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ON THE METHOD OF OBTAINING BORATELIC SUPERPHOSPHATE

Zhanyl DZHANMULDAYEVA, Galina SEITMAGZIMOVA, Aigul JANMULDAYEVA, Amid MURATOV

M. Auezov South Kazakhstan State University, 5, Tauke Khan Avenue, 160012 Kazakhstan, Shymkent, Mobil phone: + 77756135158, E-mails: a.jan_75@mail.ru, zhanyld@mail.ru

Corresponding author: zhanyld@mail.ru

Abstract

Under laboratory conditions, the effect of the amount of borate salt additive, norm and temperature of EPA on the yield and quality of the product was studied. The effect of the ratio of phosphorite: borate salt on the degree of decomposition of phosphorite, the effect of the norm and temperature of extraction phosphoric acid on the degree of decomposition of the mixture of phosphorite: borate salt was also studied. On the basis of the obtained research results, the optimal parameters of the technological process for the production of borate-double superphosphate using borate salts of the Inderskoe field are determined.

Key words: *mineral fertilizers, mycorrhoeic elements, borate double superphosphate, borate ores, phosphorites Karatau, extraction phosphoric acid*

INTRODUCTION

Currently, the use of microfertilizers is an integral part of modern crop production technology and the key to obtaining a high yield of good quality, due to their influence on biochemical processes. Along with this, some plants show an increased need for certain microelements, and microfertilizers provide a balanced set of trace elements for the needs of different cultures [1-3].

Microelements are part of compounds that have important vital functions, in particular - enzymes, vitamins, hormones, pigments and other compounds. Microelements significantly affect biochemical transformations and thus have an effect on many physiological functions in plant and animal organisms. They affect carbohydrate metabolism, enhance the use of light in the process of photosynthesis and accelerate the synthesis of proteins. Under the influence of individual microelements, the useful properties of plants are enhanced, such as drought resistance, frost resistance, acceleration of development and maturation of seeds, resistance to diseases, etc. The lack of trace elements leads to a disruption of metabolism, which in turn leads to diseases of plants and animals. But, it is necessary to take into account that the excess of trace elements can lead to harmful consequences. Boric fertilizers are the most common and are among the first micro fertilizers produced on an industrial scale. Boric fertilizers are the most common among micro fertilizers. The most concentrated boric fertilizers include boric acid H_3BO_3 and borax $Na_2B_4O_7 \cdot 10H_2O$. Industrial wastes containing small amounts of boron and some natural borates can be used as fertilizers. Natural solutions, such as brines of some salt lakes and oil drilling waters, as well as waste from boron ore enrichment, can also be used to produce borate fertilizers. In addition, boron is contained in local fertilizers (ash, peat, manure), for example 1 kg of wood ash contains 200-700 mg of boron, 1 kg of dry matter of manure and peat - about 20 mg [1-3].

Borate superphosphate is obtained by mixing superphosphate with boron-todalite fertilizer or other water-soluble boron compounds. The borate superphosphate contains 17-18% assimilated P_2O_5 and 1-2% boron in terms of H_3BO_3. One of the promising boron-containing fertilizers is borate double superphosphate. This is the most universal concentrated water-soluble fertilizer used effectively on sod-gley and limed sodpodzolic soils. Borate double superphosphate is usually obtained by treatment with phosphoric acid of datolite ore or a mixture of datolite concentrate with phosphate flour, it contains 36-40% of assimilable P_2O_5 and 6-8% of H_3BO_3. According to the requirements of TU 6-08-315-80 Superphosphate double granulated with trace elements should contain B (water) 0.4 ± 0.05% and assimilable P_2O_5 ≥42% [4].

At present, borate double superphosphate is used mainly for seed crops of leguminous grasses (clover, alfalfa), for root roots, sugar beet, flax, fruit and berry and vegetable crops. Usually, borate double superphosphate is applied to the soil before sowing of crops, and is also used for extra-fertilizing the plants (spraying and pollination).

MATERIALS AND METHODS

Laboratory studies were carried out in the following way: in the extractive phosphoric acid with a P_2O_5 content of 21,6% heated to 50-90^{0}C, a mixture of Karatau phosphoresces and borate salt, preliminarily mixed, depending on the component ratio was added. The decomposition of a mixture of phosphoresces and borate ore with extraction phosphoric acid was carried out under conditions of an unabated pulp. Under these conditions, the borate ore is uniformly distributed throughout the volume of the reaction mixture and decomposes in the phosphoric acid pulp. Then, the resulting pulp was dried at a temperature of 105-110°C for 60 minutes. The obtained product was analyzed for the content of total, digestible and free forms of P_2O_5 by standard methods in accordance with GOST 20851.2-75 and on the content of water-soluble boron (B).

Following raw materials were applied for the laboratory research: Karatau phosphorites of composition (mass %): P_2O_{5total} - 25.0; CaO – 37.04; MgO – 2.4; Fe_2O_3 – 1.18; Al_2O_3 – 0.8; insoluble residue – 21.62; F – 2.38; moisture – 0.32 and wet-process phosphoric acid produced from these raw materials; its composition (mass %): P_2O_5 $_{total}$ – 21.6; CaO – 0.57; MgO – 1.49; Fe_2O_3 – 0.99; Al_2O_3 – 0.86; F – 1.74; SO_4 - 2.22. Wet-process phosphoric acid used for the experiments was produced at the Plant of mineral fertilizers of “Kazphosphate” LLP. A complete analysis of Karatau phosphorites and WPA was conducted in the central laboratory of “Kazphosphate”.

RESULTS AND DISCUSSIONS

In the laboratory, the effect of the amount of borate salt additive, the rate and temperature of the EFC on the yield and quality of the product was studied. In laboratory studies the ratio of the mass part of phosphorite was used: the mass part of the borate salt (m.ch.ph: m.ch.b). To determine the effect of the amount of the borate salt additive on the decomposition process of the "phosphorite: borate salt" mixture, the EFK rate was 120% from stoichiometry at a temperature of 800°C, a reaction time of 1 hour and a drying temperature of 105-110°C. The results of laboratory studies are presented in Table 1.

Table 1. Effect of the amount of borate salt additive on the phosphorite decomposition factor

№	The amount of borate salt addition, «M.ch.ph: m.ch.b.»	Decomposition temperature, ° C	P_2O_5 com %	P_2O_5 assimilable %	B_2O_3, %	Degree of decomposition, %
1	100:30	80	38.2	32.89	1.80	86.1
2	100:40	80	36.1	31.21	2.36	86.4
3	100:50	80	34.5	27.65	2.90	80.1
4	100:60	80	31.7	25.11	3.11	79.2

Source: Our own experimental data, which were not previously published.

As can be seen from Table 1, with an increase in the amount of the borate salt addition, the B_2O_3 content of the product increases. However, at a ratio of "m.h.ph: m.ch.b." = 100: 60, the content of P_2O_5sv. in the product decreases, i.e. the degree of decomposition of phosphorite decreases. Perhaps in these conditions, the EFC norm is not sufficient, which is the object of further research. Under these conditions, the optimal ratio of "m.ch.ph: m.ch.b." is 100: 40.

The mixture of phosphorite and borate salt was decomposed by extraction phosphoric acid. In the thermal polycondensation of phosphates in the presence of boron compounds, copolymers of phosphorus and boron of complex composition with P-O-B bonds are formed. As a result, the degree of polymerization of the phosphate part is lower than in the absence of boron compounds. This leads to an increase in the solubility of the product. In addition, boron compounds accelerate the dehydration of phosphates, which leads to an increase in the content of total and assimilated P_2O_5. The absence of sulfate ions in the process of obtaining calcium polyphosphate, which is a ballast in the fertilizer, which also leads to an increase in the total and assimilated P_2O_5 in the product. As a source of boron, we used borate ores of the Inder deposit containing 11% of B_2O_3. The use of borate ores with this percentage is optimal. Since the use of borate ores with a B_2O_3 content of less than 5% leads to a decrease in the P_2O_5 content of the product due to an increase in the insoluble precipitate. The higher the concentration of ore in B_2O_3, the higher the concentration of the product by P_2O_5. A decrease in the process temperature leads to a deterioration in the dehydration process, and an increase in the reduction in the water soluble form of P_2O_5 in products.

The process of dehydration of phosphates in the presence of boron compounds intensifies, which makes it possible to increase the nutritional properties of fertilizers by introducing beneficial properties of the components: boron and magnesium, while simultaneously increasing the content of P_2O_5. Due to the fact that the amount of phosphoric acid is taken slightly higher than the stoichiometric norm for the formation of dihydrogen phosphates, the added boron compounds lead to complete neutralization of free acidity, the products somewhat swell and become lighter.

Borates in phosphoric acid solutions easily transform into a soluble form. With further dehydration of the resulting suspension, the process of polycondensation of phosphates and borates occurs with the formation of polymeric compounds of phosphorus and boron, the role of boron is reduced to that under these conditions boron participates in reactions of joint polycondensation with phosphates, forming heteropolymer compounds containing P-O-B bonds. Bohr exerts an accelerating effect on the process of polycondensation, as a result of which the dehydration process intensifies, which allows to increase the content of P_2O_5 in the product, to lower the temperature of the process. The resulting heteropolymers with P-O-B bonds are hydrolytically unstable, which leads to an increase in the content of the water-soluble form of P_2O_5. As a useful microelement, boron improves the quality of the product obtained. In addition, natural borates contain magnesium, which is also a useful component in fertilizers, whose presence increases the nutritional properties of the fertilizer.

Using the optimal ratio of extraction acid and borate salt to decomposition of phosphate raw materials allows to increase the degree of decomposition of raw materials, intensify the process of dehydration of phosphates in the presence of boron compound, eliminate the stages of warehouse ripening and obtain a conditioned product for a short time. The product contains useful components: phosphorus, boron. The product is characterized by good physical properties, non-hygroscopic, no free acidity, boron in the product is in a water-soluble form and evenly distributed.

The amount of boron added is limited by the requirements of agrochemistry. Since excess boron content has a harmful effect on plants. Calculation of the borate salt consumption was carried out taking into account the ratio B: P_2O_5 in granular borate double superphosphate 1: 100.

A study of the influence of the EFC norm on the degree of decomposition of phosphorite was carried out at the temperature of EFC 80^0C, the ratio "m.h.ph: m.ch.b." is 100: 40, the duration of the interaction is 60 minutes and the drying temperature is $105\text{-}110^0$C. The rate of EFC consumption was varied within 110-130% of the stoichiometry. The results of laboratory studies are presented in Table 2.

From the data given in Table 2 it can be seen that with the increase in the rate of consumption of the ESP, the degree of decomposition of the "phosphorite: borate salt" mixture increases, however, the content of P_2O_5 spore. the same increases. At an acid rate above 120% of stoichiometry, the degree of decomposition of phosphorite does not increase significantly, but the content of free unreacted P_2O_5 increases. The optimal norm of EFC in this case is 120% of stoichiometry. Under these conditions, a relatively high degree of decomposition of the "phosphorite: borate salt" mixture is achieved. The product obtained under these conditions has good physical properties.

Table 2. Influence of the EFC rate of application on the decomposition factor of the Karatau phosphorite mixture and the borate salt

№	EFC consumption rate,% of stoichiometry	Decomposition temperature, ° C	Drying temperature, ° C	P_2O_5 com., %	P_2O_5 free., %	Degree of decomposition,%
1	110	80	105-110	34.5	1.2	80.2
2	120	80	105-110	36.1	3.2	86.4
3	130	80	105-110	39.1	4.3	86.1
4	140	80	105-110	41.5	5.6	89.5

Source: Our own experimental data, which were not previously published.

A study of the effect of temperature on the degree of decomposition of the "phosphorite: borate salt" mixture was carried out within the temperature range of ESP 70-90^{0}C at a ratio of "m.h.ph: m.ch.b." of 100:40 and an EFC rate of consumption of 120% of stoichiometry. From the literature data it is known that the degree of decomposition of phosphorite decreases with increasing temperature of the ESP, this is explained by the nature of the change in solubility in the system of $CaO-P_2O_5-H_2O$ [5-7].

At a temperature of 70°C, the degree of decomposition of the "phosphorite: borate salt" mixture is somewhat higher, but the temperature of the superphosphate mass is reduced due to the relatively low ratio of the amount of heat released from the decomposition reaction. In the drying process, evaporation of moisture occurs and the content of phosphoric acid in the liquid phase increases, i.e. the activity of hydrogen ions of the liquid phase increases, which leads to an additional decomposition of the "phosphorite: borate salt" mixture. As a result of drying the pulp obtained at different temperatures to the same moisture content, the degree of decomposition of the "phosphorite: borate salt" mixture is practically the same. The results of the studies showed that when the temperature is raised above 90^{0}C, a more viscous and dense pulp is obtained. At an acid temperature of 90^{0}C, a more mobile pulp is obtained, which is easily transported to further stages of the manufacturing process. From the literature data it follows that an increase in temperature is undesirable, since the content of the assimilated form of P_2O_5 decreases. Reducing the temperature leads to a deterioration of the process.

Based on the results of the studies, it was determined that the optimum temperature of extraction phosphoric acid is 90^{0}C. Under these conditions, the product of the composition was obtained,% (by mass): P_2O_5 com. 36.1; P_2O_5 assim. 33.2; B_2O_3 2.36 (in terms of B – 0.37), which fully meets the requirements for the quality of borate double superphosphate.

CONCLUSIONS

Thus, under laboratory conditions, the influence of the ratio of phosphorite: borate salt on the degree of decomposition of phosphorite, the effect of the rate and temperature of extraction phosphoric acid on the degree of decomposition of the phosphorite: borate salt mixture was studied.

On the basis of the obtained research results, optimal parameters of the technological process for obtaining borate double-superphosphate using borate salts of the Inder deposit are determined:

-the ratio "mass part of phosphorite: mass part of borate salt" ("m.ch.ph: m.ch.b.") is equal to 100: 40;

-EFK consumption rate - 120% of stoichiometry;

-temperature of EFC - 90^{0}C.

The product obtained under these conditions contains,% (by mass): P_2O_5 total. 36.1; P_2O_5 assim. 33.2; B_2O_3 2.36 (in terms of B – 0.37), which fully meets the requirements for the quality of borate double superphosphate.

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