Research paper

Effects of zinc borate and magnesium nitrate on the explosion energy of ammonium nitrate

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Received: April 12, 2024 Accepted: June 11, 2025

Abstract

In fields of agriculture, ammonium nitrate is the most often used chemical fertilizer. Its physicochemical qualities are also applied in the explosive sector because of its affordability and ease of accessibility. But for anti-social objectives, this characteristic has made it more appealing. In order to avoid this, scientists have concentrated on adding different compounds to the ammonium nitrate synthesis process in order to lower its enthalpy.

The primary focus of this study was on the effects of ammonium nitrate on the plant's ability to reduce nitrogen concentration and minimize caking phenomena. The plant's ability to absorb heavy metals was not affected by the addition of zinc borate and magnesium nitrate, as evidenced by the significantly reduced results of calorimetry tests.

The findings of the instrumental examination showed that even with the addition of 0.1% of the study's ingredients—zinc borate, and magnesium nitrate—considerably enhanced the crushing strength of ammonium nitrate. With the results in this instance, it can be said that ammonium nitrate's inclination to deteriorate reduces and its shelf life improves. It was discovered that the reaction medium with the highest crushing strength is the one to which all three chemicals are introduced, even if their crushing strengths are comparable when applied separately.

The peak heights in the ammonium nitrate content in anion and cation analysis in ion chromatography, however, show that the low quantities of boron content—a heavy metal of the chemicals used—are the cause of this. According to nitrogen analysis, there is no impact on the nitrogen concentration of ammonium nitrate when it comes to agricultural use. It was discovered that boron compounds significantly lowered the enthalpy of ammonium nitrate when DSC analysis was carried out as a calorimetric value. It was discovered that the tendency to detonate was greatly decreased when all three chemicals were added since there was no exothermic peak in the combustion reactions. An electron microscope was used to assess surface porosity, another component influencing the detonation process.

The addition of all three compounds to the ammonium nitrate surface results in the smallest and least number of porosity when compared to the surface where each compound is added separately. It has been discovered that reducing surface porosity may change reactivity but it does not lower detonation enthalpy.

Keywords: zinc borate, magnesium nitrate, ammonium nitrate, detonation

1. Introduction

1.1 Explosion mechanism of ammonium nitrate and historical accidents

Ammonium nitrate is the chemical fertilizer with the highest commercial quality and value since it is the nitrogen fertilizer that is applied to agricultural fields the most[1].

It is more effective for agricultural usage when the commercial value is preserved and developed[2]. However, its accessibility has made it possible for it to be used for antisocial ends. Ammonium nitrate can be used as an explosive by nature if it is combined in an ANFO-style manner[3].

There are currently a number of studies available to lower ammonium nitrate's detonation enthalpy[4]. The addition of chemicals such as dolomite[5], potassium chloride[6], mono ammonium phosphate[7], nitramine compounds[8], urea - ammonium sulfate mixture[9], phosphogypsum - powder sulfur mixture[10], potassium carbonate[11], sodium bicarbonate[12], and ammonium sulfate[13], and ammonium sulfate is the main focus of studies to lower the detonation enthalpy.

Ammonium nitrate's impact on the reaction medium's degradation process is linked to the effects of all these

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chemical additives on the detonation mechanism[14].

But chemicals are also added during production, like fly ash[15] and fluidized bed combustion ash[16], which are added as a particle surface coating.

To further lower the detonation enthalpy, it has also been reported that the following substances affect enthalpy differently: sodium chloride[17], potassium chloride[18], monomolecular nitro derivatives[19], and PBX type plastic derivatives[20].

The aim of this study is to determine an important alternative in terms of chemical composition in ammonium nitrate production by evaluating the decomposition properties of ammonium nitrate and surface properties of ammonium nitrate together, and to reduce the detonation enthalpy of ammonium nitrate by determining the explosion sensitivity of the produced ammonium nitrate compound with the added boron compounds. The same procedure was used to generate ammonium nitrate particles, and it was found that these particles' hygroscopic characteristics improved during storage and complied with the established norms for the durability of commercial ammonium nitrate.

2. Material and methods

2.1 Technique for producing ammonium nitrate

The following can be used to express the compounds utilized in the study together with their concentrations: 55% nitric acid (at 50°C, Toros Agri & Industry, Turkey, CAS No: 7697-37-2), 99.9% anhydrous ammonia (at Toros Agri Industry, Turkey, CAS No: 7664-41-7), 98% sulfuric acid (at Hicri Ercili, Turkey, CAS No: 7664-93-9), 98% zinc borate (Merck, Istanbul, CAS No: 1332-07-6), 98% magnesium nitrate (Merck, Istanbul, CAS No: 13446-18-9).

Different methods can be used to manufacture ammonium nitrate, which is utilized as a chemical fertilizer. Different chemicals might be added in the dilution stages as desired to achieve the desired chemical characteristics based on market demand. In this work, the two-step evaporation process is used to produce pure ammonium nitrate, and boron compounds indicated in the dilution stage are added to reduce detonation sensitivity.

As pertinent process information, in order to produce ammonium nitrate, gasified anhydrous ammonia at 10°C and 55% nitric acid were reacted in a tubular reactor to produce a concentration of 70−80% ammonium nitrate. Using a two-stage evaporation method, the ammonium nitrate solution of the same concentration was concentrated to a predefined concentration of 94% and subsequently 97%.

2.2 Examination of the characteristics and temperature at which ammonium nitrate detonates

A calorimeter bomb was used to ascertain the ammonium nitrate chemical fertilizer's explosion capabilities for this study. The enthalpy values and detonation characteristics of pure ammonium nitrate are used as a guide during this determination (Table 1). By using a primary explosive to blast a mixture of 94.3% ammonium nitrate and 5.7% fuel oil inside a tightly sealed steel volume, deformation on the steel volume was used to study burst energy.

Table 1 Values of the effects of the chemicals used in the study on the decomposition heat of ammonium nitrate measured with a calorimeter bomb device.

Material	Heat of explosion [J·g^{-1}]
Zinc borate - added ammonium nitrate	3.42
Magnesium nitrate added - ammonium nitrate	365.1
Zinc borate and Magnesium nitrate -added ammonium nitrate	400.2
Pure ammonium nitrate	-1500

The deformation of ammonium nitrate samples acquired by the addition of the chemicals under investigation differs significantly from the deformation achieved by pure ammonium nitrate through the respective mixture. Because no steel surface deformation was seen in ammonium nitrate studies where boron compounds were added, despite the steel chamber's outer surface being totally distorted during the blasting of pure ammonium nitrate.

2.3 Examination of nitrogen

500 mL of distilled water are used to dilute a sample of 4 g of ammonium nitrate. After passing this solution through Whatman No. 46 filter paper, 100 mL is taken, and until a red hue is achieved, a few drops of methyl red sodium salt and 0.25 M sulfuric acid are added.

0.5 M NaOH is added in order to counteract the added sulfuric acid until a yellow tint is achieved. After that, the solution medium is mixed with 10 mL of formaldehyde and a few drops of cresolphthalein indicator. One milligram of NaOH is added each time until the color turns to 20 out of 100.

$$N\,[\%] = 0.0028 \times (n_1 - n) \times \left(\frac{500}{v}\right) \times \left(\frac{100}{E}\right) \qquad (1)$$

E [g]: the sample's mass of weighed ammonium nitrate
V [mL]: the amount of dilute ammonium nitrate sample used for the titration
n [mL]: During the titration, 1 M sodium hydroxide solution was consumed.
n_1 [mL]: the amount of sodium hydroxide needed to neutralize the utilized sulfuric acid
N [%]: the amount of nitrogen in the fertilizer material

When the necessary numbers (n_1: 110 mL, n: 11.25 mL, V: 100 mL, E: 4 g) were substituted for each equation parameter, the nitrogen value for the pure ammonium nitrate generated was found to be 34.6%.

2.4 Analysis of electron microscopy

According to ASTM E986-97 standard, the surface parameters of ammonium nitrate particles produced by Carl Zeiss DSM-960A electron microscope are as follows: accelerating voltage, 1-30 kV; usable magnification, × 10-30000; resolution, 70°C.

2.5 Analysis with ion chromatography

Using a Shimadzu Prominence HIC-NSn system ion chromatography device, the effect of boron compounds supplied on ammonium nitrate particles during the manufacturing of ammonium nitrate, notably at the dilution stage, is 0.01-551200 $\mu S \cdot cm^{-1}$; flow rate was monitored at 0.001-5 $mL \cdot min^{-1}$.

2.6 Analysis of crushing strength

Using the Instron Test System (Model 4411), it was possible to analyze the ammonium nitrate stack's degrading characteristics under prolonged storage conditions by examining the impact of each boron compound on the crushing strength of the ammonium nitrate particles.

2.7 Differential Scanning Calorimetry (DSC)

Thermogravimetric Analysis (TGA) of ammonium nitrate with zinc borate and magnesium nitrate was conducted using the Seteram brand, Setsys Evolution TG-DTA/DSC 1600°C micro DSC.

3. Results and discussion

Ammonium nitrate detonation is a significant issue, and researchers are urged to concentrate on the need to restrict the areas of use. Because of the widespread use of ammonium nitrate for antisocial purposes outside the agricultural industry, it has become a focus of researchers as a problem that needs to be solved chemically. Since ammonium nitrate is solely thought of as a chemical fertilizer by the agricultural industry, In the ammonium nitrate production facility, improving the storage properties along with improving its physicochemical properties will be an important step towards solving the problem. Although it is seen as an agricultural problem, the addition of the chemicals subject to this study during ammonium nitrate production due to their heavy metal identity was considered unimportant because their concentrations are sufficient to meet the amount of plant nutrients that plants need for growth and development. As a result of the tests and researches, it was seen that the calorific value of ammonium nitrate obtained in the calorimeter bomb is directly related to the reaction enthalpy released during the explosion. Therefore, it was concluded that chemical additives are needed to reduce the energy of ammonium nitrate measured in the calorimeter bomb in ammonium nitrate production. However, the effect of ammonium nitrate on the enthalpy value affects the selection of compounds such as zinc borate and magnesium nitrate to be added during the dilution stage of ammonium nitrate production.

The effect of the lowering of the enthalpy value, together with any problems in the dissolution process of the chemicals, did not play a decisive role in the selection of the chemical substance.

During the production of ammonium nitrate, the melt is passed through a perforated prilling equipment at 169°C for the granulation stage and granulated. At this stage, the viscosity of the ammonium nitrate melt is important in terms of its droplet formation capacity within a certain period of time, which can be called the viscosity change rate. Since ammonium nitrate's melting temperature, 169°C, does not affect the boron compound's non-degrading structure, the effect of boron compounds on the viscosity change rate of ammonium nitrate for phase conversions of ammonium nitrate in the granulation step, is related to the crystal structure of ammonium nitrate. The final product's temperature is greatly influenced by the rate of viscosity change, not the linear, and is dependent upon the kind of fluid used for cooling. Using a scanning electron microscope to analyze the surface, it was determined how the addition condition of each boron compound affected the surface porosity. Surface analyses for ammonium nitrate samples in which all chemical additives were included in the production process were performed using electron microscopy to study porosity. The aim here is to reduce the sensitivity to explosion in parallel with the increase in particle porosity during ammonium nitrate production. The results of the electron microscopy analysis indicate that the addition of 0.1% zinc borate and 0.1% magnesium nitrate reduces the number of pores in ammonium nitrate. Moreover, the number of pores is minimal when all two chemical additives are added.

The ammonium nitrate porosity structure is significantly impacted by the insertion of a single wire-structured crystal

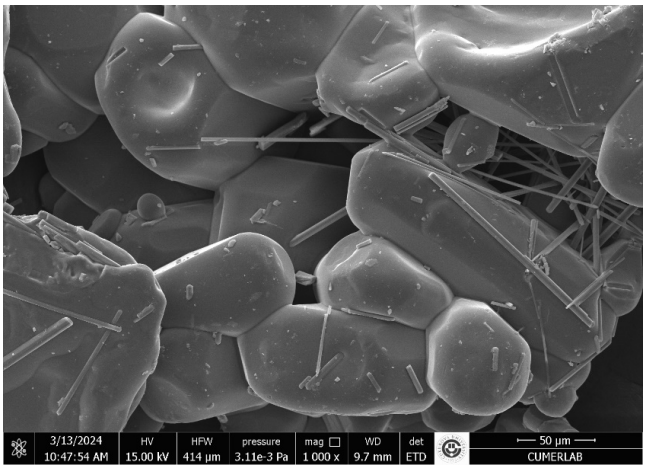


Figure 1 SEM image of the ammonium nitrate with 0.1% zinc borate.

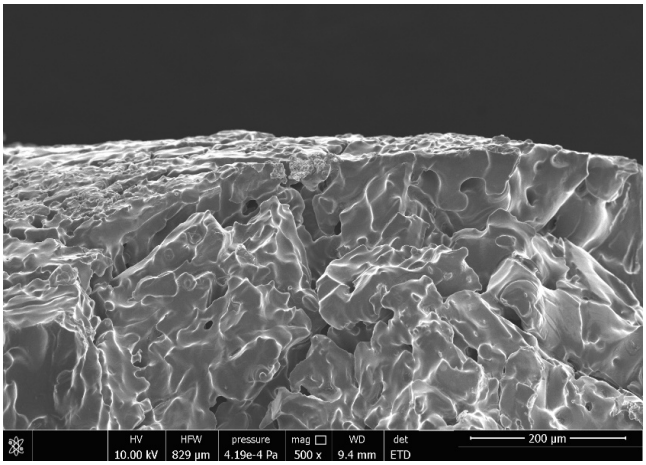


Figure 2 Pore structure of the ammonium nitrate with 0.1% zinc borate.

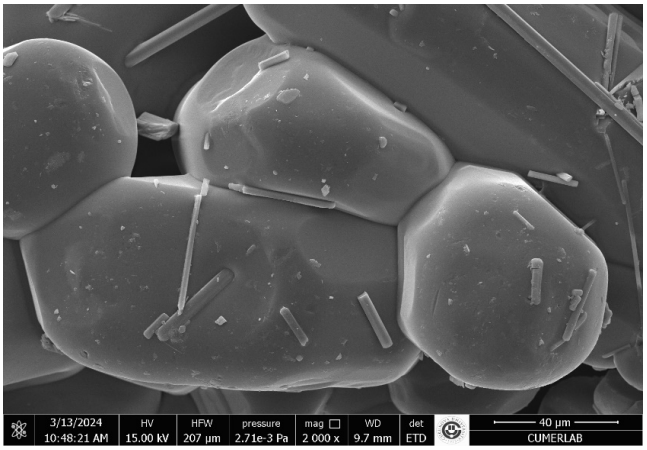


Figure 3 SEM image of the ammonium nitrate with 0.1% magnesium nitrate.

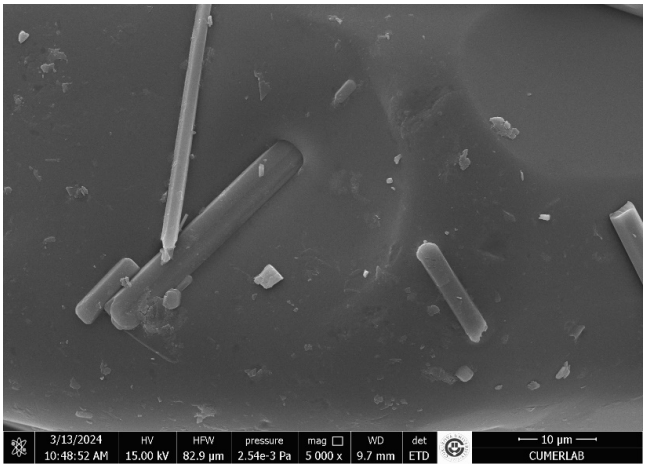


Figure 5 SEM image of the ammonium nitrate with 0.1% zinc borate and 0.1% magnesium nitrate.

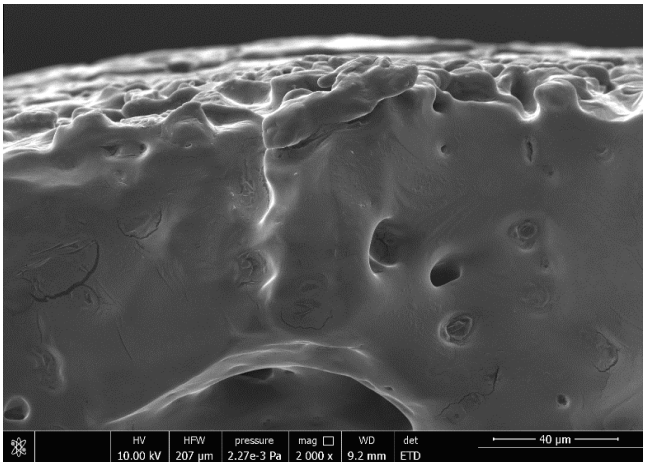


Figure 4 Pore structure of the ammonium nitrate with 0.1% magnesium nitrate.

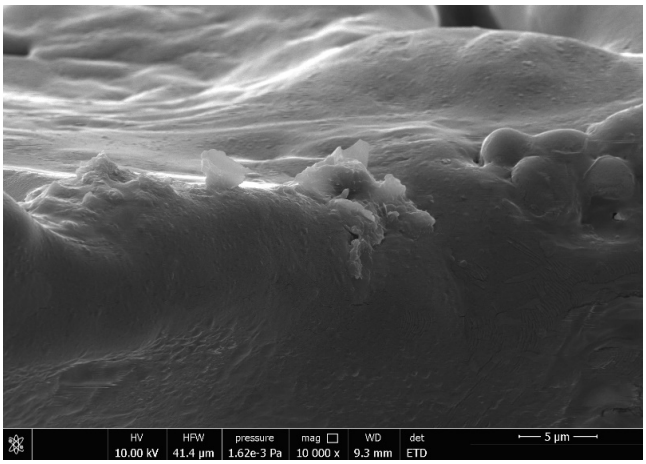


Figure 6 Pore structure of the ammonium nitrate with 0.1% zinc borate and 0.1% magnesium nitrate.

of zinc borate or magnesium nitrate, as the SEM photos demonstrate. One of the physical factors affecting the enthalpy of ammonium nitrate explosion is the porous structure of ammonium nitrate along with the enthalpy of reaction. Consequently, one of the factors that causes detonation is increasing porosity. SEM pictures were used to examine how ammonium nitrate affected the porous structures of the two compounds that were the focus of this investigation. Ammonium nitrate containing 0.1% zinc borate (Figure 1, Figure 2) exhibits the highest porosity and has the lowest pore diameter, followed by ammonium nitrate containing 0.1% magnesium nitrate (Figure 3, Figure 4). Ammonium nitrate containing both compounds has the least porosity and the largest pore diameter structure (Figure 5, Figure 6).

The impact of the compounds utilized on the crushing strength of ammonium nitrate was examined in the crushing strength analysis. This measurement is necessary because the ammonium nitrate's storage life and the particles' propensity to form clumps are both impacted by the crushing strength. In this regard, the addition of 0.1% zinc borate, and 0.1% magnesium nitrate results in an increase in crushing strength with boron compounds. It is found that the maximum crushing strength (2.75 kg/prill) is obtained when each chemical compound is added together. Therefore, it may be concluded that the boron compounds under investigation have considerably raised ammonium nitrate's crushing strength.

To examine the impact of these additives on crushing strength, a caking apparatus was used to assess the effects of all three additives on ammonium nitrate in a manner that replicated the storage process. The effects of the chemicals used in the study, such as zinc borate and magnesium nitrate, on the crushing strength of ammonium nitrate as a result of their addition to the ammonium nitrate production process, either alone or together, are shown in Table 2. It can be stated that the fracture strength has the highest value in the particles obtained as a result of the inclusion of all three chemicals in the ammonium nitrate production process. When it comes to reducing plant absorption and controlling heavy metal concentration, ammonium nitrate with zinc borate's lowest crushing strength can be seen as a significant improvement.

The effect of boron compounds added to the reaction medium on the nitrogen concentration of ammonium nitrate was investigated using ion chromatography with the goal of

Table 2 Nitrogen content and Crushing strength of boron compounds added ammonium nitrate.

Material	Nitrogen [%]	Crushing strength [kg/prills]	Moisture [%]
Zinc borate - added ammonium nitrate	34.08	2.33	0.77
Magnesium nitrate - added ammonium nitrate	34.15	2.45	0.66
Zinc borate and Magnesium nitrate - added ammonium nitrate	34.31	2.55	0.58
Pure ammonium nitrate	34.45	1.71	0.82

lowering the detonation sensitivity. From this result, it is possible to conclude that boron compounds such as zinc borate have no effect on the nitrogen concentration of ammonium nitrate when added at very low concentrations such as 0.1%.

Furthermore, Figures 4 and 5 show the results of an ion chromatography study, the quantity of boron metal dissolved in ammonium nitrate during the production process, and the amount of borate in the solution atmosphere. It is recognized that, in relation to the overall amount of boron that the plant is capable of absorbing, the amount of boron in all the compounds will not have a hazardous effect (Figures 7, 8). When the ion chromatography results are examined, it is understood that there is no decrease in the nitrogen content of ammonium nitrate with the addition of boron compounds, and the concentrations of ammonium and nitrate ions remain constant (Figure 7, 8).

Furthermore, since no distinct double salt production is seen, it may be said that boron compound functions well in this regard. When the nitrogen contents of ammonium nitrate fertilizers were chemically analyzed after production, it was observed that they changed at negligible levels (<0.1%) during the 1-month storage period (Table 2). In order to maintain the long-term use of plant fertilizer's nitrogen content and the commercial values of nitrogenous fertilizers, this circumstance is thought to be crucial.

The ammonium nitrate generated has a nitrogen concentration that the plant can use, as evidenced by the ion chromatography results, which show that the boron compounds introduced to the process at the dilution step do not appreciably diminish the nitrogen concentration of the ammonium nitrate. Since boron has the heavy metal feature of toxicity[21], it can be said that the amount of boron provided to the process won't have a harmful effect. The boron is added at a rate of 0.1%, which is less than the boron content required by the plant. Furthermore, in order to lower the ammonium nitrate's detonation enthalpy, the impact of boron compounds added to the reaction medium was assessed in this work using DSC analysis. According to DSC pictures, the effect of adding 0.1 percent magnesium nitrate, and 0.01 percent zinc borate to the reaction medium in experimental investigations is in the direction of lowering exothermic peaks (Figure 6). However, samples of ammonium nitrate seem to yield a totally endothermic peak when all two chemicals are put to the same reaction media.

When the DSC analysis of pure ammonium nitrate is examined, ammonium nitrate produced very exothermic peaks during decomposition, while ammonium nitrate with zinc borate and magnesium sulfate added produced mainly endothermic peaks during decomposition (Figure 9).

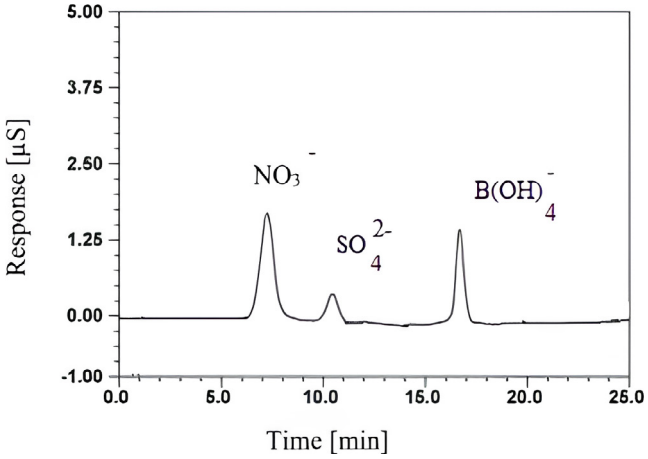


Figure 7 Anion analysis of ammonium nitrate with zinc borate and magnesium sulfate added.

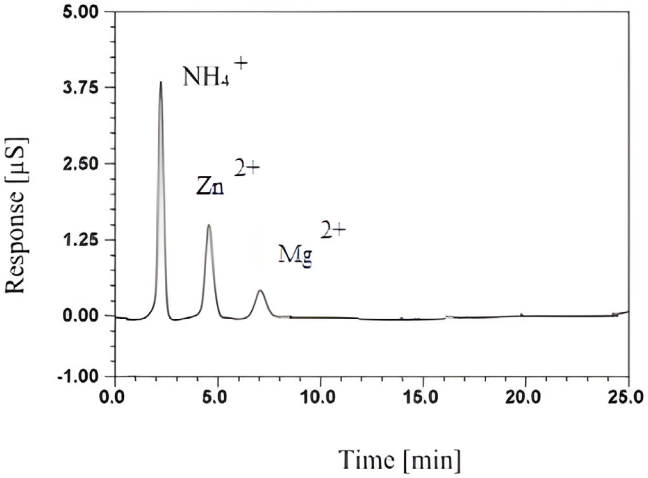


Figure 8 Cation analysis of ammonium nitrate with zinc borate and magnesium sulfate added.

In the Thermogravimetric (TGA/DSC) analysis to understand the effects of zinc borate and magnesium nitrate additions on the reaction medium to reduce the reaction enthalpy of ammonium nitrate, an endothermic peak value of 342 $J \cdot g^{-1}$ was observed at 153°C. This can be expressed as the effect of zinc borate on the enthalpy value of ammonium nitrate. On the other hand, in the study conducted to determine the reaction temperature of ammonium nitrate doped with zinc borate and magnesium nitrate, another endothermic peak of 365.1 $J \cdot g^{-1}$ was observed at 239°C. This can be expressed as the effect of the addition of magnesium nitrate on the enthalpy value of

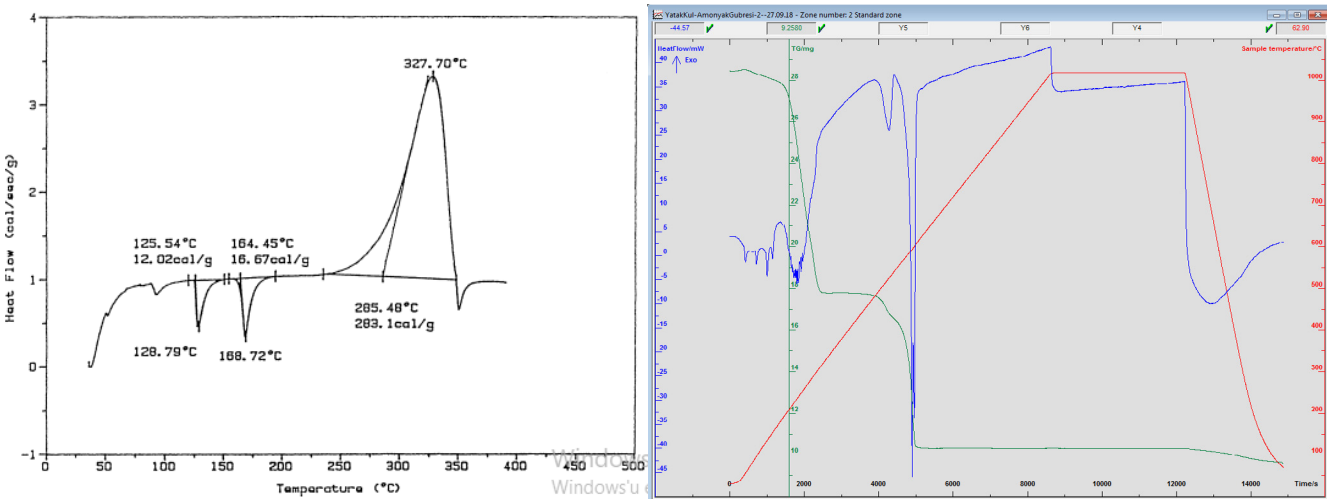


Figure 9 a) DSC analysis of pure ammonium nitrate, b) Thermogravimetric (TGA/DSC) analysis of ammonium nitrate doped with zinc borate and magnesium sulfate.



Figure 10 Cylindrical surface deformation as a result of explosion test.

ammonium nitrate. Because only the effect of magnesium nitrate on the decomposition of pure ammonium nitrate results in an endothermic peak value of 400.2 $J \cdot g^{-1}$.

The fact that boron compounds in the ammonium nitrate DSC analysis continue to show endothermic peaks shows that boron compounds are an effective choice to create endothermic peaks even with the possible temperature increase during the reaction of ammonium nitrate, which is the main purpose of the study.

The ammonium nitrate samples created by the addition of boron compound did not exhibit a substantial deformation in the detonation test tube volumes, as a result of the decrease in the severity of the explosion (Figure 10).

These findings are similar to those obtained in the DSC study. This leads to the conclusion that the chosen boron compound are suitable substitutes for ammonium nitrate in order to lower its detonation enthalpy.

It can be concluded from the TGA analysis that the boron compound added in the dilution step will not have a toxic effect even if the boron element remains in it as a result of the combustion reaction because of the endothermic effect they have on the ammonium nitrate, taking into account the mass losses of the nitrate in the combustion reaction.

There is no indication that borate has a harmful effect in Figure 6. Nevertheless, throughout the combustion reaction, it was mentioned how ammonium nitrate affects thermal energy[22]. Furthermore, the impact of borate compound on combustion reactions and the breakdown of ammonium nitrate can be investigated in relation to mass loss. It is significant how borate compounds affect thermal decomposition of ammonium nitrate. The mechanism of action shown in green in Figure 6 shows the mass loss of the borate compound due to the thermal decomposition of the ammonium nitrate material. The quantity of mass loss makes sense given that the borate component has a decomposition-slowing effect. The least amount of mass lost during the combustion reaction can be used to evaluate how much ammonium nitrate breaks down because the chemicals utilized lessen the nitrate's inclination to break down. However, when evaluated in terms of its compounds, boron can be considered as a metalloid with toxic properties and since it is used in less than the amount needed by the plant, the amounts in the decomposition process shown in green in Figure 6 will not create a toxic effect for the boron compounds that will be formed.

In order to reduce the thermal energy released during the explosion, zinc borate and magnesium nitrate were used as diluents during the production of ammonium nitrate in this study. Additionally, both of the three salts are used alone to limit the tendency of ammonium nitrate to form double salt. The porous structure of ammonium nitrate is one of the parameters that triggers the explosion event or accelerates the explosion process already. Therefore, its use as a salt, similar to the reduction of the number of pores and particle diameter, can be considered as a phenomenon that reduces the intensity of the explosion. The use of boron compounds as diluents in the ammonium nitrate production process is also a good development, because boron compounds such as zinc borate increase the crushing strength of ammonium nitrate, preventing it from deteriorating in storage

environments. According to this evaluation, ammonium nitrate is commercially conserved since it satisfies the 2-year storage life[23], during which the degradation characteristics are reduced. In this scenario, it is determined that the ammonium nitrate containing boron compound is exclusively suitable for use in agriculture.

4. Conclusions

As a metalloid compound, the internal addition of boron compound such zinc borate to the ammonium nitrate production process is not being researched.

Nonetheless, an essential production alternative has been provided by the process's development and the discovery of these compounds' beneficial effects on ammonium nitrate's physicochemical qualities, which decrease issues like degradation, caking, and unintentional use.

This means that it provides a different approach and technique for researchers to work on and enhance the preservation of ammonium nitrate's commercial value, such as nitrogen loss, to set standards for long-term storage procedures, and to reduce the amount of non-agricultural use by lowering detonation sensitivity.

An important alternative in ammonium nitrate production can be suggested because of the metalloid properties of boron compound and the distance approach to the process in this regard, which can help to minimize the nitrate losses of ammonium nitrate fertilizers and quantitatively be added to the process not more than the needs of the plant. This study, which involves measuring crushing strength and a series of thermal and chemical analyses, offers significant possibilities for resolving the ammonium nitrate-related issues.

Due to the metalloid properties of the boron compound and the fact that it can be added in the dilution stage without any pretreatment to the production process, an important alternative can be suggested in ammonium nitrate production. However, the decomposition rate of the boron compounds used in the study during the heat treatment can be associated with the dissolution rate of ammonium nitrate in the soil. This situation, together with the use of ammonium nitrate in agricultural areas, can positively affect the slow release mechanism. The addition of 0.1% zinc borate in ammonium nitrate production, which is the subject of this study, does not create any toxic effects on plant development, and can also be shown in greenhouse and field studies. This situation can be the focus of possible future research studies on boron compounds. Making important choices for resolving the aforementioned ammonium nitrate concerns involves testing physical characteristics using physical methods like measuring crushing strength and conducting a series of thermal and chemical analyses during the study.

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