EVALUATION OF CALCIUM AMMONIUM NITRATE MODIFIED WITH POTASSIUM CHLORIDE: APPLICATION AND CONSUMER PROPERTIES

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Abstract: *Potassium-calcium-ammonium nitrate samples were obtained by varying the amounts of dolomite mineral (DM) and potassium chloride (KCl) from 0.5 to 25 g per 100 g of ammonium nitrate (AN) melt. The carbonate-chloride-nitrate melt was granulated by the prilling method. At 170 °C, the nitrate melt activated the dolomite mineral, converting CaO and MgO into plant-available forms. The simultaneous addition of DM and KCl significantly improved the mechanical strength of the fertilizer granules while reducing caking, porosity, and diesel fuel absorbency by a factor of 2–3 compared with AN granules containing magnesite. The optimal composition (AN:DM:KCl=100:12:12) was characterized by EDS, SEM, and DTA analyses, which confirmed its favorable structural and physicochemical properties. These findings demonstrate the potential of NKCaMg as a mechanically stable and agronomically effective fertilizer formulation.*

Keywords: *ammonium nitrate melt, dolomite mineral, potassium chloride, fertilizer granulation, potassium-calcium-ammonium nitrate, mechanical strength, physicochemical properties*

Introduction

The global population, including that of Uzbekistan, has been increasing rapidly. In 1975 the population of Uzbekistan was 14.1 million, whereas today it has reached approximately 38 million. During the same period, irrigated land per capita decreased from 0.22 ha in 1970 to only 0.12 ha [1,2]. Together with global climate change, natural disasters, and depletion of land and water resources, these demographic pressures pose serious challenges for agricultural sustainability [3]. Ensuring adequate food and raw material supplies under such conditions requires more intensive and efficient agricultural practices, including the rational use of mineral fertilizers. It has been demonstrated that mineral fertilizers, when applied rationally, can increase crop productivity by 40–50% [4].

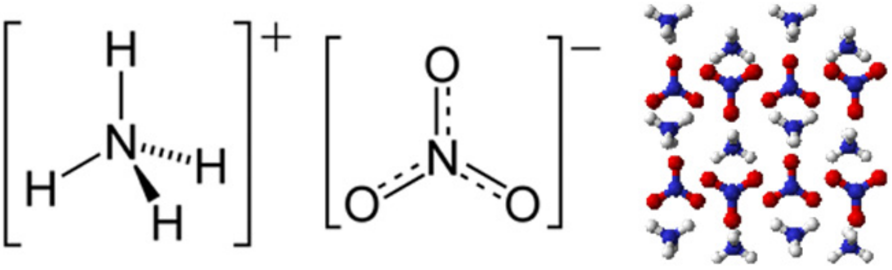

Fig. 1. Structure of ammonium nitrate

Uzbekistan has established large branches of the chemical industry to serve agriculture, producing millions of tons of grain, cotton, fruits, vegetables, and other crops annually. Future agricultural development is closely linked to modern soil cultivation technologies, high-yield crop varieties, and, importantly, the integrated use of fertilizers and plant protection products. Plants require readily water-soluble nutrients, with six macronutrients—N, P_2O_5, K_2O, S, CaO, and MgO—playing a decisive role in yield formation. Among these, nitrogen, phosphorus, and potassium are most essential, forming the basis for NPK fertilizers. In addition, micronutrients such as B, Cl, Cu, Fe, Mn, Mo, Zn, Ni, and Co are vital for plant metabolism [5-7].

Ammonium nitrate (AN) is one of the most widely produced and used granular nitrogen fertilizers due to its high nitrogen content. Pure AN (NH_4NO_3) is synthesized by neutralizing nitric acid with ammonia [8], and its structural formula is shown in Fig. 1.

Although AN is primarily used in agriculture, it is also applied as a blasting agent in mining [9-11]. In 2005, AN accounted for 20% of global nitrogen fertilizer consumption, with 13% of fixed atmospheric nitrogen used for its production [12]. However, AN has two major drawbacks: a high tendency to cake during storage and significant explosiveness [13]. Several industrial accidents, including the 2001 Toulouse explosion in France, as well as its use in terrorist attacks, have led to stricter quality and storage requirements. In response, many countries restricted or banned the use of AN in agriculture.

To mitigate these risks while maintaining its agrochemical effectiveness, manufacturers began adding calcium and magnesium carbonates, resulting in calcium ammonium nitrate (CAN). This modification eliminates most of the hazards associated with AN while improving its agronomic performance, especially on acidic soils [14-15]. Consequently, CAN currently represents around 7% of global nitrogen fertilizer production capacity.

This article analyzes methods for reducing the explosive properties of ammonium nitrate. The study found that additives such as ZnO, Na_2HPO_4, and $Mg_2(OH)_2CO_3$ effectively decrease explosiveness by stabilizing the crystal structure. Additionally, controlling granule size, maintaining optimal moisture content, and preventing contamination were shown to significantly reduce explosion risk. Overall, the article highlights effective chemical and technological approaches to improving the safety of ammonium nitrate [16].

In this article, the thermal decomposition of ammonium nitrate with additives. The study found that introducing additives such as ZnO, Al_2O_3, $CaCO_3$, and MgO increases the decomposition temperature of ammonium nitrate and reduces the exothermic intensity of the reaction. As a result, the risk of explosion decreases, and the thermal stability of the material improves. The article also notes that these additives interact with the crystal lattice, slowing down oxygen release and helping to control the decomposition process. Overall, this approach significantly enhances the safety of ammonium nitrate during storage and transportation [17].

Experimental part

Carbonate (dolomite) and chloride (KCl) compounds were selected as modifiers of ammonium nitrate (AN) in order to improve its physicochemical and handling properties. Potassium-containing calcium ammonium nitrate (CAN) samples were prepared by introducing two additives into the AN melt: dolomite mineral (DM, CaO_{total} 28.02%, MgO_{total} 26.27%) from the Ingichka deposit (Samarkand region) and potassium chloride (KCl, K_2O 60%) produced at the Dekhkanabad potash fertilizer plant.

Materials. For the experiments, analytical grade ammonium nitrate (NH_4NO_3, N 35%) was used as the base fertilizer. Dolomite mineral (DM) and potassium chloride (KCl), both abundant in Uzbekistan, were employed as additives to improve the granule stability against caking and explosiveness. Prior to use, DM and KCl crystals were dried at 100 °C for 2 h, crushed, and sieved to a particle size of approximately 250 μm.

The elemental composition of NH_4NO_3 (Fig. 2), DM (Fig. 3), and KCl (Fig. 4) particles was determined using energy-dispersive X-ray spectroscopy (EDS).

Powder X-ray diffraction (PXRD) was applied to identify the crystalline structure and phase composition of the raw materials. The analyses confirmed that the “pure” grade NH_4NO_3, Ingichka dolomite, and Dekhkanabad potassium chloride consisted of ordered crystalline phases.

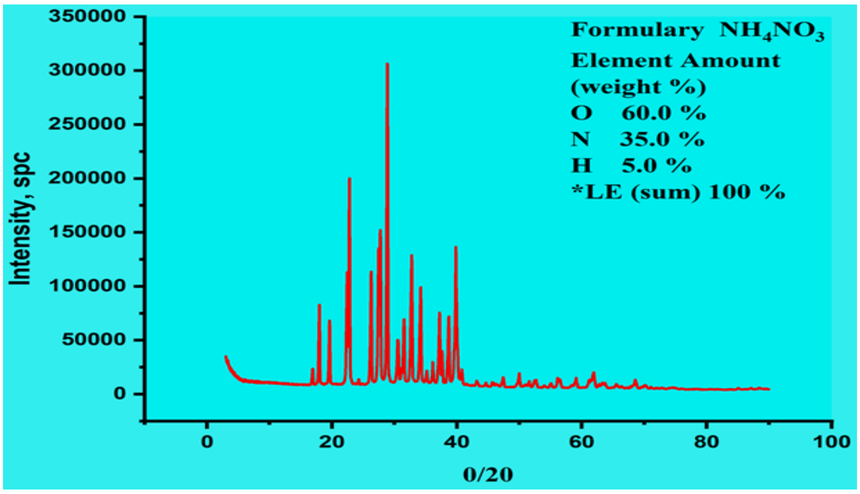

Fig. 2. EDS analysis of ammonium nitrate sample

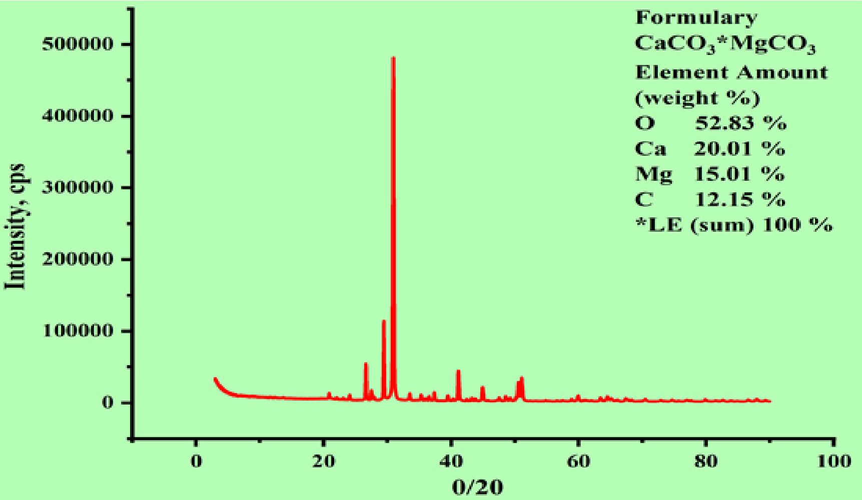

Fig. 3. EDS analysis of the DM ($CaCO_3 \cdot MgCO_3$) sample from the Ingichka deposit

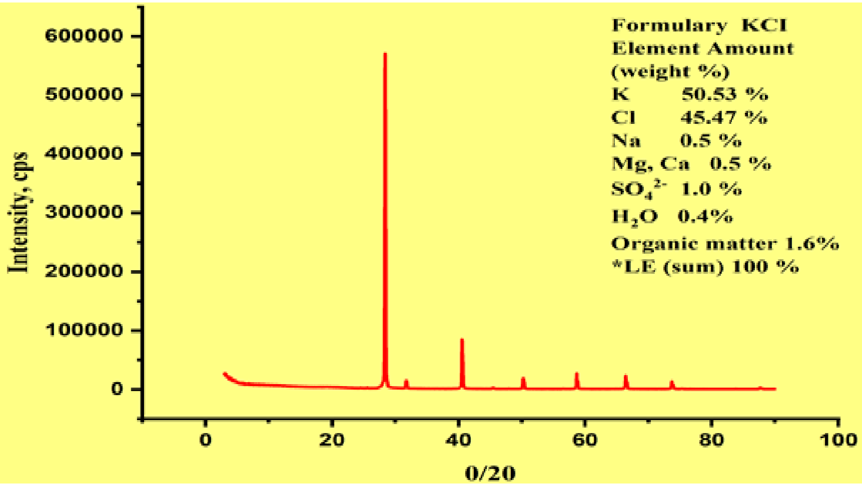

Fig. 4. EDS analysis of a sample of potassium chloride produced by the Dekhkanabad Potash Fertilizer Plant

Sample preparation. Potassium-containing CAN samples were prepared as follows. Ammonium nitrate (AN) was melted in a metal cup using electric heating. Dolomite mineral (DM) was introduced into the AN melt at mass ratios of AN:DM = 100:(0.5–25), and the carbonate–nitrate melt was maintained at 170 °C for 12 min. Subsequently, powdered KCl (particle size $\approx$0.25 mm) was added at mass ratios of AN:DM:KCl = 100:(0.5–25):(0.5–25). The carbonate–chloride–nitrate melt was stirred with a glass rod for an additional 3 min. The resulting melt was fed into a laboratory prilling unit consisting of a metal cup with a perforated bottom (hole diameter 1.2 mm).

Using compressed air, the melt was sprayed from a height of 35 m onto a polyethylene film, where solidified granules were collected. The granules were classified by particle size, and their physicochemical and commercial properties, as well as composition, were determined by standard methods [3].

Methods. **Structural and microstructural analysis.** The chemical composition of the starting materials and the optimal potassium-containing CAN sample (AN:DM:KCl = 100:12:12) was analyzed by energy-dispersive X-ray spectroscopy (EDS). Phase identification and quantitative analysis were carried out using the MATCH and ORIGIN software packages. In addition, the morphology and surface structure of the optimal granules were examined by scanning electron microscopy (SEM).

Thermal analysis. Differential thermal analysis (DTA) of the optimal composition (AN:DM:KCl = 100:12:12) was performed using a Netzsch Simultaneous Thermal Analyzer STA 409 PC/PG. The analysis was conducted to determine the temperatures of polymorphic modification transitions, the onset of decomposition, and the activation energy of the process.

Results and Discussion

The experimental results are summarized in Tables 1–2 and Fig.s 5–8.

As shown in Table 1, the incorporation of dolomite mineral (DM) and potassium chloride (KCl) into the ammonium nitrate (AN) melt at ratios of AN:DM:KCl = 100:(0.5–25):(0.5–25) resulted in the formation of multi-nutrient nitrogen–potassium–calcium–magnesium fertilizers with the following composition (wt.%): 23.21–34.62% N, 0.292–9.982% K_2O, 0.135–4.62% CaO_{total}, and 0.129–4.366% MgO_{total}.

Importantly, the obtained fertilizers exhibit a high proportion of bioavailable forms of calcium and magnesium. The ratio of water- and citric acid-soluble CaO and MgO to their total content ranges from 51.91% to 92.26% and 54.11% to 91.38%, respectively. For water-soluble forms, these values were 55.13–91.85% for CaO and 44.67–85.34% for MgO. This confirms that the modified CAN compositions provide readily accessible nutrients for plants.

It is well known that conventional CAN obtained with limestone or chalk contains only nitrogen and calcium. However, when dolomite is used as the carbonate source, magnesium is additionally incorporated into the fertilizer matrix. Furthermore, the inclusion of KCl introduces potassium. As a result, the modified CAN produced in this study contains four essential plant nutrients—nitrogen, potassium, calcium, and magnesium. These elements are crucial for plant growth and metabolic activity, and their combined presence in readily digestible forms is expected to significantly enhance crop yield and soil fertility.

The formation of water-soluble CaO and MgO indicates that at 170–175 °C a chemical reaction occurs between ammonium nitrate and the carbonate components of dolomite, yielding calcium and magnesium nitrates. This process is accompanied by the release of ammonia and carbon dioxide into the gas phase, as illustrated in the following reaction scheme:

$$4NH_4NO_3 + CaMg(CO_3)_2 \rightarrow Ca(NO_3)_2 + Mg(NO_3)_2 + 4NH_3\uparrow + 2CO_2\uparrow + 2H_2O$$

This conclusion is further supported by the data on the decarbonization degree of the dolomite mineral (DM). To evaluate this parameter, the extent of DM decarbonization was determined as a function of the reaction time (1, 5, 10, 15, 20, 25, 30 min) and the mass ratio of the initial components.

At an AN:DM:KCl ratio of 100:(0.25–25):(0.25–25), the decarbonization degree of DM after 5 minutes ranged from 12.26% to 3.35%, while after 30 minutes it decreased from 33.69% to 12.82%. These results clearly indicate that the decarbonization of DM intensifies with longer interaction times.

Table 1. Composition of potassium-containing calcium ammonium nitrate based on ammonium nitrate melt, dolomite mineral and potassium chloride

Mass ratio AN:DM:KCl	Content of components, mass. %								$\frac{CaO_{assim.}}{CaO_{total}}$ by 2% citric acid, %	$\frac{MgO_{assim.}}{MgO_{total}}$ by 2% citric acid, %	$\frac{CaO_{water}}{CaO_{total}}$ %	$\frac{MgO_{water}}{MgO_{total}}$ %
	N	K_2O	CaO_{total}	$CaO_{assim.}$ by 2% citric acid.	CaO_{water}	MgO_{total}	$MgO_{assim.}$ by 2% citric acid.	MgO_{water}.				
100 : 0.0 : 0.0	34.96	–	–	–	–	–	–	–	–	–	–	–
100 : 0.5 : 0.5	34.62	0.292	0.135	0.124	0.066	0.129	0.110	0.058	91.85	85.34	48.89	45.27
100 : 1.0 : 1.0	34.28	0.584	0.306	0.277	0.145	0.254	0.213	0.112	90.74	82.83	47.53	43.94
100 : 1.5 : 1.5	34.01	0.844	0.404	0.357	0.186	0.379	0.316	0.161	88.49	80.32	46.17	42.61
100 : 2.0 : 2.0	33.42	1.105	0.535	0.461	0.239	0.501	0.419	0.207	86.25	77.81	44.81	41.28
100 : 2.5 : 2.5	33.03	1.363	0.662	0.556	0.287	0.617	0.522	0.246	83.99	75.50	43.45	39.95
100 : 3.0 : 3.0	32.89	1.667	0.791	0.647	0.333	0.736	0.625	0.284	81.75	73.19	42.09	38.62
100 : 3.5 : 3.5	32.45	1.886	0.914	0.726	0.372	0.853	0.728	0.318	79.51	70.88	40.73	37.29
100 : 4.0 : 4.0	31.97	2.145	1.029	0.801	0.405	0.965	0.831	0.347	77.75	68.57	39.37	35.96
100 : 4.5 : 4.5	31.83	2.412	1.156	0.862	0.439	1.078	0.934	0.373	74.48	66.26	38.01	34.63
100 : 5.0 : 5.0	31.24	2.681	1.268	0.923	0.471	1.192	1.037	0.397	72.76	63.95	36.65	33.31
100 : 7.0 : 7.0	30.35	3.625	1.717	1.214	0.605	1.611	1.140	0.515	70.69	61.64	35.29	31.97
100 : 10 : 10	29.11	5.041	2.326	1.435	0.789	2.180	1.243	0.668	64.48	59.33	33.93	30.64
100 : 12 : 12	28.06	5.806	2.708	1.793	0.882	2.539	1.346	0.744	66.21	57.02	32.57	29.32
100 : 15 : 15	26.58	6.643	3.219	2.058	1.005	3.024	1.449	0.846	63.95	54.71	31.21	27.98
100 : 18 : 18	25.23	7.480	3.703	2.287	1.106	3.473	1.552	0.925	61.76	52.40	29.85	26.65
100 : 20 : 20	24.87	8.317	4.001	0.238	1.139	3.748	1.655	0.874	59.54	50.09	28.49	23.32
100 : 22 : 22	23.95	9.115	4.275	2.450	1.158	4.07	1.758	0.976	57.32	47.78	27.13	23.99
100 : 25 : 25	23.21	9.982	4.620	2.492	1.186	4.366	1.863	0.988	55.13	44.67	25.67	22.64

The trend is graphically illustrated in Fig. 5, where the optimal interaction time of the initial substances was identified as 15 minutes, corresponding to a decarbonization degree of 24.62–8.75%.

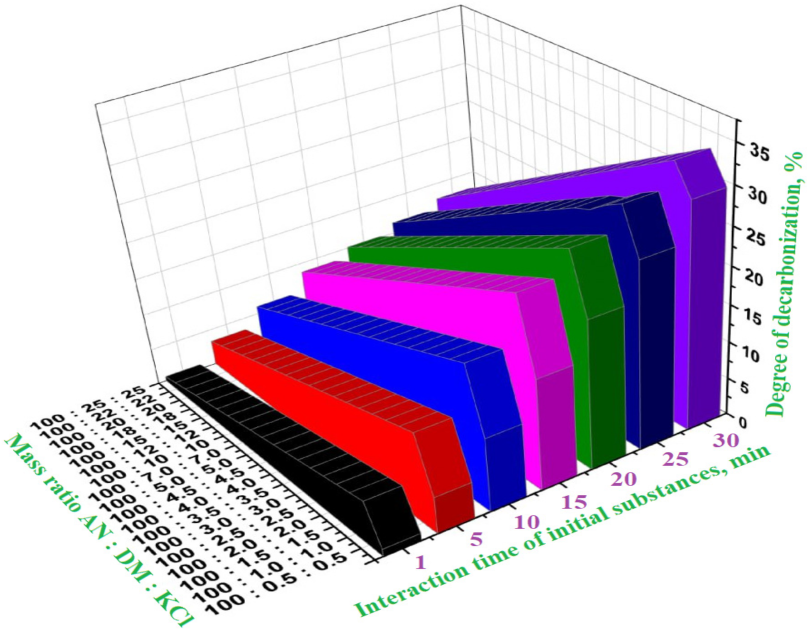

Fig. 5. The degree of decarbonization of DM depending on the amount of KCl in relation to the ammonium nitrate melt at mass ratios of AC:DM:KCl = 100:(0.5-25):(0.5-25)

However, it was also observed that under identical mass ratios of AN:DM:KCl, an increase in the absolute mass of DM and KCl from 0.5 g to 25 g per 100 g of AN melt caused a notable reduction in the decarbonization degree. This phenomenon can be attributed to the fact that the presence of KCl substantially increases the viscosity of the nitrate–carbonate melt. The higher viscosity hinders the diffusion of reactants and restricts the release of gaseous byproducts (CO_2 and NH_3), thereby suppressing the overall decarbonization process of DM.

Table 2 presents the results of determining the strength of granules of potassium-containing CAN obtained on the basis of AN melt, DM, and KCl.

Table 2. Composition of potassium-containing calcium ammonium nitrate based on ammonium nitrate melt, dolomite mineral and potassium chloride

Mass ratio AN:DM:KCl	Granule strength, MPa	Granule caking, kg/cm^2	Granule porosity, %	Granule absorption, g.
Granulated NH_4NO_3 grade "pure"	1.32	5.62	22.0	4.82
100 : 0.5 : 0.5	3.10	3.04	8.55	3.24
100 : 1.0 : 1.0	3.76	2.96	8.43	3.15
100 : 1.5 : 1.5	4.11	2.89	8.31	3.06
100 : 2.0 : 2.0	4.56	2.80	8.18	2.96
100 : 2.5 : 2.5	5.02	2.72	8.06	2.87
100 : 3.0 : 3.0	5.47	2.64	7.94	2.78
100 : 3.5 : 3.5	5.54	2.56	7.82	2.69
100 : 4.0 : 4.0	5.61	2.48	7.69	2.60
100 : 4.5 : 4.5	5.68	2.40	7.57	2.51
100 : 5.0 : 5.0	7.06	2.32	7.45	2.41
100 : 7.0 : 7.0	8.43	2.24	7.33	2.32
100 : 10 : 10	9.09	2.15	7.21	2.23
100 : 12 : 12	9.74	2.07	7.09	2.14
100 : 15 : 15	11.27	2.0	6.97	2.04
100 : 18 : 18	12.04	1.92	6.84	1.95
100 : 20 : 20	12.50	1.84	6.72	1.86
100 : 22 : 22	12.97	1.75	6.60	1.77
100 : 25 : 25	14.32	1.67	6.48	1.68

The strength of granules is one of the indicators characterizing the stability of AN.

As shown in Table 2, the introduction of both dolomite mineral (DM) and potassium chloride (KCl) into the ammonium nitrate (AN) melt markedly enhances the mechanical strength of the resulting granules. Specifically, when the mass ratio of AN:DM:KCl is increased from 100:0.5:0.5 to 100:25:25, the compressive strength of the product rises from 3.10 to 14.32 MPa, compared to the initial value of 1.32 MPa for pure granulated NH_4NO_3 (grade “pure”).

A similar trend is observed with respect to the caking properties. While the caking strength of pure NH_4NO_3 is 5.62 kg/cm^2, the corresponding values for NKCaMg-fertilizers at AN:DM:KCl = 100:0.5:0.5 and 100:25:25 are significantly reduced to 3.04 and 1.67 kg/cm^2, respectively. These values are 1.85–3.36 times lower than that of unmodified ammonium nitrate, which is a desirable property for safe storage and handling.

The addition of DM and KCl also leads to a notable reduction in granule porosity. For AN:DM:KCl = 100:(0.5–25):(0.5–25), the porosity of NKCaMg-fertilizers ranges from 8.55 to 6.48%, whereas for pure AN granules it reaches 22.0%. Since lower porosity directly reduces the capacity of granules to absorb liquid fuel, this modification enhances the safety characteristics of the product.

Indeed, as demonstrated in Table 2, absorbency is inversely correlated with porosity. For non-caking AN ($N \geq 28\%$) with the addition of small amounts of DM and KCl (100:0.5–1.5:0.5–1.5), the absorbency of granules varies between 3.24 and 3.06 g per 100 g of product. With higher additive contents (100:2–25:2–25), the absorbency further decreases to 2.96–1.68 g, in contrast to 4.82 g for pure AN granules.

These findings explain the observed enhancement in granule strength, as reduced porosity and absorbency limit the penetration of liquid fuel, thereby lowering the detonation sensitivity and increasing the thermal stability of AN-based composite fertilizers.

Among the tested compositions, the most agriculturally favorable potassium-containing CAN was identified at a ratio of AN:DM:KCl = 100:12:12. This formulation produces a fertilizer containing 28.01% N, 5.80% K_2O, 2.71% CaOtotal., and 2.54% MgOtotal., with a degree of dolomite mineral decarbonization (γDM) of 13.46%. The corresponding granule strength, caking, porosity, and absorbency were 9.74 MPa, 2.07 kg/cm^2, 7.09%, and 2.14 g, respectively, confirming its optimal balance of mechanical stability, reduced caking, and improved safety properties.

X-ray structural analysis of the optimal potassium-containing CAN sample (AN:DM:KCl = 100:12:12) demonstrated that the calcium and magnesium present in the dolomite mineral, originally in plant-unavailable forms, are transformed into plant-accessible compounds after 15 minutes of interaction with molten ammonium nitrate. Moreover, the reaction between potassium chloride and molten ammonium nitrate resulted in the formation of small amounts of potassium nitrate (Fig. 6).
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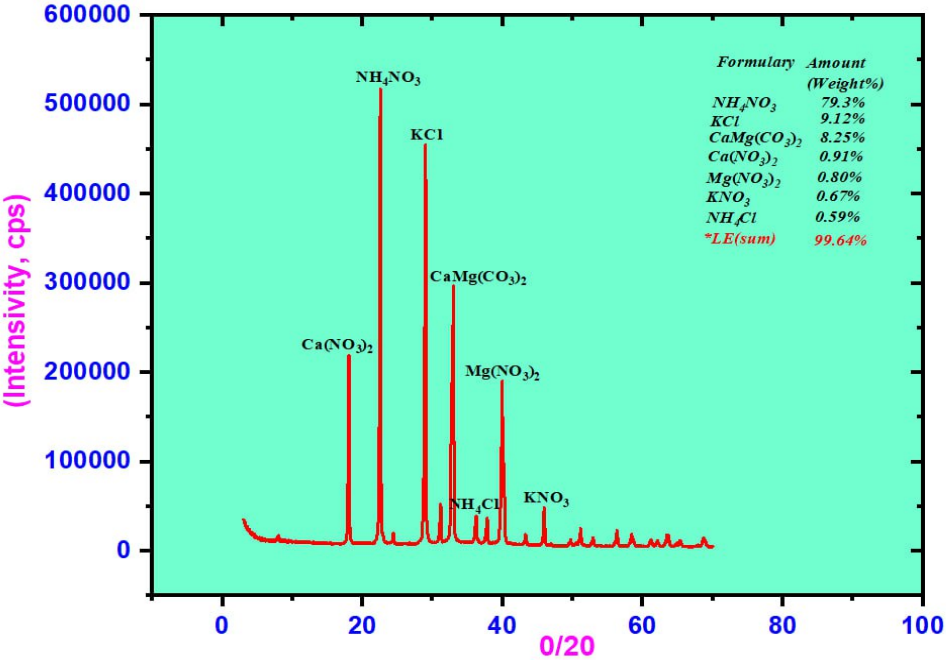
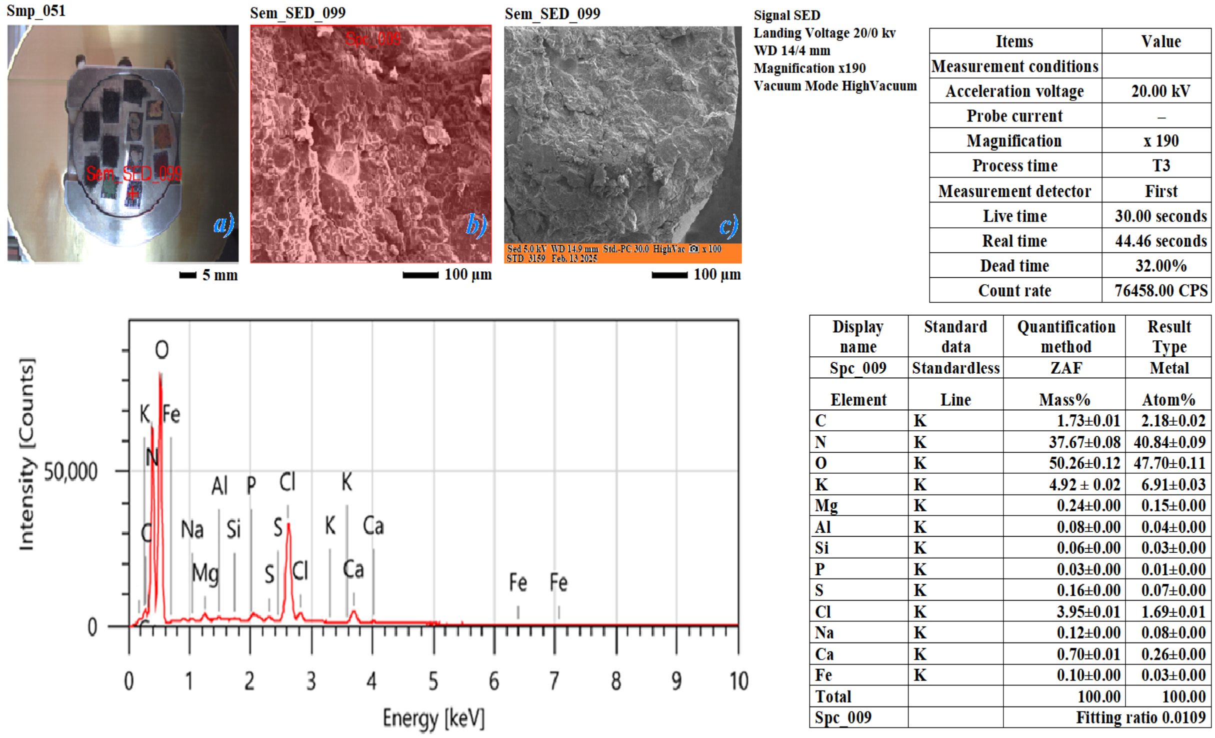


Fig. 6. EDS analysis of a sample of potassium-containing CAN, with the optimal ratio of AN:DM:KCl = 100:12:12

The SEM analysis was conducted to obtain high-resolution images of the surface and to assess the chemical composition and microstructural features of the selected optimal sample. The morphology of granules at AN:DM:KCl = 100:12:12 is shown in Fig. 7. Fig. 7-a presents the overall granule view, Figure 7-b illustrates the internal structure, and Figure 7-c reveals the surface microstructure. The SEM images indicate the presence of both micro- and macrocracks, together with uniformly distributed fine crystalline particles of DM and KCl. Notably, no large agglomerates of DM or KCl were detected. These findings confirm that each granule contains not only the primary macronutrients—nitrogen, potassium, calcium, and magnesium - but also trace elements such as iron and aluminum, which can serve as additional sources of plant nutrition. The SEM results are in full agreement with the X-ray diffraction data, validating the structural and compositional uniformity of the product.



Signal SED
Landing Voltage 20/0 kv
WD 14/4 mm
Magnification x190
Vacuum Mode HighVacuum

Items	Value
Measurement conditions	
Acceleration voltage	20.00 kV
Probe current	–
Magnification	x 190
Process time	T3
Measurement detector	First
Live time	30.00 seconds
Real time	44.46 seconds
Dead time	32.00%
Count rate	76458.00 CPS

Display name	Standard data	Quantification method	Result Type
Spc_009	Standardless	ZAF	Metal
Element	Line	Mass%	Atom%
C	K	1.73±0.01	2.18±0.02
N	K	37.67±0.08	40.84±0.09
O	K	50.26±0.12	47.70±0.11
K	K	4.92 ± 0.02	6.91±0.03
Mg	K	0.24±0.00	0.15±0.00
Al	K	0.08±0.00	0.04±0.00
Si	K	0.06±0.00	0.03±0.00
P	K	0.03±0.00	0.01±0.00
S	K	0.16±0.00	0.07±0.00
Cl	K	3.95±0.01	1.69±0.01
Na	K	0.12±0.00	0.08±0.00
Ca	K	0.70±0.01	0.26±0.00
Fe	K	0.10±0.00	0.03±0.00
Total		100.00	100.00
Spc_009		Fitting ratio 0.0109	

Fig. 7. SEM analysis of a sample of potassium-containing CAN, with the optimal ratio of AN:DM:KCl = 100:12:12

Differential thermal analysis (DTA) was employed to investigate polymorphic phase transitions in ammonium nitrate (AN) granules under varying temperature conditions. Since the commercial properties of granulated nitrate are strongly influenced by storage and transportation environments, understanding these transitions is of particular importance. Ammonium nitrate is known to exhibit five crystalline modifications within the temperature range of −50 to 169.6 °C. Each modification is stable within a specific temperature interval: modification I (169.6–125.2 °C), II (125.2–84.2 °C), III (84.2–32.3 °C), IV (32.3 to −17 °C), and V (−17 to −50 °C). These modifications differ in crystal lattice structure and volume changes.

The transition from modification III to IV is accompanied by the maximum volumetric expansion of the granules, which leads to a sharp decrease in their mechanical strength and increased tendency to agglomerate. Conversely, the most stable granules are obtained when transitions occur with minimal volumetric and structural changes, namely from modification II directly to modification V (II → V).

Table 3. Temperature of modification transition of sample AN:DM:KCl = 100:12:12

Mass ratio AN: DM: KCl	The meaning of the peak on the curve								
	IV→III	III→II	II→I	I→melt	melt→I	I→II	II→III	III→IV	II→IV
	heating from 25 to 175°C				cooling from 175 to 25°C				
NH_4NO_3 "pure"	46	85	126	169	169	125	48	30	–
100 : 12 : 12	48.2	91.4	132.8	173.2	163.4	118.4	–	–	47.2

Given this, a key objective of the present work was to evaluate the influence of DM and KCl additives on the kinetics of polymorphic transformations in AN. The transition temperatures of the modified polymorphs in the optimized composition (AN : DM : KCl = 100 : 12 : 12) during heating and cooling cycles in the range of 25 ↔ 175 °C are presented in Fig. 8 and summarized in Table 3.

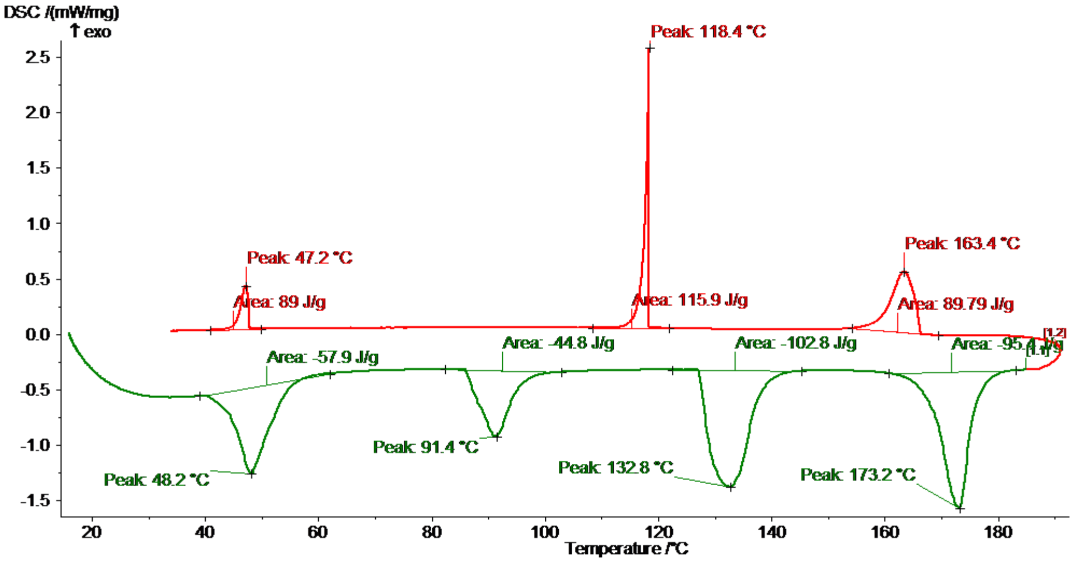


Fig. 8. DTA analysis of a sample of potassium-containing CAN, with the optimal ratio of AN:DM:KCl = 100:12:12 (heating and cooling of AN with the addition of DM and KCl)

To avoid duplication, a photograph of the DTA analysis of pure NH_4NO_3 is not provided. However, for comparative study, the results of heating ammonium nitrate from 25 to 175°C and cooling from 175 to 25°C are presented in Table 3.

According to DTA analysis, when heating pure NH_4NO_3 from 25 to 175 °C, the transition temperature of the IV→III modification occurs at 46 °C. Further polymorphic transformations are observed at 85, 126, and 169 °C, corresponding to the III→II, II→I, and I→melt transitions, respectively. Upon cooling from 175 to 25 °C, the reverse sequence of transitions (melt →I, I→II, II→III, and III→IV) takes place at 169, 125, 48, and 30 °C, respectively. Notably, in pure NH_4NO_3 the direct transition from II→IV, which is associated with more stable modifications and reduced volumetric deformation of granules, is absent.

For the optimized composition AN:DM:KCl = 100:12:12, the heating cycle revealed polymorphic transitions at 48.2, 91.4, 132.8, and 173.2 °C for the IV→III, III→II, II→I, and I→melt modifications, respectively. During cooling, the transitions melt→I and I→II were detected at 163.4 and 118.4 °C. Importantly, the DTA results indicate that the presence of dolomite mineral (DM) and potassium chloride facilitates stabilization of the IV modification by promoting a direct II→IV transition pathway. This bypasses the unstable modification III, thereby reducing lattice deformation and enhancing granule strength. Consequently, granules containing DM and KCl demonstrate improved resistance to temperature fluctuations up to ~47 °C, as no sharp volumetric changes associated with modification transitions are observed.

Table 4. Onset temperature and activation energy values of thermal decomposition of the sample AN:DM:KCl = 100:12:12

Mass ratio AN:DM:KCl	Temperature range, °C	Temperature of the onset of decomposition, °C	Activation energy, J/g
NH_4NO_3 "pure"	200-300	211.0	-915.1
100 : 12 : 12		238.4	-503.7

In addition to polymorphic stability, the thermal stability of AN was assessed by determining the decomposition onset temperature and activation energy values in the range of 200–350 °C (Fig. 9, Table 4). Literature data indicate that the decomposition of pure NH_4NO_3 commences at 211 °C. In contrast, the optimized AN:DM:KCl = 100:12:12 sample exhibited a significantly higher decomposition onset temperature of 238.4 °C, representing an increase of 27.4 °C compared with pure NH_4NO_3. This upward shift demonstrates that DM and KCl not only stabilize the polymorphic transformations of AN but also enhance its overall thermal stability.

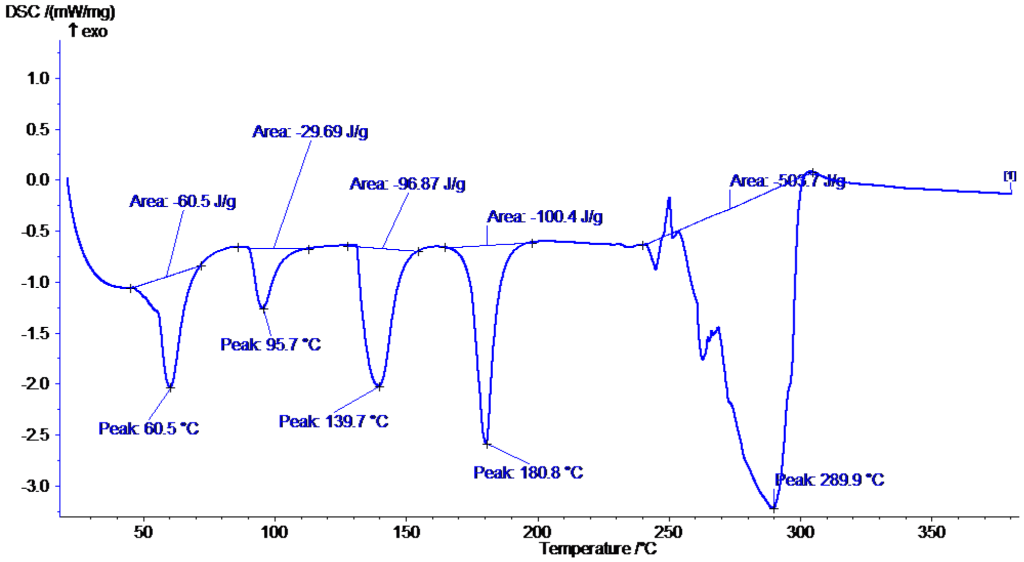


Fig. 9. DTA analysis of a sample of potassium-containing CAN, with the optimal ratio of AN:DM:KCl = 100:12:12 (decomposition onset temperature and activation energy)

The activation energy of thermal decomposition was calculated using the thermal analysis software *NETZSCH Proteus* (version 4.8.1). The results presented in Table 4 demonstrate that the thermostable AN samples containing DM and potassium chloride require significantly higher activation energy for decomposition (503.7 J/g) compared with pure NH_4NO_3 (915.1 J/g).

These findings confirm that the presence of DM and KCl exerts an inhibitory effect on the decomposition of ammonium nitrate. By increasing the energy barrier to thermal degradation, these additives contribute to improved thermal stability of AN-based compositions. Consequently, the incorporation of DM and KCl enhances the safety of ammonium nitrate during production, storage, and transportation, as well as its reliability when applied as a complex nitrogen fertilizer in agriculture.

Conclusion

In this study, the process of obtaining potassium-containing CAN samples was investigated by granulating carbonate–chloride–nitrate melts derived from AN with the addition of powdered DM and potassium chloride in ratios of AN:DM:KCl = 100:(0.5–25):(0.5–25) using the prilling method. Based on the chemical composition and physicochemical properties of the NKCaMg fertilizer samples, the formulation with AN:DM:KCl = 100:12:12 was identified as optimal.

Analyses by EDS and SEM confirmed that, in addition to nitrogen required for plant growth, the potassium-CAN also contains potassium, calcium, and magnesium. The microstructural studies revealed that the granules of the optimal sample possess finely dispersed DM and KCl crystals uniformly distributed within the matrix. Furthermore, at 170 °C, the exchange reaction between DM and AN leads to the partial formation of $Ca(NO_3)_2$ and $Mg(NO_3)_2$ in the NKCaMg-fertilizer composition.

The detonation sensitivity of potassium-CAN was evaluated by DTA analysis. Results demonstrated that the presence of DM and KCl induces a stable II→IV polymorphic transition at 47.2 °C, increases the initial decomposition temperature of NH_4NO_3 by 27.4 °C, and raises the activation energy of decomposition by 411.4 J/g. Collectively, these effects improve the thermal stability and safety of AN.

Thus, the incorporation of DM and KCl into AN produces a multi-nutrient fertilizer with enhanced agrochemical efficiency (supplying N, K, Ca, and Mg), improved granule strength, reduced caking and porosity, lower absorption of diesel fuel, and consequently, reduced detonation tendency and a higher level of explosion safety.

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