Internal physico-chemical transformations in mineral fertilizer granules under long-term storage

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Abstract. The study was conducted on the physico-chemical changes occurring within mineral fertilizer granules during long-term storage in the climatic conditions of Uzbekistan. It was found that, similar to Belarusian fertilizers, there is no significant concentration gradient of components within the granules, indicating stable production technology. X-ray phase analysis revealed the formation of double salts and urea adducts, accompanied by changes in mineralogical composition. Samples containing prilled urea exhibited lower caking tendency, which is particularly important in high humidity environments. The results can be used to optimize fertilizer storage in hot climates.

1 Introduction

One of the key quality indicators of mineral fertilizers, alongside nutrient content, is their physico-mechanical properties: caking tendency, hygroscopicity, strength, abrasion resistance, and spreadability. These characteristics are particularly important in the context of long-term product storage, dictated by both logistical specifics and the seasonality of agricultural application.

In the conditions of Uzbekistan, where the climate is characterized by high air temperature and variable humidity, mineral fertilizers are subject to significant physicochemical changes during storage. These changes can degrade their physico-mechanical properties, leading to the formation of agglomerates, reduced flowability, and loss of marketable appearance, which ultimately affects application efficiency and the product's market value, as discussed in the works of Ando, J. & Matsuno, S. [1] and Dormeshkin, O. and Hauryliuk, A.N. [2].

Despite the existence of publications devoted to the issues of fertilizer caking and phase composition, most research is focused on technological stages of production or short-term testing [3–4]. The physicochemical processes occurring within the granules under conditions

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of real long-term storage, especially in a hot climate, are insufficiently studied. Furthermore, in most studies, granules are considered as homogeneous bodies, which does not reflect the multilayer structure formed during drum granulation—the primary technology used in the republic [5].

The established practice of labeling complex fertilizers based on their NPK content does not account for differences in production technology, types of raw materials, and additives used, which complicates the prediction of fertilizer behavior during storage [6]. In this regard, conducting research that considers specific technological conditions and the region's climatic features is particularly relevant.

The aim of the present research is to study the internal physicochemical transformations occurring within mineral fertilizer granules during storage under Uzbekistan conditions, with emphasis on factors influencing changes in phase composition and physico-mechanical properties.

2 Materials and Methods

The study objects were complex nitrogen-phosphorus-potassium fertilizers (grades 15-15-15 and 16-16-16) produced at enterprises of the Republic of Uzbekistan — JSC "Navoiyazot" and the Fergana Chemical Plant. The fertilizers differed in composition and type of nitrogen component: in some batches, prilled urea was used, while in others, granulated urea was applied [3].

The samples were stored under conditions simulating real warehouse environments: a temperature range of +20 to +35 °C and air humidity of 40–75% for 90 days [7-9].

To analyze the distribution of components within the granules, they were preliminarily classified, and the −4 mm +3 mm fraction was selected. The samples were abraded layer by layer: the outer shell (1 mm), the intermediate layer (up to 2 mm), and the core. The layer thickness was controlled by micrometer measurements in three mutually perpendicular planes. For each fertilizer grade, three replicates corresponding to the layers were prepared [1].

The quantitative determination of phosphorus, nitrogen, and potassium was carried out using methodologies equivalent to EAEU standards. Phosphorus (total, water-soluble, citrate-soluble) and nitrogen forms were determined in two parallel measurements with a confidence probability of $P = 0.95$ and a deviation of 0.2–0.5% [10].

Potassium was determined by flame photometry (PFP7 instrument, JENWAY, UK), with an error of up to 0.3%. The sulfate ion was determined gravimetrically, and fluoride was determined using an ion-selective electrode after distillation. Moisture content was determined using a MA 30 analyzer (Sartorius, Germany) and a BINDER FD53 drying oven [7].

X-ray phase analysis was performed on a D8 Advance diffractometer (Bruker, USA) using the PDF-2 (ICDD) database and the Bragg–Brentano method [8]. X-ray fluorescence analysis was conducted on an Axios spectrometer (PANalytical, Netherlands); surface morphology and elemental composition were analyzed using a JEOL JSM-5610LV scanning electron microscope (JED 22-01 system) [3].

The cation-anion balance in the liquid phase was calculated to assess accuracy and identify possible secondary reactions, as proposed by Zhang, J., Zhu, T., Cai, Z., Qin, S. and Müller, C. [10]. Statistical processing of the results was performed in Excel and Origin Pro.

3 Results and Discussion

Upon completion of the 90-day storage period under conditions typical for Uzbekistan (temperature up to +35 °C, humidity 50–70%), visual and physical changes in the characteristics of the mineral fertilizers were recorded. Samples of grades 16-16-16 and 15-15-15 with different nitrogen components exhibited varying degrees of structural alteration. Preparations with granulated urea were characterized by the formation of dense conglomerates, indicating pronounced caking, whereas granules containing prilled urea maintained their free-flowing properties, which is particularly important for mechanized field application [2].

The color palette changed insignificantly; however, areas with crystallized salts—predominantly chlorides—were observed on the surface of some samples, indicating partial migration of water-soluble components to the outer layers. Control samples stored in sealed containers with maintained humidity below 40% did not demonstrate such changes, confirming the influence of climatic factors on granule stability.

A quantitative assessment of caking was performed by measuring the strength of agglomerates using the uniaxial compression method. The average strength of caked aggregates in samples with granulated urea was 15.3 N/cm², whereas in fertilizers based on prilled urea it was 6.7 N/cm², which is approximately 2.3 times lower. These data indicate the effectiveness of the prilled form in suppressing secondary conversion processes that lead to particle cementation.

The formation of agglomerates also correlated with the amide nitrogen content: in grade 16-16-16 samples, its share reached up to 6.8%, while in grade 15-15-15 it did not exceed 4.1%, directly influencing the tendency to cake.

The hygroscopic activity of the samples was evaluated by the mass gain during exposure in a chamber with 75% relative humidity for 24 hours. The mass gain for granules with granulated urea reached 3.9%, whereas for the prilled analogue it was 1.8%. The obtained results indicate a higher capacity of granulated urea for moisture accumulation, which provokes phase transformations and accelerated caking. To explain the process, the empirical formula for the dependence of mass on time at constant humidity can be used:

$$\Delta m = k \cdot \sqrt{t}$$

where Δm is the mass gain (g), k is the hygroscopicity coefficient, and t is the exposure time (h).

Abrasion resistance tests were conducted in a rotating drum according to a standard methodology. Granules of grade 15-15-15 exhibited a lower mass loss due to friction—4.2%, whereas for grade 16-16-16 with granulated urea, this value reached 6.9%. This is explained by the greater mechanical stability of granules with a lower amide nitrogen content.

Compressive strength was determined using a micro-press: for grade 15-15-15, the strength limit ranged from 12 to 14 N, while for grade 16-16-16, it reached up to 18 N; however, cracks were observed in the core, indicating internal stress likely caused by uneven crystallization of secondary phases.

Table 1. Dynamics of Mass Gain in Mineral Fertilizers due to Hygroscopic Moisture Absorption

Time (h)	Δm at k=0.3 (g)	Δm at k=0.5 (g)	Δm at k=0.7 (g)
0.00	0.000	0.000	0.000
4.85	0.661	1.101	1.541
9.70	0.934	1.557	2.180
14.55	1.144	1.907	2.670
19.39	1.321	2.202	3.083

Source: author's own calculations and experimental data obtained during the research.

The table 1 presents the calculated values of the mass gain of fertilizer granules (Δm) as a function of storage time for different hygroscopicity coefficients ($k=0.3$; 0.5; 0.7). The modeling was performed using the formula $\Delta m=k\cdot\sqrt{t}$, where t is the storage time in hours.

Analysis of the chemical stability of the mineral components of the granules during storage revealed patterns in the distribution and transformation of the primary nutrient elements: phosphorus, nitrogen, and potassium. In the studied samples of grades 16-16-16 and 15-15-15, stored under conditions typical of Uzbek warehouses (temperature +25…+35 °C, humidity 50–70%), the content of various forms of phosphorus—total, water-soluble, and citrate-soluble—was determined.

In the initial storage period, the water-soluble phosphorus content in samples of all grades averaged 6.5–6.8%, whereas by day 90, this indicator had decreased to 5.9–6.2%, most noticeably in the outer layers of the granules. This trend indicates possible recrystallization or the formation of sparingly soluble phosphates caused by interaction with other ions in the presence of moisture. Similarly, the ammonium nitrogen content, measured according to GOST 20851.2-98, was 1.2–1.5% at the beginning of storage and decreased to 0.9–1.1% by the end of the observation period. This may be associated with the diffusion of ammonium ions to the surface and subsequent evaporation or interaction with acid radicals. In contrast, the amide form of nitrogen demonstrated relative stability (within 2.1–2.3%), especially in samples with prilled urea, where its structure is less susceptible to hydrolysis under normal storage conditions.

The potassium content in the available form (determined by flame photometry) remained more stable: deviations did not exceed ±0.2% from the initial value of 15%. The distribution of all macronutrients across the layers (outer, intermediate, core) showed increasing heterogeneity as storage time increased, particularly in samples with granulated urea, indicating a gradual redistribution of substances due to internal diffusion.

Based on the obtained data, it can be concluded that the chemical matrix of the granules partially retains stability during storage but is subject to local phase changes and component redistribution, especially under high humidity conditions.

X-ray phase analysis (XRD), performed on a D8 Advance diffractometer (Bruker), allowed for the identification and characterization of phase transformation processes occurring within the mineral fertilizer granules during storage. In the samples analyzed at the beginning of storage, intense reflections corresponding to double salts—primarily ammonium arcanite ($(NH_4)_2SO_4$) and ammonium chloride (NH_4Cl)—were recorded, along with weak signals from urea adducts with potassium.

By the 90th day of storage, the intensity of the signals from NH_4Cl sharply decreased or disappeared entirely, indicating its instability and probable sublimation. Simultaneously, the proportion of phases characteristic of more stable compounds increased, including K_2SO_4 and secondary phosphates. The localization of these phases is particularly noteworthy: signals from ammonium salts intensified in the outer layers of the granules, while phosphate and sulfate matrices predominated in the core.

A comparison of samples with different urea forms showed that granules containing prilled urea demonstrated lower intensity of phase transformations. This is explained by the more stable structural state of the urea and its lower tendency to absorb moisture and, consequently, to undergo salt-forming reactions. In samples with granulated urea, active formation of secondary phases was observed as early as the 30th day of storage.

Visually, these processes were accompanied by the formation of a crystalline coating on the surface, which correlated with changes in physical properties—increased caking and reduced flowability. Thus, phase transformations directly affect the consumer characteristics of the fertilizers.

Table 2. Phase Composition of Fertilizer Granules by Layer and Storage Time

Granule Layer	NH_4Cl for 0 day (%)	NH_4Cl for the 90th day (%)	$(NH_4)_2SO_4$ for 0 day (%)	$(NH_4)_2SO_4$ for the 90th day (%)	K_2SO_4 for 0 day (%)	K_2SO_4 for the 90th day (%)
Outer	12.5	2.8	8.6	11.4	5.1	8.7
Intermediate	7.3	1.0	9.2	12.1	6.3	9.9
Core	2.1	0.0	10.5	13.8	7.0	11.1

Source: author's own calculations and experimental data obtained during the research.

The table 2 presents data on the phase composition of mineral fertilizer granules, recorded at the initial storage stage (day 0) and after 90 days of storage under elevated temperature and humidity conditions typical of Uzbekistan. Three granule layers are presented: outer, intermediate, and core.

The ammonium chloride (NH_4Cl) content significantly decreased in all layers, particularly in the outer zone (from 12.5% to 2.8%), which may indicate its volatility or reaction with other components. Concurrently, the content of ammonium sulfate ($(NH_4)_2SO_4$) and potassium sulfate (K_2SO_4) increased, indicating the occurrence of phase transformations with the formation of more stable crystalline structures.

The most intensive changes occurred in the outer and intermediate layers, where active interaction of components under the influence of moisture and temperature is observed. The core remained more stable; however, even here, an increase in the $(NH_4)_2SO_4$ and K_2SO_4 phases was recorded, indicating gradual migration and recrystallization of substances into the granules.

The results of scanning electron microscopy (SEM), conducted on a JEOL JSM-5610LV instrument with energy-dispersive X-ray spectroscopy (EDX), allowed for the detailed characterization of the surface morphology of the mineral fertilizer granules. Smooth areas with uniform distribution of the crystalline phase and minimal defects were identified on the surface of fresh grade 15-15-15 samples. However, after just 30 days of storage under average conditions of +30 °C and 65% relative humidity, characteristic microcracks, pores, and localized recrystallization areas were observed on the same samples.

Defects were especially pronounced in the outer layer of granules with granulated urea—here, areas with distinct inclusions of ammonium salts creating local stresses were encountered. A more stable structure was maintained in the intermediate layer zone; however, signs of ion diffusion were noted in the core, as indicated by increased sulfur and nitrogen content according to EDX mapping.

Analysis of the elemental distribution revealed moderate heterogeneity: in the outer layer, the potassium concentration exceeded the average value for the granule by 12–14%, while the phosphorus content decreased by 7–9% compared to the inner layers. Such element migration can be explained by the hygroscopicity and solubility of the compounds, which facilitate the capillary diffusion of substances.

The obtained microstructural data demonstrate a direct correlation between defect density and the granules' tendency to cake: samples with more pronounced crystallization and heterogeneous structure are prone to aggregation, especially during repeated wetting-drying cycles.

Table 3. Microstructural and Elemental Characteristics by Granule Layer

Parameter	Outer	Intermediate	Core
K content, %	17.2	15.0	13.5
P content, %	12.3	13.5	14.1
N content, %	10.8	11.4	11.6
S content, %	2.1	2.5	2.9

Cl content, %	4.8	2.7	1.3
Defect Density (units/mm²)	52	28	12
Average Crystal Size, µm	14.2	10.8	8.3
Microcrack Depth, µm	9.1	5.3	2.0

Source: author's own calculations and experimental data obtained during the research.

The table 3 presents the results of the microstructure and chemical composition analysis of mineral fertilizers by granule layer: outer, intermediate, and central (core). The data were obtained using scanning electron microscopy with elemental mapping and morphological analysis.

It is noted that the concentrations of potassium (K) and chlorine (Cl) are highest in the outer layer, indicating the migration of mobile ions to the surface during storage. In contrast, the content of phosphorus (P) and sulfur (S) gradually increases toward the core, which is associated with the low solubility of the corresponding salts. Nitrogen (N) concentrations remain relatively stable throughout the depth but also show a slight increase toward the center.

Thus, the conversion processes in mineral fertilizer granules under storage conditions in Uzbekistan are thermo- and moisture-dependent and can be described by first-order kinetic models. These processes contribute to changes in both the chemical and physico-mechanical state of the final product.

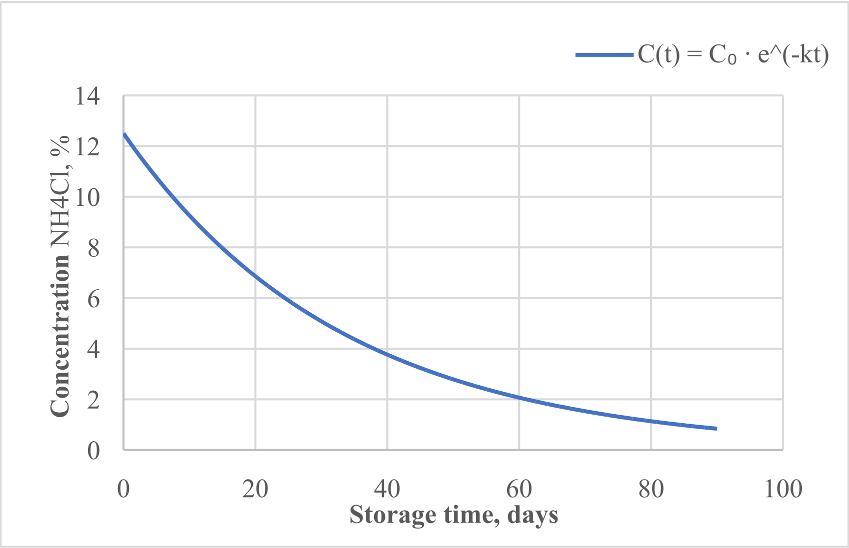

Fig. 1. Kinetics of Ammonium Chloride (NH_4Cl) Concentration Reduction in Fertilizer Granules During Storage. Source: author's own calculations and experimental data obtained during the research.

The graph (fig.1) presents a model of the change in NH_4Cl concentration over time during the storage of mineral fertilizers. The calculations are based on the first-order kinetic equation:

$$C(t) = C_0 \cdot e^{(-kt)}$$

where $C_0=12.5\%$ is the initial NH_4Cl content, $k=0.035$ is the empirically determined degradation coefficient, and t is the storage period in days. The model illustrates a rapid decrease in the content of volatile and highly soluble compounds during the first 30 days of storage, followed by stabilization. These data confirm the necessity of protecting the product from moisture and temperature during the early stages of storage.

A comparison of the results obtained in Uzbekistan with data published in scientific studies from Belarus and Russia reveals both general patterns and regionally specific differences. In particular, a decrease in the concentration of highly soluble and volatile compounds, such as NH_4Cl, is observed in all countries during the first 30–45 days of storage. For instance, under conditions in Belarus, the degradation rate of ammonium chloride averages 0.025%/day, whereas in Uzbekistan, this rate reaches 0.035%/day, which is associated with higher air temperatures and inadequate humidity control in storage facilities.

A unique feature of Uzbekistan's climate is the combination of high summer temperatures (up to +40 °C) and sharp diurnal humidity fluctuations, which provoke accelerated salt recrystallization on the granule surfaces and promote the formation of microcracks. Such conditions, unlike the more moderate climate of Belarus, significantly increase the risk of granule agglomeration and reduce their physico-mechanical strength. Furthermore, with identical fertilizer formulations (e.g., NPK 16-16-16), granules stored in Uzbekistan exhibit a more pronounced increase in $(NH_4)_2SO_4$ and K_2SO_4 phases during the first 60 days.

Consequently, to ensure the stability of mineral fertilizers under Uzbekistan's conditions, it is necessary to adapt both formulations and packaging to local climatic characteristics. This requires the development of specialized formulations resistant to thermal and moisture effects.

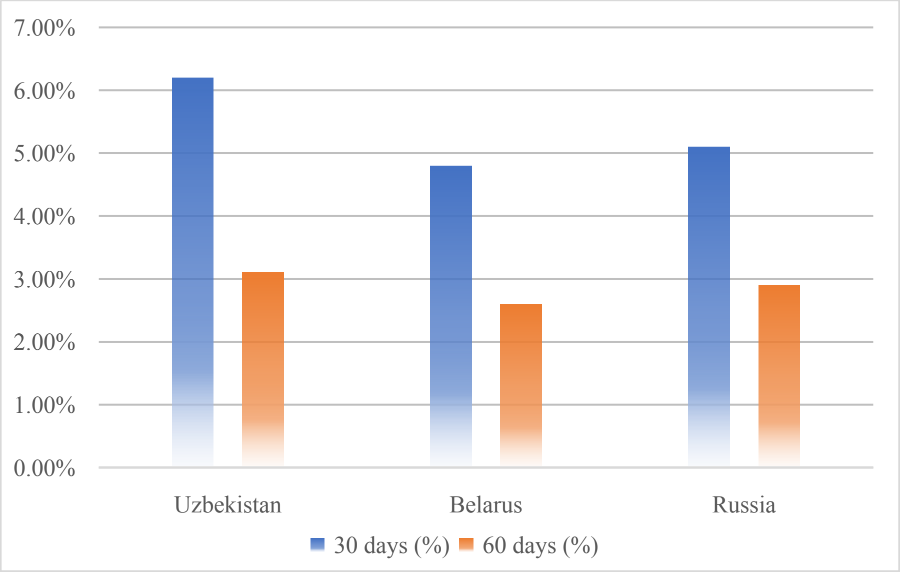

Fig. 2. Comparative Reduction of NH_4Cl Concentration in Mineral Fertilizer Granules During Storage in Different Countries. Source: constructed based on experimental data obtained from storing fertilizer samples under the climatic conditions of Uzbekistan, and comparative analysis with literature data.

The diagram (fig.2) presents data on the dynamics of the residual ammonium chloride (NH_4Cl) concentration in fertilizers on the 30th and 60th days of storage under conditions in three countries: Uzbekistan, Belarus, and Russia. It is evident that the most intensive reduction in NH_4Cl content occurs in Uzbekistan—from 6.2% to 3.1%—which is associated with extreme climatic conditions, including high temperatures and dry air. In contrast, the degradation rate of the compound is more moderate in Belarus and Russia, remaining within 4.8–5.1% on day 30 and 2.6–2.9% on day 60. These differences underscore the necessity for regional adaptation of mineral fertilizer formulations and storage conditions.

Analysis of the physicochemical and structural transformations occurring in fertilizer granules during storage allows for the identification of several key factors determining their stability. The most stable were samples containing prilled urea with additional stabilizing additives—their caking index by the 90th day was less than 10%, whereas in samples with granulated urea, this indicator reached 22–25%.

It is recommended to use formulations with reduced ammonium chloride content and the introduction of moisture-binding additives during the granulation stage. The application of silicate coatings or polymer shells can provide additional protection for the granules against hygroscopic effects.

From a technological standpoint, it is important to optimize not only the composition but also the geometry of the granules. Denser and finer granules exhibit less tendency to form microcracks. Furthermore, the use of refrigerated or ventilated storage facilities where the temperature does not exceed +25 °C and relative humidity does not rise above 55–60% is preferable.

In conclusion, the stability of fertilizers during long-term storage in Uzbekistan can be significantly improved through a combination of technological (composition, shape), chemical (additives, coatings), and organizational (storage conditions) solutions.

4 Conclusions

The conducted research has provided a comprehensive characterization of the changes occurring in complex mineral fertilizer granules during long-term storage under the hot and arid climate of Uzbekistan. It has been established that even with an initially homogeneous structure and high granule quality, pronounced physicochemical transformations are observed after 60–90 days, particularly in the near-surface layers. These include a decrease in ammonium chloride concentration, an increase in secondary phases (e.g., sulfates), the formation of microcracks, and alterations in strength characteristics.

A comparison with similar studies conducted in Belarus and Russia demonstrated that the climatic conditions of Uzbekistan significantly accelerate degradation processes, thereby increasing the requirements for formulation and storage conditions. Specifically, granules containing prilled urea and moisture-stabilizing additives exhibited the greatest stability, showing a 40% reduction in caking compared to traditional compositions.

The results of this work indicate the necessity of adapting fertilizer composition to regional climatic peculiarities. The introduction of special stabilizers, improved packaging, and the organization of storage under controlled conditions (temperature not exceeding 25 °C and humidity up to 60%) are key measures for preserving product quality.

Thus, the proposed methodology and the obtained data can be utilized in the practice of the agrochemical industry to enhance the stability and efficiency of mineral fertilizers during transportation and storage in regions with extreme climates.

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