Chemical Technology
Ammonium Nitrate
Ammonium Nitrate

- Very important nitrogenous fertilizer because of its
  - high nitrogen content (33%)
  - Cheapness of its manufacture
Properties

- Mol. Wt. 80.05
- M.P. 170°C
- B.P. Decomposes at 200°C or higher
- Solubility Soluble in water (900 gm/lit at 20°C), alcohol and NH3

- It’s a Explosive when mixed with combustible materials or exposed to high temperature
Ammonium nitrate is marketed in several forms, depending upon its use. Liquid ammonium nitrate may be sold as a fertilizer, generally in combination with urea.

- Liquid ammonium nitrate may be concentrated to form an ammonium nitrate "melt" for use in solids formation processes.

- Solid ammonium nitrate may be produced in the form of prills, grains, granules, or crystals.

- Prills can be produced in either high or low density form, depending on the concentration of the melt. High density prills, granules, and crystals are used as fertilizer, grains are used solely in explosives.
Production

The process of production of Ammonium Nitrate is based on the reaction of nitric acid and ammonia with principal variations in methods of producing the product in solid form as pellets, crystals or flakes.
Ammonium nitrate is made by reacting nitric acid (made by oxidizing ammonia) with ammonia.

\[ \text{NH}_3(g) + \text{HNO}_3(aq) \rightarrow \text{NH}_4\text{NO}_3 \]  
\[ (\Delta H = -20.6 \text{ Kcal}) \]

If properly proportioned and preheated, the reaction can be run continuously to produce molten ammonium nitrate containing very little water (1–5%) formed in to small spheres by dropping the reaction product through a shot tower or in to flakes by cooling it on belts or drums.
Raw Materials

- 57–60% HNO₃ from oxidation–absorption tower
- Liquid NH₃
- Clay, for coating on end product to avoid explosions.
Quantitative Requirements

- **Basis:** 1 ton of Ammonium Nitrate (98% yield)
- **Ammonia:** 0.22 ton
- **60% HNO₃:** 1.38
- **Plant Capacity:** 100–500 tons/day
Prilling Process

- The ammonia vapors reacted with aqueous nitric acid in a stainless steel reaction vessel with agitation.
- The heat of reaction causes water to boil off and the final salt solution is 75% and 140°C when pumped to a vacuum evaporator to concentrate further to 95% solids.
- The hot liquor is sprayed from the top of a prilling tower (60–75 meters high) counter-current to conditioned air flow.
The solidified spherical pellets or prills are about 1.5 mm in diameter and must be screened and dried before coating with clay.

Fines and oversized material are re-dissolved and sent to the neutralizing for recycle.
Nitrolime Process

- The same process which produced a 95% melt for prilling can be utilized for the production of nitrolime.
- The melt flows from a storage tank to pug mill which is a screw mixer consisting of two sets of mixing blades rotating in opposite directions.
- Pulverized lime (325 mesh) is admixed here with some heat of reaction evolved.
The product flows to a rotary drum granulator, then to a co-current direct heated flue gas dryer where product moisture is reduced to 0.5–0.6 % H₂O.

Screen classifying separates 2–4 mm particles which move on to a coating drum where fine limestone is added to yield a free flowing product.

Oversize material (> 4 mm) is recycled.

Undersize (< 2 mm) is returned to the pug mill for size buildup.
This process, patented by L.A. Stengel, and assigned to Commercial Solvents Corp., involves vapor phase reaction in a packed stainless steel reactor.

Ammonia vapor is preheated to 140–150 °C in a single stage heat exchanger while 60 % HNO₃ is preheated first to 95 °C in a stainless steel unit and then to 160 °C in a tantalum unit avoid high temperature HNO₃ corrosion.
The molten NH$_4$NO$_3$ and water vapor at 200 °C are passed through the tangential entry of a cyclone separator where air aids in removal of steam from the molten salt.

The latter is removed at the bottom and solidified on a water-cooled stainless steel belt.

The solids are crushed, ground to flake size and screened.

Oversize is reground and fines are dissolved and returned to HNO$_3$ pre-heater stream.

The product flakes are coated with clay, and bagged or bulk shipped.
Major Engineering Problems

- Corrosion

Carbon steel can only be used in the NH$_3$ storage and feed system.

Up to about 120$^\circ$C, Type 304, extra–low carbon (ELC) stainless steel is used for aqueous or 100 % HNO$_3$. This MOC is used throughout most of the remainder of an ammonium nitrate plant.

In the Stengel process, where it is necessary to preheat 60% HNO$_3$ to 170$^\circ$C, expensive tantalum metal is needed for this heat exchanger.
Crystallization:

This problem occurs in the vacuum crystallization process. An Oslo–Krystal classifier is used since it provides adequate growth of seed crystals to the proper size, shape and strength in a continuous manner. Prior to this equipment, the paddle type grainer was used, but only small crystals could be produced.
Safety:
The extreme reactivity of NH₄NO₃ with combustible materials and its sensitivity to explosive decomposition requires safety precautions different from most in organic processing. Any air used in drying must be free oil and other combustibles. The Stengel process has the greatest inherent safety in its design since the equipment is designed for short residence times and low hold-up.
Conditioned Air Requirements:

Both NH$_4$NO$_3$ and nitrolime are hygroscopic so that humidity and temperature requirements of the air in the materials handling area are critical.
Ammonium sulfate

Auxiliary in many sectors of industry, e.g. the chemical, industrial chemicals, woodworking, pharmaceutical, leather, paper, textile and wood pulp industries and biological water treatment plants.
Product description

White, crystalline powder without anticaking agent.

Chemical Name:

Ammonium sulfate
ammonium sulphate
diammonium sulfate
Sulfuric acid diammonium salt
Chemical formula

\[(\text{NH}_4)_2\text{SO}_4\]

Molecular weight

132.14 g/mol
Properties

Hardens during prolonged storage, especially when under pressure, without any modification of chemical properties.

Briefly striking the bags restores pourability once again.

When alkaline substances are added ammonia is liberated. Has a weakly acid reaction.
<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Melting point</td>
<td>approx. 350°C</td>
</tr>
<tr>
<td>Decomposition</td>
<td>from approx. 235°C</td>
</tr>
<tr>
<td>Bulk density</td>
<td>1000 kg/m³</td>
</tr>
<tr>
<td>Solubility in water (20°C)</td>
<td>754 g/l</td>
</tr>
<tr>
<td>Solubility in water (50°C)</td>
<td>843 g/l</td>
</tr>
<tr>
<td>pH (100 g/l H₂O)</td>
<td>approx. 5</td>
</tr>
</tbody>
</table>
Applications

In biological treatment plants: As nutrient for bacterial cultures.

In the chemical industry: In the production of persulfates. In the precipitation of protein.

In the industrial chemicals sector: Production of fire extinguisher powder and flame proofing agents. In the production of metals (e.g. chromium) and noble metals (e.g. gold).
In the paper industry: Production of fire-resistant papers.

In the pharmaceutical industry: As a nutrient for microorganisms.

In the textile industry: As an additive to dye baths and for flame proofing fabrics, wadding and wicks. In the production of auxiliaries for textiles processing.

In the wood pulp industry: In the production of yeast and sulfite liquor.
About 90 percent of ammonium sulfate is produced by 3 different processes:

1. as a byproduct of caprolactam [(CH₂)₅COHN] production,
2. from synthetic manufacture, and
3. as a coke oven byproduct.

The remainder is produced as a byproduct of either nickel or methyl methacrylate manufacture, or from ammonia (NH₃) scrubbing of tail gas at sulfuric acid (H₂SO₄) plants.
Ammonium sulfate is produced as a byproduct from the caprolactam oxidation process stream and the rearrangement reaction stream.

Synthetic ammonium sulfate is produced by combining anhydrous ammonia and sulfuric acid in a reactor.

Coke oven byproduct ammonium sulfate is produced by reacting the ammonia recovered from coke oven off gas with sulfuric acid.
After formation of the ammonium sulfate solution, manufacturing operations of each process are similar.

Ammonium sulfate crystals are formed by circulating the ammonium sulfate liquor through a water evaporator, which thickens the solution. Ammonium sulfate crystals are separated from the liquor in a centrifuge.

In the caprolactam byproduct process, the product is first transferred to a settling tank to reduce the liquid load on the centrifuge.
The saturated liquor is returned to the dilute ammonium sulfate brine of the evaporator. The crystals, which contain about 1 to 2.5 percent moisture by weight after the centrifuge, are fed to either a fluidized-bed or a rotary drum dryer. Fluidized-bed dryers are continuously steam heated, while the rotary dryers are fired directly with either oil or natural gas or may use steam-heated air.
At coke oven byproduct plants, rotary vacuum filters may be used in place of a centrifuge and dryer. The crystal layer is deposited on the filter and is removed as product. These crystals are generally not screened, although they contain a wide range of particle sizes. They are then carried by conveyors to bulk storage. At synthetic plants, a small quantity (about 0.05 percent) of a heavy organic (i.e., high molecular weight organic) is added to the product after drying to reduce caking.
Dryer exhaust gases pass through a particulate collection device, such as a wet scrubber. This collection controls emissions and reclaims residual product. After being dried, the ammonium sulfate crystals are screened into coarse and fine crystals. This screening is done in an enclosed area to restrict fugitive dust in the building.
Ammonium sulfate particulate is the principal emission from ammonium sulfate manufacturing plants. The gaseous exhaust of the dryers contains nearly all the emitted ammonium sulfate. Other plant processes, such as evaporation, screening and materials handling, are not significant sources of emissions. The particulate emission rate of a dryer is dependent on gas velocity and particle size distribution. Gas velocity, and thus emission rates, varies according to the dryer type.
Generally, the gas velocity of fluidized-bed dryers is higher than for most rotary drum dryers. Therefore, the particulate emission rates are higher for fluidized-bed dryers.

At caprolactam byproduct plants, relatively small amounts of volatile organic compounds (VOC) are emitted from the dryers. Some plants use baghouses for emission control, but wet scrubbers, such as venturi and centrifugal scrubbers, are more suitable for reducing particulate emissions from the dryers. Wet scrubbers use the process streams as the scrubbing liquid so that the collected particulate can be easily recycled to the production system.