

Green Chemistry: Controlling the NO_x level

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Abstract

NO and NO₂ are hazardous gases for animals as well as for plants. They are known as NO_x and are needed to be controlled in order to save our environment. By reducing the ignition and combustion temperature and by applying other methods like catalytic decomposition and absorption, the formation of NO_x can be controlled. But in the present study, hazardous NO_x gas production has been controlled by applying the absorption method *en route* to its recycling process during synthesis of raw material like C@Al₂O₃ composite powder (required for the industrial synthesis of aluminum nitride powder by carbothermal nitridation). The principles of Green Chemistry were also followed in this process.

KEYWORDS: NO_x, Green Chemistry, Carbon Alumina Composite, Recycling.

Introduction

Among the major air pollutants produced mainly due to automobiles and industries are the oxides of nitrogen. The prevalent oxides of nitrogen formed at high temperatures are mainly NO₂ and NO, collectively written as NO_x, formed due to oxidation of N₂ ($N_2 + O_2 \rightarrow 2NO$, $2NO + O_2 \rightarrow 2NO_2$). The main sources of NO_x are *Internal Combustion Engines* (Combustion of Diesel Fuel or Gasoline in automobiles), *Natural Sources* (Extreme heat produced during large thunderstorms leading to reaction between aerial N₂ and O₂), *Biological sources* (Some bacteria can produce NO_x), *Power Plants* (Burning of fossil fuels like coal and natural gas to produce electricity) and *Industrial synthesis* (During synthesis of fertilizers, nylon, ceramic powders etc.) [1]. The effects of NO_x as pollutant are [2]: (i) creation of the pollutant acid rain causing hazardous impact on fish and wildlife and deterioration of stone building, (ii) formation of smog and contribution to the formation of other toxic chemicals such as O₃, PAN, Organic peroxides etc., (iii) Playing the role of one of the Greenhouse Gases and (iv) Hampering plant growth. The toxic effect of NO on human body resembles that of CO as, $Hb \text{ (Haemoglobin)} + NO \rightarrow HbNO$. But HbNO is much less stable than HbCO, hence NO is comparatively less hazardous. But the effect of NO₂ is lethal. The safety level of NO₂ is 0.05ppm. But intake of the same in higher concentration affects human body by damaging lungs and causing Broncholitis and even may lead to death on intake at 150-200 ppm concentration [3].

The extensive NO_x reduction techniques such as reducing the temperature of the ignition flame by means of steam flow, reducing the combustion temperature by making excess air flow, external flue gas re-circulation, air and fuel staging and water [4] and steam injection, catalytic decomposition of NO into N₂ and O₂ by using CuO, ZnO etc. [5] have already been employed. A noble attempt by utilizing the evolved NO_x collections for getting back the raw materials by means of absorption by suitable precursor (Fig.1) during synthesis of nanocomposites [6, 7, 8, 9] has been made in the present study.

The novelty of the present study is to make the industrial synthesis of Aluminum Nitride (AlN) environment friendly by controlling the evolution of NO_x

gases in one of the intermediate steps. AlN ceramics is finding wide applications in micro and opto electronic components, high voltage insulation and structural components for armour. It is a very good heat conductor and at the same time a very good electrical insulator. There are several methods available for synthesizing AlN powder out of which, carbothermal nitridation is the most commonly used and the cheapest method, and hence commercially exploited. It undergoes intimate mixing of carbon and alumina followed by nitridation and decarbonisation (burning out excess carbon). The latest method of intimate mixing is coating of alumina on carbon nano particles by heterogeneous nucleation in order to form C@Al₂O₃ composites [6]. Hazardous NO_x gases are produced during synthesis of this C@Al₂O₃ composite material. But since this technology has some novelty [7], the controlling of NO_x emission becomes very necessary.

Materials and Methods

The specifications of the raw materials used are presented in Table 1. Water, as it is safer to the environment, has been selected as the solvent instead of other organic solvents that could produce greenhouse gases.

The experimental flow diagram of synthesis of aluminum nitride powder by carbothermal nitridation of alumina is shown in Fig.2. The overall synthesis procedure of aluminum nitride powder has already been reported [4,5], where hazardous NO_x gases emitted during the “Drying” and “Pyrolysis” steps, were released to the atmosphere. In the present study, they have been passed through a colloidal suspension of aluminum hydroxide (4gm/250ml) with excess air flow during the course of their emission. The pH level of the supernatant, obtained by centrifuging the sol at 20k rpm, has been monitored at two temperatures (273K and 301K), by using the 335 Digital pH Meter of Systronics India Ltd., India. The centrifugation was done by R-24 apparatus of Remi Elektrotechnik Ltd., India.

DTA/TG analysis of the dried carbon@alumina composite sol (transformed via gelation) was carried out in order to investigate its decomposition temperature as well as to optimize the temperature for its drying and pyrolysis steps by using the STA409C apparatus of NETZSCH, Germany. In this operation, 79mg of the sample was taken in an alumina crucible and 68mg α -Al₂O₃ as reference was introduced into the DTA/TG furnace. These were heated from 298K to 1283K maintaining a heating rate at 10 K.min⁻¹ in protective (oxygen) gas flow. Temperature changes were monitored and compared with respect to a standard sample (α -Al₂O₃) to find out the DTA peaks whereas beam balance technique having an electromagnetic compensation set up was used to note the weight changes of the sample with respect to the standard sample (α -Al₂O₃).

Transformation of aluminum hydroxide into aqueous aluminum nitrate solution has been performed in the recycling plant designed as in Fig.3, where a 214.5 gm batch of the previously prepared carbon sol [6,7] was used in the heating and mixing unit. Before its drying and pyrolysis, the sol was sonicated at 20kHz (VPL-P-1 Ultrasonic Horn, Vibronics, India) and each batch of this sol was containing 11.2 gm carbon black, 1.12 gm of Tween80, 41.176 gm aluminum nitrate nonahydrate and 182.3 gm water.

The centrifugate (AO2, at 273K) at the middle of the absorption process was dried and undergone characterization by Fourier Transform Infra Red (FTIR) Spectrometry. The result was compared with the FTIR spectra of pure aluminum hydroxide powder (AO1). The FTIR experiment was carried out with the help of Perkin Elmer FTIR 1615 equipment. In this process the sample was mixed with KBr

by 1:300 (w/w) (approx.) ratio in an Agate Mortar followed by pressing under hydraulic press to prepare a pellet of 13 mm diameter. Then it was placed in a sample holder and the FTIR spectrograph was obtained from total 16 scans at a 4 cm^{-1} resolution. The percent transmittance (% T) was plotted against wave number from 4000 cm^{-1} to 400 cm^{-1} .

The supernatant after the absorption process completed was undergone evaporative crystallisation [10] and was characterised by X-Ray Diffraction (XRD) and elemental analyses. XRD of AO1, AO2 and purchased aluminum nitrate nonahydrate were also done for comparison. The XRD analysis was performed by taking 0.1gm of the solid samples in an Al sample holder with Cu-K α radiation ($\lambda=1.54056\text{ \AA}$) at 40 kV and 20.0 mA by using XRD Tool (X'Pert PRO, Phillips Analytical X-ray & B.V., Holland) and the Hydrogen and Nitrogen content of the synthesized Aluminum Nitrate crystals had been determined by introducing a small amount of sample in the sample holder crucible of an Element Analyser (Perkin Elmer, UK).

Results and Discussion

Decomposition of carbon@alumina composite powder shows an endothermic peak at 383.4K (Fig.4). The peak at 383.4K corresponds to the decomposition of nitrate to form oxides/hydroxides of aluminum. The temperature was thus optimized and the temperature of the heating and mixing unit was fixed above 383.4K.

The pH monitoring of the aluminum hydroxide sol has been described in Table 2, showing almost no change in pH after 180 minutes of run at 273K. The increase in the acidity level has been explained by the formation and increasing concentration of aluminum nitrate.

Trapping of NO_x has been confirmed via FTIR characterization of the centrifugate (AO2) where peak for nitrate at 1385 cm^{-1} has been detected (Fig.5). This confirmation was done by comparing the FTIR peak of raw aluminum hydroxide powder (AO1).

The crystals thus produced (3.6 gm crystals were recovered) by evaporative crystallization of the final supernatant (ANH) was analyzed qualitatively and was confirmed to be $\text{Al}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$ by characterization via XRD analysis (Fig.6.a). Two parameters viz. time and temperature has been varied to see the yield. The yield is directly proportional to time and inversely proportional to temperature. The optimum temperature of trapping NO_x was observed to be 273K (the lowest temperature limit for aqueous medium). The results of the Elemental Analysis (CHN) (C-0%, H-4.9%, N-11.1%) were at the vicinity to the theoretical weight percentage of hydrogen and nitrogen (H-4.8384%, N-11.20184%). This result confirms the formula of the synthesized product to be $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$.

As the reactions are taking place in presence of excess oxygen, it is assumed that unstable NO is oxidized into NO_2 that has passed through the basic aluminum hydroxide solution. N_2O_4 , the dimer of NO_2 has redox potential [12] of -0.86 Volt for $\text{NO}_3^-|\text{N}_2\text{O}_4$ system and +0.88 Volt for $\text{N}_2\text{O}_4|\text{NO}_2^-$ system favoring the conversion of nitrogen oxide into both nitrate and nitrite since the Gibbs Free Energy of the conversion $\text{NO}_3^- \rightarrow \text{N}_2\text{O}_4$ is positive (so the backward reaction takes place) while that of the $\text{N}_2\text{O}_4 \rightarrow \text{NO}_2^-$ conversion is negative (that is the forward reaction takes place). Nitrite converts into nitrate in oxygen atmosphere.

There are twelve principles of Green Chemistry [11], viz., (1) Prevention, (2) Atom Economy, (3) Less Hazardous Chemical syntheses, (4) Designing Safer Chemicals, (5) Safer Solvents and Auxiliaries, (6) Design for Energy Efficiency, (7)

Use of Renewable Feedstocks, (8) Reduce Derivatives, (9) Catalysis, (10) Design for Degradation, (11) Real Time Analysis for Pollution Prevention and (12) Inherently Safer Chemistry for Accident Prevention, out of which two (No.5 &7) are followed. As a result, the industrial application of this technology of synthesizing AlN powder becomes environment friendly.

Conclusion

NO and NO₂ are hazardous gases for animals as well as for plants. By reducing the ignition and combustion temperature and by applying other methods like catalytic decomposition and absorption, the formation of NO_x can be controlled. Selection of appropriate solvent and allowing the product gas to synthesis of raw materials *en route* to its recycling process reduces the chance of hazards. The principles of Green Chemistry can be followed by this way.

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Tables and Figures

Table 1: Specifications of raw materials as per manufacturers' data.

<i>Name of raw materials (Manufacturers)</i>	<i>Impurity content and other specifications</i>
H ₂ O (Eco Still Mark 1500 SQD, Qualigens Fine Chemicals, India)	Conductivity- 1 μ Siemens cm ⁻¹ .
C-black, N-110 Grade (Phillips Carbon Black Industries, India)	Impurity-Not Available Surface area-142m ² gm ⁻¹ , Particle Size-11nm
Polyoxyethylene(20)-sorbitanmonooleate (Tween80) (Aldrich Chemicals, USA)	-
Al(OH) ₃ (Aluminum Hydroxide Hydragylite); AR Grade (Merck KGaA, Germany)	Chloride (Cl) 0.01%, Sulphate (SO ₄) 0.05%, Iron (Fe) 0.01%, Sodium (Na) 0.3%.
Al(NO ₃) ₃ .9H ₂ O; (Aluminum Nitrate Nonahydrate) AR Grade (Merck Speciality Pvt. Ltd., India)	Chloride (Cl) 0.005%, Sulphate (SO ₄) 0.03%, Iron (Fe) 0.01%, Heavy metals (as Pb) 0.005%, Substances not precipitated by ammonia 0.5%

Table 2: pH monitoring of the supernatant collected at 273K and 301K.

<i>Sample Mark</i>	<i>Run time (Passing of NO_x)</i>	<i>pH of the supernatant at 273K</i>	<i>pH of the supernatant at 301K</i>
AO1	0 min	7.14	7.15
AO2	90 min	6.55	6.76
AON	180 min	6.22	6.34
ANH	240 min	6.20	6.23

Fig.1: Controlling the NO_x emission.

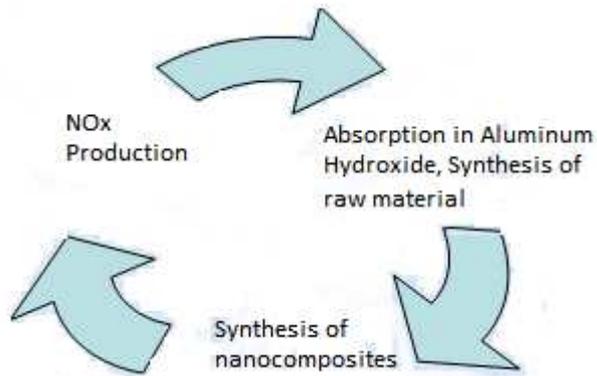


Fig.2: Experimental Flow Diagramme.

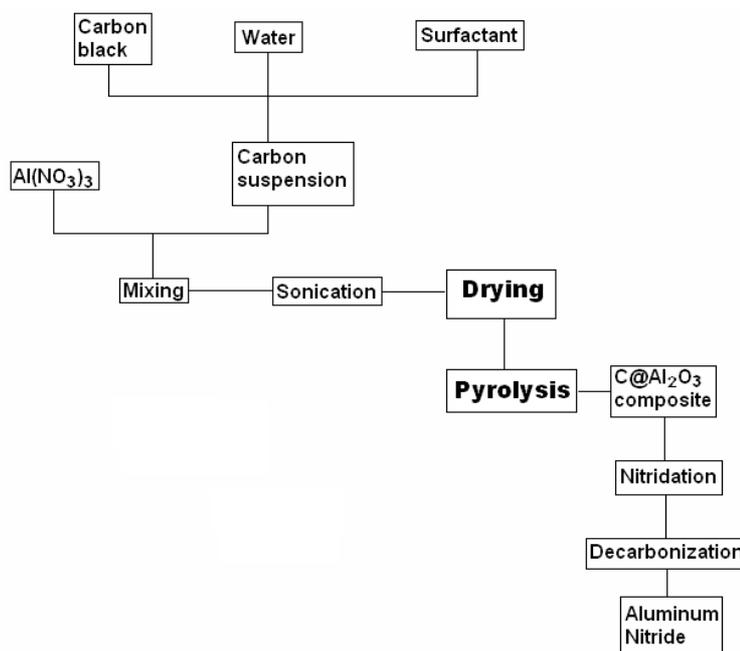


Fig.3: Schematic of the Recycling Unit

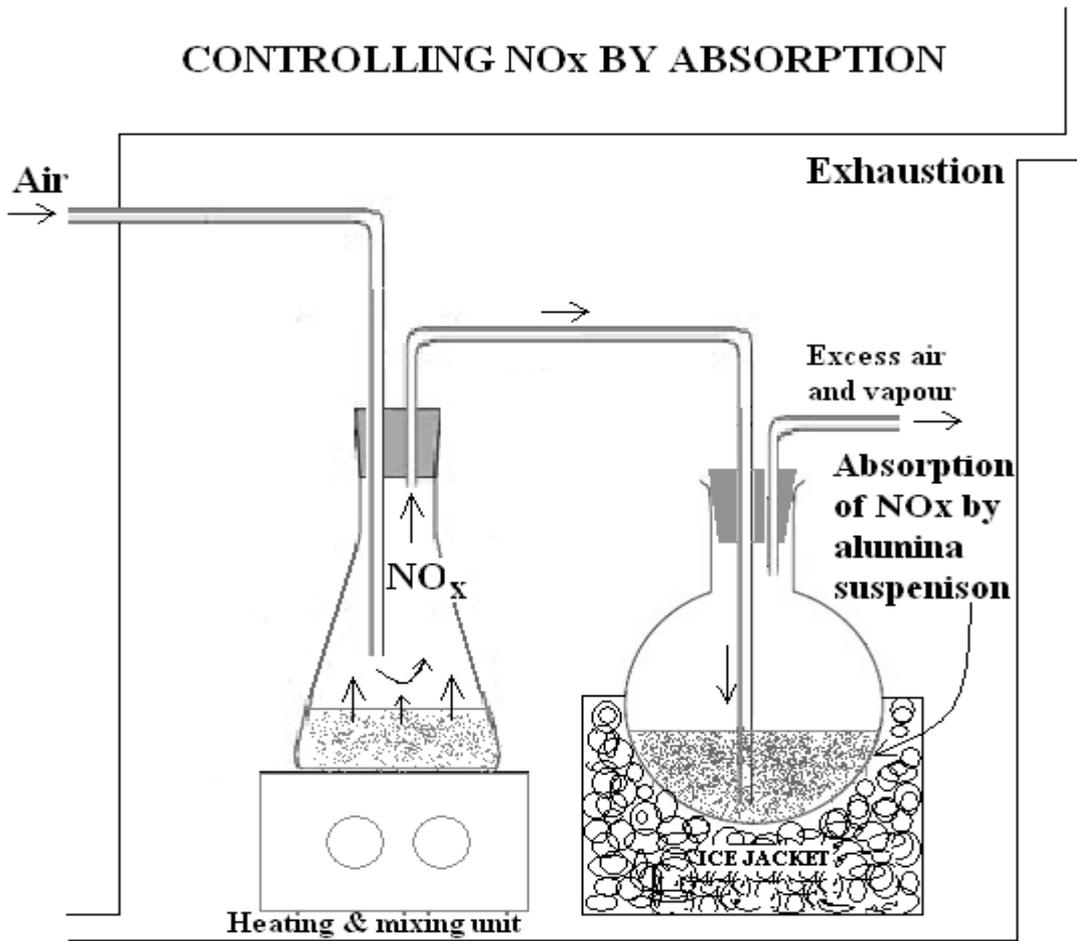


Fig.4: Result of the DTA/TG Analysis of the carbon@alumina composite powder

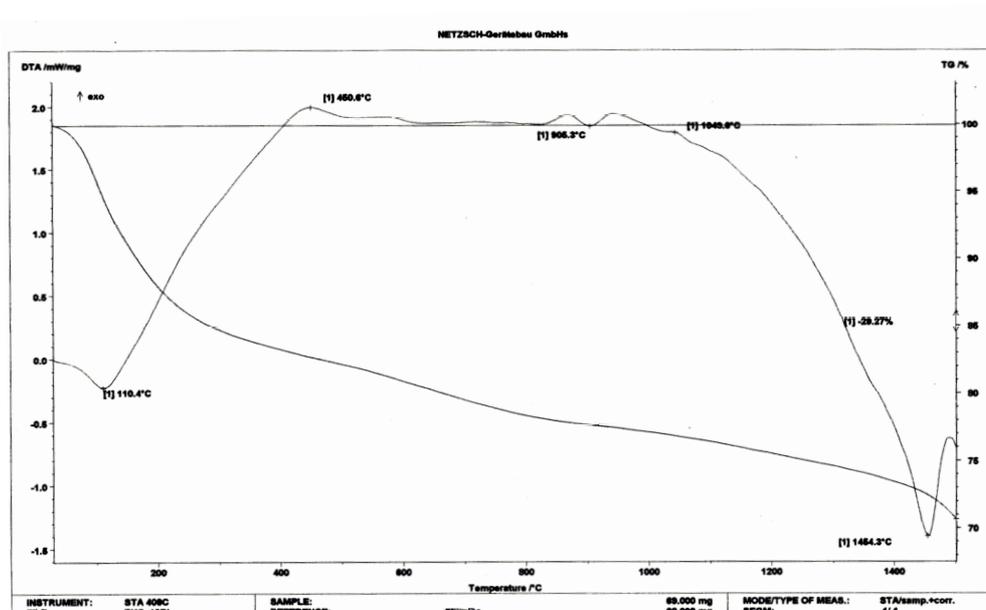


Fig.5: FTIR spectra of aluminum hydroxide before (AO1) and after (AO2) absorption of NO_x .

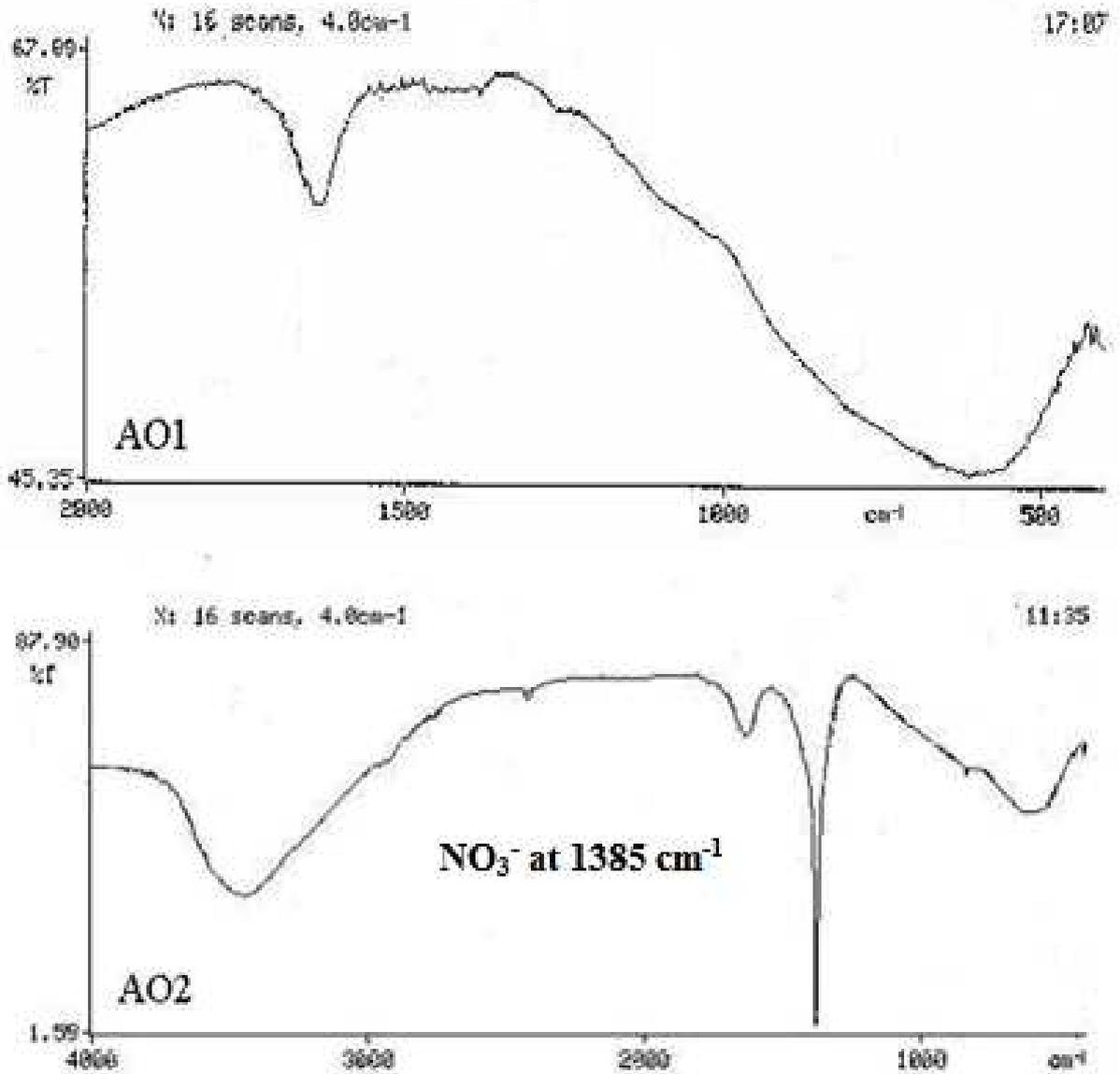


Fig.6: XRD patterns of (a) pure aluminum hydroxide before absorption of nitrogen oxide, (b) the centrifugate during the reaction, (c) synthesised aluminum nitrate and (d) purchased aluminum nitrate nonahydrate (manufacturer's).

