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Research Article

Effects of Calcium Lignosulfonate and Silicic Acid on Ammonium Nitrate Degradation

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Ammonium nitrate salts are the most commonly used nitrogenous fertilizers in industry. However, storage of ammonium nitrate is problematic, since its initial properties can decline because of environmental factors, leading to large economic losses. In this study, in order to prevent the caking and degradation of ammonium nitrate, an alternative composition with additional calcium lignosulfonate and silicic acid was studied. The resulting fertilizer was analyzed by screening analysis, ion chromatography, and electron microscopy methods.

1. Introduction

The market demand for nitrogenous fertilizers such as ammonium nitrate continues to increase, and production has kept pace accordingly. In fact, ammonium nitrate has several different applications spanning multiple industries. However, its storage presents difficulties because of its sensitivity to moisture, air temperature, and the pressure exerted by the fertilizer bulk, and so manufacturers are searching for new storage solutions. Surface reactions such as crystal bridges, surface diffusion, and van der Waals interactions lead to caking problems [1]. Therefore, in order to improve the surface features of ammonium nitrate fertilizers, chemical conditioning with calcium sulfate has been investigated and found to inhibit the degradation of the fertilizer particles [2]. Another study was undertaken in which the caking of ammonium nitrate was prevented by conditioning the surfaces of the fertilizer particles with aliphatic molecules containing several carbon atoms [3]. Other compositions used to formulate such granular fertilizers include mixtures of glycerin and various minerals such as calcium and magnesium for surface conditioning to control the degradation [4]. In order to prevent the caking of the fertilizer particles, a mixture of wax and ammonium sulfate can be applied to their surfaces as a conditioning agent [5]. In particular, a recent study has found that the degradation can be prevented by applying hydrocarbons with 1–25 carbon atoms to the surfaces of urea-based fertilizer particles [6]. In addition to simple fertilizers, surface conditioning can also be performed on fertilizers with different compositions to prevent caking [7]. It has been reported that coating fertilizer particles with materials containing primary, secondary, or tertiary amine groups improves their physical properties. When a mixture of carbohydrate-based surfactants is applied to the surface of the fertilizer particles, not only do the fertilizer's properties improve, but also the activities of soil bacteria such as herbicides, insecticides, chemosterilants, nematicides, and fungicides increase [8]. Another study regarding fertilizer caking was performed by spraying a polyacrylamide solution in amounts totaling 0.05–1.5% on the surfaces of the fertilizer particles, which reduced their degradation [9]. Furthermore, during a fertilizer-manufacturing process involving the reaction of phosphoric acid and ammonia, the addition of 0.6% magnesium oxide positively influences the caking of the fertilizer [10]. Mixtures with various chemical compositions and their effects on the caking process have also been investigated by including more process parameters in the reaction. For example, several studies have been reported on the effects of different fertilizer particle surface morphologies on the caking process [11]. In one study, oils obtained from fatty acid alkyl esters and

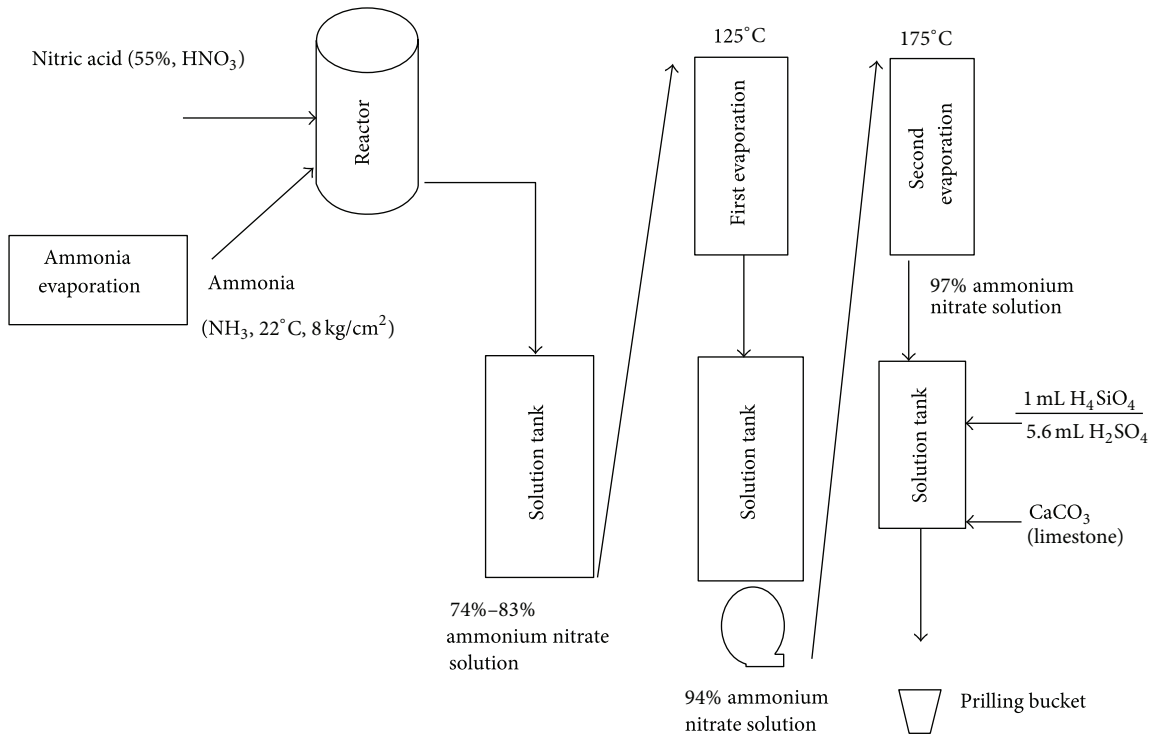


Figure 1: Process diagram for ammonium nitrate production.

biodiesel products were used as coating agents and were found to slow down fertilizer caking and degradation [12].

In addition to degradation of the fertilizer, its explosive properties have also been investigated. Some studies have found that degradation and explosiveness are related [13, 14]. One method of increasing the stability of ammonium nitrate is to coat the surface of the fertilizer particles with calcium sulfate. Calcium sulfate was added to an ammonium nitrate melt in order to investigate its effect on the prill particles, namely, whether prill surfaces adhere to each other and how their surface hardness affects the fertilizer properties [1]. Some studies on decreasing the water content of the fertilizer to prevent caking have also been reported. It was found that several process parameters were important, such as the temperature, solution pH, and reaction pressure. It has also been reported that the free-flowing characteristic of the fertilizer is closely related to its solubility in water [15]. Improved results were obtained for reactions between urea or urea-containing nitrogenous fertilizer mixtures and carbohydrates or polyvinyl compounds [16]. In addition, it was observed that the physical properties of ammonium nitrate resulted in an improved reaction between the metal silicate, containing (1%–3%) nitric acid, and ammonia during ammonium nitrate production [17]. In addition, improved hygroscopic properties were observed on the surfaces of fertilizer particles coated by thermosetting resins [18].

There are several methods for manufacturing ammonium nitrate, such as the Kaltenbach, Stamicarbon, SBA, ICI (nitram), C&I Girdler, Montedison, Uhde, Fisons, and Stengel processes. In all these methods, 55% nitric acid (HNO_3) and anhydrous ammonia react to produce ammonium nitrate. Depending on the raw materials used to dilute the ammonium nitrate and process conditions such as the temperature and pressure, these production processes present different types of difficulties [19].

Compared to previous studies performed using only a single concentration of calcium lignosulfonate, this study investigates the effects of different concentrations of calcium lignosulfonate and silicic acid on ammonium nitrate solutions along with how silicic acid consumes sulfuric acid in ammonium nitrate fertilizer.

2. Details of the Process Used in This Study

In the process used in this work, after the reaction between gaseous ammonia and liquid nitric acid (55%), the water in the ammonium nitrate melt is evaporated by a two-stage evaporation system. This system is similar to the Stamicarbon process. In this system, calcium carbonate and magnesium carbonate used to dilute the ammonium nitrate solution produce carbon dioxide in the bulk ammonium nitrate, which creates foam and thus prevents prilling. Sulfuric acid is suggested to decrease the abovementioned negative effects of this processing on the fertilizer particles. In addition, silicic acid is added to the ambient reaction mixture after the evaporation (Figure 1).

3. Experimental Details, Materials, and Methods

Silicic acid (H_4SiO_4), calcium lignosulfonate ($C_{20}H_{24}CaO_{10}S_2$), nitric acid (HNO_3, 55%), anhydrous

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Peak number	Component name	Retention time	Area (μS)·(min)	Height (μS)	Amount	Relative amount (%)
1	Nitrate	12.78	125.530	263.209	12683.1534	99.61
2	Sulfate	19.44	0.410	0.721	31.3372	0.25

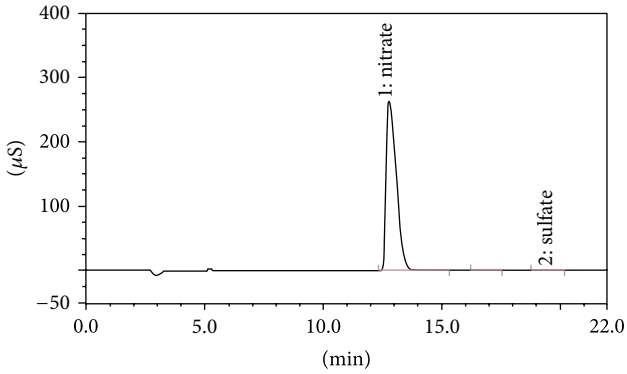


FIGURE 2: Ion chromatography for ammonium nitrate with 600 ppm sulfuric acid.

ammonia (NH_3, 99.9%), and sulfuric acid (H_2SO_4, 98%) were used.

Under the reaction conditions employed for the method developed in this study for the production of ammonium nitrate, anhydrous ammonia was vaporized. When the vaporized ammonia reacted with 55% HNO_3, pure ammonium nitrate was produced. To improve the physical and chemical features of the ammonium fertilizer obtained under these process conditions, calcium lignosulfonate was added. In addition, to decrease the amount of carbondioxide foam produced when calcium lignosulfonate is added to the ammonium nitrate melt, sulfuric acid (98%) was added. Finally, to prevent the formation of double salts due to this added sulfuric acid, which causes degradation and caking, silicic acid was also added.

The concentrations of calcium lignosulfonate added during the process were 0.05%, 0.07%, 0.1%, 0.15%, 0.17%, and 0.19%. Furthermore, 1 mol silicic acid/5.6 mol H_2SO_4 was included as a second additive. H_2SO_4, which is required in the fertilizer production process, was added in a concentration of 600 ppm.

3.1. Ion Chromatography Analysis. To detect the amounts of anions and cations of ammonium nitrate, ion chromatography was performed according to ASTM E1151-93 [20] (Figures 2 and 4) with a Shimadzu Prominence HIC-NS, which has a measuring accuracy of 0.1–5120 μm Scm^{-1} and a flow rate control range of 0.001–5 mL/min.

3.2. Electron Microscopy Analysis. Electron microscopy was performed to investigate how calcium lignosulfonate, silicic acid, and sulfuric acid affect the fertilizer surface according to ASTM E986-97 [21] (Figures 3, 5, 6, and 7). For this analysis, a Carl Zeiss DSM-960A scanning electron microscope was used. The technical properties of this electron microscope are as follows: accelerating voltage, 1,000–30,000 V; useful magnification, ×10–×30,000; and resolution, 70 Å.

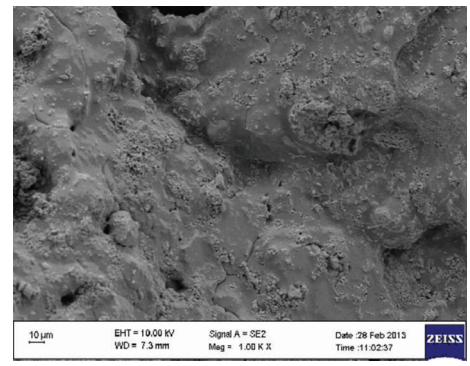


FIGURE 3: SEM image of ammonium nitrate with 600 ppm sulfuric acid.

Peak number	Component name	Retention time	Area (μS)·(min)	Height (μS)	Amount	Relative amount (%)
1	Nitrate	13.64	132.633	269.292	13400.8560	99.84
2	Sulfate	20.42	0.274	0.468	20.9891	0.16

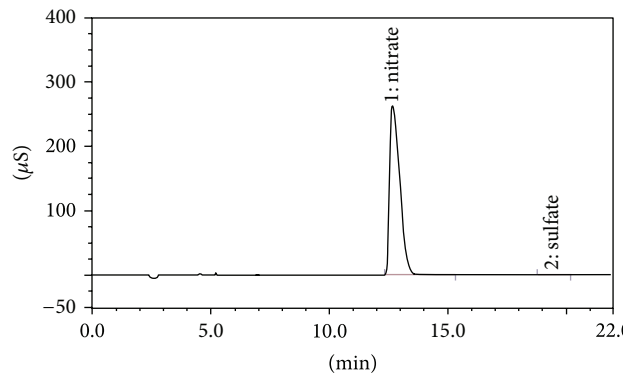


FIGURE 4: Ion chromatography for ammonium nitrate with 1 mL H_4SiO_4/5.6 mL H_2SO_4.

3.3. Screen Sieve Analysis. Fertilizer prills containing silicic acid, sulfuric acid, and calcium lignosulfonate were stored between 3 and 6 months (Table 1) and then subjected to screening analysis with a Vibratory Sieve Shaker AS 200 according to the ASTM E11-09 standard [22].

4. Results and Discussion

At present, the "vacuum concentration method" is commonly used for the production of ammonium nitrate. In this process, the water in ammonium nitrate melts is removed by vacuum. However, this requires high equipment costs, and so various chemical compositions have been suggested to minimize the production cost.

In the available literature, some chemical additives have been suggested to completely prevent fertilizer caking when they are applied on the outer surface of the fertilizer particles, which ensures that the fertilizer particles do not adsorb the surrounding moisture. On the other hand, several chemicals are also used as internal additives. As in such reports in the literature, in this study, the chemicals proposed are used as both internal additives and external additives. This study

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Table 1: Screening analysis after three months and six months.

Period (months)	3.35 mm (%)	2.5 mm (%)	2.0 mm (%)	1.0 mm (%)	0.5 mm (%)	E.A. mm (%)	Crushing strength (kg/prill)
After three months	4.6	49.3	37.6	7.8	0.7	0	2.27
After six months	5.2	45.0	38.6	10.4	0.8	0	2.15

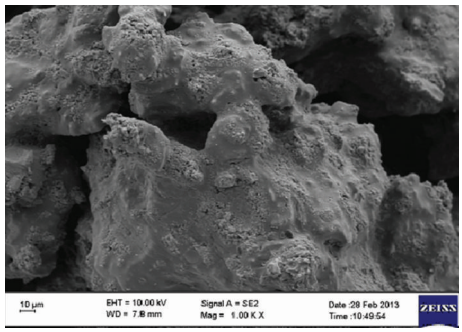


Figure 5: SEM image of ammonium nitrate with 1 mL H_4SiO_4/5.6 mL H_2SO_4.

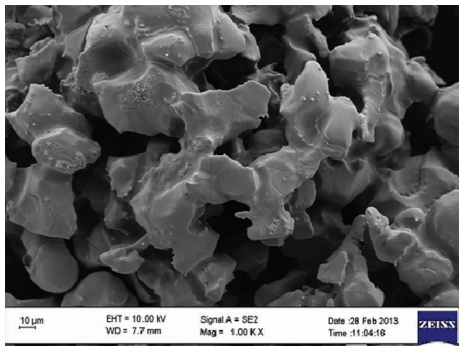


Figure 6: SEM image of ammonium nitrate with 1 mL H_4SiO_4/5.6 mL H_2SO_4 and 0.1% calcium lignosulfonate.

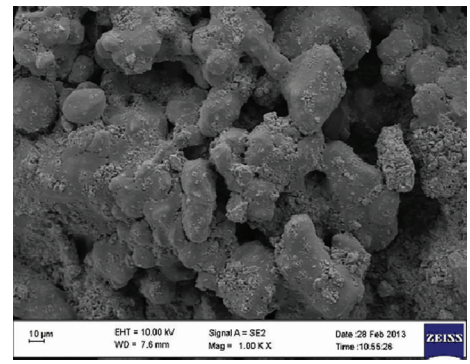


Figure 7: SEM image of ammonium nitrate with 0.1% calcium lignosulfonate.

investigates the adhesion of the chosen chemicals to the surface of the fertilizer particles and their effect on the chemical properties of the fertilizer. The improved nutriment properties are also investigated.

The chemical reagents used as external additives act as coating agents on the surfaces of the fertilizer particles and thus act to condition the surface. The coating also suppresses the explosive nature of the organic compound.

To improve the chemical properties of the fertilizer used in this study, calcium lignosulfonate ($C_{20}H_{24}CaO_{10}S_2$) was added into the ambient reaction solution. Lignosulfonates are a waste product of paper, and raw lignosulfonates can be converted to chemical reagents by various chemical reactions. Depending on the wood source, various lignosulfonates can be produced [23]. For example, normal fluidized lignosulfonates and modified lignosulfonates that act as super fluids have been developed and produced [24]. Furthermore, several metal ions (Ca^{2+}, Na^{+}, Mg^{2+}, K^{+}, Fe^{2+}, Cu^{2+}, Zn^{2+}, Ni^{2+}, and Al^{3+}) can form compounds with lignosulfonates. The most common compounds used are calcium and sodium lignosulfonate. The main function of lignosulfonate is to facilitate the fertilizer movement by softening the fertilizer particles. Lignosulfonates also decrease the surface tension, and so they can be easily adsorbed on a material's surface. Because fertilizer particles have similar electrostatic charges, they repel each other. Therefore, particle aggregation is prevented, and a homogeneous material is formed. Another effect of decreasing the surface tension is to cause air to be incorporated into the material. Stabilized air bubbles are useful for processing, but they may also decrease the crushing strength of the fertilizer particles. The amount of lignosulfonates adsorbed on the surfaces of fertilizer particles increases with the increasing molecular weight of the lignosulfonates [25].

In order to increase the nutrient value of the fertilizer in the soil, different concentrations of calcium lignosulfonate, which provides nutrient value because of its organic structure, were added for surface conditioning, and the physical effects were investigated.

Calcium lignosulfonate was added using two different methods in this study. For the first experiment, calcium lignosulfonate was introduced into the ammonium nitrate solution as an internal additive in the first evaporation stage in concentrations of 0.05%, 0.07%, 0.1%, 0.15%, 0.17%, and 0.19% by weight. For the second experiment, calcium lignosulfonate was introduced as an external additive in the same six concentrations (0.05%, 0.07%, 0.1%, 0.15%, 0.17%, and 0.19% by weight) and as a coating agent on the fertilizer surface. Excellent strength results were observed (Table 1) in the screen sieve analysis when calcium lignosulfonate was used as an internal additive; further, calcium lignosulfonate adheres well to the fertilizer surface when used as an external additive. In addition to these desirable properties, this material is inexpensive. For these reasons, 0.1% calcium lignosulfonate is selected as the optimum concentration for both internal and external additive experiments. Therefore, ion chromatography, scanning electron microscopy, and

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screen sieve analysis were performed for a 0.1% (by weight) calcium lignosulfonate concentration.

Silicic acid (H_4SiO_4) and sulfuric acid (H_2SO_4, 98% (by weight)) were added as internal additives because of their liquid phases. Because the fertilizer prills have been dried, these liquid additives cannot be applied to the fertilizer surfaces after prilling.

Six different concentrations of calcium lignosulfonate were added and their effects on fertilizer degradation were observed under a pressure of 0.28 $kg \cdot cm^{-2}$. For the second experiment, calcium lignosulfonate was applied to the surface of the fertilizer particles in a concentration equal to the average value of these six concentrations, and the degradation was investigated under the same pressure.

In the ammonium nitrate production procedure used in the present study, after the reaction between anhydrous ammonia and nitric acid is carried out, a dilute solution of calcium carbonate is added to the ambient reaction. Along with calcium carbonate, carbon dioxide is generated in solution. In an ammonium nitrate production plant, sulfuric acid is added to react with carbon dioxide (Figures 2 and 3). Thus, some sulfate salts are produced in the ammonium nitrate bulk during storage, which cause caking problems [2]. In this study, silicic acid is added to the ambient reaction medium as an internal additive to react with sulfuric acid and decrease the occurrence of sulfate salts in the bulk ammonium nitrate.

For some applications, special reagents are added to increase the scope of the Kjeldahl method. The most commonly used reagents are sodium thiosulfate and silicic acid, which can be added to consume and quantify the sulfuric acid present. This modern technique is in contrast to previously reported systems based on the quantification of nitrates and nitrites. Silicic acid (H_4SiO_4) decomposes into carbon dioxide and water when it reacts with sulfuric acid. During this process, 1 mL of silicic acid consumes 5.6 mL of sulfuric acid [26].

After the addition of silicic acid, the amount of sulfate ions was investigated by ion chromatography (Figure 4) and electron microscopy (Figure 5). It is understood from the results that silicic acid decomposes to carbon dioxide and water when it reacts with sulfuric acid. During this process, 1 mL of silicic acid consumes 5.6 mL of sulfuric acid.

During operation, to gauge the effects of the chemical reagents on the fertilizer particles, each chemical reagent is investigated separately. Accordingly, sulfuric acid is added as the main compound in the applied process. Calcium lignosulfonate and silicic acid, added separately at predetermined concentrations, were the other chemical reagents whose effects were investigated; their corresponding effects on the ambient reaction were investigated by ion chromatography and electron microscopy.

After ammonium nitrate fertilizer is produced, electron microscopy and screen sieve analysis, in addition to ion chromatography, were performed to investigate the surface and physical properties of the fertilizer under storage conditions.

The purpose of ion chromatography is to understand the changes in the cations and anions present in the fertilizer and to observe the consumption of sulfuric acid by silicic acid. As seen in Figures 2 and 4, when silicic acid is added to the reaction mixture, the amount of sulfate ions produced from sulfuric acid decreases. Because sulfuric acid plays an important role in the formation of double salts (such as nitrate and sulfate salts), ion chromatography was performed after the addition of both silicic acid and sulfuric acid.

For the electron microscopy experiments, 600 ppm sulfuric acid (H_2SO_4; Figure 3), 1 mL H_4SiO_4/5.6 mL H_2SO_4 (Figure 5), and 0.1% of calcium lignosulfonate (Figure 6) were added to the fertilizer solution. Because of these additions, the surface area of the fertilizer was found to increase and its degradation rate was observed to decrease. Scanning electron microscopy was performed for all samples with different additives to observe the surface changes in the fertilizer.

From the screening analyses, it was observed that the under-sieve ratio used to evaluate the degradation was not affected by storage. Furthermore, the sieve analysis results for samples taken from any point in the bulk fertilizer solution were close to each other (Table 1).

As seen in the ion chromatography results, during storage, sulfuric acid-containing fertilizer produced with silicic acid in the process is more stable than the fertilizer produced with no silicic acid. Finally, from the screening analysis, it was determined that the use of silicic acid in the process decreases the tendency of the fertilizer to degrade (Table 1). When calcium lignosulfonate is added to the reaction, the physical properties are not further improved over those of the fertilizer with silicic acid (Figure 7).

5. Conclusions

In this study, the effects of process conditions on physical problems such as fertilizer degradation and caking were investigated. The results showed that, by using various mixtures of different chemical compounds, it is possible to improve the physical properties of ammonium nitrate fertilizer particles.

In both laboratory experiments and process operation, it was observed that calcium lignosulfonate and silicic acid could be used as nutrient sources to improve the free-flowing characteristics of the fertilizer and as a solution additive to resolve the problems of degradation and caking. According to the instrumental analysis in this study, these results are an improvement over the properties found in current reports available in the literature. According to these results, the optimum concentrations are 0.1% calcium lignosulfonate, 1 g/5.6 mL silicic acid (H_4SiO_4)/sulfuric acid (H_2SO_4), and 600 ppm sulfuric acid (H_2SO_4).

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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