Effect of Silicate, Carbonate, Calcium Lignosulphonate, and Silicic Acid Additives on Ammonium Nitrate Degradation

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Abstract
Ammonium nitrate is the most commonly used nitrogen fertilizer in the agriculture and plays an important role in the development of leaves and stems in plants. The storage and production of ammonium nitrate at the industrial scale can result in degradation and caking. Various solutions have been proposed, however, to date, an effective solution to the degradation problem has not been identified. The addition of silicic acid during the production of ammonium nitrate prevents the double salt formation caused by sulphuric acid additive, which is a process requirement. Silicic acid was combined with calcium carbonate in the dilution stage in order to increase the fracture strength of ammonium nitrate. With the addition of calcium lignosulphonate, the phase conversion of ammonium nitrate granules was completed more rapidly, and thus the problem of degradation was prevented. Thus, chemical and physical degradation of the ammonium nitrate structure were prevented during the 2-year storage period, which was adopted as the standard for the ammonium nitrate production process.

Keywords
Ammonium nitrate, degradation, caking, calcium lignosulphonate, silicic acid, limestone

1 Introduction
Ammonium nitrate is typically commercially produced with a nitrogen content of 26 % or 33 %. Reduction in the nitrogen content is achieved by adding limestone (calcium carbonate) during the production process of ammonium nitrate. Reducing the nitrogen content limits the moisture withdrawal properties of ammonium nitrate, but long-term storage (> 1 year) of this product is not successful. Therefore, different chemicals are included in the process to prevent degradation of ammonium nitrate.

Some important compounds that have been studied are calcium trialkylamine, potassium dimethyloctylamine, dimethyl decylamine, and dimethyl laurylamine. These salts were found to significantly affect the crystalline structure of ammonium nitrate. In another study, ammonium sulphate and urea were used to prevent crystallization of ammonium nitrate over a two-year period. This process was also found to improve the fracture strength.

Yet another study found that adding ammonium sulphate reduced the nitrogen content in ammonium nitrate by 21 %, thus mitigating the degradation problem significantly. However, this nitrogen ratio does not meet consumer’s expectations, and an application for this product could not be found. The addition of potassium chloride solution to the solution medium of potassium nitrate improves dusting characteristics. Thus, the effect of mineral content on the degradation characteristics of ammonium nitrate during its use as chemical fertilizer has been described. The addition of magnesium ammonium phosphate hexahydrate to ammonium nitrate solution containing urea was found to improve the moisture-withdrawing properties of ammonium nitrate.

The effect of phosphoric acid on the degradation characteristics of ammonium nitrate has been studied, and it has been reported that crystal bridges do not form in solid ammonium nitrate particles over the six months storage period when phosphoric acid is added. On the other hand, trace elements such as sulphates, oxysulphates, nitrates, borates, and chlorides were reported to improve the properties of ammonium nitrate. In addition, the effect of monoammonium phosphate on physical properties such as moisture tension and fracture strength has been reported.

The physical form of ammonium nitrate affects its dehumidification properties. Therefore, prilling or granulation in the production process provides important information on the crushing strength of ammonium nitrate, a degradation parameter. It was found that the urea solution increased fracture strength, while ammonium nitrate had a significant effect on crystal bridges. It is understood that the ammonium ions in urea act as a stabilizer in ammonium nitrate and, therefore, have a significant effect on correcting the degradation problem. NH4 groups in urea have been reported to inhibit water diffusion by reacting with sulphate ions during the production process. Besides, it is observed that added phosphate salt solutions provide an important storage mechanism for dilution up to 40 % concentration.

The 2-year period is the standard period for the degradation problems of ammonium nitrate to become evident. To avoid this problem, the working performance of all recommended chemicals was evaluated. The effect of chemicals, such as sodium sulphate, on the degradation
of ammonium nitrate was measured by observation over a two-year period. In addition, the porous structure of ammonium nitrate triggered the problem of degradation; it was detected by the manufacturer of urea. The crystalline structure was also examined as a parameter affecting the degradation of ammonium nitrate, and changes in the crystalline structure were investigated with the physicochemical properties of ammonium nitrate at various temperatures.

The decomposition of ammonium nitrate should be analysed accurately. Various methods have been developed for this purpose, such as the Classical Nucleation Theory (CNT) model. For the CNT test method, humidity must be between 0 – 60 % and temperature at 25 °C. The experimental conditions in the present study were relative humidity ranging from 65 to 73 % and air temperature ranging from 24 to 35 °C. Due to the ambient conditions, the CNT model was not suitable, and instead, 6 pieces of 50 kg ammonium nitrate samples were stacked and subjected to a caking test.

In the present study, ammonium nitrate was produced in HNO₃ (w = 55 %), using anhydrous ammonia, limestone, and sodium silicate as dilution stage chemicals in the two-stage ammonium nitrate production process. However, sulphuric acid was used to minimize the amount of carbon dioxide formed by the addition of limestone. Silicic acid was used to reduce the formation of a double salt through the reaction of sulphate ions in sulphuric acid with nitrate ions.

During granulation of the final ammonium nitrate solution through the prilling process, calcium lignosulphonate was added as binding salt solution to complete the phase laying of ammonium nitrate during the cooling period.

2 Materials and methods

During ammonium nitrate production, nitric acid (w = 55 %), anhydrous ammonia, H₂SiO₄, H₂SO₄, Na₂SiO₃, and limestone were used as raw materials.

2.1 Production process and operating conditions

In two-stage ammonium nitrate production, under the conditions of 10 °C and 12.5 kg cm⁻², anhydrous ammonia is gassed by heating to 20 °C, 5.6 kg cm⁻² via an evaporator. Under the same conditions, ammonia is reacted with liquid nitric acid (w = 55 %) at approximately 50 °C to obtain a maximum of ammonium nitrate solution (w = 85 %). At the first stage, the solution is concentrated to 94 % (w/w) and then to 99.7 % by vacuum application. It is then diluted with the addition of limestone to produce commercially developed ammonium nitrate with 26 % or 33 % nitrogen content. Calcium carbonate addition causes carbon dioxide gas formation during solution formation, which leads to foaming in the solution tank. To minimize this foaming problem, sulphuric acid (max. w = 1 %) is added to the ammonium nitrate reaction medium. Although ammonium nitrate produced in this way seems to be smooth, it has been shown that double salt formation (nitrate-sulphate) is another factor that triggers the degradation problem under storage conditions. To minimize this double salt formation, it is necessary to remove the sulphate ions from the solution medium. In the experiments conducted here, H₂SiO₄ was used to eliminate sulphate ions (1 ml H₂SiO₄/5.6 ml H₂SO₄) (Fig. 1).

Commercially produced pure ammonium nitrate contains 35 % nitrogen. Commercially, the preferred ammonium nitrate fertilizer is the calcium ammonium nitrate fertilizers

![Fig. 1 - Two-stage vacuum ammonium nitrate production process](image-url)
with 26 \% and 33 \% nitrogen content. Limestone is added at the dilution step during the production of ammonium nitrate. For 26 \% nitrogen content, limestone is added at a rate of 25 \%, and 60 kg of limestone in ammonium nitrate with 33 \% nitrogen content.\textsuperscript{27} In this study, 1 \% sulphuric acid was used to minimize the excess carbon dioxide production that is caused by the addition of limestone.

2.2 Electron microscopy analysis

A Carl Zeiss DSM-960A electron microscope was used for surface analysis of the ammonium nitrate particles obtained by the two-stage production process. Electron microscopy analysis was conducted by using the ASTM E986-97 standard. Device analysis parameters were determined as follows: accelerating voltage 1–30 kV; useful magnification 10–30000 ×; resolution 70 Å.

2.3 Ion chromatography analysis

In this study, analysis of anions and cations in ammonium nitrate particles was carried out using ion chromatography to determine and monitor double salt formation, which triggers degradation during post-production storage. The analysis was performed according to the ASTM E1151-93 standard, using a Shimadzu Prominence HIC-Nssn system. The working parameters were conductivity 0.01–51200 μS cm\(^{-1}\), and flow rate of 0.001–5 ml min\(^{-1}\).

2.4 Screen sieve analysis

The desired standard particle size desired in the fertilizer production process is 2 mm. However, owing to the geometrical structure of the equipment used for prilling, a particle size of 2 mm is often not uniformly obtained. The equipment hole diameter and conical shape can be increased to 3.35 mm depending on the speed. The particle size distribution obtained in the granulation process was performed using an electronic shaker in the fertilizer industry. In this study, the vibratory sieve shaker AS 200 was used as an electronic shaker, and the analysis was performed according to the ASTM E11-09.\textsuperscript{27}

2.5 Analysis of sulphate

The formation of a double salt is possible during the production process in the presence of sulphate ions. It is important to quantitatively know how \( \text{H}_2\text{SO}_4 \) which is the sulphate source, behaves during the production and storage processes. To determine the sulphuric acid content in the ammonium nitrate product, the fertilizer sample is prepared by diluting with 10 ml of HCl, 50 ml of \( \text{H}_2\text{SO}_4 \), and 300 ml of pure water. This mixture is boiled and 20 mg BaCl\(_2\) is added. After boiling, the mixture sits for 1 h, and then the solution is formed. The precipitate is washed with AgNO\(_3\) to remove any possible chloride ions. The precipitate obtained is baked for 1.5 h at 500 °C.

\[ S(\%) = n \cdot 0.137 \cdot \left( \frac{V_1}{V_2} \right) \cdot m \]  
\[ \text{SO}_4(\%) = S(\%) \cdot 2.5 \]  

\( n \): amount of barium sulphate in precipitation, \( V_1 \): sample volume, \( V_2 \): total volume, \( m \): sample mass.

2.6 Determination of silicic acid

To determine the amount of silicic acid required to minimize the effects of sulphuric acid in the ammonium nitrate fertilizer production process, 0.25 g of ammonium nitrate is heated at 500 °C for 1 h, and then 10 ml of hydrochloric acid (\( w = 50 \%) \) is added, which is further diluted with 100 ml of pure water. The water is then completely evaporated, and after the addition of 10 drops of HCl, 50 ml of water is added. The solution is sealed and filtered with No. 42 filter paper. Three drops of sulphuric acid are then added to the filter paper and left to cool for a half-hour at 1000 °C, followed by the addition of two drops of sulphuric acid. After the addition of 25 ml of hydrofluoric acid (\( w = 48 \%) \), the solution is diluted to 25 ml. The final solution was kept at 250 °C for 1 h, and then baked in an ash oven at 1000 °C for a half hour, left to cool, and weighed.

\[ \gamma(\text{SiO}_2)/\text{mg l}^{-1} = \left( \frac{\text{weight loss} \cdot 100}{V(\text{sample})/\text{ml}} \right) \]  

2.6.1 Calculations

\[ N(\%) = (50 - A) \cdot F \]  

\( N \) is the amount of nitrogen in percent in the ammonium nitrate sample analysed, \( A \) is the quantity of NaOH during volumetric analysis, and \( F \) is the dilution factor.

2.7 Analysis of nitrogen

For nitrogen analysis, 7 g of ammonium nitrate sample is diluted with 500 ml of pure water. 10 ml of this solution is then mixed with 50 ml of 20 % NaOH and titrated with sulphuric acid (\( w = 98 \%) \).

2.8 FTIR analysis of calcium lignosulphonate in ammonium nitrate

Fourier transform infrared spectroscopy (FTIR) analysis of ammonium nitrate was performed to determine the lignosulphonate salt content in calcium ammonium nitrate.
Lignosulphonate has an effect on the completion of physicochemical properties such as phase transformations of ammonium nitrate during the prilling process, and maintenance of this effect during the storage process is an important step to mitigate the degradation problem. This aforementioned observation was used for the analysis of device conditions in the FTIR and the Bruker spectrophotometer in the frequency range of 400–4600 cm\(^{-1}\) at 4 cm\(^{-1}\) with 32 co-addition scans. The spectra were analysed using Nicolet hardware, and analyses were performed using a KBr disk.

3 Results and discussion

During this study, 6 pieces of 50 kg ammonium nitrate samples were studied using the caking test at 24–35 °C, 1 atm, 65–73 % relative humidity after production and during storage.

Although different production processes of ammonium nitrate are provided in the literature, the most commonly used is the two-stage vacuum process. In this process, however, as shown in Table 1, many parameters such as pressure and temperature need to be controlled.

| Stage                        | Pressure / kg cm\(^{-2}\) | Temperature / °C |
|------------------------------|---------------------------|-----------------|
| ammonia evaporation          | 6.1                       | 15              |
| ammonium nitrate production reactor | 5.6                      | 125             |
| I. stage evaporation         | 3                         | 125             |
| II. stage evaporation        | 3                         | 175             |
| dilution with filler as CaCO\(_3\) | 1                        | 175             |
| prilling                     | 1                         | 175             |

In the two-stage vacuum ammonium nitrate production process, ammonium nitrate produced at 80 % concentration is concentrated to 94 % in the first stage, and 99 % in the other stage, during its reaction with anhydrous ammonia with 55 % HNO\(_3\). At this time, it can be diluted to commercially develop ammonium nitrate with 26 % and 33 % nitrogen content. In this study, 12.5 % calcium carbonate (limestone) and 12.5 % Na\(_2\)SiO\(_3\) has been added at the dilution stage of ammonium nitrate production process. When limestone is added, the conversion of carbonate to CO\(_2\) causes foaming in the solution. Therefore, to minimize foaming from the addition of carbonate, the addition of sulphuric acid is required. It has been observed that the addition of sulphate in the ammonium nitrate production process, to date, has led to the formation of sulphate-nitrate salts together with nitrate during storage, and accelerated the degradation of ammonium nitrate. Therefore, in this process, silicic acid was chosen as the chemical agent to eliminate sulphate ions.

Sulphuric acid-based sulphate ions on ammonium nitrate particles were analysed by SEM analysis (Figs. 2–4), and sieve analysis (Tables 2 and 3).

![Fig. 2](image1.png) – a) SEM images of ammonium nitrate that contains only limestone (w = 25 %); b) SEM images of ammonium nitrate containing calcium carbonate (w = 12.5 %), and sodium silicate (w = 12.5 %)

![Fig. 3](image2.png) – a) SEM image of ammonium nitrate particles, containing H\(_4\)SiO\(_4\) (1 ml silicic acid/5.6 ml sulphuric acid), calcium carbonate (w = 12.5 %), and sodium silicate (w = 12.5 %); b) SEM image of ammonium nitrate particles containing calcium carbonate (w = 25 %) after a two-year storage period

![Fig. 4](image3.png) – a) SEM image of ammonium nitrate, containing calcium carbonate (w = 12.5 %) and sodium silicate (w = 12.5 %) after two years of storage; b) SEM image of ammonium nitrate, containing silicic acid (1 ml silicic acid/5.6 ml sulphuric acid), calcium carbonate (w = 12.5 %), and sodium silicate (w = 12.5 %) after two years of storage

This study is unique in that instrumental analysis methods have been used, such as electron microscopy and ion
chromatography, to analyse the production of ammonium nitrate on an industrial scale. Owing to the moisture absorption potential and oxidative properties of ammonium nitrate, it is very difficult to maintain quality standards.\textsuperscript{27} This is because the physicochemical property of ammonium nitrate during the storage process depends on ambient temperature and relative humidity of air.\textsuperscript{16} To control this process, limestone and Na$_2$SiO$_3$ are added to complete the phase transformation in the reaction medium. Both chemical salts provide additional nutrients for the plant in soil applications. However, limestone and silicic acid have been found to play an important role in preventing the formation of crystal bridges, one of the most important parameters that accelerate the degradation process of ammonium nitrate. This process was analysed using electron microscopy and ion chromatography.

Sieve analysis of the particle size of ammonium nitrate was used to determine the product quality after a 2-year period; this is accepted as the standard procedure to measure the degradation process and was used to evaluate the performance of the chemicals used to mitigate degradation. In the sieve analysis, it was observed that the particle size of calcium-carbonate-doped ammonium nitrate (Table 2) was smaller than that of sodium-silicate-doped ammonium nitrate. The mean particle diameter was determined to be 2 mm when sodium silicate and calcium carbonate were added together (Table 3). Therefore, the best results, in terms of particle size, were obtained through the process in which both chemicals were added at the same ratio (12.5%).

With the addition of sulphuric acid, ammonium bridges are formed by hydrogen bonds in ammonium nitrate, and thus, double salts of nitrate-sulphate are formed.\textsuperscript{27} To minimize the concentration of sulphate-nitrate double salts, it is necessary to minimize the activity of sulphate in ammonium nitrate. Therefore, silicic acid was used. In the optimization studies, it was concluded that 1 ml of silicic acid removes 5.6 ml of sulphuric acid. As seen on the SEM images in Figs. 3b and 4b, sodium silicate produced less deformation on ammonium nitrate than on calcium carbonate under bulk storage conditions (0.28 kg cm$^{-2}$).

In another SEM analysis, as Figs. 2a and 3b show, the surface when calcium carbonate is added as the diluting chemical was observed. In addition, Figs. 2b and 4a show the SEM analysis results of the effect of adding calcium carbonate ($w = 12.5\%$) and sodium silicate ($w = 12.5\%$) to ammonium nitrate.

The effect of $H_2SiO_3$ on the elimination of sulphuric acid is shown in Figs. 3a and 4b. In this case, the perfect surface features are obtained in the process in which Na$_2$SiO$_3$, limestone, and $H_2SiO_3$ are added. Crushing strength, another quality parameter, is listed in Table 3. The crushing strength of ammonium nitrate containing Na$_2$SiO$_3$, limestone, and $H_2SiO_3$ is better than that containing only limestone (Table 2).

In the present study, the effect of silicic acid on double salt was found to be beneficial in the two-year storage period, and it created no deformation of the ammonium nitrate particles. In ion chromatography (Figs. 5a and 5b), the effect of silicic acid on the elimination of sulphate ions is observed. Ion chromatography also shows the results of the anion and cation analysis of the ammonium nitrate solution. According to these results, the nitrogen loss in ammonium nitrate particles is negligible during the two-year storage period, with no loss in quality.

A different number of trials were performed for the various parameters indicated in this study. For example, when the amount of sodium silicate exceeds 12.5%, the particle size of ammonium nitrate decreases and the proportion of particles of an average diameter of 2 mm, which is accepted as a standard by the EFMA, falls below 75%.

Another chemical additive used in this study was calcium lignosulphonate. The effect of calcium lignosulphonate on the acceleration of the phase conversion of ammonium nitrate during prilling was positive. This effect was observed in the FTIR analysis, in which it was shown to significantly

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**Table 1** – Screen sieve analysis for ammonium nitrate containing only calcium carbonate at the end of the two-year storage duration

| Time period     | 3.35 mm | 2.5 mm | 2.0 mm | 1.0 mm | 0.5 mm | U.S. / mm | Crushing strength | SO$_4^{2-}$/ppm | N/%   |
|-----------------|---------|--------|--------|--------|--------|-----------|------------------|-----------------|-------|
| Final production| 5.6     | 42.9   | 33.9   | 17.5   | 0.1    | 0         | 2.27             | 6.5923          | 26.70 |
| Final production after two years | 5.3     | 41.7   | 37.2   | 14.8   | 1.0    | 0         | 1.83             | 6.5552          | 26.42 |

**Table 2** – Screen sieve analysis for ammonium nitrate containing only calcium carbonate at the end of the two-year storage duration

| Time period     | 3.35 mm | 2.5 mm | 2.0 mm | 1.0 mm | 0.5 mm | U.S. / mm | Crushing strength | SO$_4^{2-}$/ppm | N/%   |
|-----------------|---------|--------|--------|--------|--------|-----------|------------------|-----------------|-------|
| Final production| 8.3     | 49.2   | 40.1   | 2.1    | 0.3    | 0         | 2.35             | 1.0004          | 26.49 |
| Final production after two years | 7.7     | 50.0   | 38.1   | 3.4    | 0.8    | 0         | 2.21             | 0.9952          | 26.25 |

**Table 3** – Screen sieve analysis for ammonium nitrate containing calcium carbonate (12.5%), sodium silicate (12.5%), and silicic acid (1 ml silicic acid/5.6 ml sulphuric acid), and analysis at the end of the two-year storage duration

| Time period     | 3.35 mm | 2.5 mm | 2.0 mm | 1.0 mm | 0.5 mm | U.S. / mm | Crushing strength | SO$_4^{2-}$/ppm | N/%   | SO$_2$/ppm |
|-----------------|---------|--------|--------|--------|--------|-----------|------------------|-----------------|-------|-----------|
| Final production| 8.3     | 49.2   | 40.1   | 2.1    | 0.3    | 0         | 2.35             | 1.0004          | 26.49 | 0.1765    |
| Final production after two years | 7.7     | 50.0   | 38.1   | 3.4    | 0.8    | 0         | 2.21             | 0.9952          | 26.25 | 0.1756    |
retard degradation (Fig. 6). Lignosulphonate served as a filler material in the porous structure of ammonium nitrate after the addition of Na$_2$SiO$_3$ and limestone; it was found to have an enhancing effect on the crushing strength by minimizing the surface cracks.

The function of calcium lignosulphonate addition in this study can be interpreted in various ways. With the addition of calcium lignosulphonate to the ammonium nitrate production process during granulation, the phase conversion of ammonium nitrate can occur more rapidly, causing it to complete, cool, and reach atmospheric conditions faster. When the concentration of calcium lignosulphonate was less than 0.5 %, it was found that the solidification process was not sufficient during the transition of ammonium nitrate from the liquid (molten) state to the solid phase, and thus phase conversion could not be completed sufficiently. When the calcium lignosulphonate concentration exceeded 0.5 %, it was found that larger particles had formed during granulation, which tends to adhere to the granulated/prilled ammonium nitrate particles.

4 Conclusion
In this study, the effect of Na$_2$SiO$_3$, limestone (calcium carbonate), silicic acid, and calcium lignosulphonate on ammonium nitrate produced by the two-stage vacuum concentration process was analysed with the aim of eliminating degradation and caking, which are considered the major problems in the production and use of ammonium nitrate at an industrial scale. Analyses using SEM, ion chromatography, sieve analysis, and FTIR were conducted. The selected chemicals are easily accessible and inexpensive. In this study, 12.5 % calcium carbonate, 12.5 % sodium silicate, 1 ml silicic acid, 5.6 ml sulphuric acid, and 0.5 % calcium lignosulphonate were used.

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SAŽETAK
Utjecaj silikata, karbonata, kalcijeva lignosulfonata i aditiva silicijeve kiseline na razgradnju amonijeva nitrata
Ahmet Ozan Gezerman

Amonijev nitrat najčešće je dušično gnojivo u poljoprivredi i ima važnu ulogu u razvoju lišća i stabljika. Skladištenje i proizvodnja amonijeva nitrata u industrijskim razmjerima može rezultirati razgradnjom i stvrdnjavanjem. Predložena su razna rješenja, međutim do danas nije pronađeno učinkovito rješenje problema razgradnje. Dodavanje silicijeve kiseline tijekom proizvodnje amonijeva nitrata sprječava stvaranje dvostruke soli uzrokovano dodatkom sumporne kiseline, što je preduvjet postupka. Silicijska kiselina kombinirana je s kalcijevim karbonatom u fazi razrjeđivanja kako bi se povećala čvrstoća amonijeva nitrata. Dodavanjem kalcijeva lignosulfonata brže je dovršena fazna pretvorba granula amonijeva nitrata, čime je spriječen problem razgradnje. Dakle, spriječeno je kemijsko i fizičko propadanje strukture amonijeva nitrata tijekom dvogodišnjeg skladištenja, što je prihvaćeno kao standard za postupak proizvodnje amonijeva nitrata.

Ključne riječi
Amonijev nitrat, razgradnja, stvrdnjavanje, kalcijev lignosulfonat, silicijeva kiselina, vapnenac

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Izvorni znanstveni rad
Prispjelo 12. srpnja 2019.
Prihvaćeno 7. rujna 2019.