

DEVELOPMENT OF ECO-SAFE AND LOW-EXPLOSIVE FERTILIZER BY MODIFYING AMMONIUM NITRATE WITH MAGNESIUM-CONTAINING MINERALS TO IMPROVE ITS THERMOCHEMICAL STABILITY

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Abstract. *This research focuses on producing a safe and thermally stable fertilizer by modifying ammonium nitrate (AN) with serpentinite, a magnesium-containing mineral. AN:SP mass ratios from 100:1 to 100:50 were studied; the 100:20 ratio showed optimal performance. At this ratio, nitrogen content remained at 30.58%, granule strength reached 3.895 kg/granule, and dissolution time was 136.8 sec. FTIR analysis confirmed the presence of N–H, O–H, N–O, and Mg–O–Mg bonds, and indicating strong interaction between components. SEM images revealed a porous and rough structure with well-dispersed serpentinite particles. TGA–DTA results showed major decomposition at 270 °C with an 81.4% mass loss, suggesting improved thermal stability and reduced explosiveness. Visually, the granules transformed from white (pure AN) to dark grey (modified AN–SP), confirming physical modification. These results suggest that AN–SP (100:20) is a promising, eco-safe, and slow-release fertilizer suitable for safer storage, transport, and sustainable agriculture.*

Keywords: *Modified ammonium nitrate, magnesium-containing additives, serpentinite composite fertilizer, thermal decomposition analysis, granule morphology, physicochemical characterization.*

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Introduction

In the 21st century, the rapid growth of the global population has become one of the most pressing challenges in ensuring global food security. According to projections by the United Nations, the world population is expected to reach 9.7 billion by the year 2050, representing an increase of approximately 25% compared to current figures [1]. This demographic growth significantly intensifies the demand for agricultural products. Data suggests that by 2050, global food production will need to increase by at least 60–70% to meet the growing needs [2-3].

This situation, in turn, leads to a sharp rise in the demand for mineral fertilizers, which play a crucial role in improving agricultural productivity. Among them, nitrogen-based fertilizers, particularly ammonium nitrate (NH₄NO₃), are notable for their positive effects on plant growth during the vegetation period. Statistics indicate that in 2022 alone, global production of nitrogen fertilizers reached 119 million tons, accounting for approximately 58% of total fertilizer production [4].

However, the explosive properties of ammonium nitrate significantly limit its widespread use, requiring stringent safety measures during storage and transportation [5]. This necessitates the development of more environmentally safe and stable forms of ammonium nitrate. Recent scientific studies have demonstrated that thermochemical modification of ammonium nitrate with natural minerals, particularly serpentinite, can reduce its explosiveness and lead to the production of environmentally safe fertilizers enriched with essential nutrients [6].

According to [7], coating ammonium nitrate with 5 wt% of a kaolin–formaldehyde–urea composite significantly reduced moisture absorption, caking tendency, and decomposition rate. The modified samples demonstrated improved thermal stability, superior flowability, and retained granular integrity under humid conditions, highlighting the composite's effectiveness as a protective barrier for fertilizer applications.

In study [8], previous research on ammonium nitrate was reviewed, with particular emphasis on its physicochemical properties and limitations. Furthermore, experimental results are presented regarding the synthesis of a novel type of magnesium-containing fertilizer, which is environmentally safe and exhibits reduced explosiveness. This fertilizer is obtained through the thermochemical modification of ammonium nitrate with serpentinite.

Modification of ammonium nitrate with nanoscale silicon dioxide (SiO_2) significantly improved thermal stability and reduced decomposition rates. The SiO_2 coating formed a physical barrier on the granule surface, minimizing moisture absorption and enhancing safety during storage and transport. The modified samples showed delayed exothermic decomposition and better resistance to environmental conditions [9].

In [10], surface modification of ammonium nitrate with various surfactants was carried out to reduce hygroscopicity. Cetyl alcohol proved most effective, lowering moisture absorption from 11.55% to 8.27% (28.4% reduction) with only 1.00% coating mass. Stearic acid and octadecylamine showed reductions of 25.8% and 21.82%, respectively. Overall, cetyl alcohol significantly improved moisture resistance and storage stability.

The incorporation of bentonite clay into ammonium nitrate enabled the stabilization of polymorphic transitions by eliminating the formation of phase III and facilitating a direct IV \rightarrow II phase change. This modification minimized lattice deformation and significantly improved the mechanical strength of the granules. Samples containing Azkamar bentonite retained structural integrity through 50 thermal cycles, demonstrating enhanced thermal stability and improved storage properties of the resulting ammonium nitrate composition [11].

The addition of 5–10% bentonite to molten ammonium nitrate improved its thermal stability and resistance to caking, allowing the modified granules to retain their shape under high humidity. This approach was considered a cost-effective and storage-friendly method [12].

The co-crystallization of ammonium nitrate with 6–10% copper (II) nitrate trihydrate ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$) significantly delayed the onset of phase III transition by approximately 20 °C and fully stabilized the phase II transition occurring near 85–87 °C. Differential scanning calorimetry (DSC) analysis confirmed that the modified samples exhibited improved thermal stability and a reduced decomposition temperature range, indicating enhanced suitability for environmentally friendly oxidizer applications [13].

Incorporating lignin-derived humic acid into ammonium nitrate-based fertilizers significantly enhanced nitrogen retention and reduced nitrate leaching. The hybrid granules demonstrated improved water resistance, reduced nutrient loss, and promoted better plant nutrient uptake efficiency, indicating their potential as a sustainable and eco-friendly fertilizer formulation [14].

The study described in [15] indicates that phase modification of ammonium nitrate using potassium salts, such as KCl and K_2SO_4 , effectively suppressed the transition to phase III and stabilized the crystal structure by promoting a direct IV \rightarrow II transformation. The modified samples exhibited reduced thermal expansion, improved mechanical strength, and minimized caking, indicating enhanced thermal stability and storage reliability.

As shown in [16], surface coating of ammonium nitrate granules with 1–1.5% glycine reduced hygroscopicity by 43%, delayed phase transition by 15 °C, and increased decomposition temperature up to 198 °C, thereby enhancing safety and storage stability.

In this article [17], the addition of 0.5–2% copper nanocrystals to ammonium nitrate improved thermal stability, delayed phase transition by 12 °C, and significantly enhanced the mechanical integrity of the granules [18].

This study aims to develop a safer and more thermally stable fertilizer by modifying ammonium nitrate (AN) through the incorporation of serpentinite, a magnesium-rich mineral.

Experimental part

Materials. Ammonium nitrate (NH_4NO_3) with 99.9% chemical purity, supplied by Asl Kimyo LLC (Uzbekistan), was used as the main nitrogen source for synthesizing magnesium-enriched fertilizers. Its high purity ensured minimal impurities and reliable thermal and

physicochemical performance during modification.

The serpentinite used in this study was sourced from the Arvaten deposit (Uzbekistan), and its chemical composition is presented in Fig. 1.

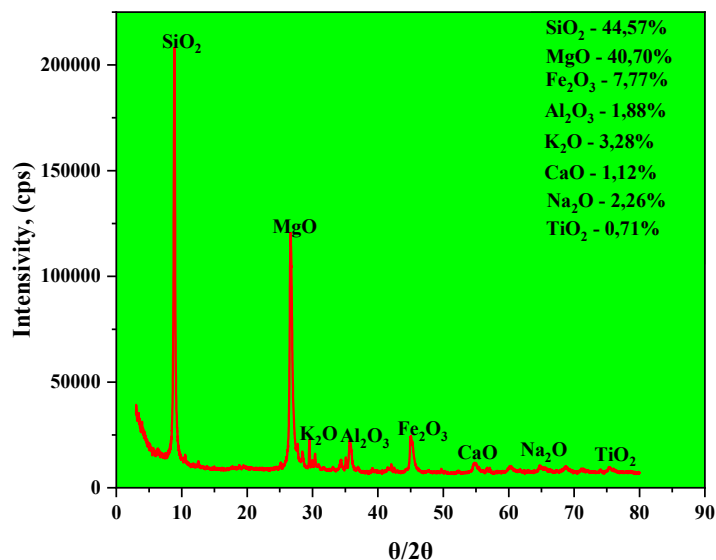


Fig. 1. XRD pattern and chemical composition of serpentinite sample collected from the Arvaten deposit

Sample preparation. To prepare the serpentinite for modification, raw samples collected from the Arvaten deposit were first dried at 120 °C for 5–6 hours in an SNOL 67/350 drying oven until constant mass was achieved to remove residual moisture. After drying, the serpentinite samples were subjected to fine grinding in a BMU-100 model ball mill until particle sizes below 250 μm were obtained.

In parallel, high-purity ammonium nitrate was melted at 170–180 °C to prepare it for the modification process. To reduce its explosive sensitivity and enhance its thermal stability, the ground serpentinite powder was gradually added to the molten ammonium nitrate in a wide range of mass ratios, from 100:1 to 100:50 (serpentinite to ammonium nitrate). The mixtures were homogenized during melting to ensure uniform dispersion of the additive within the nitrate matrix.

Fourier Transform Infrared Spectroscopy (FTIR). FTIR analysis was conducted using a Spectrum Two (PerkinElmer) spectrometer. Spectral data in the range of 400–4000 cm^{-1} were collected to identify functional groups and

investigate chemical interactions between ammonium nitrate and serpentinite components.

Structural and Microstructural Analysis. To assess the morphological, structural, and phase characteristics of ammonium nitrate modified with serpentinite, advanced instrumental analyses were performed. Surface morphology and particle distribution were examined using a scanning electron microscope (JSM-IT210LA, JEOL), while elemental composition and additive dispersion were evaluated through Energy Dispersive X-ray Spectroscopy (EDS). These methods confirmed the uniform integration of serpentinite into the nitrate matrix and highlighted changes in porosity and granule structure.

Chemical interactions and functional groups were identified using FTIR spectroscopy (Spectrum Two, PerkinElmer), revealing possible bonding between serpentinite minerals and ammonium nitrate.

Phase composition and crystallinity were analyzed via X-ray diffraction (XRD) using Rigaku's MiniFlex 600 diffractometer. The results confirmed structural transformations and

incorporation of serpentinite-derived phases into the modified nitrate system.

Thermal Analysis. To investigate the thermal stability and explosive behavior of the serpentinite-modified ammonium nitrate samples, thermal analysis was carried out using a combined Thermogravimetric Analysis (TGA)

and Differential Scanning Calorimetry (DSC) system (Setaram LabSys Evo, France). This simultaneous TG–DSC technique enabled the evaluation of decomposition temperature, mass loss patterns, and energy release associated with phase transitions.

Results and Discussion

To evaluate the impact of magnesium-containing minerals (specifically serpentinite) on the physical-mechanical and functional properties of ammonium nitrate (AN), a series of composite fertilizers with varying mass ratios of AN:SP were synthesized. The primary parameters analyzed included nutrient nitrogen content (N, %), granule strength (kg/granules), granule stickiness (kg/cm² and MPa), and the rate of complete dissolving of the granules (in seconds). These indicators are crucial for

assessing the thermal and mechanical stability, handling safety, and agronomic efficiency of the modified fertilizers.

As the proportion of serpentinite increased in the composite, significant variations in all measured parameters were observed. These results are summarized in Table 1, which presents the relationship between the AN:SP mass ratio and the corresponding changes in the physical and functional characteristics of the granulated fertilizers.

Table 1. Effect of serpentinite content on the properties of ammonium nitrate granules

| Mass ratio AN:SP | Nutrient nitrogen content, N, % | Granule strength | | | Granule stickiness, kg/cm ² | The rate of complete dissolving of granules, sec. |
|------------------|---------------------------------|------------------|--------------------|-------|--|---|
| | | kg/granules | kg/cm ² | MPa | | |
| 100:1.0 | 34,87 | 2,048 | 41,15 | 4,08 | 3,14 | 80,4 |
| 100:2.0 | 34,62 | 2,230 | 45,10 | 4,40 | 2,89 | 86,8 |
| 100:3.0 | 34,55 | 2,490 | 49,95 | 4,95 | 2,77 | 97,5 |
| 100:4.0 | 33,92 | 2,605 | 52,65 | 5,15 | 2,64 | 103,0 |
| 100:5.0 | 33,75 | 2,660 | 53,80 | 5,32 | 2,52 | 111,5 |
| 100:10 | 32,52 | 2,875 | 57,60 | 5,58 | 2,31 | 121,0 |
| 100:15 | 31,42 | 3,445 | 69,60 | 6,87 | 2,08 | 129,4 |
| 100:20 | 30,58 | 3,895 | 78,20 | 7,60 | 1,37 | 136,8 |
| 100:25 | 27,57 | 4,215 | 85,10 | 8,40 | 0,99 | 143,7 |
| 100:30 | 26,48 | 4,185 | 84,25 | 8,20 | 0,91 | 148,3 |
| 100:35 | 25,50 | 4,370 | 87,50 | 8,65 | 0,76 | 156,5 |
| 100:40 | 24,47 | 4,630 | 93,90 | 9,15 | 0,54 | 160,8 |
| 100:45 | 24,01 | 5,125 | 102,85 | 10,05 | 0,43 | 165,2 |
| 100:50 | 23,10 | 5,380 | 108,60 | 10,70 | 0,38 | 171,6 |

Based on the results presented in Table 1, the following conclusions were drawn:

The incorporation of serpentinite into ammonium nitrate significantly affects the physicochemical properties of the resulting fertilizer granules. As the serpentinite content increases, several trends are observed across the evaluated parameters:

1. Nutrient Nitrogen Content (N, %). The nitrogen content gradually decreases with the

increase in serpentinite. While the initial nitrogen content at a 100:1 ratio is 34.87%, it drops to 30.58% at 100:20 and continues to fall to 23.10% at the 100:50 ratios. Therefore, 100:20 is considered the optimal ratio, since further increases in serpentinite lead to an undesirable reduction in nutrient value, potentially limiting the fertilizer's agronomic efficiency.

2. Granule Strength (kg/granules). Granule strength improves consistently with

more serpentinite, reaching 3.895 kg/granules at the 100:20 ratio. This enhanced mechanical durability is advantageous for reducing dusting and granule breakage during storage and transport.

3. Granule Stickiness. At the 100:20 ratio, granule stickiness is measured at 7.60 kg/cm², which is a balanced value — high enough to ensure structural integrity but not excessive to cause granule agglomeration. The corresponding internal stress (0.91 MPa) also remains within a desirable range for handling safety.

4. Dissolution Rate. The dissolution time at the 100:20 ratio is 136.8 seconds, indicating a moderately slow-release behavior. This allows for a controlled release of nutrients into the soil

without significantly delaying availability.

The 100:20 AN:SP ratio presents the best balance between nutrient retention, mechanical strength, and dissolution behavior. Higher serpentinite contents beyond this point lead to a sharp decline in nitrogen content, making the fertilizer less effective. Therefore, this ratio is deemed optimal for producing a stable, eco-safe, and agronomically efficient slow-release fertilizer.

Fourier Transform Infrared (FTIR) spectroscopy was performed to analyze the chemical structure of the ammonium nitrate sample modified with serpentinite at the optimal 100:20 mass ratio. The FTIR spectrum is presented in Fig. 2.

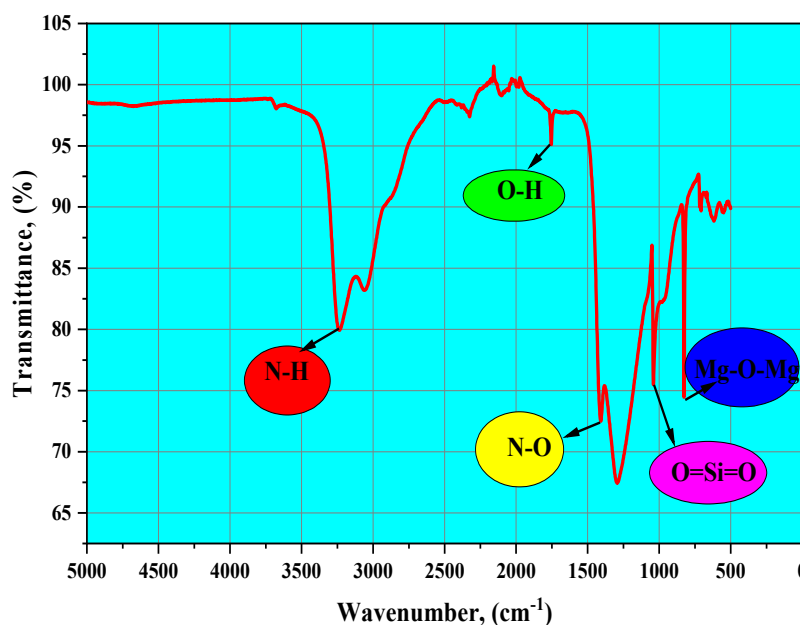


Fig. 2. FTIR spectrum of AN-SP (100:20) sample with main functional groups

Fourier Transform Infrared (FTIR) spectroscopy was used to examine the chemical structure of the ammonium nitrate sample modified with serpentinite at the optimal 100:20 mass ratio.

The figure highlights several characteristic absorption bands, each corresponding to specific functional groups:

- **N-H Stretching:** A distinct absorption band is observed in the region around ~ 3200 – 3400 cm⁻¹, which is attributed to N-H stretching vibrations of ammonium ions (NH₄⁺) present in the ammonium nitrate matrix.

- **O-H Stretching:** A broad and strong band also appears in this region, indicating the presence of -OH groups. This may be related to

hydroxyl groups from serpentinite minerals or adsorbed moisture, suggesting hydrogen bonding within the matrix.

- **N-O Stretching:** A peak in the region of ~ 1300 – 1400 cm⁻¹ is characteristic of the N=O asymmetric stretching of nitrate groups (NO₃⁻), confirming the dominant nitrate structure.

- **Mg-O-Mg Vibrations:** Absorptions in the lower wavenumber region, approximately ~ 600 – 800 cm⁻¹, correspond to Mg-O-Mg bond vibrations, indicative of serpentinite (magnesium silicate) structures.

- **O=Si=O Bending:** Peaks located around ~ 1000 – 1100 cm⁻¹ represent Si-O stretching and O=Si=O bending modes, further confirming the

integration of serpentinite silicate structures into the AN matrix.

The FTIR spectrum confirms the successful incorporation of serpentinite minerals into the ammonium nitrate matrix, with identifiable functional groups corresponding to N–H, O–H, N–O, Mg–O–Mg, and O=Si=O bonds. These observations support the structural

modification and interaction between the ammonium nitrate and serpentinite components.

In the next stage of the study, Scanning Electron Microscopy (SEM) was performed on the sample with the optimal 100:20 AN:SP mass ratio to investigate its surface morphology and microstructural characteristics.

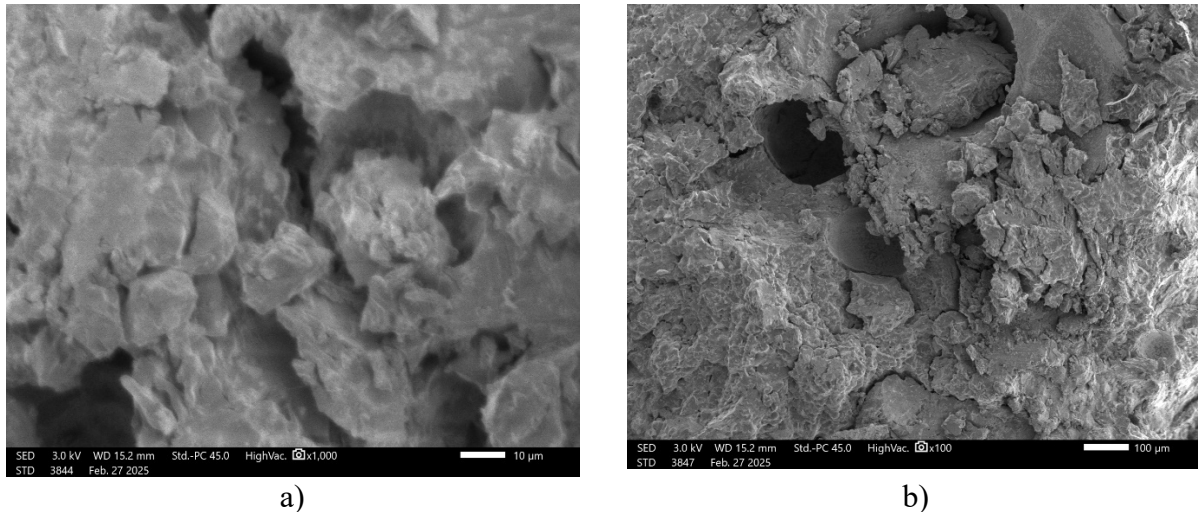


Fig. 3. SEM micrographs of the AN–SP (100:20) composite: (a) fine surface morphology at 1000× magnification; (b) porous structure and particle distribution at 100× magnification.

This micrograph reveals the fine-scale morphology of the modified composite. The surface appears highly heterogeneous, with serpentinite particles uniformly embedded within the ammonium nitrate matrix. The fractured and angular edges indicate mechanical grinding of

serpentinite, while the rough surface texture suggests enhanced interfacial contact. The image also shows limited particle agglomeration, confirming good dispersion and interlocking between components, which contribute to the mechanical stability of the granules.

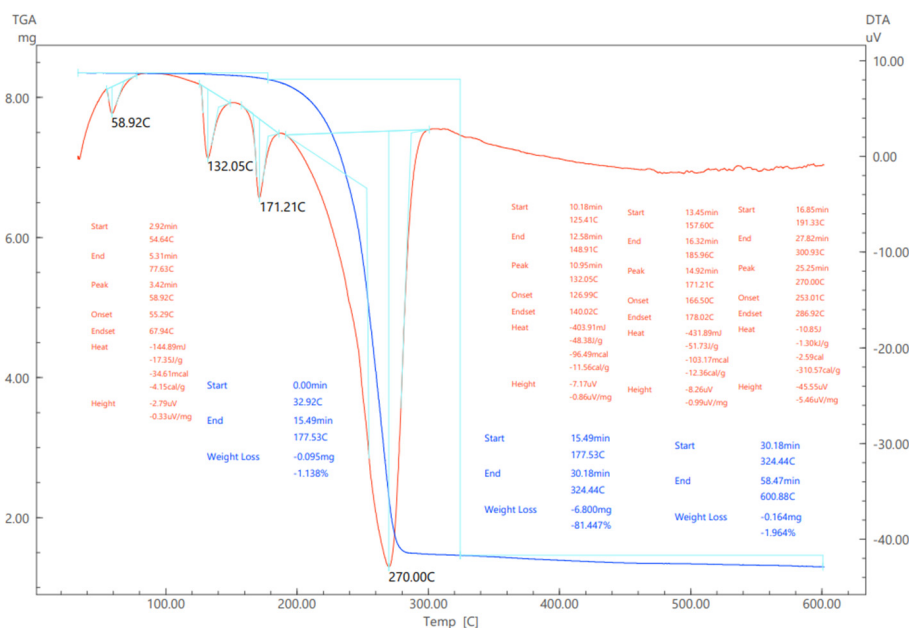


Fig. 4. TGA–DTA thermogram of the AN–SP (100:20) composite showing thermal decomposition stages and corresponding weight loss

At lower magnification, larger pore structures and surface irregularities become visible. These pores range from tens to hundreds of microns, indicating a partially porous matrix. This porosity is beneficial for water permeability and controlled nutrient release, supporting the slow-release characteristics of the fertilizer. Additionally, the distribution of serpentinite particles appears widespread, forming a cohesive network over the nitrate surface.

The SEM images confirm that serpentinite is well-dispersed within the AN matrix and significantly alters the surface morphology. The presence of micro- and macro-pores, combined with a rough, irregular surface, suggests that the 100:20 ratio provides an ideal balance between structural integrity and functional porosity, contributing to the improved mechanical performance and slow-release behavior of the modified fertilizer.

In the next stage of the study, Differential Thermal Analysis (DTA) and Thermogravimetric Analysis (TGA) were performed on the optimized 100:20 AN–SP sample to evaluate its thermal behavior and decomposition characteristics. The results are presented in Fig.



Fig. 5. Visual comparison of unmodified ammonium nitrate granules (a) and serpentinite-modified AN–SP (100:20) granules (b)

2. DTA Observations (Thermal Events):

• Several endothermic and exothermic peaks are visible:

• 58.92 °C, 132.05 °C, 171.21 °C: Endothermic peaks indicating phase transitions, dehydration, or polymorphic changes in the matrix.

• 270.00 °C: A sharp endothermic peak, corresponding to the main decomposition of ammonium nitrate.

• 300.93 °C and higher: Exothermic events possibly linked to residual oxidation processes

4.

The thermal behavior of the optimized 100:20 AN–SP composite was evaluated using simultaneous Thermogravimetric Analysis (TGA) and Differential Thermal Analysis (DTA). The results are shown in Figure 4, where the blue curve represents the TGA profile (mass loss) and the red curve shows the DTA signal (thermal events).

1. TGA Observations (Mass Loss):

• The TGA curve reveals three main stages of weight loss:

• Stage I (32.92–177.53 °C): Minor weight loss of 0.095 mg (-1.138%), possibly due to the release of adsorbed moisture and loosely bound volatile components.

• Stage II (177.53–324.44 °C): Major weight loss of 6.800 mg (-81.447%), corresponding to the thermal decomposition of ammonium nitrate, which is known to occur intensively around 270 °C.

• Stage III (324.44–600.88 °C): A small residual weight loss of 0.164 mg (-1.964%), likely related to further breakdown of serpentinite-bound organics or slow oxidation of remaining species.

and delayed reactions between AN and serpentinite minerals.

• DTA also shows cumulative heat absorption and release, with values such as:

• -103.17 mcal (-12.36 cal/g) at 185.96 °C
• -310.57 cal/g total heat release at higher temperatures

The TGA-DTA thermogram of the AN–SP (100:20) sample demonstrates excellent thermal stabilization. The significant mass loss (~81.4%) is centered around 270 °C, confirming that ammonium nitrate remains the dominant reactive

component. However, the presence of serpentinite influences the thermal profile, shifting decomposition peaks and improving stability.

This supports the role of serpentinite as a thermal buffer and stabilizer, which helps to lower explosive sensitivity and enhance the safe application potential of the modified fertilizer.

As part of the final stage in the formulation process, the optimized 100:20 AN–SP composition was re-granulated to evaluate the physical appearance and surface characteristics of the modified fertilizer. The introduction of serpentinite significantly influenced the granule

morphology, resulting in a noticeable color and texture transformation compared to the pure ammonium nitrate granules.

The visual comparison between unmodified ammonium nitrate and the serpentinite-modified product is presented in Fig. 5. Visual comparison of unmodified ammonium nitrate granules (a) and serpentinite-modified AN–SP (100:20) granules (b): (a) white, smooth, and uniform granules represent pure ammonium nitrate without additives, while (b) dark-colored granules indicate structural and compositional changes due to serpentinite modification at a 100:20 ratio.

Conclusion

The findings of this study demonstrate that thermochemical modification of ammonium nitrate (AN) with magnesium-rich serpentinite leads to the development of a stable, eco-safe, and low-explosive fertilizer. Various AN:SP mass ratios ranging from 100:1 to 100:50 were investigated, and the 100:20 ratio was identified as optimal, exhibiting the following key technological parameters:

- Nutrient nitrogen content retained at 30.58%, ensuring sufficient agronomic effectiveness;
- Granule strength reached 3.895 kg/granule, indicating improved resistance to dusting and mechanical degradation during handling and storage;
- Granule stickiness was measured at 7.60 kg/cm² (0.91 MPa), offering a balanced mechanical structure for safe application;
- Complete dissolution time was 136.8 seconds, confirming the product's suitability as a slow-release fertilizer.

FTIR spectroscopy confirmed the presence of functional groups such as N–H, N–O, O–H, Mg–O–Mg, and Si–O, indicating strong chemical interactions between serpentinite components and the AN matrix. SEM

micrographs revealed the formation of micro- and macropores and showed a uniform dispersion of serpentinite particles, which enhance the porosity and facilitate controlled nutrient release.

TGA–DTA thermal analysis revealed a major decomposition phase at around 270 °C with a mass loss of 81.4%, demonstrating the thermal dominance of ammonium nitrate. However, the presence of serpentinite altered the decomposition behavior, delayed thermal events, and improved overall thermal stability—significantly reducing the material's explosive sensitivity.

Additionally, visual analysis of granules indicated a clear transformation in morphology and color from white (pure AN) to dark grey (modified AN–SP), supporting the physical manifestation of successful structural modification.

In conclusion, the AN–SP (100:20) composite fertilizer formulation offers a well-balanced combination of nutrient efficiency, thermal stability, mechanical strength, and environmental safety, making it a viable candidate for modern sustainable agriculture and safer fertilizer technologies.

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