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Influence of granule structure mineral fertilizers for their physical and chemical properties

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ABSTRACT
In this article, maintaining the quality and commercial properties of mineral fertilizers during repeated transshipment and long-term transportation is an important issue. The purpose of the research work is to study the structure of granules in complex mixed fertilizers and to develop methods to improve it at the production stage, thereby improving the physical and mechanical properties of the finished product. In order to improve the granular structure of the mineral fertilizer, the static strength of the granules, the mass fraction of moisture, the chemical composition, and the structural shape of the granules were determined using an electron microscope. To improve the structure and increase the strength of mineral fertilizers, a method of encapsulation was used using 0.5% aqueous solutions of organic polymers of modified polyacrylamide, followed by granulation and drying at a temperature of 75 °C and a tralchet granulator. A comparative analysis was conducted to study the structure of mineral fertilizers, diammonium phosphate, and encapsulated superphosphate using modern instrumental methods. The structure of encapsulated superphosphate was studied, and its strength was increased using 0.5% aqueous solutions of modified polyacrylamide at a temperature of 750 °C, with an increase from 40 to 2000 times. Spectral studies of superphosphate treated with polymer solutions were carried out, and structural features corresponding to the functional groups of organic compounds were identified. The research results showed that aqueous solutions of modified polyacrylamide allow structure formation, creating a polymer shell and increasing the strength of mineral fertilizer granules.

Keywords: mineral fertilizer, strength, structure, grain, research.

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Introduction

The manufacture of mineral fertilizers is an important area of the Kazakh agro complex, occupying a leading position in non-hydrocarbon, non-resource exports.

The country is experiencing an increase in the production of complex mixed mineral fertilizers for export.

The range of mineral fertilizers produced in the Republic of Kazakhstan today is changing in favor of mineral fertilizers, which meet modern consumer

preferences. Complex mixed fertilizers, as a rule, are more concentrated and require lower costs for transportation, storage, and application compared to single-component fertilizers.

Improved quality of exported mineral fertilizers is a prerequisite for increasing export potential and an important factor in maintaining the competitiveness of Kazakhstani producers. Thus, the problem of preserving the quality of mineral fertilizers during numerous transshipments and long-term transportation is one of the key ones for the industry as a whole. In addition, improving the physicochemical properties of mineral fertilizers can significantly increase the efficiency of their use and avoid losses at the application stage [[1],[2]].

The consumer properties of granular mineral fertilizers - static strength of granules, caking, dustiness - are interrelated and depend on the substance constituents and building of the granules, which is largely determined by the technological parameters of the production process [[3], [4]].

Currently, modern non-destructive methods for studying the structure of solids, such as scanning electron microscopy (SEM), have appeared and become available. The use of these methods allows us to study in detail the structure and distribution of chemical elements in granules of complex mineral fertilizers, as well as their relationship with physical and chemical properties [[5],[6]].

The importance of scientific work is to study the structure of granules of complex mixed fertilizers, as well as to search and develop methods for improving them at the production stage to improve the physical and mechanical features of the eventual product.

Experimental part

Object of research. To study the properties of granular mineral fertilizers, the most popular brands of mineral fertilizers produced by Kazphosphate LLP were selected. Sample preparation and sampling for experimental work were carried out in accordance with the established procedure [7].

Research methods. *Determination of the static strength of sample granules.* The static strength of sample granules was measured according to GOST 21560.2-82. The static strength of the granules was studied using an automatic dual Rockwell hardness tester HRS150/45T-Z. The strength measurement range is from 3.0 to 20 MPa, with a relative error ±1%.

Determination of mass fraction of water. The mass fraction of hygroscopic and total water was determined by drying in an oven in accordance with [8].

Study of the structure and chemical composition of granules using scanning electron microscopy. The microstructure and a cut of a sample of the mineral fertilizers was an instrumental method determined using scanning microscopy SEM (JSM-6490lV, Jeol, Tokyo, Japan). The scale of this microstructure is x50-2000 times the increase from the actual state (600 micron, spectral 0 - 20 keV).

Study the structural features of the studied sample. An IR Fourier spectrometer (Zhimadzu IR Prestige-21 with an attenuated total internal reflection attachment, Miracle Pike Technologies (Tokyo, Japan)) was used to study the structural features of the studied sample.

To improve the structure and increase the strength of mineral fertilizers, a method of encapsulation was used using 0.5% aqueous solutions of organic polymers of modified polyacrylamide, followed by granulation and drying at a temperature of 75 °C and a tralchet granulator.

The discussion of the results

The structure of granules of complex fertilizers is determined, first of all, by the technology of their production: the method of granulation, as well as the modes of the method of introducing raw materials. In turn, the structure of granules affects the physico-chemical and physico-mechanical characteristics of granular fertilizers - static strength [[9], [10]].

The work of the author (Kochetova I.M.) presents experimental images of the results of microphotography and the distribution of chemical elements on a chip of a DAP granule of grade 18-46, treated with I-40 oil (magnification x200).

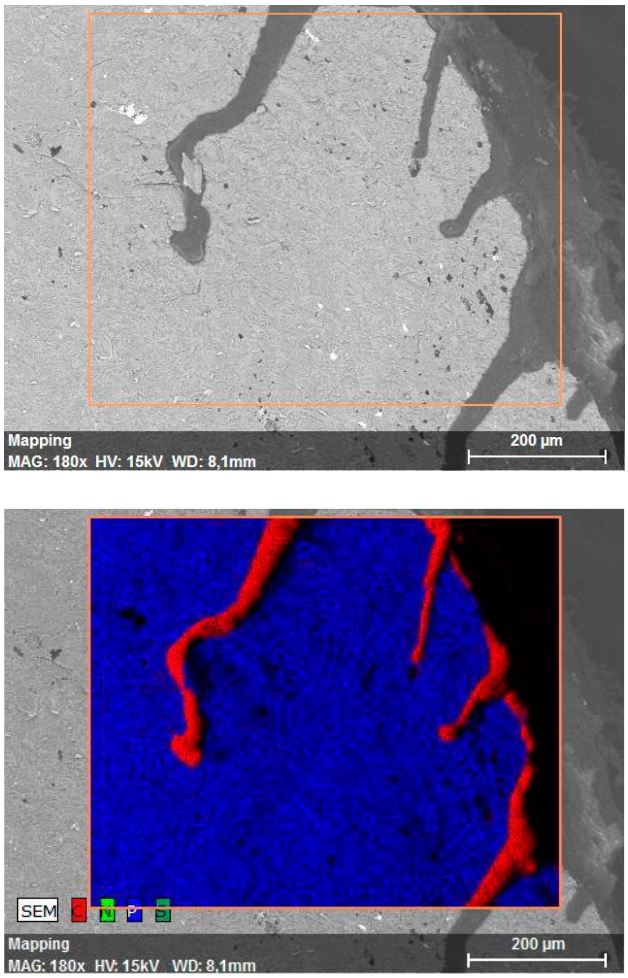

Figure 1 - Microphotograph and distribution of chemical elements on a chip of DAP granule grade 18-46 treated with I-40 oil (magnification x200)

It is noted here that the presence of surface pores largely determines the hygroscopic characteristics of the product and can also increase the consumption of conditioning additives (Figure 1).

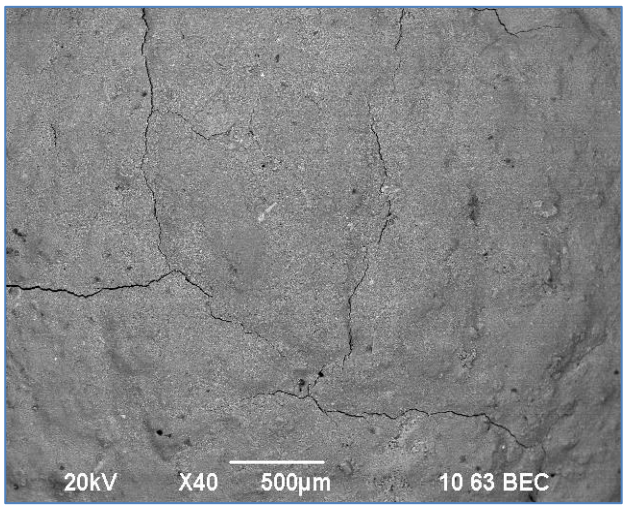

Figure 2 - The microstructure of a sample of the modified superphosphate (magnification x40)

From Figure 2, it follows that the microstructure of superphosphate granules with an X40 magnification and treated with 0.5% aqueous solutions of polycarilamide appears amorphous at a temperature of 75 ^{0}C. In the top layer of superphosphate, the formation of links occurs, leading to structuring in the form of amorphous and crystalline structures with the formation of a polymer layer on the surface of the granules. The binding of components with polymer solutions during granulation and the polymer layer on the surface of superphosphate have a positive effect on the structure and strength of the granules.

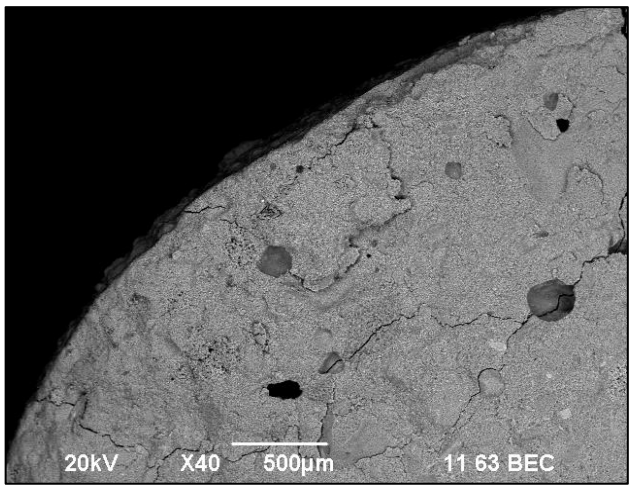

Figure 3 - The microstructure with a cut of the sample of the modified superphosphate (magnification x40)

From Figure 3, it follows that the pores of superphosphate granules are associated with cracks and are the centers for cracks, and the formation of a thin film on the surface of the granules provides an increase in strength up to 17 MPa.

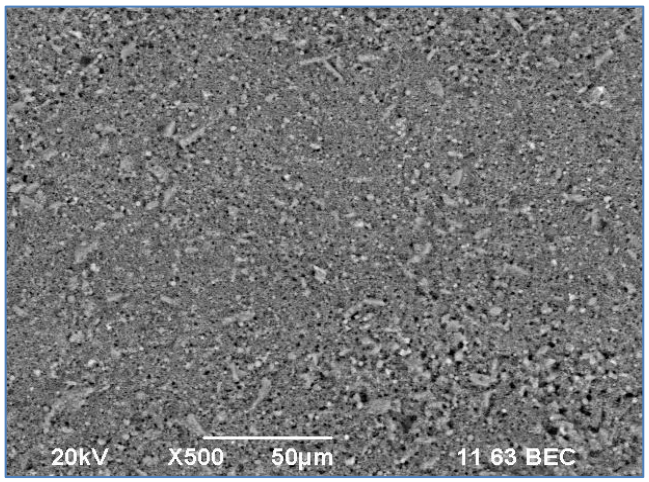

Figure 4 - The microstructure of a sample of the modified superphosphate (magnification x500)

Figure 4 shows that barrel-shaped structures with properties characteristic of phosphorus compounds were detected.

This indicates that the appearance of these fragments in the fertilizer structure is associated with the aggregation of fertilizer particles and the subsequent formation of large interconnected units due to the adsorption properties and functional groups of the polymer solutions, which influence the structural strength of the entire system (Fig.4).

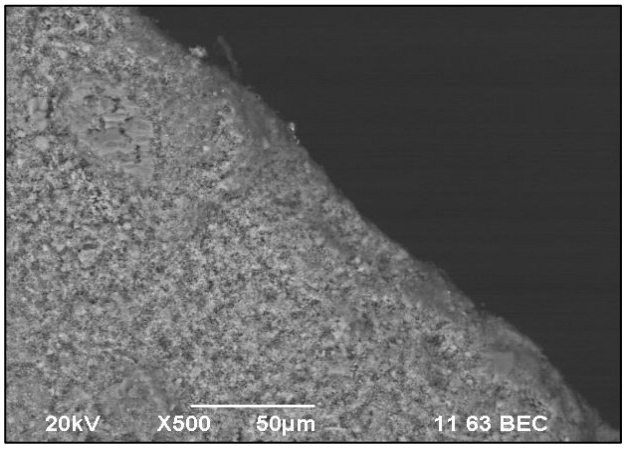

Figure 5 - The microstructure with a cut of the sample of the modified superphosphate (magnification x500)

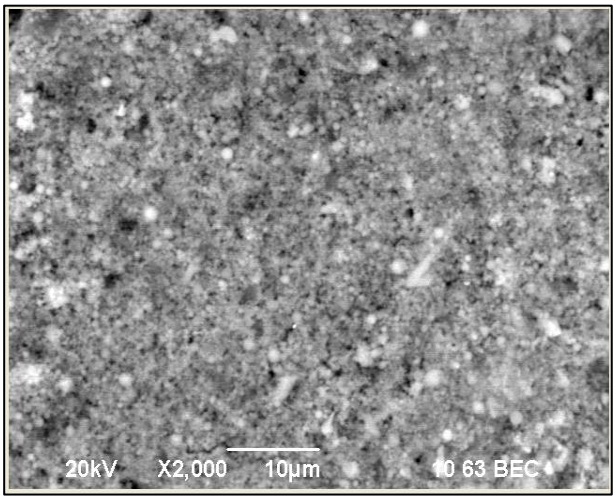

Figure 6 - The microstructure of a sample of the modified superphosphate (magnification x2000)

From Figure 6, it follows that there is a secondary adsorption layer in which the molecules are directed, and on the outside, there is a hydrophilic part that promotes coagulation binding of particles.

From Figure 7, it follows that the structure is observed on the surface of the granules, and in parallel, it is visible how a polymer layer is formed due to the interaction of the active centers of mineral fertilizers and the active functional groups of aqueous solutions of the polymer with the formation of thin films.

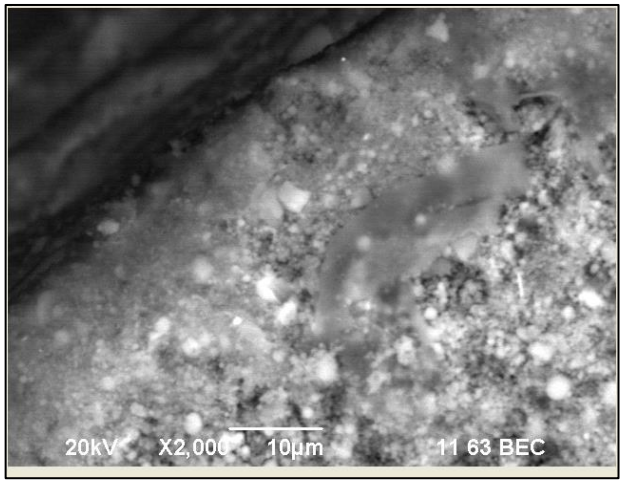

Figure 7 - The microstructure with a cut of the sample of the modified superphosphate (magnification x2000)

The improved mechanical properties of superphosphate positively impact the fertilizer's effectiveness. For example, due to its greater strength, dust formation during application is eliminated.

The obtained modified superphosphate had the following functional groups during research. The superphosphate was analyzed in an IR spectrometer (Shimadzu IR Prestige-21), and the results of the studies are shown in the table. 1 and Fig. 8.

Table 1 – Spectral data of modified superphosphate

No	Peak	Intensity	Corr. intensity
1	601.79	81.382	1.048
2	690.52	73.207	5.766
3	752.24	75.802	0.256
4	775.38	74.927	1.098
5	875.68	81.125	0.797
6	910.40	75.602	3.854
7	1002.98	68.732	3.190
8	1026.13	70.113	1.435
9	1365.60	86.484	0.112
10	1377.17	86.282	5.189
11	1558.48	86.358	0.447
12	3390.86	87.240	0.241
13	3618.46	91.620	0.855
14	3691.75	94.343	1.326

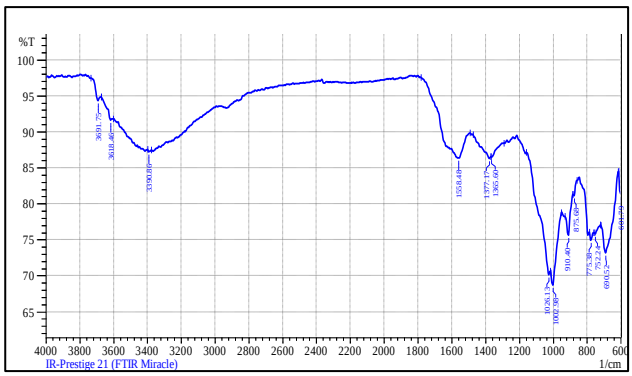

Figure 8 - IR-spectrum of modified superphosphate

As can be seen from the data in Figure 8, there are the following IR absorption spectra:

-non-intensive absorption spectra with wavelengths of 3691.75–3390.86 cm^{-1} characterize the presence of bonds (RC–COOH) carboxylic acids, bonds (RC–COH) aldehydes and ketones (R–CO–R) functional groups of superphosphate;

-non-intensive absorption spectra with wavelengths of 1558.48–1365.60 cm^{-1} characterize the presence of bonds (C–C) between carbons and (C–H) hydrocarbon groups in superphosphate;

-intensive absorption of 1026.13–910.40 cm^{-1} determines the compounds of hydroxyl, sulfur, nitrogen molecules – OH, N, S;

-Intensive absorption values of 875.68-752.24 cm^{-1} are characterize the presence of a bond between phosphorus and sulfur (P=S).

-intensive absorption values of 690.52-601.79 cm^{-1} are are characteristic of Ca^{+2} compounds in the valence state O-Ca-O.

The authors' work presents data on determining the basic physicochemical properties of fertilizer for its mechanized application to improve soils and increase crop yields [[11], [12]]. Using additions that improve the properties and increase the effectiveness of waste-based fertilizers corresponds with the modern approach to creating waste-free technologies, observed in agriculture and other branches of the economy [[13], [14]].

This work presents the results of research on the leaching of solid phosphorus-containing waste with humic acid. Such waste includes the by-products of the electrothermal processing of phosphate raw materials—phosphorus sludge and cottrel dust [[15], [16]].

Conclusions

A literature review was conducted of scientists who contributed to the study of the structure of granules and their influence on the physicochemical properties of mineral fertilizers[[17], [18], [[19], [20]].

A comparative analysis was conducted to study the structure of mineral fertilizers, diammonium phosphate, and encapsulated superphosphate using modern instrumental methods.

The structure of encapsulated superphosphate was studied and its strength was increased using 0.5% aqueous solutions of modified polyacrylamide at a temperature of 750 °C with an increase from 40 to 2000 times.

Spectral studies of superphosphate treated with polymer solutions were carried out, and structural features corresponding to the functional groups of organic compounds were identified. The research results showed that aqueous solutions of modified polyacrylamide allow structure formation, creating a polymer shell and increasing the strength of mineral fertilizer granules.

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CRediT author statement: **B. Smailov:** Conceptualization, formal analysis, investigation, data writing, original draft preparation, writing–review and editing. **O. Beisenbayev:** Data curation, writing draft preparation, methodology, **A. Anarbayev:** Resources, supervision. **B. Zakirov:** Investigation, visualization. **U. Aravind:** software, validation.

Conflicts of Interest. On behalf of all authors, the corresponding author declares that there is no conflict of interest.

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Минералды тыңайтқыштар түйіршіктерінің құрылымының олардың физика-химиялық қасиеттеріне әсері

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ТҮЙІНДЕМЕ

Минералды тыңайтқыштарды қайта тиеу және ұзақ мерзімге тасымалдау кезінде олардың сапасы мен тауарлық қасиеттерін сақтау маңызды мәселелердің бірі болып табылады. Ғылыми-зерттеу жұмысының мақсаты – күрделі аралас тыңайтқыштардың түйіршіктерінің құрылымын зерттеу, сонымен қатар дайын өнімнің физика-механикалық қасиеттерін жақсарту мақсатында өндіріс сатысында оны жетілдіру әдістерін табу және әзірлеу. Минералды тыңайтқыштың түйіршікті құрылымын жақсарту мақсатында түйіршіктердің статикалық беріктігі, ылғалдың массалық үлесі, түйіршіктердің химиялық құрамы мен құрылымдық пішіні электронды микроскоптың көмегімен анықталды. Минералды тыңайтқыштардың құрылымын жақсарту және беріктігін арттыру үшін модификацияланған полиакриламидтің органикалық полимерлерінің 0,5% сулы ерітінділерін қолданып, кейіннен түйіршіктеу және контейнерлік гранулятордың көмегімен 75 °С температурада кептіру арқылы капсуляция әдісі қолданылды. Заманауи аспаптық әдістерді қолдана отырып, минералды тыңайтқыштардың диаммоний фосфаты мен капсулаланған суперфосфаттың құрылымына салыстырмалы талдау жасалды. Капсулаланған суперфосфаттың құрылымы мен оның беріктігі модификацияланған полиакриламидтің 0,5% сулы ерітінділерін 75 °С температурада 40-тан 2000 есеге дейін арттыру арқылы зерттелінді. Полимер ерітінділерімен өңделген суперфосфатқа спектрлік зерттеулер жүргізіліп, органикалық қосылыстардың функционалдық топтарына сәйкес келетін құрылымдық ерекшеліктері анықталды. Зерттеу нәтижелері модификацияланған полиакриламидтің сулы ерітінділері құрылымды қалыптастыруға, полимер қабықшасын жасауға және минералды тыңайтқыш түйіршіктерінің беріктігін арттыруға мүмкіндік беретінін көрсетті.

Түйін сөздер: минералды тыңайтқыш, беріктілік, құрылым, түйіршік, зерттеу.

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Влияние структуры гранул минеральных удобрений на их физико-химические свойства

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АННОТАЦИЯ

Сохранение качественных и товарных свойств минеральных удобрений при многократной перевалке и длительной транспортировке является одним из важных вопросов. Цель научно-исследовательской работы – изучить структуру гранул комплексных смешанных удобрений, а также найти и разработать методы ее улучшения на этапе производства с целью улучшения физико-механических свойств готового продукта. С целью улучшения зернистой структуры минерального удобрения с помощью электронного микроскопа определяли статическую прочность гранул, массовую долю влаги, химический состав и структурную форму гранул. Для улучшения структуры и повышения прочности минеральных удобрений был использован метод капсуляция с применением 0,5% водных растворов органических полимеров модифицированного полиакриламида, с последующей грануляцией и сушкой при температуре 75 °C с помощью таральчетного гранулятора. Проведен сравнительный анализ структуры минеральных удобрений диаммонийфосфата и инкапсулированного суперфосфата с использованием современных инструментальных методов. Изучена структура инкапсулированного суперфосфата, и его прочность была повышена с использованием 0,5%-ных водных растворов модифицированного полиакриламида при температуре 750°C с увеличением от 40 до 2000 раз. Проведены спектральные исследования суперфосфата, обработанного полимерными растворами, и идентифицированы структурные особенности, соответствующие функциональным группам органических соединений. Результаты исследований показали, что водные растворы модифицированного полиакриламида позволяют формировать структуру, создавая полимерную оболочку и повышая прочность гранул минерального удобрения.

Ключевые слова: минеральное удобрение, прочность, структура, зерно, исследование.

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