtain superphosphate fertilizers with microelements, secondary raw materials with acidic microelements of the PH environment formed during molybdenum processing of Almalyk mining and metallurgical combine joint-stock company were used. Studies have shown that under the influence of micronutrients (copper, zinc, molybdenum, etc.), important physiological and biochemical processes can be controlled, thereby increasing the yield and quality of agricultural products. The use of microelements together with basic fertilizers is an effective and economically important (convenient) agrochemical method. The purpose of the research is to implement new types of phosphoric fertilizers based on incomplete standards of mineral fertilizers and acids, which are widely used in agriculture, or their salt mixtures, using trace element salts and secondary raw materials containing trace elements of hydrometallurgy.

1 Introduction

The rapid growth of the world's population, the reduction of arable land resources and water reserves are increasing the problem of production of new types of fertilizers on a global scale. Therefore, one of the important tasks of the fertilizer production industry and agriculture is to fully satisfy the population's demand for quality products. Providing agriculture with mineral fertilizers at a high level of efficiency is one of the urgent problems.

Today, there are problems in the world of increasing the efficiency of using mineral fertilizers and improving production methods, as well as applying advanced technologies, a scientifically based system of agricultural management, and increasing environmental

* Corresponding author: dilmurod.uktamov@mail.ru

protection measures. One of the effective ways of producing mineral fertilizers is to obtain complex fertilizers containing trace elements. In this way, even distribution of micronutrients in the planted areas is achieved. In our country, research is being carried out on increasing the efficiency of mineral fertilizers and developing production methods, researching the improved system of the agricultural agro-complex. Creation and improvement of production technology of micronutrient fertilizers based on local raw materials, their effective use is one of the important tasks of today.

2 Materials and methods

If we look at the history, mineral fertilizers began to spread in the 19th century. It has grown rapidly since the middle of the 20th century due to the production and application of mineral fertilizers. Until then, mainly manure, ash and other waste were used as fertilizers. Mineral fertilizers are a tool that strongly affects the soil (its physical, chemical and biological properties); they enrich the soil with nutrients, change the reaction of the soil solution, affect microbiological processes, etc. Due to the fact that plants are fed mainly through the roots, when mineral fertilizers are applied to the soil, they actively affect the growth and development of plants, as a result, the general biological productivity of fields and meadows. Mineral fertilizers are divided into direct and indirect fertilizers. Directly used fertilizers contain nitrogen, phosphorus, potassium, as well as elements such as magnesium, boron, zinc, copper, molybdenum, manganese, sulfur, necessary for plant nutrition. Fertilizers belonging to this group are mainly mononutrient, nitrogenous, phosphorous or potassium, and complex, that is, mixed and complex fertilizers. Indirectly used mineral fertilizers (calcareous fertilizers, gypsum, etc.) are mainly used to improve the agrochemical and physical properties of the soil. Mineral fertilizers are produced in the form of solid, i.e. powdery, granular and liquid-ammonia water, liquid ammonia, and ammonia [1].

In the works of S.Kh. Azimov, B.S. Zakirov, A.Kh. Narkhodjaev, the composition and structure of molecules of complexes were analyzed physico-chemically (X-ray phase, thermal and IR-spectra) in order to create a technology for obtaining new effective micronutrient stimulants for plant growth. For this purpose, new micronutrient complex fertilizers were synthesized on the basis of ammonium nitrate and acetic acid monoethanolamine copper acetate monohydrate ($NH_4NO_3 \cdot NH_2C_2H_4OH \cdot (CH_3COO-)CU \cdot H_2O$), and to determine the molecular composition of the obtained new complex-nitrateammonium acetic acid monoethanolamine copper acetate monohydrate, physical-chemical analysis studies were carried out [2].

The use of micronutrients together with macrofertilizers is of great importance in increasing the productivity of agricultural crops. In this case, not only the yield and quality of crops will increase, but also the fertility of the soil will improve. Therefore, the production of nitrogen-phosphorus fertilizers based on industrial waste containing microelements such as copper and molybdenum and the determination of the effect of fertilizers on the agrochemical properties of soil and plants when applied to cotton are urgent issues [3].

14 vitally important trace elements have been identified. They include B, Mo, Cu, Zn, Mn, Co, etc. Microelements, together with enzymes, vitamins, hormones, pigments, etc. in the body, affect the vital processes of organisms. They participate in biochemical changes and affect the physiological functions that occur in the plant organism through enzyme systems. Increases the use of light in the process of photosynthesis, accelerates protein synthesis. Some microelements activate the beneficial properties of plants, that is, they strengthen properties such as resistance to drought and cold, acceleration of seed germination and development, and increase of resistance to diseases. Their lack leads to disruption of metabolic processes, disease of plants and living organisms [4].

Microfertilizers are fertilizers that are applied in small amounts (grams and kilograms per hectare). Boric acid, copper (II) sulfate, ammonium molybdate and other technical salts are used in the composition. Coal ash, manganese sludge (slurry), precipitated magnesium borate and other micronutrient wastes are insoluble in water. They are processed into a water-soluble form or used directly as fertilizer. Water-soluble and insoluble microfertilizers are used in agriculture. Complex fertilizers are fertilizers containing at least two nutrients. Secondary complex fertilizers (for example, nitrogen-phosphorus, nitrogen-potassium, phosphorus-potassium) and tertiary complex fertilizers (for example, nitrogen-phosphorus-potassium) are divided into types. Tertiary fertilizers are called complete fertilizers. Complex fertilizers may also contain micronutrients, pesticides, and plant growth additives [5].

G. Gospodarenko and others, plants without microelements suffer from various diseases and productivity decreases spontaneously, and even if plants are supplied with nitrogen, phosphorus, and potassium fertilizers as needed, due to the lack of microelements, plants do not fully absorb the nitrogen, phosphorus, and potassium compounds contained in the fertilizer or get diseases [6, 7] mentioned.

3 Results and discussion

Experiments were carried out with low-quality phosphorite flour, non-enriched phosphorite flour and washed-burned (thermoconcentrate) phosphorite concentrates (UzDSt 2825:2014) obtained on the basis of phosphorites of the Central Kyzylkum.

Also, in order to obtain micronutrient superphosphate fertilizers, secondary raw material with acidic micronutrients (MECSRM) produced in the process of molybdenum processing of Almalyk Mining and Metallurgical Combine (AMMC) JSC was used.

Table 1. Chemical composition of the MECSRM sample of hydrometallurgy, %.

Sample №	N_{total}	Microelements									H_2O
		Total	Fe	Co	Mn	Cu	Zn	Mo	Ni	Mg	
1	4.87	0.35	0.0371	0.00012	0.0086	0.24	0.012	0.0371	0.00086	-	87.61

Microelement containing secondary raw materials of hydrometallurgy are H_2O-87.61% in liquid green color, acid environment 2.35, total N content - 4.87%, microelements in secondary raw materials (Fe, Mn, Su, Zn, Ni, Co, Mo) and other salts are 12.73%. The secondary raw materials with trace elements contain NH_4NO_3-13.09%; $(NH_4)_2CO_4$-1.37%; trace elements-0.35% g/l, crystallization temperature is 10.6ºC, ρ-1.150, μ -1.289, Tct -(-10.6), Tbp is -101 °C.

Studies have shown that under the influence of micronutrients (copper, zinc, molybdenum, etc.), important physiological and biochemical processes can be controlled, thereby increasing the yield and quality of agricultural products. The use of microelements together with basic fertilizers is an effective and economically important (convenient) agrochemical method.

High carbonated Central Kyzylkum (low-grade P_2O_5–12.38%, CaO–43.68%, CO_2–13.48%, non-enriched P_2O_5–16.38%, CaO–45.93%, CO_2–18.15) %, SO_3-1.86%, and thermoconcentrate P_2O_5-27.40%; CaO-54.68%; CO_2-4.52%) phosphorite samples were activated to obtain micronutrient phosphate suspension [8-10].

MECSRM was observed to be activated at certain ratios by phosphorite as the pH of the medium was 2.35 (Table 2). As the amount of low-grade phosphorite flour in the composition of liquid industrial waste increases, its activation and decarbonization levels decrease.

For example, the level of activation (degradation) of phosphate raw materials in the MECSRM:phosphorite 80:20 ratio is 58.92%, that is, 1.42% of the total P_2O_5 of 2.41% is in a form that can be absorbed by plants. It was found that 83.45% of the total 8.52% of calcium

(CaO) in phosphorite was transformed into a form that could be assimilated by plants. In the process of activation, complete decarbonization of phosphorite flour in the suspension was observed. And the environment of the suspension changes from 2.35 to 5.85. It was determined that the micronutrient suspension contains 3.79% nitrogen, 0.27% micronutrients, and 0.66% SO_3.

Table 2. Chemical composition of phosphate suspension with trace elements, %.

MECSRM: Phosphorite	N	P_2O_5		CaO		∑ micro-element	Coefficient (consumption degree)		CO_2	H_2O	SO_3	pH
		Total	Digestible	Total	Digestible		P_2O_5	CaO				
With low grade phosphorite flour												
80:20	3.79	2.41	1.42	8.52	7.11	0.27	58.92	83.45	0.00	67.93	0.66	5.85
60:40	2.84	4.81	1.85	17.02	6.99	0.20	38.46	41.06	2.55	50.91	0.50	6.24
40:60	1.95	7.48	2.11	27.62	10.08	0.14	28.21	36.50	3.84	35.04	0.33	6.30
With unenriched phosphorite flour												
80:20	3.76	3.16	3.06	8.86	7.56	0.27	96.83	85.33	0.00	67.28	0.66	6.11
60:40	2.84	6.37	2.94	17.86	9.65	0.20	46.15	54.03	4.35	50.90	0.50	6.57
40:60	1.91	9.65	2.82	27.05	12.68	0.14	29.22	46.88	8.87	34.39	0.33	6.94
Thermoconcentrate with flour												
80:20	3.86	5.43	2.06	10.84	9.37	0.28	37.94	86.44	0.00	69.19	0.66	5.57
60:40	2.87	10.76	2.79	21.47	15.39	0.21	25.92	71.68	0.00	51.41	0.50	6.17
40:60	1.93	14.64	2.71	26.26	11.16	0.14	18.51	42.49	0.90	35.04	0.33	6.33

MECSRM-microelement containing secondary raw material

Phosphorite flour (MECSRM:phosphorite in the proportions 80:20, 60:40, 40:60) that was not enriched with secondary raw materials with an acidic pH medium was also activated. As the ratio of MECSRM increases in the process, it was observed that the activation of phosphorite also increases. For example, 29.22% of 9.65% of total phosphorus in the MECSRM:phosphorite suspension at a ratio of 40:60 is absorbed by plants, while at a ratio of 80:20, 96.83% of 3.16% of total phosphorus (P_2O_5), 85.33% of 8.26% of total calcium (CaO) is absorbed by plants. it was observed that it was transformed into a form. It was observed that the suspension contained 3.76% total nitrogen, 0.27% trace element salts, and 0.66% SO_3. It was found that the pH of the microelement suspension is neutral, i.e. 6.11.

Also, thermal concentrate flour with secondary raw materials was activated in different proportions, and their chemical composition was analyzed. The results of the obtained analysis showed that in the suspensions obtained on the basis of thermoconcentrate, it was observed that the transition of calcium to the absorbed state was higher than that of phosphorus. For example, in the MECSRM:phosphorite suspension in the ratio 40:60, the absorbable state of phosphorus is 18.51%, in the ratio 60:40 it is 25.92%, in the ratio 80:20 it is 37.94%, while the absorbed state of calcium is 42.49%, 71.68%, 86.44%, respectively. it became known that he organized In the process of activation, complete decarbonization of phosphorite flour in the suspension was observed, and the medium of the suspension was in the range from 5.57 to 6.33. It was found that the percentage of nitrogen in the obtained micronutrient phosphate suspension was from 1.93% to 3.86%, micronutrients from 0.14% to 0.28%, SO3, which is a nutrient element, was from 0.33% to 0.66%.

The obtained results show that the amount of micronutrients in the suspension is sufficient to obtain complex micronutrient fertilizers. Also, during the activation of phosphorites, the consumption of acid is reduced and the cost of the enterprise is significantly saved from the economic point of view.

Micronutrient phosphate suspensions were obtained on the basis of MECSRM and phosphorite samples (MECSRM:FS=80:20) of Almalyk Mining and Metallurgical Combine JSC. The obtained suspension and superphosphates were mixed in a ratio of 1:1 and complex fertilizers with micronutrients of a new variety were obtained. Their chemical composition (Table 3) was analyzed based on known methods.

The plant-absorbable form of P_2O_5 in the total 9.55% of superphosphate obtained on the basis of low-grade phosphorite flour (acid standard 60%) and micronutrient suspension is 68.90%, the form of microelements that can be absorbed by plants is 44.76%, and the water-soluble form is 22.65 is %. In micronutrient fertilizers made on the basis of low-grade phosphorite flour, as the acid level increased, the plant-absorbable and water-soluble form of micronutrients decreased, as in the fertilizers studied above. For example, 60% of the acid, 0.22% of microelement superphosphate taken in moderation, the plant-absorbable form of microelements is 44.76%, and the water-soluble form is 22.65%. In the fertilizer obtained at the rate of 80% of the acid, the absorbable state of the total 0.22% trace element was observed to be 4.78% less than the fertilizer obtained at the rate of 60%, and the water-soluble state was 2.12% less.

Table 3. Chemical composition of superphosphate fertilizers with microelements, % (superphosphate:ME suspension 1:1).

H_2SO_4, %	N	P_2O_5		∑ microelement			level of assimilation of microelements%		H_2O	pH
		Total.	Dige stible	Total.	Dige stible	Woter-soluble	Dige stible	Woter-soluble		
With low grade phosphorite flour										
60	2.92	9.55	6.58	0.22	0.098	0.050	44.76	22.65	1.98	6.49
80	2.92	9.09	7.14	0.22	0.088	0.045	39.98	20.53	2.89	6.26
100	2.97	8.83	7.59	0.22	0.079	0.041	35.81	18.49	2.62	6.07
With unenriched phosphorite flour										
60	2.89	12.02	9.65	0.22	0.089	0.047	40.28	21.24	2.62	6.51
80	2.94	11.48	9.92	0.22	0.081	0.064	37.01	19.05	2.17	6.13
100	2.94	10.86	10.66	0.22	0.073	0.038	33.12	17.33	3.09	5.59
Thermoconcentrate with flour										
60	2.96	18.69	11.32	0.22	0.078	0.044	35.68	19.88	2.00	6.01
80	2.96	17.34	12.65	0.22	0.074	0.039	33.73	17.52	2.54	6.13
100	3.01	16.86	13.98	0.22	0.070	0.034	31.99	15.63	1.53	6.27

Also, in superphosphate fertilizers based on non-enriched phosphorite flour, micronutrients were 0.22%, but their plant-absorbable and water-soluble form is less compared to micronutrient fertilizers based on low-grade phosphorite flour. For example, in micronutrient containing superphosphates obtained on the basis of low-grade and non-enriched phosphorite flour with an acid value of 60%, the amount of micronutrients is the same, that is, 0.22%. But in the fertilizer based on non-enriched phosphorite flour, microelements absorbed by plants are 4.48% less, and water-soluble ones are 1.41% less. This pattern was also observed in fertilizers with acid content of 80 and 100%. It was found that the nitrogen content of new varieties of fertilizers based on unenriched phosphorite flour ranged from 2.89% to 2.94%, and their pH range was from 5.59 to 6.51.

Also, the above law was observed in the composition of superphosphate fertilizers decomposed thermoconcentrate flour with different rates of sulfuric acid. It was found that nitrogen content of micronutrient fertilizers obtained on the basis of thermoconcentrate ranges from 2.96% to 3.01%, and the pH of fertilizers is neutral.

Also, in the studies, the process of granulation of superphosphate mass obtained at different levels of sulfuric acid with the presence of micronutrient phosphate suspension was studied. The amount of micronutrient phosphate suspension in the granulation process was 20% (superphosphate: suspension 1:0.2). Granular micronutrient superphosphate fertilizers (Table 4) were dried at a temperature of 90-105 °C and their chemical composition was analyzed.

Table 4. Chemical composition of granulated superphosphate fertilizers in the presence of microelement suspension, % (superphosphate:ME suspension 1:0.2).

H_2SO_4	N	P_2O_5		∑microelement			level of assimilation of microelements%		H_2O	pH
		Total.	Dige stible	Total.	Dige stible	Woter-soluble	Digestible	Woter-soluble		
With low grade phosphorite flour										
60	0.73	10.16	7.19	0.05	0.020	0.009	46.09	23.00	1.37	6.01
80	0.74	9.69	7.98	0.05	0.011	0.008	40.45	20.54	1.36	5.77
100	0.75	9.28	8.50	0.05	0.012	0.007	34.79	18.17	1.88	5.48
With unenriched phosphorite flour										
60	0.74	12.80	9.69	0.06	0.024	0.011	45.47	21.95	1.33	5.97
80	0.75	12.06	9.96	0.05	0.012	0.007	39.76	19.64	1.48	5.62
100	0.76	11.42	11.02	0.05	0.012	0.007	34.48	17.28	1.48	5.36
Thermoconcentrate with flour										
60	0.74	19.11	12.51	0.06	0.022	0.010	42.76	20.16	1.55	5.68
80	0.74	17.63	14.33	0.06	0.023	0.009	37.70	18.01	1.05	5.43
100	0.74	16.71	15.73	0.06	0.012	0.008	31.76	15.85	1.74	5.22

The presence of nitrogen and microelements in the composition of superphosphate fertilizers with microelements improves its quality, in addition to the plant-absorbable phosphorus feed. Ammonium nitrate and ammonium sulfate salts in the composition of micronutrient phosphate suspension obtained by activating phosphorite samples with the help of MECSRM increase the strength of superphosphate grains, in addition to being a nitrogen nutrient for plants.

Analyzing the composition of micronutrient fertilizers made on the basis of non-enriched phosphorite flour, it was found that the product obtained at the rate of 80% of sulfuric acid contains 0.74% nitrogen, 12.80% total phosphorus, and 82.59% plant-absorbable form. Also, the content of microelements in the fertilizer is 0.05%, and their plant-absorbable form is 39.76%. When analyzing the water-soluble form, it was found to be 19.64%. Fertilizer with acid level of 100% contains total nitrogen 0.75%, total phosphorus 11.42%, and its plant-absorbable form is 96.50%. It was observed that microelements make up 0.05%, their plant-absorbable form is 34.48%, and water-soluble form is 17.28%. In these fertilizers, as the acidity level increased, it was observed that microelements absorbed by the plant and water-soluble form decreased. The amount of microelements in the fertilizer with 100% acidity is 0.05%, their plant-absorbable form is 34.48%, water-soluble form is 17.28%. It was found that these indicators are 5.28% less than the plant-absorbable form of micronutrients in superphosphate with an acid level of 80%, and 2.36% less than the water-soluble form. It was observed that microelements contained in superphosphate fertilizer obtained at the rate of 60% of acid are 10.99% less than the plant-absorbable form, and 4.67% less than the water-soluble form.

This pattern was also observed in superphosphate fertilizers obtained on the basis of low-grade phosphorite flour and thermoconcentrate. The presence of phosphorous in one of the phosphorites, in addition to the acid norm, has an effect on the reduction of the absorbable and water-soluble form of microelements. For example, although the rate of acid used for decomposing phosphorite samples of Central Kyzylkum is 60%, micronutrient suspension is 20%, the absorbable and water-soluble forms of micronutrients in them are different. The plant-absorbable form of microelements in the fertilizer based on thermoconcentrate with an acid value of 60% is 42.76%, and the water-soluble form is 20.16%. This indicator is 2.71% compared to the absorbable form of microelements in the fertilizer based on unenriched phosphorite flour with an acid value of 60%, and 1.79% compared to the water-soluble form. % less. It was observed that microelements contained in the superphosphate fertilizer obtained on the basis of low-grade phosphorite flour are 3.33% less than the plant-absorbable form, and 2.84% less than the water-soluble form.

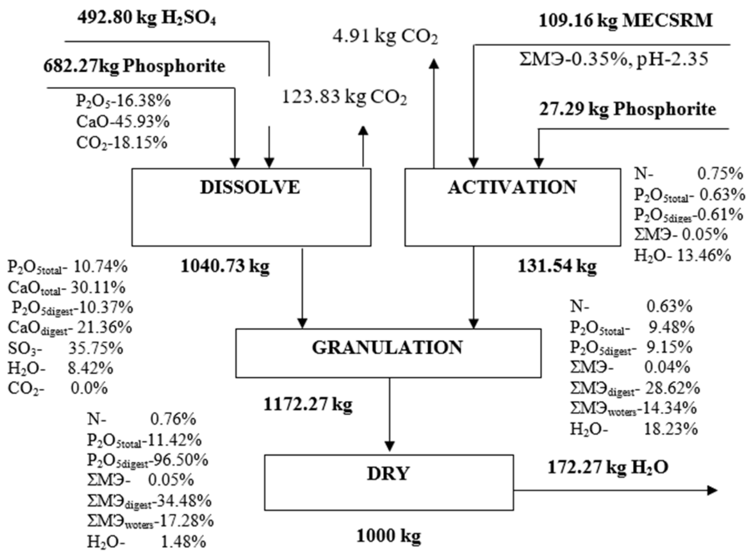

Fig. 1. Material balance of granulated superphosphate fertilizer in the presence of microelement suspension.

Figure 1 shows the material balance of granulated superphosphate fertilizer in the presence of micronutrient suspension.

To obtain 1 ton of micronutrient fertilizer, 25.58 kg of non-enriched phosphorite flour and 102.33 kg of Almalyk mining and metallurgical combine JSC are activated with secondary raw materials of micronutrients, which are formed during molybdenum processing. Also, 639.59 kg of non-enriched phosphorite flour is activated with 461.97 kg of 92.5% sulfuric acid for 15-20 minutes to obtain simple superphosphate fertilizer. The resulting superphosphate fertilizer is granulated in the presence of micronutrient suspension (1:0.2 ratio). new type micronutrient superphosphate fertilizer contains 0.76% of nitrogen nutrients, 11.42% of total phosphorus (P_2O_5), 11.02% plant absorbability of phosphorus, 0.05% of total microelements, 34.48% plant absorbability, and 17.28% water-soluble form. Dried micronutrient superphosphate fertilizer contains 1.48% H_2O.

4 Conclusion

Microelement phosphate suspension was obtained by activating highly carbonated Central Kyzylkum phosphorite samples (MECSRM:FS in the proportions 80:20, 60:40, 40:60) on the basis of microelement containing secondary raw materials of Almalyk mining metallurgical combine JSC.

When microelement containing secondary raw materials are introduced into the technology of obtaining fertilizers, in addition to performing the function of raw materials for obtaining microelement fertilizers, the acid consumption in the activation of phosphorites is reduced and the cost of the enterprise is significantly saved from the economic side, and the environment is cleaned from waste from the ecological side, and the large-scale utilization of secondary raw materials collected at the enterprise will be achieved.

The advantage of using microelements in the composition of macrofertilizers is that there is little risk of toxic effect on the plant even if its norm is exceeded. The material balance of superphosphate fertilizers of a new type obtained in the presence of micronutrient suspension activated on the basis of phosphorite samples and micronutrient secondary raw materials of the industry was developed.

It has been proved that it is possible to obtain a new type of superphosphate fertilizers based on samples of Central Kyzylkum phosphorite and microelement containing secondary raw materials produced during molybdenum processing of Almalyk mining and metallurgical combine JSC.

References

1. Ormon Orozovich Choriev, Oriental renaissance: Innovative, educational, natural and social sciences. Scientific journal impact factor **2(9)** (2022)
2. S.Kh. Azimov, B.S. Zakirov, A.Kh. Narkhodzhaev, Uzbek chemical journal **1**, 80-87 (2018)
3. Begzod Tillabekov, Begali Niyazaliev, Agro Science **1(64)**, 5 (2020)
4. Q. Gafurov, I. Shamshidinov, *Technology of mineral fertilizers and salts* Textboo (T., Science and technology, 2007), pp. 8-9
5. A.I. Fateev, M.M. Myroshnychenko, NSC Institute of Soil Science and Agrochemistry named after O.N. Sokolovsky, 115-118 (2003)
6. G. Gospodarenko, Agrobusiness today **19-20**, 26-29 (2010)
7. I.V. Zherdetsky, Agronomist **4**, 28-30 (2009)
8. D. Uktamov, G' Ochilov, Solid State Technology **63(6)** (2020)
9. D. Uktamov, M Alieva, E3S Web of Conferences **390**, 05034 (2023). https://doi.org/10.1051/e3sconf/202339005034
10. D. Uktamov, Journal of Pharmaceutical Negative Results **13(06)** (2022). https://doi.org/10.47750/pnr.2022.13.S06.482