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Zh. K. Dzhanmuldaeva[1], A.A. Kadirbaeva[1], G.M.Seitmagzimova[1], Zh.M. Altybayev[2], Sh.K. Shapalov[2]

[1]M.Auezov South Kazakhstan State University, Shymkent, Kazakhstan;
[2]South Kazakhstan Pedagogical University, Shymkent, Kazakhstan
Zanyld @mail.ru, arsenal_575@inbox.ru, shermahan_1984@mail.ru

ON THE METHOD OF MANUFACTURE OF ORGANOMINERAL FERTILIZER BASED ON DOUBLE SUPERPHOSPHATE

Abstract. The paper considers features and advantages of using organomineral fertilizers. Large amount of weakly alkaline lignin-containing solutions being a hard-recyclable waste of cellulose production is formed as a result of the steam-explosive catalysis of herbal agricultural raw materials. The paper considers the possibility of using it as an organic component of organomineral fertilizer. Optimal parameters of the process of double superphosphate production were determined based on laboratory investigation results. The obtained product does not meet requirements of the State standard for double superphosphate, but it is similar to double superphosphate composition. We offer to conduct the process of product granulation in the presence of lignin-containing solution which is a waste of cellulose production to improve the quality, increase the assortment and the agrochemical composition of the fertilizer. Based on the research results we suggest a technological scheme of organomineral fertilizer production on a basis of double superphosphate with the use of lignin-containing solution. The obtained organomineral fertilizer has good physical qualities: it does not clump, does not cake up and does not lose its friability.

Key words: organomineral fertilizers, delignification, lignin-containing solution, double superphosphate, wet-process phosphoric acid (WPA).

Introduction. It is known that organomineral fertilizers combine the advantages of individual organic and mineral fertilizers, strengthen and prolong the action of each of the components and simultaneously remove disadvantages of both fertilizers. The mineral part of organomineral fertilizers dissolve well in the soil solution and ensure fast assimilation by plants. Organic components have a prolonged effect and guarantee the supply of plants with nutrients for a long time. The separate application of organic and mineral fertilizers does not give such an effect. Organic and mineral parts of organomineral fertilizers interact between each other and nutrients (nitrogen, phosphorus and potassium) pass into more accessible compounds for plants. When using organomineral fertilizers, nitrogen mobility reaches 95-98%, phosphorus - 90-95%, potassium - 95%, and they are completely used by plants, while these elements are used in mineral fertilizers only by 30-35%. Therefore, the average doses of granular organomineral fertilizers are about 10 times lower compared to organic fertilizers and 2-3 times lower compared to mineral fertilizers. The ecological component is also very important in the production of organomineral fertilizers, i.e. the amount of both mineral and organic waste on the Earth will decrease. The effectiveness of the use of organomineral fertilizers has been confirmed by numerous tests, while it has been established that the content of organic matter in the soil increased on average by 16-25%. Agrochemical analysis of soil showed a significant increase of the level of macro- and microelements in the soil. The amount of nitrogen in the soil, compared with control sites, increased by an average of 2.2-2.8 times, the content of phosphorus increased by 1.3-2.0 times, potassium by 1.3-2.5 times, calcium by 1,3-1,9 times, magnesium by 1,3-1,6 times [1].

Organomineral fertilizers are characterized by high agrochemical efficiency. There are physiologically active substances in the organomineral fertilizers, which influence the growth of plants, create a loose soil structure, increase the total surface of the finished product volume. Organomineral fertilizers promote to adsorption and retention of moisture (up to 50%), as well as nutrients such as nitrogen, phosphorus, potassium, calcium, minor-nutrient elements. They have good physical qualities: they do not clump, do not cake up and do not lose their friability even when the moisture content in them is up to 50% (absolute). The use of organomineral fertilizers prevents and eliminates the possibility of elution of nutrient elements and allows to reduce significantly (by 25-50%) the norm of introducing nutrients into the soil. In addition, the use of organomineral fertilizers will allow to reduce soil salinity, provide optimal water and air regime, increase humus content in the soil, reduce the harmful effects of high doses of NPK fertilizers, pesticides, toxic chemicals and radionuclides, to increase soil fertility, crop yield, their quality value and ensure environmental safety [2].

Scientists of M. Auezov South Kazakhstan State University have developed a technology of cellulose production based on the process of steam-explosive autocatalysis of herbal agricultural raw materials, such as wheat straw and rice hulls. The developed cellulose technology is associated with the formation of large amount of weakly alkaline lignin-containing solutions. They have studied the process of explosive autocatalysis of wheat straw and rice hulls in the presence of weak alkaline solutions of cellulose production; paper or corrugated cardboard are produced from the cellulose hereafter. It has been established that the use of steam explosion of straw or rice hulls with subsequent extraction by alkaline solutions allows obtaining cellulose with better strength characteristics than that at acid delignification. Lignin is removed from these solutions; this process is called as delignification. At that, weakly alkaline lignin-containing solutions are formed, which are hard-recyclable wastes of paper production [3,4]. Further processing or recycling of these wastes is an actual production problem and an essential element of the creation of non-waste technology.

In this context, the development of the technology of organomineral fertilizer with the possibility of utilization of delignification extract is topical issue. Its use as an organic component of organomineral fertilizer based on double superphosphate can be one of such methods. To prepare an organomineral fertilizer on the basis of double superphosphate, we suggest adding the delignification extract at the granulation stage.

The proposed technology of organomineral fertilizer based on double superphosphate consists of several stages: 1) decomposition of phosphate raw materials with wet-process phosphoric acid (WPA); 2) drying the pulp; 3) granulation of the product in the presence of the lignin-containing solution; 4) drying and sifting the finished product. To determine optimal parameters of the process of obtaining organomineral fertilizer on the basis of double superphosphate, the influence of WPA norm, concentration and temperature on phosphorite decomposition degree and the additive of lignin-containing solution influence on the process conditions and the quality of the product were studied.

Materials and methods. Laboratory experiments of the decomposition of Karatau phosphorites with wet-process phosphoric acid for obtaining double superphosphate were carried out as follows. The WPA stoichiometric norm was calculated according to a simplified procedure that does not take into account the mineralogical composition of raw materials [5]. The required amount of wet-process phosphoric acid was heated up to a certain temperature and then mixed with phosphorite for 1 hour at stirring. The formed pulp was dried for 1.5 hours in a dryer at 105-110°C (to approach the temperature regime of ageing the double superphosphate in production conditions). The obtained chamber double superphosphate was analyzed for moisture content and all forms of P_2O_5 content by standard methods in accordance with GOST 20851.2-75 and GOST 20851.4-75.

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 discussion. To study the influence of WPA norm on the phosphorite decomposition degree the interaction process was carried out at a temperature of 70°C during 1 hour and a drying process was carried out at a temperature of 105-110°C. The WPA consumption coefficient was varied within 70-110% of the stoichiometry. The results of laboratory studies are presented in Table 1.

As can be seen from Table 1, the phosphorite decomposition degree increases when increasing the WPA consumption rate, the content of P_2O_{5free}. also increases. In the dried samples, the P_2O_{5total} ranges as 33,3-38,0%, and P_2O_{5free} is 5.6-7.9%. At the acid norm above 90% of stoichiometry, the phosphorite decomposition degree does not increase significantly. At the norm of 110% of stoichiometry the decomposition degree is 91.8%, however, the content of free P_2O_5 is also high. Therefore, the optimal WPA norm is 90% of stoichiometry.

Table 1 - Influence of WPA consumption rate on the phosphorite decomposition degree at 70 °C

№	WPA consumption rate, % of stoichiometry	Drying temperature, °C	$P_2O_{5\,total}$, %	$P_2O_{5\,free}$, %	Decomposition level, %
1.	70	105-110	33,3	5,6	80,2
2.	80	105-110	34,6	6,2	85,1
3.	90	105-110	35,7	6,9	89,3
4.	100	105-110	36,9	7,2	90,5
5.	110	105-110	38,0	7,9	91,8

Under these conditions, a relatively high phosphorite decomposition degree is attained and a product with good physical properties is obtained, i.e. the prepared product can be processed further. The next step of the product treatment is granulation in the presence of the lignin-containing solution.

To study the effect of temperature on the phosphorite decomposition degree, decomposition temperature was varied within 40-90°C, the WPA consumption rate was 90% of the stoichiometry as an optimal value determined earlier. It is known that the phosphorite decomposition degree decreases with increasing temperature, this is explained by the nature of the change in solubility in CaO-P_2O_5-H_2O system [5]. When temperature increasing the supersaturation degree with calcium hydrophosphate increases. As a result, calcium hydrophosphate film is formed on the surface of the phosphorite grains, which leads to decomposition process deceleration. At temperature below 70°C, the phosphorite decomposition degree 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 to the weight of the superphosphate mass. This will increase the moisture content of the product. Evaporation of moisture takes place and the content of phosphoric acid in the liquid phase increases in the process of drying. The calcium hydrophosphate film formed on the surface of the phosphorite grains dissolves, an activity of hydrogen ions in the liquid phase increases, as a result of which the phosphorite further decomposition takes place. The results of studies showed that increasing the temperature above 70^0C causes more viscous and dense pulp formation. At a temperature of 70°C, more mobile pulp is obtained, which will easily be transported to the dryer.

Thus, optimal parameters of the process of obtaining double superphosphate were determined: WPA consumption rate is 90% of stoichiometry; the decomposition temperature is 70°C. Under these conditions, the product of the following composition was obtained, (mass %): P_2O_{5total} - 35.7; $P_2O_{5available}$ - 31.9 and P_2O_{5free} - 6.9. This product does not meet the requirements for the double superphosphate GOST, but it is similar to double superphosphate composition.

The lignin-containing solution obtained as a result of a steam explosion of rice hulls is an alkaline water extract containing 26% of lignin with pH = 12-13. After complete evaporation of this extract, the chemical composition of the obtained precipitate, determined from scanning electron microscopy, (mass %) is following: C-34.85; O-35.68; Na-0.62; Si-1.15; S-0.16; K-24.52. As can be seen from the data, the dry residue is mainly represented by carbon, oxygen, and potassium; there are sodium, sulfur and silicon in relatively small amounts.

Studying the fertilizer granulation process in the presence of lignin-containing solution has shown that the use of lignin-containing solution leads to the neutralization of free acidity forming potassium phosphates in the complex of phenylpropyl functional groups and the enrichment of the product additionally with potassium nutrient. As a result of double superphosphate preparation in laboratory conditions with the use of delignification solution at the granulation stage we have obtained the organomineral fertilizer of the composition, mass %: P_2O_{5total} – 33,8; $P_2O_{5available}$ – 32,11; P_2O_{5free} – 0; organic constituent – 5,39.

The results of investigations of lignin-containing solution additive influence on commodity fraction product output from the granulation stage are given in Figure 1.

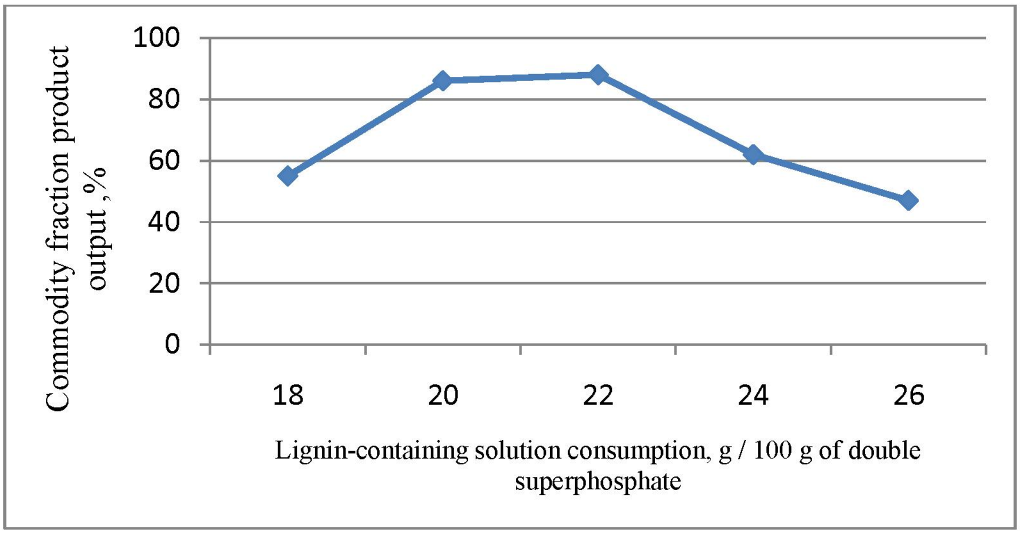

Figure 1 – Dependence of commodity fraction product output on lignin-containing solution consumption

It demonstrates that optimal lignin-containing solution additive, providing maximum of commodity fraction product output, has very narrow range. Outside the range either pelletizing does not take place or spontaneous agglomeration takes place. Insignificant additive increase or decrease leads to sharp reduction of commodity fraction product output. It is explained that the additive decrease is accompanied with moisture input decrease, i.e. there is the lack of moisture for complete wetting fertilizer grain surface; at that pelletizing does not take place. And when the additive increasing the amount of moisture input increases which results in excessive growth of charge moisture content and formation of large lumps and agglomerates.

The results of laboratory testing have shown that optimal lignin-containing solution additive is 20-22 g / 100 g of powdered double superphosphate. The maximal commodity fraction product output – 86-88% is observed at this condition.

The proposed technological scheme for the production of organomineral fertilizer based on double superphosphate consists of several stages: 1) the decomposition of phosphate raw materials with WPA of P_2O_{5total} 21.6% concentration (by mass), at 90% WPA consumption rate for 1 hour at 70-90°C, while the phosphate raw material decomposing by 55-60%: 2) Drying the pulp at 105-110^{0}C. During the drying process, the decomposition of raw materials continues and the total decomposition degree of raw materials increases to 85-90%; 3) Granulation of the product in the presence of the lignin-containing solution; 4) Drying the prepared granules to the moisture content of 3-4% in warm conditions at the temperature of 60-70^{0}C.

Conclusion. Optimal parameters of the process of double superphosphate production were determined based on laboratory investigation results: decomposition of phosphate raw materials with WPA for 1 hour at 70-90°C with further decomposition during the drying process, then lignin-containing solution addition with the norm of 20-22 g / 100 g of powdered double superphosphate on the granulation stage. When using lignin-containing solution at the granulation stage of double superphosphate production we can prepare the new mineral fertilizer of improved quality. It will promote to increase product output and to increase the assortment and the agrochemical composition of the organomineral fertilizer. Simultaneously the cellulose production waste can be utilized completely. The prepared organomineral fertilizer based on double superphosphate contains P_2O_5 in easily assimilated form for plants and an organic part that is of prolonged action. The use of such a fertilizer extends the term of its effective action in the soil.

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Ж.К. Жанмолдаева[1], А.А. Қадірбаева[1], Г.М. Сейтмагзимова[1], Ж.М. Алтыбаев[2], Ш.К. Шапалов[2]

[1]М.Әуезов атындағы Оңтүстік Қазақстан мемелекеттік университеті, Шымкент, Казахстан;
[2]Оңтүстік Қазақстан педагогикалық университеті, Шымкент, Казахстан

ҚОС СУПЕРФОСАТ НЕГІЗІНДЕ ОРГАНОМИНЕРАЛДЫ ТЫҢАЙТҚЫШТЫ ДАЙЫНДАУ ӘДІСІ БОЙЫНША

Аннотация. Мақалада органоминералды тыңайтқыштардың ерекшеліктері мен артықшылықтары көрсетілген. Шөпті ауылшаруашылық шикізаттарын целлюлоза алу мақсатымен бу-жарылыс катализ арқылы өңдеу нәтижесінде көп мөлшерде әлсіз сілтілі лигнинқұрамдас ерітінділер пайда болады. Мақалада осы ерітіндіні органоминералды тыңайтқыштың органикалық құрамдас бөлігі ретінде қолдану қарастырылған. Зертханалық зерттеулер нәтижесінде қос суперфосфат алу процесінің тиімді технологиялық параметрлері анықталған. Алынған суперфосфат қос суперфосфатқа қатысты стандарт талаптарына сәйкес келмейді, бірақ құрамы бойынша қос суперфосфатқа жақын. Тыңайтқыштардың сапасын жоғарылату, ассортиментін көбейту және агрохимиялық құрамын жақсарту мақсатымен оны целлюлоза өндірісінің қалдығы –лигнин-құрамдас ерітіндінің қатысында түйіршіктеу ұсынылған. Зерттеу нәтижелері бойынша лигнинқұрамдас ерітінділерді қолдану арқылы қос суперфосфат негізінде органоминералды тыңайтқыш алудың технологиялық сызба нұсқасы ұсынылған. Алынған органоминералды тыңайтқыштың физикалық қасиеттері жақсы: жұмырланбайды, нығыздалмайды және үгілгіштігін жоғалтпайды.

Түйін сөздер: органоминералды тыңайтқыштар, дәнекерлеу, лигнинді ерітінділер, қос суперфосфат, экстракциялық фосфор қышқылы.

Ж.К. Жанмолдаева[1], А.А. Қадірбаева[1], Г.М. Сейтмагзимова[1], Ж.М. Алтыбаев[2], Ш.К. Шапалов[2]

[1]Южно-Казахстанский государственный университет им. М.Ауэзова, Шымкент, Казахстан;
[2]Южно-Казахстанский педагогический университет, Шымкент, Казахстан

ПО МЕТОДУ ИЗГОТОВЛЕНИЯ ОРГАНОМИНЕРАЛЬНОГО УДОБРЕНИЯ НА ОСНОВЕ ДВОЙНОГО СУПЕРФОСФАТА

Аннотация. В статье представлены особенности и преимущества использования органоминеральных удобрений. В результате паро-взрывного катализа травянистого сельскохозяйственного сырья с целью получения целлюлозы образуется большое количества слабощелочных лигнинсодержащих растворов, которые являются трудноутилизируемым отходом. В статье рассмотрена возможность применения его в качестве органической составляющей органоминерального удобрения. По результатам лабораторных исследований определны оптимальные параметры процесса получения двойного суперфосфата. Полученный продукт не соответствует требованиям стандарта на двойной суперфосфата, но по своему составу схож с двойным суперфосфатом. С целью улучшения качества, увеличения ассортимента и агрохимического состава удобрения предлагается процесс грануляции продукта проводит в присутствии лигнинсодержащего раствора – отхода производства целлюлозы. По результатам исследований предложена технологическая схема производства органоминерального удобрения на основе двойного суперфосфата с использованием лигнинсодержащего раствора. Полученное органоминеральное удобрение имеет хорошие физические качества: не комкуются, не слёживаются и не теряют своей рассыпчатости.

Ключевые слова: органоминеральные удобрения, делигнификация, лигнинсодержащие растворы, двойной суперфосфат, экстракционная фосфорная кислота (ЭФК).

Information about authors:

Dzhanmuldaeva Zh.K. – candidate of technical Sciences, Professor, Department "Chemical technology of inorganic substances", M.Auezov South Kazakhstan State University, Shymkent, Kazakhstan;

Kadirbaeva A.A. - candidate of technical Sciences, Associated Professor, Department "Chemical technology of inorganic substances", M.Auezov South Kazakhstan State University, Shymkent, Kazakhstan;

Seitmagzimova G.M. - candidate of technical Sciences, Professor, Department "Chemical technology of inorganic substances", M.Auezov South Kazakhstan State University, Shymkent, Kazakhstan;

Altybayev Zh.M. - PhD, Senior teacher, Department of chemistry and biology, M.Auezov South Kazakhstan State University, Shymkent, Kazakhstan;

Shapalov Sh.K. - PhD, Senior teacher, Department of chemistry and biology, South Kazakhstan Pedagogical University, Shymkent, Kazakhstan.