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table

VIII AMMONIUM SALTS, NITRIC ACID, AND NITRATES

6/20

Introduction

As mentioned previously, ammonia is the source of more than 95% of the chemical nitrogen fertilizer currently produced in the world. Ammonia may be used directly as a fertilizer (see chapter X) or converted to ammonium salts, nitrates, or urea. No accurate estimates are available as to the percentage of these various products in world use. In Europe the leading form of nitrogen fertilizer is ammonium nitrate, either as such, in mixtures with calcium carbonate, or in compound fertilizers including nitrophosphates. In Asia urea is the leading form either as such or in compound fertilizers. In North America anhydrous ammonia is the leading form of nitrogen fertilizer. Individual countries within these and other continents may have other preferences.

The purpose of this chapter is to describe the technology of production of ammonium salts for fertilizer use other than ammonium phosphates (which are covered in chapter XIV) and the production of nitric acid and nitrates except potassium nitrate which is covered in chapter XVIII.

Ammonium Sulfate

Ammonium sulfate was once the leading form of nitrogen fertilizer, but it now supplies a relatively small percentage of the world total nitrogen fertilizer because of the more rapid growth in use of urea, ammonium nitrate, and anhydrous ammonia. The main advantages of ammonium sulfate are its low hygroscopicity, good physical properties (when properly prepared), chemical stability, and good agronomic effectiveness. It is a good source of sulfur as well as nitrogen. Its reaction in the soil is strongly acid forming (see chapter XXII) which is an advantage on alkaline soils and for some crops such as tea; in some other situations its acid-forming character is a disadvantage. Its main disadvantage is its low analysis (21% N), which increase packaging, storage, and transportation costs. As a result, the delivered cost at the farm level usually is higher per unit of nitrogen than that of urea or ammonium nitrate. However, in some cases, ammonium sulfate may be the most economical source of nitrogen when the transportation distance is short, when it is available as a byproduct at low cost, or when a credit can be taken for its sulfur content.

Ammonium sulfate is available as a byproduct from the steel industry (recovered from coke-oven gas) and from some metallurgical and chemical process. One large source is a byproduct from production of caprolactam.

Properties of Ammonium Sulfate

Table 1 shows the more important properties of crystalline ammonium sulfate.

TABLE 1. PROPERTIES OF PURE AMMONIUM SULFATE

Color	White
Molecular weight	132.14
N.Content	21.2%
Density of solid, 20°/4°C	1.769
Specific gravity of saturated solutions	1.2414 at 20°C 1.2502 at 93°C
Specific heat of solid	0.345 at 91°C
specific heat of saturated Solutions	0.67 at 20°C 0.63 at 100°C
Heat of crystallization	11.6 cal/kg in 42% solution
Heat of dilution	6.35 cal/kg from 42% to 1.8% solutions
Melting point	512.2°C
Thermal stability	Decomposes above 280°C
pH	5.0
Loose-bulk density	962 kg/m ³
Angle of repose	28°
Stoichiometric requirements, tons per ton of product	NH ₃ 0.2578 H ₂ SO ₄ 0.7422
Critical relative humidity	At 20°C 18% At 30°C 81.1%
Solubility, g/100 g of water	
At 0°C	70.6
At 100°C	103.8

Production Methods

Several different methods are used for ammonium sulfate manufacture, in accordance with available raw materials and local conditions.

The principal methods are:

1. Reacting ammonia and sulfuric acid in a saturator evaporated under vacuum or at atmospheric pressure and recovering the crystals via a centrifuge or filter;
2. Scrubbing town gas or coke-oven gas with sulfuric acid in saturator units of special design and recovering the crystals by centrifuging or filtration;
3. Reacting ammonium carbonate with anhydrite or gypsum derived from natural or byproduct sources, removing the calcium carbonate by filtering, evaporating, and crystallizing ammonium sulfate from the mother liquor prior to centrifuging;

4. Evaporating byproduct liquors containing ammonium sulfate produced from other processes and separating the nearly pure salt by: (a) crystallization and centrifuging or alternatively (b) recovering by slurry granulation on a moving bed and recycling in a drier-screening system to give granules of the required size range;
5. Directly reacting gaseous ammonia with sulfuric acid in a spray tower to form a dry, amorphous product;
6. Simultaneously producing ammonium sulfate and other ammonium salts in granulated fertilizer processes to produce phosphate, nitrate, and nitrophosphate multinutrient fertilizers containing ammonium sulfate;
7. Using other miscellaneous process, such as recovering ammonium sulfate from SO_2 in flue gas or in sulfuric acid tail gas (see chapter XII), which are in use or have been proposed.

Crystallization Technology

Except in special cases, such as those described in subparagraphs 4, 5, and 6 above, crystallization is of major importance in ammonia sulfate production as well as in the manufacture of other salts. Hence it is appropriate at this stage to review briefly the fundamental process and design features which control crystal formation and influence plant performance (2,3,4,5).

Two major considerations arise in crystallization technology—first, the formation of nuclei in a supersaturated solution and, secondly, the growth of these particles to the product size-range required. In both of these stages, the driving force is the degree of supersaturation in the mother liquor, which, if allowed to rise appreciably, may induce uncontrollable nucleation. Subsequent crystal growth, however, is generally directly proportional to supersaturation and, as a rule, is easier to control than nucleation.

When a solution is supercooled to a point just before fine, solid nuclei appear, it is termed metastable. After initial precipitation, this solution is said to be unstable or labile, and a constant addition of metastable liquor will cause each nucleus to grow into a single crystal. Thus, control of metastable conditions is a major factor in the design and operation of crystallization units; critical items include residence time, agitation, and equipment surface characteristics, as well as the pH, temperature, and soluble and insoluble impurities contained in the liquor. Hence, for continuous, stable operation, an equilibrium has to be established whereby the number of grown crystals removed equals the number of fresh nuclei formed. Under these conditions, uniformly sized crystals should result when a constant feed is supplied, and average crystal size becomes a function of the production rate divided by the nucleation rate.

When the production rate is held constant, as in continuous operation, average crystal size is thus largely controlled by nucleation rate. One gram of typical nuclei may represent 1 billion particles; hence, a continuous crystallizer must provide a way of controlling the number of nuclei and fines produced in this system and also contain provisions for classifying the product in order to minimize subsequent washing, drying, and storage problems. Modern crystallizers are designed to incorporate these features and are also provided with control equipment to ensure virtually automatic operation.

After growth and classification to the required size ammonium sulfate crystals are removed from the unit by various means, such as a salt catchpot, an airlift, or a helical screw, separated from the mother liquor by a centrifuge; washed with water (and/or ammonia liquor); and dried in a rotary drier prior to screening and storage. In some plants, the production of large, well-washed crystals and the use of high-efficiency centrifuges eliminate the need for a drier. However, when small crystals are produced and particularly when impurities are present, drying, cooling and, perhaps, conditioning with an anticaking agent may be unavoidable. When large, closely sized crystals are desired, the crystals may be screened and the fines redissolved and returned to the crystallizer.

Other methods of crystal recovery and treatment include the use of a top-feed rotary vacuum filter-drier and also the granulation of small crystals by roll compaction equipment. Such machines are especially suitable for the relatively small tonnages of sulfate produced in some coke-oven byproduct units. In a few instances, pugmills or drum-type pelletizers are used to produce granulated sulfate from byproduct caprolactam liquor or other waste streams containing ammonium sulfate in appreciable quantities.

Chemical and Physical Specifications

Fertilizer-grade ammonium sulfate specification normally indicate a minimum nitrogen content, which is usually not less than 20.5%. Limitations on free acidity and free moisture are also generally demanded; typical figures are 0.2% for free H_2SO_4 and 0.2% for free H_2O . Occasionally, maximum values for certain organic or inorganic impurities may also be specified for byproduct material.

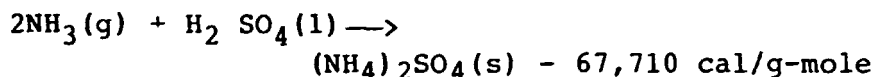
Crystal size-range specifications depend on customer requirements and the type of application. For direct application or bulk blending, large crystals, mainly in the range of 1-3 mm, are preferred although somewhat smaller crystals may be acceptable in some countries for direct application, such as 90% retention on an 0.8-mm screen. To obtain crystals of this size, considerable design and operating skill is usually needed, and in some plants

additives are used to promote crystal growth or modify the crystal shape (6). For use in production of compound fertilizers, small crystals are acceptable. There is a trend toward production of small crystals (mainly 0.2-0.8 mm) which are sold as is to producers of granular compound fertilizers or are granulated by roll compaction for direct application or bulk blending. The roll compaction granulation process is described in chapter XVIII.

Production Details

Combined Reaction-Evaporation Methods--Large tonnages of ammonium sulfate are produced from anhydrous ammonia and strong sulfuric acid in continuous saturator-crystallizer units operating either under vacuum or atmospheric pressure. In installations of the vacuum type, the heat of reaction is removed by evaporating water either present in the feed acid or added to the system for temperature-control purposes. This technique is also used for saturators of the atmospheric type; alternative cooling can be achieved in the latter by blowing large volumes of air through the slurry.

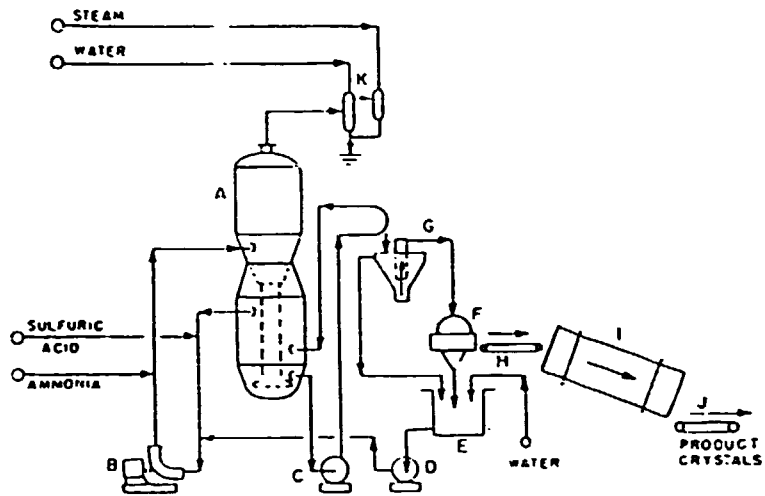
The reaction between gaseous, anhydrous ammonia and sulfuric acid can be shown as follows:



In practice the exothermic heat of the reaction given above is approximately equal to 2,350 kcal/kg of N.

Units of the vacuum type are designed in accordance with the basic principles of crystallization previously reviewed and are usually built in the form of a suspension vessel surmounted by a flash chamber. Ammonia and sulfuric acid are introduced via a slurry recycle line, wherein they react and superheat the recirculating slurry, which is subsequently flashed in the upper chamber at a reduced pressure generally between 55 and 58 cm of mercury. The loss of water in this zone supersaturates the slurry, which recirculates to the lower suspension vessel via an internal pipe and comes into contact with small crystals and nuclei, thereby inducing further crystal growth in terms of size rather than in number. Slurry is recycled by a thermal syphon and/or by an external pump, and as it is brought into contact with newly added reactants, the exothermic heat produced destroys undesirable nuclei and fines. Skilled design of the suspension vessel and the means of slurry withdrawal permits considerable size classification to be attained in the unit, and proper instrumentation ensures long periods of uniform operation.

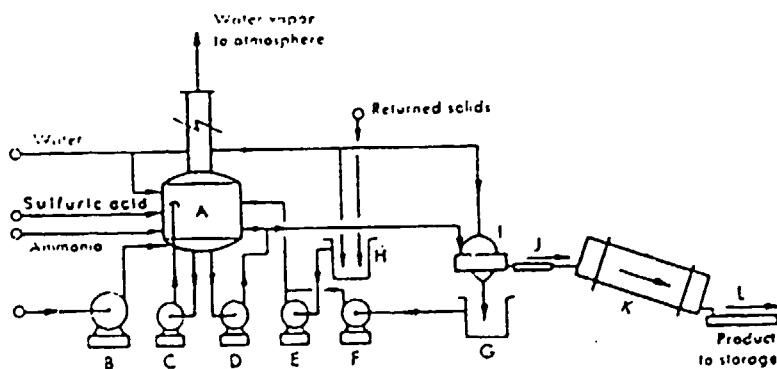
This type of crystallizer is generally known as the "Krystal" or "Oslo" unit and was developed in Norway by Isaacsen and Jeremiassen (7). Figure 1 illustrates diagrammatically the use



Legend

- A "Krystal" type of vacuum evaporator-crystallizer
- B Forced-circulation pump
- C Slurry-recirculation pump
- D Mother-liquor recycle pump
- E Mother-liquor tank
- F Continuous or batch centrifuge
- G Slurry concentrator
- H Drier conveyor
- I Rotary drier
- J Dried-product conveyor
- K Vacuum condenser-ejector unit

Figure 1. "Krystal" type of Unit for Ammonium Sulfate Production.



Legend

- | | |
|-----------------------------|----------------------------------|
| A Evaporator-crystallizer | G Mother-liquor tank |
| B Air blower | H Sump tank |
| C Liquor-recirculation pump | I Batch or continuous centrifuge |
| D Slurry-recirculation pump | J Drier conveyor |
| E Makeup pump | K Rotary drier |
| F Mother-liquor pump | L Product conveyor |

Figure 2. Atmospheric-Pressure Process for Ammonium Sulfate Manufacture.

of forced circulation in conjunction with this design of crystallizer for ammonium sulfate production. During operation, it is important to control the pH within fairly close limits, e.g., 3.0-3.5, since a lower value yields undesirable, thin crystals. Excessive acidity also promotes an overgrowth of crystals, especially in pipelines, and necessitates frequent redissolving or "killing" with steam. Insufficient acidity, on the other hand, not only produces inferior crystals which are difficult to wash and store but may cause ammonia losses as well. For these reasons, some producers maintain free acidity of 1.0-1.5 g of H_2SO_4 /liter of solution.

Another popular type of reduced-pressure crystallizer is the draft tube baffle unit, in which a vigorous upward slurry recirculation is maintained by means of an internal impeller and draft tube (8). Growing crystals are brought to the surface of the flashing slurry, where supersaturation induces maximum crystal growth, and sufficient nuclei are present to minimize scale formation inside the unit.

Atmospheric pressure units are of several types and are preferred by some producers to vacuum crystallizers, especially for small and medium outputs, because of their simplicity and somewhat lower investment costs. Ammonia can be added via a sparger tube or a jet type of mixer. In one proprietary process, a simple absorption column incorporating a few large slotted bubble-hoods is used. Another design employs a single vessel for both reaction and crystallization, and reaction heat is removed by evaporation of water, supplemented in many cases by air blowing, as shown in figure 2. In other designs, separate neutralizing and crystallizing vessels are used to provide easier operation and closer control. An optimum balance between cooling-air energy and crystal yield is usually obtained when crystallization temperatures are controlled in the range of 63°-66°C.

In most cases, crystals are recovered from ammonium sulfate slurry by recycling through the continuous or the automatic batch type of centrifuge, wherein the product is screened and spin-dried, washed with water and weak ammonia, and again spin-dried before being conveyed to the drier. In some plants, continuous top-feed filters are used instead of centrifugals. As previously mentioned, for small outputs, top-feed filter-driers can sometimes be employed with advantage since the product can be separated, washed, and dried in a single machine.

As is well known, ammonium sulfate liquors are quite corrosive, and wetted parts of equipment are usually made of stainless steel or of rubber-lined mild steel. In some earlier plants, vessels constructed in wood and mild steel were employed, and corrosion was minimized by careful pH control. Modifiers intended to improve crystal size and shape include small amounts of trivalent metallic salts. Such corrosion inhibitors as traces of phosphoric acid or arsenic compounds are also added in some cases.

Gasworks Byproduct Methods-- Before the availability of synthetic ammonia in the early 1920s, virtually all ammonia was obtained from solid-fuel carbonization plants. Typical bituminous coals used for gas and coke production contain about 1%-2% of nitrogen, and some 15%-20% of this can be recovered as ammonia, amounting to approximately 2.5-3.0 kg of NH_3 /ton of coal used. Most of this ammonia is believed to be formed at temperatures in the range of 1000°C, after coking has taken place. Hence, most byproduct ammonia is usually associated with high-temperature carbonization units, e.g., coking plants for iron and steel production, where the amount of ammonium sulfate produced may be equivalent to about 20 kg/ton of steel.

Ammonia is removed from gas for two principal reasons; first, to prevent subsequent corrosion and plugging problems in distribution mains and fittings and, secondly, to produce a useful byproduct at a reasonable profit. However, in more recent years, world ammonium sulfate prices have fluctuated widely, and, from time to time, byproduct material from gasworks and coke ovens has been sold at prices levels not much greater than the cost of the sulfuric acid needed as a raw material. As a result, some producers have converted their units to ammonium phosphate production as a more profitable alternative. Other byproducts recovered from gas-washing units, because of necessity or additional financial return, include ammonium thiocyanate, ferrocyanides, pyridins, and tar.

Three principal methods are available for ammonia and/or ammonium salt recovery; they are known as the direct, indirect, and semidirect processes, respectively. In the first method, the entire gas stream is cooled to remove as much tar as possible and is then passed through a saturator of the bubbler type (or, in more recent plants, a scrubber of the spray type), wherein it is washed with sulfuric acid. The ammonium sulfate slurry produced is withdrawn, centrifuged, washed, dried, and sent to storage. Advantages of this type of unit include high recoveries, relatively low investment and operating costs, low steam needs, and small effluent liquor volumes. Nevertheless, in many instances, the product is unavoidably contaminated with tar and pyridines and may be unacceptable unless, perhaps it is recrystallized prior to sale. In addition, chlorides present in the fuel or water may react to form ammonium chloride and create additional corrosion problems unless linings of rubber or plastic material are used. Furthermore, except in cases where a separate crystallizer is employed, flexibility with regard to size, shape, and purity of product is likely to be very limited since it becomes difficult to maintain an optimum balance between the free acidity needed to suppress impurities and the optimum pH needed to promote good crystal growth.

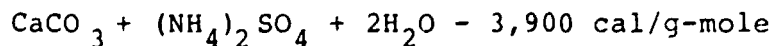
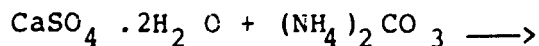
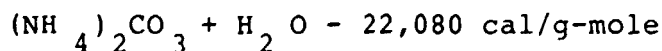
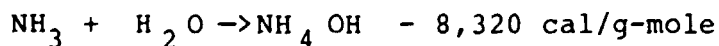
Earlier problems of direct operation led to the development of the indirect method, whereby the gases are first cooled by contact with recirculating wash liquor, followed in some cases by a further scrubbing with water. Combined liquors are sent to the upper section of an ammonia still of the bubble-cap type, in which contact with steam releases the "free" ammonia present as ammonium carbonate, ammonium sulfide, and other easily dissociated salts. The liquor then passes to an

adjoining lime leg, where treatment with lime liquor decomposes the "fixed" ammonium salts, e.g., ammonium chloride. Steam passing upwards from the base of the column strips virtually all of the ammonia gas produced, which is recovered as a crude ammonia solution or is sent to a sulfuric acid washer for ammonium sulfate production. Advantages of this method include the production of a salt substantially free from impurities and also having considerable flexibility, plus an ability to make aqua ammonia and derivatives. However, operating costs are high, and effluent disposal problems may arise. In addition, ammonia losses may be appreciable, owing to incomplete reaction and absorption.

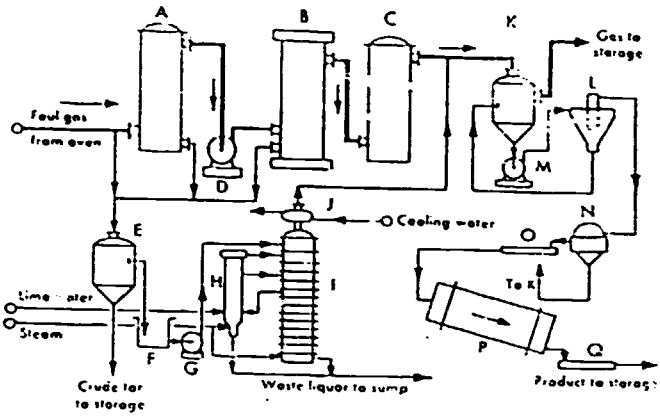
The semidirect process offers a compromise between direct and indirect operation, whereby the gas is first cooled and washed to deposit tar and an aqueous condensate (9). The latter is "sprung" in a relatively small ammonia still, and the released NH_3 is combined with the main gas stream, which is reheated to about 70°C and scrubbed with a solution containing nearly saturated ammonium sulfate and 5%-6% of sulfuric acid at about $50^\circ\text{--}70^\circ\text{C}$, in units either of the spray-absorber type or of the older saturator type incorporating a cracker pipe (or bubbler ring.) Because this process gives ammonia recoveries greater than those attainable by direct operation and also produces a salt largely free from tar, pyridine, and other impurities, it has become the most popular for large installations. Figure 3 shows the basic flow diagram of a semidirect gas scrubber/ammonium sulfate unit, as well as an illustration of an ammonium sulfate saturator.

Several varieties and modifications of these systems are found throughout the world, principally developed by the Koppers, Otto and Wilputte organizations (10).

Ammonium Carbonate-Gypsum Process-- This method, which is also known as the Merseburg Process, was originally developed in Germany and has long been used in Austria, India, Pakistan, and the United Kingdom (11,12). It is based on combining ammonia and carbon dioxide to produce ammonium carbonate, which is then reacted with gypsum or anhydrite (of natural or byproduct origin) to yield ammonium sulfate and calcium carbonate, as follows:



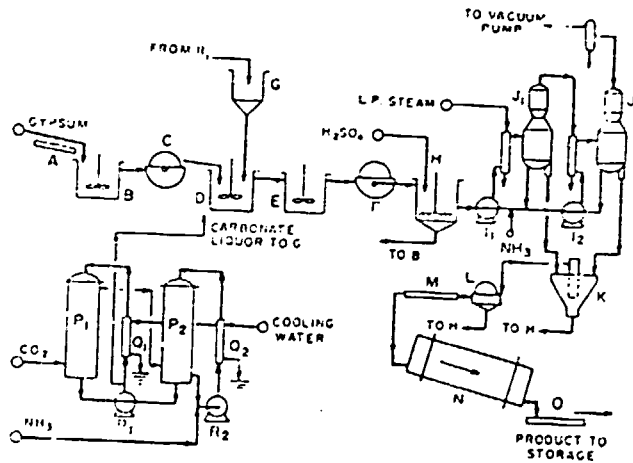
Under certain circumstances, this process has several advantages, for example, countries without indigenous sulfur supplies but having natural or byproduct sources of gypsum



Legend

- | | |
|--------------------------------|----------------------------------|
| A Primary gas-cooler | J Dephlegmator |
| B Electrostatic precipitator | K Sulfate saturator-crystallizer |
| C Gas reheater | L Slurry concentrator |
| D Main gas-blower | M Slurry feed-pump |
| E Tar separator | N Batch or continuous centrifuge |
| F Crude ammonia liquor storage | O Drier conveyor |
| G Still feed-pump | P Rotary drier |
| H Line leg | Q Product conveyor |
| I Ammonia still | |

Figure 3. Semidirect Process for Ammonium Sulfate Production from Coke-Oven Gas.



Legend

- | |
|--|
| A Gypsum conveyor |
| B Gypsum washing tank |
| C Gypsum dewatering filter |
| D Primary reactor |
| E Secondary reactor |
| F Calcium carbonate filter |
| G Ammonium carbonate storage tank |
| H Sulfate-liquor clarifier |
| J ₁ , J ₂ Evaporator feed-pumps |
| J ₁ , J ₂ Vacuum evaporator-crystallizers |
| K Slurry concentrator |
| L Batch or continuous centrifuge |
| M Drier conveyor |
| N Rotary drier |
| O Product conveyor |
| P ₁ , P ₂ Ammonium carbonate towers |
| Q ₁ , Q ₂ Heat exchanger-coolers |
| R ₁ , R ₂ Carbonate liquor recirculating pumps |

Figure 4. Gypsum Process for Ammonium Sulfate Production.

(or anhydrite) can produce ammonium sulfate without purchasing sulfur from abroad (13). In addition, the byproduct calcium carbonate can be used for cement production or other purposes, such as for agricultural lime or in calcium ammonium nitrate manufacture. One disadvantage is the large amount of energy (steam) required to recover solid ammonium sulfate from the relatively dilute solution.

In one Indian plant (Sindri), ammonia gas is absorbed in water and carbonated at a pressure of about 2.1 kg/cm^2 (or 30 psig) in two series-connected aluminum towers since this pressure allows a higher cooling-water temperature to be employed than if atmospheric pressure were used. Carbon dioxide is introduced at the base of the primary tower, which is packed with 5-cm (2-in) stoneware rings wetted with a solution of ammonium hydroxide and recycling ammonium carbonate. Final absorption is undertaken in the secondary tower, and reaction heat is removed by recirculating liquor through water-cooled heat exchangers in closed circuit with each tower. The preferred liquor strength corresponds to approximately 170 g of ammonia and 225 g of carbon dioxide per liter. Stainless steel is used for the wetted parts of pumps, and liquor piping is made of aluminum.

In another Indian plant (Fertilizers and Chemicals Ltd., Travancore), jet absorbers are used to prepare both the ammonia solution and the ammonium carbonate liquor in conjunction with a carbonating tower. Cooling is undertaken by recycling liquor through water-cooled heat exchangers, and the heat of reaction thereby vaporizes the liquid anhydrous ammonia used in the process. When the desired strength has been reached, the solution is sent to storage and subsequent reaction. The relation between liquor strength, moisture in the gypsum, and the resulting ammonium sulfate liquor concentration has been reported by George and Gopinath (14).

When natural gypsum or anhydrite is used, it is crushed and ground before reaction. In one case, the preferred final size is about 90% through 120-mesh although, under certain circumstances, there are indications that a coarser is permissible. When using byproduct gypsum of phosphoric acid-plant origin, it may be preferable to remove impurities by repulping the filter cake in an agitated vessel (or, alternatively, by scalping in liquid cyclones) prior to washing and dewatering to the maximum extent on a drum or disc filter before reacting with ammonium carbonate. Some methods of purifying byproduct gypsum will be described in chapter XIII.

Reaction can be undertaken either in a series of wooden vessels or mild-steel tanks fitted with steam coils and agitators, and the reaction train is usually designed to give a total retention time of 4-6 hours. The slurry produced is filtered and the calcium carbonate cake washed and dewatered on continuous vacuum machines of the traveling-belt type, or alternatively, on a two-stage drum-filter installation provided with intermediate repulping. (In some earlier plants, plate-frame filter presses were installed for this purpose). Final clarification by pressure filtration or settling is sometimes employed to ensure maximum purity of product, followed by neutralization with sulfuric and heating to about 110°C to

remove excess ammonia prior to concentration and crystallization. The evaporator feed-liquor usually contains about 500-520 g of ammonium sulfate and less than 0.1 g of ammonia per liter.

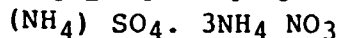
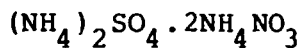
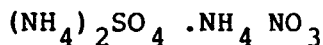
Evaporation is undertaken in continuous multiple-effect evaporator crystallizers, and production can be supplemented, if desired, by adding ammonia and sulfuric acid to the crystallizer recirculating line as previously described. Crystals of the required size range are separated and washed in a centrifuge, dried in a rotary drier at 120°-130°C, and sent to storage. Alternatively, a vertical tray type of drier-cooler can be used since this is said to give reduced crystal breakage and dust formation, compared with the use of a rotary drier and cooler. A diagram of a gypsum-process ammonium sulfate plant is given in figure-4.

Recovery of Byproduct Liquor-- Byproduct units have been installed in many countries for producing ammonium sulfate from the waste streams of caprolactam, acrylonitrile, and certain other processes. In such cases, the waste liquor should normally contain at least 35% of ammonium sulfate in solution. Otherwise, recovery may not be justified unless for the purpose of preventing stream pollution. Since recovery often is unprofitable, processes have been developed recently for making caprolactam that produce less byproduct ammonium sulfate or none (15).

Occasionally, spent sulfuric acid from petroleum refineries, petrochemical plants, and soap factories can be used for ammonium sulfate production if impurities do not cause insurmountable frothing or corrosion problems or render the product unacceptable. If the acid is too badly contaminated, it may be more expedient to burn off the impurities in a specially designed furnace and to produce fresh acid for ammoniation. Another alternative is to ammoniate the contaminated acid and granulate the slurry in a drum or pugmill type of granulating system, similar to those used for producing granular fertilizers.

Spray-Tower Ammoniation-- Substantial tonnages of ammonium sulfate have been made for many years in Japan in spray towers from the chamber or contact type of sulfuric acid and anhydrous ammonia. The acid is sprayed into ammonia vapor inside the tower, and the heat of reaction produces a dry, amorphous product, mostly below 300-mesh, which is continuously removed from the base of the tower by a screw conveyer. This form of ammonium sulfate is particularly suitable for use in granular compound fertilizers.

Double-and Mixed-Salt Production-- By ammoniating mixtures of sulfuric and nitric acid or by combining their ammonium salts in special ways, it is possible to produce compounds containing both ammoniacal and nitrate nitrogen in the form of true double salts. Three double salts have been identified:



One German process produces an ammonium sulfate nitrate corresponding approximately to $(\text{NH}_4)_2\text{SO}_4 \cdot \text{NH}_4\text{NO}_3$ and containing 62% ammonium sulfate and 38% ammonium nitrate. Total nitrogen content is 26%, about three-quarters being present in ammoniacal form and one-quarter as nitrate nitrogen. It is made by ammoniating the requisite mixture of sulfuric and nitric acid, evaporating to a moisture content of 3%, adding about 1% of ferrous sulfate (to reduce subsequent caking), cooling to 100°C, chilling, and flaking. After further conditioning by spraying with dilute ammonia solution, the double salt is granulated (sometimes with additional ammonium sulfate), dried, cooled, and bagged.

In a simpler process, also of German origin, ammonium nitrate solution is evaporated under vacuum to a 95% concentration, cooled to about 130°C, and reacted with solid ammonium sulfate in a pugmill granulator system having a recycle ratio of 2 or 3:1 of product until a pH of 4.0 is attained, after which the product is dried, cooled, and bagged. Processes for prilling the product have also been developed.

For several years, TVA produced an ammonium nitrate-sulfate containing 30% N mainly for use in sulfur-deficient areas. The process involved ammoniation of a mixture of nitric and sulfuric acid followed by pan granulation of the resulting slurry. The product consisted mainly of the double salt $(\text{NH}_4)_2\text{SO}_4 \cdot 3\text{NH}_4\text{NO}_3$. Compared with ammonium sulfate, ammonium sulfate nitrate of the usual grade (26% N) contains an additional 5% N. Its storage properties are superior to ammonium nitrate or mixture of solid ammonium sulfate and ammonium nitrate since free ammonium nitrate is absent. However, the large-scale manufacture of urea, as well as of binary and ternary high-analysis fertilizers, has diminished the importance of ammonium sulfate nitrate in most countries.

When mixtures of sulfuric acid and phosphoric acid are ammoniated, a variety of mixed and double-salt products can

be made. One of the most popular is "ammo-phos," containing 16% N and 20% P₂O₄. After ammoniation, the slurry formed is granulated in a pugmill or drum unit, then dried and screened (and sometimes cooled) to give a water-soluble product containing about two-thirds ammonium sulfate and one-third ammonium phosphate by weight. This material has good storage properties under normal conditions (see chapter XIV).

Granular urea-ammonium sulfate mixtures have been produced by TVA for use in sulfur-deficient areas. The process is similar to the pan granulation of straight urea (chapter IX). One such product contained 40% N and 4% S (16). Hydro Agri is also developing fluid bed cogranulation process based on solutions of ammonium nitrate or urea and ground crystalline solids of ammonium sulfate.

Miscellaneous Process-- Numerous processes have been proposed or developed for recovering sulfur from flue gas based on scrubbing with ammonia or injection of ammonia into the flue gas; these processes yield ammonium sulfite, sulfate, or mixtures of these compounds. Ammonium sulfate can be produced as a final product, and some commercial use has been reported in Japan. However, the demand for ammonium sulfate is small in comparison to the potential supply from flue-gas sulfur; therefore, most processes involve disposal of the sulfur as calcium sulfate or sulfite and recycling of the ammonia.

Storage and Handling

Several factors contribute to trouble-free storage of ammonium sulfate and other fertilizers. First, the product should be of uniform crystal size and should contain a low percentage of fines. Secondly, it should be dry and preferably have below 0.1% free moisture. Thirdly, no free acidity should be present on the crystal surfaces. Fourthly, the product should be cooled with dry air under controlled conditions after drying if the ambient temperature and humidity are sufficiently high to cause subsequent moisture condensation after cooling in a bulk storage pile or in sealed bags.

Ammonium Chloride

General Information

Ammonium chloride contains 26% N when pure; the fertilizer-grade product contains 25% N. Ammonium chloride is used in a variety of compound fertilizers (19); examples are:

18-22-0 (ammonium phosphate -chloride)
16-0-20 (ammonium-potassium chloride)
14-14-14
12-18-14

Also ammonium chloride is used in other grades of compound fertilizers in combination with urea or ammonium sulfate.

Coarse crystalline or granular forms are preferred for direct application; whereas, fine crystals can be used in compound fertilizers.

Advantages of ammonium chloride are that it has a higher concentration than ammonium sulfate and a somewhat lower cost per unit of N (in Japan). It has some agronomic advantages for rice (20); nitrification is less rapid than with urea or ammonium sulfate and, therefore, N losses are lower and yields are higher.

Although ammonium chloride is best known as a rice fertilizer, it has been successfully tested and used on other crops such as wheat, barley, sugarcane, maize, fiber crops, sorghum, etc., in a variety of climatic conditions. Of particular note, however, is the use of ammonium chloride on palms. The importance of chlorine as an indispensable nutrient for coconut and oil palms was first reported in 1971 by von Uexkul, et al., who noted that chlorine content was closely related to the amount of copra obtained. Further studies by Menoza in 1975 indicated a linear response of coconut to chlorine in terms of copra yield per tree. The highest copra yield was almost 70% above the yields obtained from trees receiving no chlorine (17).

Ammonium chloride contains a very high (66%) chlorine content hence it can be regarded as a very suitable fertilizer for coconut where the soil is sufficient in potassium but deficient in nitrogen and chlorine. Where potassium is also deficient in soils, the combined application of ammonium chloride and potassium chloride could be more effective.

Ammonium chloride is as highly acid forming as ammonium sulfate per unit of N which can be a disadvantage. Other disadvantages are its low N content compared with urea or ammonium nitrate and the high chloride content which can be harmful on some crops or soils.

Nevertheless, it is possible that ammonium chloride fertilizer could become a useful outlet for surplus supplies of chlorine or byproduct hydrochloric acid that arise from time to time in various countries, provided the above-mentioned precautions were observed. Another useful feature of ammonium chloride is that it can be applied to rice with safety in the presence of certain fungi which would reduce ammonium sulfate to toxic sulfides. The industrial uses of ammonium chloride are worldwide, although in relatively small tonnages. The major applications include dry-battery manufacture and use as a flux for soldering and brazing.

Properties of Ammonium Chloride

The properties of ammonium chloride are given in table 2.

TABLE.2 PROPERTIES OF PURE AMMONIUM CHLORIDE

Color	White
Molecular weight	53.5
Density, 20°/4°C	1.526
Nitrogen content	26%
Solubility, g/100 g of water at Temperature (°C)	

0	29.4
20	37.2
40	45.8
60	55.3
80	65.6
100	77.3
115.6 (boiling-point)	87.3
Effect of heat	
Ammonium chloride begins to dissociate at 350°C and sublimes at 520°C	
Critical relative humidity	
At 20°C (68°F)	79.2
At 30°C (86°F)	77.5

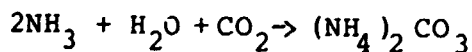
Production Methods

Several methods for producing ammonium chloride are used; the order of importance is as follows:

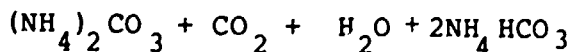
1. The dual-salt process, whereby ammonium chloride and sodium carbonate are produced simultaneously;
2. Direct neutralization of ammonia with hydrochloric acid;
3. Miscellaneous methods.

The Dual-Salt Process-- Most ammonium chloride used in India, China, and Japan for fertilizer purposes is produced by the dual-salt process (or in suitably modified Solvay plants) which is described in monograph 4 of the U.N. Fertilizer Industry Series (19). In this method, ammonium chloride is salted out by the addition of solid, washed sodium chloride instead of being decomposed by lime liquor to recover ammonia as in the Solvay ammonia-soda process.

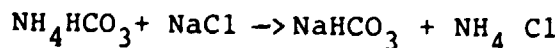
In conventional Solvay plants, an ammoniated solution of about 30% sodium chloride is treated with carbon dioxide in large absorber towers to form ammonium carbonate:



Additional carbonation produces ammonium bicarbonate:

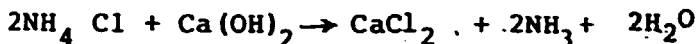


The addition of sodium chloride yields sodium bicarbonate and ammonium chloride:



The sodium bicarbonate is separated by centrifuging or filtration and calcined to produce sodium carbonate and CO_2 ; the latter is recycled to the system. In the Solvay process,

reaction reaches equilibrium at about 75% completion, and the mother liquor is reacted with lime liquor to recover ammonia for reuse in the process, i.e.:

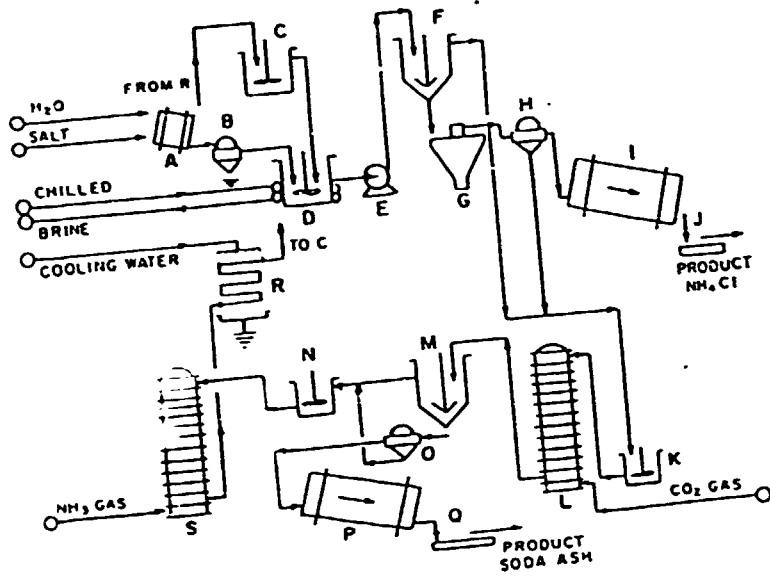


The calcium chloride liquor can sometimes be sold but may have to be discarded in the absence of suitable markets.

In the dual-salt process (or the modified Solvay process), the mother liquor remaining after separation of sodium bicarbonate is ammoniated, cooled below 15°C, and salted out by adding washed, solid sodium chloride. The precipitated ammonium chloride is centrifuged, washed, and dried. The fine crystals can be granulated by roll compaction or used in compound fertilizers. In Japan, a method of producing large ammonium chloride crystals of rice grain shape, 2-3 mm in size, has been developed by undertaking cooling, nucleation, and crystallization of the ammonium chloride under closely controlled conditions in separate vessels of special design.

Slurry from the last crystallizer is centrifuged, washed, and dried to about 0.25% free moisture in a rotary drier at 105°C. After removal of ammonium chloride, the liquor is reammoniated and returned to the carbonating tower to produce further sodium bicarbonate and to commence a new cycle of operations. A basic flow diagram of this process is shown in figure 5.

The ammonium chloride produced by this method, particularly when granulated or produced in coarse crystal form, is reported to have good physical properties. A typical analysis is given in table 3.



Legend

- A Salt washer
- B Salt centrifuge
- C Ammoniated-brine tank
- D Salt reactor
- E Slurry pump
- F Ammonium chloride slurry tank
- G Ammonium chloride concentrator
- H Ammonium chloride centrifuge
- I Ammonium chloride drier
- J Ammonium chloride product conveyer
- K Mother-liquor tank
- L Carbonating tower
- M Bicarbonate slurry tank
- N Bicarbonate mother-liquor tank
- O Bicarbonate centrifuge
- P Soda-ash calciner
- Q Soda-ash product conveyer
- R Ammoniated-brine cooler
- S Ammoniation tower

Figure 5. Dual-Salt Process for Ammonium Chloride Production.

TABLE 3. TYPICAL ANALYSIS OF DUAL-SALT PROCESS AMMONIUM CHLORIDE

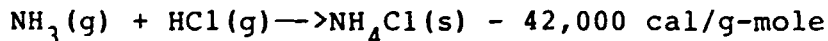
	%
NH ₄ Cl (minimum)	95.0
NaCl	1.5
Carbonates as CO ₂	0.5
Sulfates as SO ₄	0.3
Insoluble material	0.1

The economics of the process must be evaluated in comparison with alternative methods for producing soda ash. This subject is discussed in a UNIDO publication (19). The comparison is most favorable when the process is carried out adjacent to an ammonia plant which serves as a source of CO₂.

As previously mentioned, in a conventional Solvay process precipitation of sodium bicarbonate is taken to about 75% completion only. The modified Solvay process and the dual process permit the attainment of considerable reductions in sodium chloride requirements, perhaps to 1.25-1.5 tons/ton of soda ash, compared with approximately 2 tons for the orthodox Solvay process. This can represent appreciable savings in foreign exchange to countries compelled to import commonsalt. Also the dual process avoids the requirements for burned lime and the disposal problem of waste calcium liquor.

In most countries the demand for nitrogen fertilizers greatly exceeds the demand for soda ash; therefore, ammonium chloride from this source is not likely to supply a large percentage of nitrogen fertilizer needs.

The Direct-Neutralization Method-- Ammonium chloride of high purity is made in several countries by the direct reaction between anhydrous ammonia vapor and hydrochloric acid gas, according to the reaction.



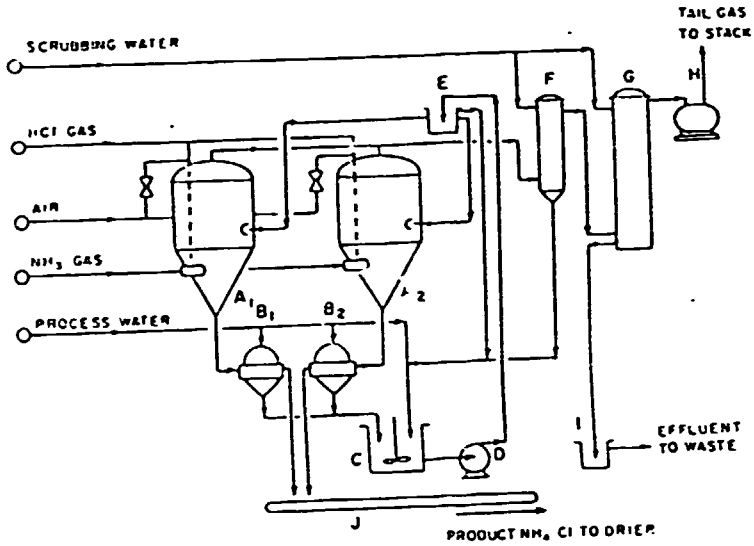
In most cases, neutralization is undertaken at reduced pressures of 250-300 mm of mercury in one or more rubber-lined steel vacuum reaction vessels protected with an additional inner lining of inert brick. Concentrated hydrochloric acid gas is passed through an aspirator, wherein it is diluted with air to about 20% concentration and enters the reactor via a vertical sparger tube. According to preference, ammonia gas is introduced either by a second sparger or by tangential nozzles in the base of the reaction vessel. Agitation is provided by the large volume of air entering the reactor with the hydrochloric acid vapor, thus avoiding the need for a mechanical agitator with its additional power requirements and maintenance problems.

Similarly, operation under vacuum not only provides excellent cooling but simultaneously prevents the escape of noxious vapors and eliminates the need for hydrochloric acid-vapor blowers, plus their attendant cost and maintenance charges. A reduced pressure of 250-330 mm of mercury and a corresponding slurry temperature of 75°-80°C represent typical operating conditions.

In most cases, it is usual to maintain a uniform acid feed for the desired output level and to control the ammonia addition to achieve a steady pH of 8.0. The control system should include an audible alarm and provisions for shutting off the acid feed if the pH falls below 7.0; otherwise, those components in the system not protected by rubber or plastic linings (e.g., the centrifuge) would be quickly damaged by corrosion. Slurry is withdrawn from the saturator at about 80% solids concentration, and the ammonium chloride crystals are separated and rinsed in stainless-steel centrifuges. In some cases, drying is also undertaken in the separator by blowing hot air through the crystal bed before discharge. Alternatively, a top-feed filter-drier can be used instead of centrifuges.

Mother liquor from the centrifuges is pumped back to the saturator(s) via storage tank. Saturator offgases must be well scrubbed before entering the vacuum pump or ejector unit to prevent corrosion and to eliminate air pollution. A two-stage scrubbing system is usually employed and may consist of a direct, barometric scrubber-condenser followed by a wetted, packed tower. Liquor from the scrubber-condenser is returned to the mother-liquor tank and is evaporated in the saturator, thus providing a means of temperature control, as well as of acid recovery. Figure 6 shows the basic flow diagram for a typical direct-neutralization unit.

As with other processes involving reactions between hydrochloric acid (or chlorides) and ammonia, traces of free chlorine in the acid feed can lead to disastrous explosions caused by the formation of nitrogen trichloride in the saturator. Hence, adequate safety precautions must be installed whereby the HCl gas feed is monitored and the flow shut off when chlorine is detected. This can be accomplished by such means as bypassing a small stream of gas through a photocell-colorimeter unit containing potassium iodide



Legend

- A₁, A₂ Neutralizer-crystallizers
- B₁, B₂ Batch or continuous centrifuges
- C Mother-liquor tank
- D Neutralizer feed-pump
- E Splitter feed-box

- F Primary scrubber
- G Secondary scrubber
- H Vacuum pump
- I Seal-pot
- J Product conveyer

Figure 6. Direct-Neutralization Process for Ammonium Chloride Production.

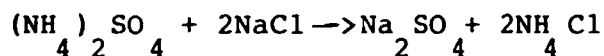
or using a modern continuous gas analyzer of the absorptiometric or chromatographic type.

After separation and drying, the crystalline ammonium chloride is packed as quickly as possible in moisture-proof bags to minimize subsequent storage and application difficulties. Recent trials have shown that such anticaking agents as certain fatty acid derivatives or inert powders; either applied to the crystals after drying or added to the saturator, can be helpful in reducing caking tendencies after manufacture. Granulation by roll compaction would provide a good material for direct application; fine crystals could be used in compound fertilizers.

In accordance with the purity of the feed materials (plus any reworked product) and provided the plant has been properly designed and maintained in good condition, the direct-neutralization method will produce ammonium chloride of high purity. For example, in one Indian plant a product of a quality well in excess of British Pharmacopoea specifications can be achieved.

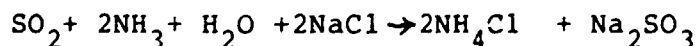
Byproduct HCl from production of potassium sulfate by the Mannheim process (see chapter XVIII) can be used. Also substantial amounts of byproduct HCl are available from other industries. Production of ammonium chloride could be a convenient way to utilize byproduct HCl which often has a low value and poses a difficult disposal problem.

Miscellaneous Processes-- Ammonium chloride can be made from ammonium sulfate and sodium chloride according to the reaction:



In one method, the ammonium sulfate and a 5% excess of common salt are added to an ammonium sulfate solution followed by heating and stirring for several hours. The resulting slurry is filtered or centrifuged while it is hot and is washed with hot water to separate the solid sodium sulfate from the ammonium chloride liquor. The latter is concentrated, cooled, and crystallized in leadlined pans and the crystals centrifuged, washed with water, and dried. Normally, only ammonium chloride for chemical purposes would be made by this method and in relatively small quantities since the ammonium sulfate used as a raw material could be considered a preferable fertilizer.

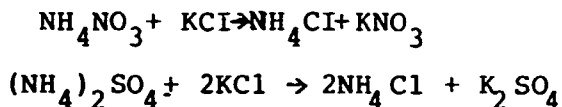
Another method is the use of SO₂ or sulfite liquor in conjunction with ammonia and sodium chloride, as shown below:



Ammonia and sulfur dioxide or sulfite liquor are added to a solution of common salt, and an excess of SO₂ equivalent to about 2% bisulfite is initially maintained, which is

reduced to about 1% as the reaction reaches equilibrium. As the temperature approaches 60°C, the sodium sulfite precipitates and is centrifuged, washed, and dried. The ammonium chloride mother-liquor is concentrated, crystallized, and centrifuged to yield a product of high purity after washing and drying.

Although the deliberate production of ammonium chloride for fertilizer use is rare in regions other than East Asia, it is a very common constituent of compound fertilizers (granular or liquid) in Europe and North America. It is formed in NPK fertilizers by reaction of ammonium nitrate and/or ammonium sulfate with potassium chloride:



These reactions go substantially to completion in most granulation processes, in nitrophosphate processes, and in liquid compound fertilizer processes. Ando, *et al.*, found that ammonium chloride was one of the most common forms of nitrogen in representative grades of NPK granular fertilizers in the United States (21). Thus, the production and use of compound fertilizers containing ammonium chloride is well established on a worldwide basis even though some people in the industry are not aware of it.

Nitric Acid

Historical Development

Nitric acid has an interesting history and was made in medieval times, if not earlier. About 1100, Geber described a method of preparing agua fortis by distilling nitre with copper sulfate and alum. In the mid-17th century, Glauber made fuming nitric acid by distilling nitre with strong sulfuric acid. Cavendish, in 1785, established that nitric acid was composed of nitrogen and oxygen by passing electric sparks through a mixture of these gases. Milner of Cambridge obtained nitric acid in 1788 by passing ammonia over heated manganese dioxide and absorbing the vapors in water (22). In 1839, Kuhlman patented a method of nitric oxide formation using platinum to oxidize a mixture of ammonia and air, which has become the basis of virtually all nitric acid manufacture today.

In 1895, Rayleigh demonstrated that nitrogen and oxygen could be removed from air and combined to form oxides of nitrogen by means of an electric arc. This phenomenon was also investigated by Crookes, and a small pilot plant using this principle was operated in Manchester, England, in 1900. However, the yield of nitric oxide by this method was only 1.5%-2.0%, despite high power requirements. A commercial plant was built by Brikeland and Eyde in Norway in 1902 using 350,000 hp (261,000 kw) from hydro sources and was operated for

several years. However, this process gave way to the ammonia-oxidation method using a platinum catalyst, developed by Ostwald and Brauer, and first operated in Germany about 1908 (23). This method also eventually rendered obsolete the nitre process (formerly the major source of nitric acid) whereby sodium nitrate, principally from Chile, was distilled with concentrated sulfuric acid and the vapors simultaneously oxidized and absorbed in water, using stoneware equipment.

The principal use for nitric acid is for fertilizer production, mainly for ammonium nitrate either as such or in compound fertilizers, nitrophosphates, nitrogen solutions, or mixed salts. Smaller fertilizer uses are for calcium and potassium nitrate. Nitric acid also has many industrial uses of which manufacture of explosives is the largest.

Properties of Nitric Acid

Nitric acid is a strong acid and a powerful oxidizing agent.

Anhydrous HNO_3 does not normally exist in liquid form. On distilling strong solutions under reduced pressure with concentrated sulfuric acid and ozone, one obtains almost pure nitric acid having a concentration of 99.7% and a specific gravity of 1.52. On freezing a 98% solution, colorless crystals having a melting point of -41.6°C separate. When heated at atmospheric pressure, concentrated nitric acid boils at 78.2°C but begins to decompose and eventually yields a 68% HNO_3 solution with a maximum boiling point of 120.5°C . This corresponds approximately to $2\text{HNO}_3 \cdot 3\text{H}_2\text{O}$ but is not a true hydrate since its composition and concentration are functions of pressure. The more important properties of nitric acid are summarized in table 4.

Two solid hydrates can be prepared-- $\text{HNO}_3 \cdot \text{H}_2\text{O}$ and $\text{HNO}_3 \cdot 3\text{H}_2\text{O}$ having melting points of approximately -38°C and -18.5°C , respectively. Heat of dilution is at a maximum, corresponding to $3\text{HNO}_3 \cdot \text{H}_2\text{O}$, although no true hydrate having this analysis has been found. When dilute solutions of nitric acid are concentrated under atmospheric pressure, a maximum boiling-point solution again corresponding to 68% HNO_3 results. The relation between specific gravity and percentage of nitric acid at 15°C is given in figure 7.

TABLE 4. PROPERTIES OF NITRIC ACID

Molecular weight	63.02
Color	
In liquid state	Transparent to yellow
As gaseous oxides	Transparent to yellow or brown (Color darkens on prolonged exposure to light)
Odor	Sweet to pungent
Hazards	
In liquid state	Rapidly attack flesh and most organic matter.
As gaseous oxides	Anesthetic to dangerously toxic.
Melting point	-41.6°C .
Boiling point of constant	120.5°C
boiling point mixture containing	
68% HNO_3 , at 760 mm. Hg	
Density of 68% HNO_3 , $20^\circ/4^\circ\text{C}$	1.41
Refractive index at 16.4°C	1.39
Solubility in water	Totally soluble at all concentrations.
Acidity	A strong acid, having

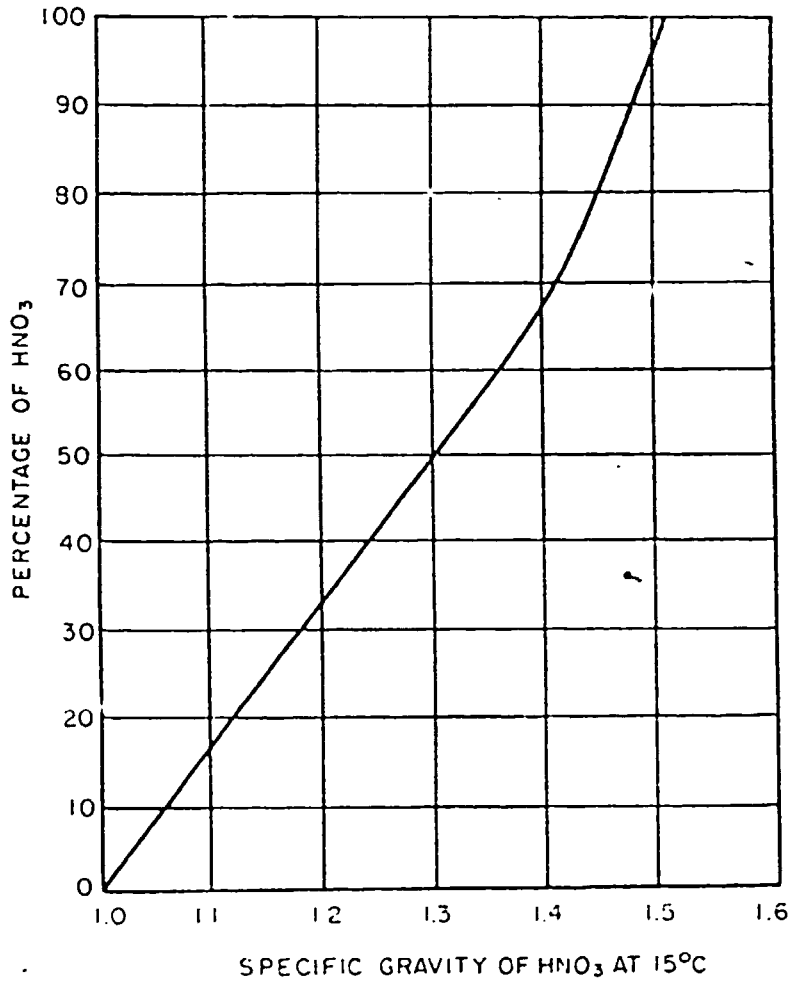


Figure 7. Specific Gravity at 15° C, Nitric Acid Solutions.

having pronounced oxidizing characteristics. Will passivate some metals such as iron and aluminum.

Entropy

Liquid at 16°C	37.19 cal/g-mole
Gas at 25°C	63.62 cal/g-mole
Heat of fusion	2,503 cal/g-mole
Heat of vaporization at 20°C	9,426 cal/g-mole
Heat of infinite dilution at 25°C	-7,971 cal/g-mole
Heat capacity at 27°C	26.24 cal/g-mole
Typical impurities in HNO ₃ of ammonia origin	Cl ₂ -- less than 5ppm HNO ₂ --less than 5 ppm

Oxides of Nitrogen

The oxides of nitrogen that are of interest in nitric acid production are:

Nitrous oxide	N ₂ O
Nitric oxide	NO
Nitrogen dioxide	NO ₂
Dinitrogen tetroxide	N ₂ O ₄

Of these, NO and NO₂ are of primary importance. N₂O₄ exists in equilibrium with NO₂ (2NO₂ \rightleftharpoons N₂O₄) and is not present in significant proportions at temperatures above about 100°C. It acts as a transitory intermediate in low temperature absorption of NO₂ in nitric acid. N₂O is seldom present in significant amounts. A mixture of nitrogen oxides, usually NO NO₂, is commonly referred to as NO_x particularly in pollution control parlance.

Chemical and Theoretical Considerations in Production of Nitric Acid from Ammonia

The chemical reactions that occur in the production of nitric acid from ammonia, including both the desired reactions and some undesirable reactions, are listed in table 4.A together with their heats of reaction.

The overall reaction is strongly exothermic. Of the total heat released more than half is released in the ammonia oxidation step (reaction 2) at a high temperature permitting economical recovery as steam or for other purposes (described later). Also part (about half) of the heat released by reaction 7 can be recovered at a useful temperature level. The remainder of the heat is released at a temperature too low for useful recovery and requires a net consumption of energy for circulation of cooling water, acid, and process gas and in some processes, for refrigeration.

Chemical Reaction Occuring in Nitric Acid Production
and Standard Heats of Reaction

Data from National Bureau of Sciences Technical Note 270-3,
Selected Values of Chemical Thermodynamic Properties, January, 1992.

No.	Reaction	Heat of Reaction ^a	
		Joules/ g mole	Cal/ g mole
1	$\text{NH}_3(\text{g}) + 2\text{O}_2(\text{g}) \rightarrow \text{HNO}_3(\text{aq}) + \text{H}_2\text{O}(\text{l})$	-436,918	-104,423
2	$4\text{NH}_3(\text{g}) + 5\text{O}_2(\text{g}) \rightarrow 4\text{NO}(\text{g}) + 6\text{H}_2\text{O}(\text{g})$	-226,523	-54,139
3	$4\text{NH}_3(\text{g}) + 3\text{O}_2(\text{g}) \rightarrow 2\text{N}_2(\text{g}) + 6\text{H}_2\text{O}(\text{g})$	-316,832	-75,723
4	$2\text{NH}_3(\text{g}) + 2\text{O}_2(\text{g}) \rightarrow \text{N}_2\text{O}(\text{g}) + 3\text{H}_2\text{O}(\text{g})$	-275,780	-65,911
5	$4\text{NH}_3(\text{g}) + 6\text{NO}(\text{g}) \rightarrow 5\text{N}_2(\text{g}) + 6\text{H}_2\text{O}(\text{g})$	-451,296	-107,860
6	$2\text{NO}(\text{g}) \rightarrow \text{N}_2(\text{g}) + \text{O}_2(\text{g})$	-90,309	-21,583
7	$2\text{NO}(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{NO}_2(\text{g})$	-57,108	-13,649
8	$2\text{NO}_2(\text{g}) \rightarrow \text{N}_2\text{O}_4(\text{g})$	-28,617	-6,839
9	$3\text{N}_2\text{O}_4(\text{g}) + 2\text{H}_2\text{O}(\text{l}) \rightarrow 4\text{HNO}_3(\text{aq}) + 2\text{NO}(\text{g})$	-15,747	-3,764
10	$3\text{NO}_2(\text{g}) + \text{H}_2\text{O}(\text{l}) \rightarrow 2\text{HNO}_3(\text{aq}) + \text{NO}(\text{g})$	-58,672	-14,023
11	$4\text{NO}(\text{g}) + 3\text{O}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l}) \rightarrow 4\text{HNO}_3(\text{aq})$	-144,334	-34,496
12	$4\text{NO}_2(\text{g}) + \text{O}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l}) \rightarrow 4\text{HNO}_3(\text{aq})$	-87,226	-20,847
13	$2\text{N}_2\text{O}_4(\text{g}) + \text{O}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l}) \rightarrow 4\text{HNO}_3(\text{aq})$	-58,509	-14,008

a. Heats of reaction per g mole of the underlined compound. All reactions are exothermic.

In the ammonia oxidation step, reaction 2 is the desired reaction, and reactions 3,4,5 and 6 are undesirable reactions which must be held to a minimum. The ammonia conversion efficiency, expressed as a percentage of the ammonia that is converted to NO, is mainly a function of the catalyst activity, temperature, pressure, thoroughness of mixing of the incoming air and ammonia, and velocity of gas flow through the catalyst. Conversion efficiencies above 94% can readily be obtained over a wide range of temperatures, 800°-1000°C. Above 1000°C the decomposition of NO (reaction 6) becomes significant, and loss of catalyst by volatilization of platinum and rhodium oxides becomes serious even at somewhat lower temperatures. The following tabulation shows the usual interrelationship of temperature (measured at the catalyst surface), operating pressure, and conversion efficiency (24). The data are typical of good practice and subject to some variation.

<u>Pressure,</u> <u>atm</u>	<u>Temperature,</u> <u>°C</u>	<u>Conversion</u> <u>Efficiency, %</u>
1	790-850	97-98
3.5	870	96-97
8	920	95-96
10.5	940	94-95

Temperature is controlled by preheating the air and ammonia and by the amount of excess air. The percentage of excess air is usually such as to result in 8%-11.5% NH₃ by volume in the ammonia-air mixture. Mixtures containing more than this must be avoided as the explosive limit starts at about 12%, and the stoichiometric requirement corresponds to 14.2% NH₃.

Various alloys and metallic oxides have been tried as catalysts, but usual preference is for platinum containing between 2% and 10% Rh. In high-pressure plants (8-11 atm) the usual alloy is 90% Pt and 10% Rh. In medium-pressure plants platinum alloyed with 5%-7% Rh often is used. In the U.S.S.R. a ternary alloy containing 3.5% Rh, 4% Pd, and 92.5% Pt is also used (25). The rhodium improves the mechanical strength of the platinum wire, increases its catalytic activity, and decreases catalyst losses. However, it is more than twice as expensive as platinum.

Many other alloys of the platinum group of elements have been tried. Also, base metal oxide catalysts have been tried experimentally and used commercially in wartime when platinum was unobtainable. Various combinations of oxides of bismuth, cobalt, thorium, cerium, and other metals have shown promise, and studies are continuing (26). However, so far no commercial use of these materials is known at present.

Reaction 1 is the desired overall reaction. The steps in the process are ammonia oxidation (reaction 2), oxidation of NO to NO₂ (reaction 7), and conversion of NO₂ to nitric acid (reaction 12). Reaction 12 is the overall result of a series of steps in which NO₂ or N₂O₄ reacts with water to form nitric acid and NO (reaction 10 or reactions 7, 8, and 9). The NO formed by these reactions must then be reoxidized and reabsorbed forming more nitric acid and NO and this cycle repeated until the amount of NO_x is reduced to a very low level.

An extremely important variable is the rate of gas flowing past the catalyst. Increased flow rates not only increase the weight of ammonia available for oxidation (assuming a constant gas composition) but also probably lead to higher oxygen transport rates on the catalyst surface and quicker removal of the newly formed intermediate products. Furthermore at low velocities, nitric oxide can diffuse upstream behind the catalyst to form nitrogen dioxide, which will subsequently result in loss of fixed nitrogen (reaction 5.) The same reaction can occur if unconverted ammonia passes through the catalyst, which could occur because of poor mixing or holes in the catalyst gauze.

Increased gas velocities, plus the provision of several layers of catalyst, also help to minimize undesirable downstream reactions between unconverted ammonia and nitrogen oxides, as well as the dissociation of nitric oxide into nitrogen and oxygen (reaction 6). Undesirable side reactions are thus minimized, and reaction 2 is favored by providing high gas velocities and a short contact time, which is usually in the region of 0.001 seconds.

Naturally, there is some limiting velocity beyond which undesirable effects occur which may include increased erosion, loss of catalyst, and perhaps incomplete ammonia oxidation. The optimum velocity increases with temperature (2). A common practice is to relate the catalyst weight to the plant capacity for design purposes. The relationship is commonly expressed as the "ammonia loading rate." A publication gave usual rates as 246-29. lb of ammonia per troy ounce of catalyst per day (3.6-4.3 kg/g/day) (24). This applies to both high- and low-pressure ammonia oxidation units.

Nitric oxide produced in the ammonia burner must be oxidized to nitrogen dioxide by the excess air present before absorption in water. Some nitric oxide is formed during this absorption and must also be oxidized prior to reabsorption (reaction 7.)

This is an unusual, third-order, trimolecular reaction since it has a negative temperature coefficient and is thus assisted by decreased temperatures and increased pressures. Conversion time has been shown to be an inverse function of the square of pressure. The rate of reaction is a direct function of the cube of the pressure (24). Although this reaction has been studied by several workers in great detail, it is still not fully understood.

The principal absorption reactions of significance in nitric acid manufacture are reactions 7, 8, and 9. The overall reaction between nitrogen dioxide and water is given in reaction 12.

The absorption of nitrogen dioxide in water has been studied extensively, and several principal conclusions can be drawn from the mass of research data available (27). For example, when temperatures are reduced, the gas-phase equilibrium moves toward the formation of additional dinitrogen tetroxide and an increased solubility in HNO_3 . As a result, in some cases a reduction of 5°C not only improves the absorption rate but also increases acid concentration by about 2%. In addition, the tendency for nitric acid to decompose is diminished. Hence, the overall absorber operation is greatly improved by lower temperatures.

Absorber performance is also aided by increased pressure not only because of the simultaneous beneficial effect on reaction 7 but also because the absorption moves towards the formation of stronger nitric acid. At pressures of 50 atm and with cooler/absorber residence times as long as 15 seconds, acid concentrations as high as 72% HNO_3 can be obtained although absorption efficiency is low. In commercial operation, however, uneconomic increases in pressure are needed to obtain concentrations above 60% HNO_3 , except in absorber units of special design.

Production Considerations

General Information-- Numerous proprietary processes for nitric acid manufacture are now available, but they differ mostly in design details or selected operating conditions and not in fundamental principles. The major features usually found in modern nitric acid plants include:

1. Vaporization, superheating, and filtration of anhydrous ammonia;
2. Preheating, filtration, and compression of process air;
3. Catalytic oxidation of ammonia;
4. Cooling of nitric oxide by heat exchange with various media, e.g., process air, boiler water, tail gas, etc.;
5. Oxidation of nitric oxide to higher oxides;
6. Absorption of nitrogen oxides in water to form nitric acid;
7. Bleaching of acid by additional air or other means;
8. Treatment of tail gas to improve total plant efficiency and to reduce air pollution;
9. Recovery of energy in compressed process gases;
10. Recovery of catalyst for resale.

Commercial processes often are classified according to the pressure used. Monopressure processes use the same pressure throughout; whereas, dual-pressure processes use a lower pressure for the oxidation step than for the absorption step.

The first nitric acid plants used near-atmospheric pressure throughout. However, practically all modern plants use elevated pressures; the following general types are common: (1) mono-pressure plants using medium pressure (3-5 atm) throughout, (2) monopressure plants using high pressure (8-13 atm) throughout, and (3) dual-pressure plants using medium-pressure combustion and high-pressure absorption. Simplified flow diagrams of each of these types of plants are shown in figures 8, 9, 10 and 11.

In commenting on the process diagrams, figures 8-11, it should be noted that each diagram is based on information supplied by a different engineering and construction organization. Each of the organizations offers a range of processes to meet various client needs. For instance, figure 8, identified as an Uhde process is only one of several processes offered by that company. Also several other companies offer nitric acid process, and there is no intention to imply that processes offered by the four companies mentioned by name are necessarily superior to those offered by other companies.

Some features of specific processes, which may not be evident from the flow diagrams, should be pointed out. In the Uhde medium pressure process, the air required for burning the ammonia is supplied by an uncooled air compressor. The operating pressure is governed by the maximum final pressure obtainable in an uncooled compressor, i.e., $P(\text{abs}) = 4-5$ bar in the case of radial compressors (for a plant capacity of up to 250 t.p.d. HNO_3 100%) and $P(\text{abs}) = 5-6$ bar with axial flow compressors (for a plant capacity of over 250 t.p.d. HNO_3 100%).

Hence, plant capacities of 1000 t.p.d. HNO_3 100% can be realized by employing only one ammonia combustion element and two absorption towers.

The air compressor is normally driven by a steam turbine and by a tail gas expansion turbine, the steam being generated within the plant.

The compressor may alternatively be driven by a high-voltage asynchronous or synchronous motor.

In this case, the entire steam generated is available for export.

The energy requirements of the plant can be adapted to prevailing conditions. For instance, if the credit for steam is high, the reaction heat may be used extensively to generate steam or, conversely, to heat the tail gas for power recovery in the tail gas turbine.

With this plant type, it is possible to produce an acid with a concentration of up to 68% HNO_3 or two acids with different concentrations, e.g. 60% HNO_3 and 68% HNO_3 , while the NO_x content in the tail gas can be reduced to less than 500 ppm.

The NO_x concentration may be further lowered to less than 200 ppm by selective catalytic reduction using a non-noble-metal catalyst and ammonia as the reducing agent according to the BASF NO_x abatement process.

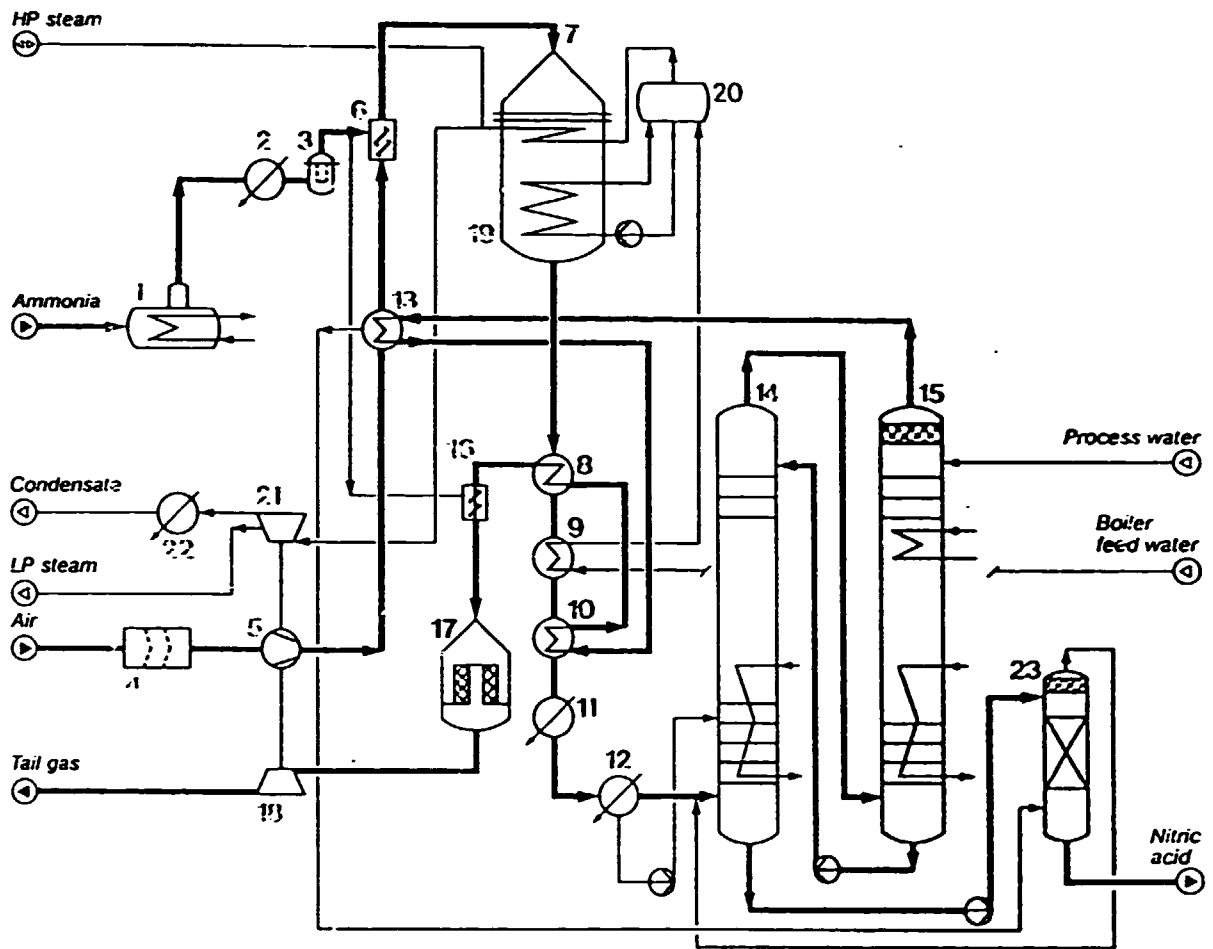
Over all nitrogen yield is about 96.2 or 95.8% in conjunction with the BASF process. Uhde also offers a high-pressure process (8-10 atm), a dual pressure process (ammonia oxidation at 5 atm and absorption at 10-14 atm), and a process for making highly concentrated nitric acid (98-99% HNO₃).

The Grande Paroisse dual-pressure extended absorption process (figure 9) typically operates at a pressure of 4 atm for ammonia oxidation and 10 atm for the absorption step. The absorption is carried out in single tall tower (40 m high) although, for improving the recovery in an existing plant which has a shorter tower, a second tower may be added. Chilled water from the ammonia vaporizer is used to cool the upper part of the absorption tower. The NO content of the tail gas is 200 ppm or less. The company also offers a medium-pressure process. The usual nitric acid concentration is 60%.

The Weatherly high-pressure process typically operates at about 10 atm pressure for both ammonia oxidation and absorption steps. As in other processes there is some pressure drop as the gas passes through the various process steps so the pressure of the tail gas entering the expander may be about 1.6 atm lower than the pressure at the air compressor discharge. All units are built to operate at pressures up to about 13 atm; therefore, by increasing the air compressor speed, the pressure and throughput can be increased. Also, the arrangement permits the operator to take advantage of the increased compressor output when the atmosphere air is cooler and therefore denser. Thus, the plant can be operated at up to 120% of design capacity.

The various heat exchangers from the ammonia oxidizer to the platinum filter are butted against each other to form a compact train and minimize construction costs. Spool pieces are inserted in the train to increase retention time and thereby increase the percentage of NO oxidized to NO₂ at a temperature high enough for economical recovery of the heat of reaction. As in other processes, cooling water is recirculated through the ammonia vaporizer.

In the extended recovery option illustrated in figure 10, the upper part of the absorption tower is cooled to about 2°C using refrigerated potassium carbonate brine as the coolant. Water is chilled in coils by the cold gas leaving the top of the tower and is circulated through heat exchange coils in a middle section of the tower to precool the ascending gas. Refrigeration of the brine may be done in a



- | | |
|----------------------------------|--|
| 1. NH ₃ evaporation | 13. Tail gas heater I |
| 2. NH ₃ gas preheater | 14. Absorption lower I |
| 3. NH ₃ gas filter | 15. Absorption lower II |
| 4. Air filter | 16. NH ₃ tail gas mixer |
| 5. Air compressor | 17. NO _x abatement unit |
| 6. NH ₃ /air mixer | 18. Tail gas expansion turbine |
| 7. NH ₃ burner | 19. La Mont waste heat boiler |
| 8. Tail gas heater III | 20. Steam drum |
| 9. Economizer | 21. Condensing turbine with extraction steam |
| 10. Tail gas heater II | 22. Steam turbine condenser |
| 11. Feed water preheater | 23. Bleaching tower |
| 12. Cooler condenser | |

Figure 8: Medium pressure Nitric Acid Process (Uhde)

- | | | |
|-------------------|---------------------------|----------------------|
| 1 VAPORIZER | 10 ECONOMIZER | 19 STARTUP TANK |
| 2 SUPERHEATER | 11 COOLER-CONDENSER | 20. STEAM TURBINE |
| 3 FILTER | 12 WEAR ACID SEPARATOR | 21 CONDENSER |
| 4 PREHEATER | 13 NITROUS GAS COMPRESSOR | 22 BLEACH AIR COOLER |
| 5 FILTER | 14 TAIL-GAS PREHEATER | 23. BLEACHER |
| 6 COMPRESSOR | 15 COOLER-CONDENSER | |
| 7 MIXER | 16 ABSORBER | |
| 8 CONVERTER | 17 SEPARATOR | |
| 9 TAIL-GAS HEATER | 18 TAIL-GAS EXPANDER | |

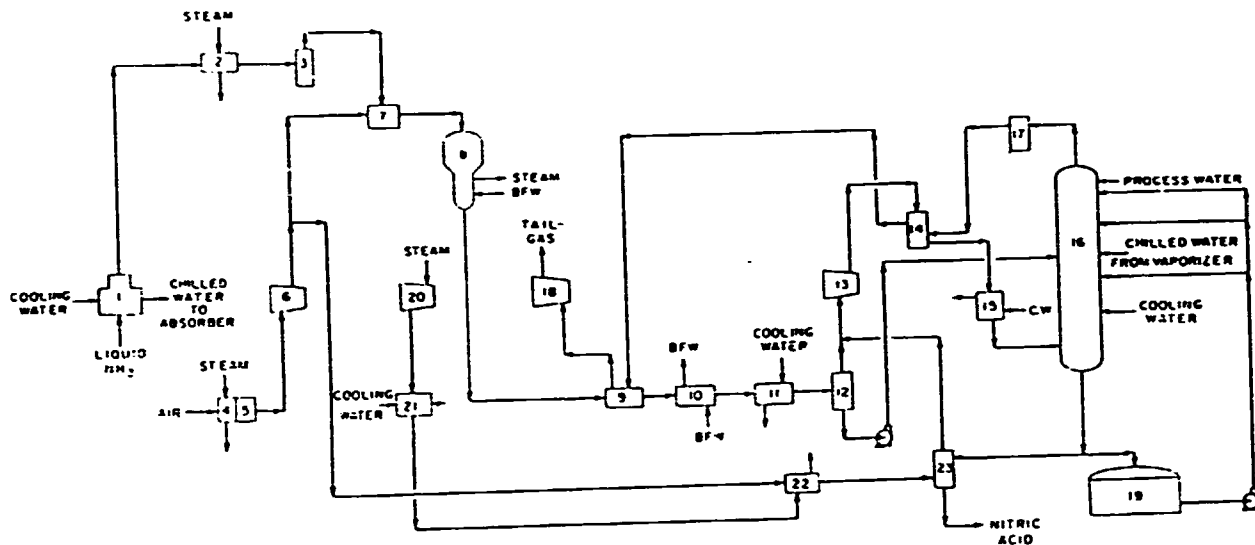


Figure 9. Dual-Pressure Nitric Acid Process (Grande Paroisse).

low-pressure ammonia vaporizer with the ammonia vapor going to ammonium nitrate production. Alternatively, mechanical refrigeration can be used. With the extended absorption system, the NO_x concentration can be lowered to less than 200 ppm. The company also offers the alternative of reduction of tail gas by combustion with fuel gas. The usual nitric acid concentration is 58%.

The C&I Girdler process (figure 11) is a high-pressure (about 10 atm) process. Refrigerated water is used in the upper part of the absorption tower to reduce the NO_x content of the tail gas to less than 200 ppm. Nitric acid concentrations range from 55% up to 65%. As in other processes higher concentrations are attained at the expense of higher NO content of tail gas unless special provision is made for its reduction by additional cooling, a greater number of plates in the absorber column, or chemical reduction.

Ammonia Preparation The anhydrous ammonia used must be free from the catalyst poisons mentioned below, and the oil content must be limited to a few parts per million to avoid fouling the vaporizer and catalyst screens. Liquid anhydrous ammonia produced to the required specifications is vaporized, filtered, and superheated to eliminate any possibility of liquid droplets entering the catalyst chamber and burning holes in the screens. The superheated vapor is thoroughly mixed with process air in various ways, e.g., by venturis, spargers, diffusers, etc. according to the type of process. Some plants also use specially designed ducts, baffles, and even packed columns to ensure complete mixing.

Process-Air Preparation-- Process air must also be free from catalyst poisons, dust and oil. In some plants, ambient air is given a preliminary wash with water in a spray tower or packed column before being compressed, filtered, preheated, and mixed with superheated ammonia vapor for subsequent combustion.

In certain plants employing atmospheric or low-pressure oxidation, the process air can be raised to the required pressure by suitably designed fans. For medium- and high-pressure oxidation, rotary machines of the lobe, vane, centrifugal or axial-flow design can be used, with an increasing preference for the two last types, since these units can be combined with various turbine drives and expanders in the form of one large single-shaft installation. (In some designs the heat of compression provides sufficient air preheat).

The ratio of ammonia to air, as well as the flow rate of each component, must be carefully controlled to ensure maximum conversion efficiency, freedom from explosion, and maximum plant output. Hence, reliable instrumentation in this section, as well as in other parts of the plant, is of the utmost importance.

Catalytic Ammonia Oxidation-- The customary choice is a platinum - rhodium gauze since this alloy promotes reaction and also meets other operating criteria, such as the severe conditions of service. A rhodium content of 4%-10% is usual. Since higher

- 1 AIR FILTER
- 2 EXPANDER TURBINE
- 3 AXIAL CENTRIFUGAL COMPRESSOR
- 4 STEAM TURBINE
- 5 TAIL GAS PREHEATER
- 6 ENTRAINMENT SEPARATOR
- 7 ECONOMIZER
- 8 AIR HEATER
- 9 ABSORBER
- 10 MIXER
- 11 GAUGE
- 12 CONVERTER
- 13 EXPANDER GAS HEATER
- 14 WASTE HEAT BOILER
- 15 GAS HEATER
- 16 PH 7.0 FILTER
- 17 WASTE HEAT EXCHANGER
- 18 COOLER-CONDENSER
- 19 ACID SEPARATOR
- 20 INTERCHANGER
- 21 VAPORIZER
- 22 FILTER
- 23 SUPERHEATER

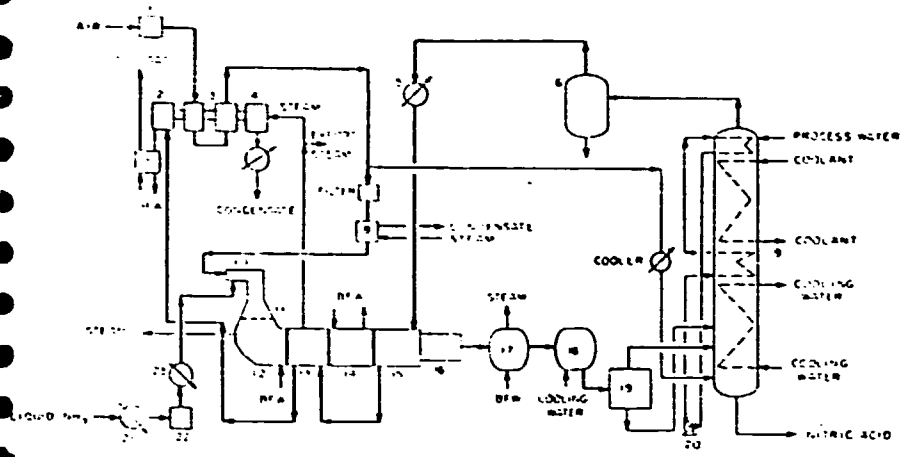


Figure 10. High Pressure Nitric Acid Process (Weatherly).

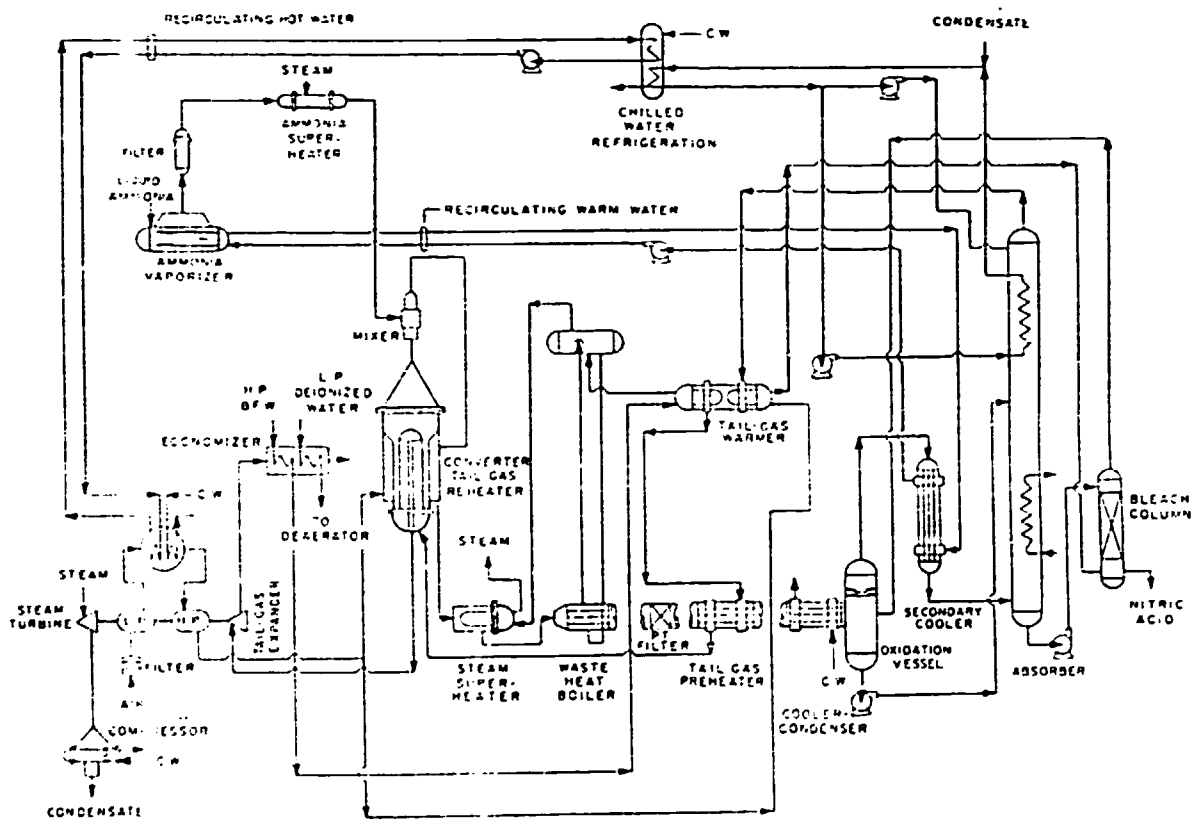


Figure 11. High Pressure Nitric Acid Process (ICI Girdler).

percentages tend to give slightly greater conversions and longer life, a 10% rhodium content has become standard in many processes.

The need to minimize and control contact time in order to suppress unwanted reactions and to minimize catalyst requirements led to the early adoption of fine screens as a suitable catalyst form. These are usually circular in shape and are stacked in multiple array, as the use of several (5 to 50) screens permits the residence time and contact time to be easily varied in order to obtain the maximum yield of nitric oxide. The use of multiple platinum gauzes in conjunction with preheated air was patented in 1909 by Kaiser in Germany, and these principles are still standard practice today. High-pressure burners are frequently fitted with gauzes having wires 0.076 mm in diameter woven with 1,024 meshes/cm². Finer gauzes with wires in the range of 0.051-0.057 mm are preferred by some for installation in low-pressure units. Modern looms are capable of weaving catalyst gauzes up to 5 meter width, as a result of which it is possible to produce 1000 tons of nitric acid per day in one single burner. Even larger burners can be manufactured, the upper limit is dictated solely by transport restrictions and flange machining. Chrome-nickel alloy grids are used to support these fine screens because they have a very low mechanical strength when they are operating in the 900°C range and, simultaneously, are being subjected to appreciable differential pressures caused by the high gas velocities in the burner chamber.

When first installed, a new gauze exhibits a relatively low activity, but after several days of operation under proper conditions, catalytic efficiency rises to a satisfactory level and remains nearly constant during the usual life of the screen, which should be several weeks, or, even months for high- and low-pressure burners, respectively. During operation, the crystalline structure of the platinum alloy is modified by the severity of service, and distortion takes place. Erosion also occurs if vibration is present especially at high temperatures and pressures, which also results in diminished activity. Eventually, the screen wears out and has to be replaced.

As is well known, platinum catalysts for most processes can be poisoned by such elements as As, Bi, P, Pb, S, Si and Sn, and ammonia-oxidation gauzes are no exception. Fortunately, synthetic ammonia is normally of high purity, unless accidentally contaminated. However, since air can be contaminated with dust or many other pollutants, thorough air cleaning is necessary. Location of the air intake in an area relatively free from contaminants will help. If poisoning by impure ammonia (Contd....P/38.)

or air should arise, deep penetration may occur, leading to the formation of inactive compound in the wires and, perhaps, to ruination of the catalyst. In other instances, contamination by traces of Cr, Fe, or Ni may temporarily reduce conversion efficiency, but this can often be restored by treatment with hydrochloric acid or certain salts. Frequently, activity can also be assisted by dismantling the catalyst screen assembly from time to time and removing accumulated solids by gently brushing the gauzes, which also helps to reduce the pressure drop across the burner. However, catalyst screens should be handled to the minimum extent because they become brittle during service.

Ammonia burners are classified into low-medium, and high-pressure types in accordance with conditions of operation. New plants are usually built with medium-(3-6 atm) or high-(8-12 atm) pressure burners although some plants with low-pressure burners are still in operation. Burners for atmospheric and low-to-medium pressures are often 3-4 m in diameter and perhaps may incorporate up to five or so catalyst screens; whereas, high-pressure burners usually are smaller in diameter-perhaps 1.2-1.5 m and may contain 25-45 gauzes. High-pressure units of this size can produce 250 ton of HNO_3 , or even more, per 24-hour day. Larger-size plants are now common; up to 1,100 tpd can be produced with a single burner with either high-or medium-pressure burners although two burners may be preferable for the lower range of medium-pressure processes. Gas velocities are much greater in high-pressure burners, and efficiencies are usually less, e.g, in the 93%-95% range, compared with 96%-97% or so for low-and medium-pressure units.

However, recent designs of some high-pressure burners, in which diameters are increased to reduce gas velocities, are said to approach efficiencies formerly only attainable in low-pressure units. Most low-pressure burners operate in the region of 865°C and high-pressure units at about 940°C. The higher temperatures, pressures, and gas velocities associated with high-pressure reflect greater catalyst losses. As a typical guide, Mukherjee, *et al.*, gave the following relative losses before recovery (28).

<u>Ammonia-Burner Pressure</u>	<u>Absorption Pressure</u>	<u>Relative Platinum Losses</u>
Atmospheric	Atmospheric	1
Atmospheric	3.2 x atmospheric	1
3.2 x atmospheric	3.2 x atmospheric	3
8.0 x atmospheric	8.0 x atmospheric	5

It should be noted that the cost of reprocessing used catalyst screens and of recovering and refining platinum and rhodium recovered in filters is appreciable. In a paper that compared a dual-pressure process (low-pressure oxidation) with a high-pressure process, the following data were given showing that total catalyst costs were \$1.81/ton of HNO₃ higher for the high-pressure process than for the low pressure (24).

Catalyst Cost per ton of Nitric Acid in Plants Using
Low-and High-Pressure Ammonia Oxidation

Pressure (Absolute)

	<u>High Pressure(10.1 atm)</u>		<u>Low Pressure(3.4 atm)</u>	
	<u>mg/ton</u>	<u>Cost,\$/ton</u>	<u>mg/ton</u>	<u>Cost,\$/ton</u>
Net loss of Pt	206	1.52	94	0.70
Net loss of Rh	29	0.48	7	0.10
Recovery, refining, etc.	-	<u>0.81</u>	-	<u>0.20</u>
Total catalyst cost.		2.81		1.00

Note: Cost of platinum-\$230/troy ounce -\$7.40/g.
 Cost of rhodium-\$511/troy ounce-\$16.63/g.
 (Since the paper was written the cost of platinum has increased greatly)

Most plants, particularly those with high-pressure burners, have filters of some sort that recover part of the platinum that is lost from the catalyst. Reported net consumption of platinum catalysts is in the range of 100-200 mg/ton of HNO₃ for medium-and high-pressure units. The downtime for catalyst renewal is relatively greater in high-pressure burners for a given weight of installed catalyst. Nonetheless, in some high-pressure plants, an average screen-life of about 60 days of continuous operation is obtained and further improvement is likely by more thorough cleaning of the combustion air and ammonia.

Cooling of Reaction Products-- Hot gases leaving the burner are cooled in order to increase the formation of nitrogen dioxide and to recover heat for use elsewhere in the plant, thereby contributing to the self-sufficiency of the process. In most medium and high-pressure plants, different sequences are used; the gases may pass in turn through a waste-heat boiler, a tail gas heater, a cooler-condenser, a compressor (in dual-pressure plants), and a second cooler-condenser. In some cases the gases also may pass through a steam superheater and a combustion air preheater. A platinum-recovery filter usually precedes the cooler-condenser. In one process all

Major heat exchangers are mounted horizontally end-to-end to simplify plant design and to reduce capital costs (see figure 10). In several European processes, some of the heat exchangers are built as an integral part of other equipment, for example, the burner or the waste-heat boilers. Heat recoveries of the order of 82%-85% are attained in some plants; higher figures are limited by dew point and corrosion considerations. In certain cases, about 1.1 tons of steam per ton of 100% HNO_3 can be produced. Most of this is normally used for power purposes within the nitric acid plant, but as much as 0.4 ton may be available for export.

The optimum gas-cooling sequence is closely associated with the number and types of energy recovery units and also the operating temperatures and pressures selected for each stage of the process. Plant capacities, ammonia costs, and capital and operating costs must also be taken into consideration when selecting the best cooling sequence for a specific installation.

Nitric Oxide Oxidation-- In atmospheric and some low-to-medium-pressure processes, one or more separate oxidation-cooling units are often included prior to gas absorption. These are built in the form of vertical towers cooled with external water curtains, shell-and-tube units, and also drum and cascade coolers. Excess air in the gas promotes initial oxidation, and some of the water vapor also present condenses to form weak nitric acid, which is later concentrated in the absorption section. Additional air for oxidation usually is injected at some point in the process, often in the absorption tower. In some plants, the gas is rapidly cooled in specially designed units to condense the water vapor without forming much weak acid, thereby helping to increase final acid concentration. A combined multistage condenser-cyclone separator unit, designed to remove water from the system and capable of yielding an acid concentration of about 63% HNO_3 has been described (29).

Some high-pressure processes seek to maximize the extent of oxidation of NO to NO_2 in the heat recovery train so that the heat generated by this reaction can be recovered at a relatively high temperature level. This can be accomplished by inserting extra chambers in the train to increase retention time, for instance between the waste heat boiler and the tail gas heater. Up to 80% of the NO can be oxidized to NO_2 before it enters the cooler-condenser by this means. In some other high-pressure processes, gas cooling and NO oxidation may be undertaken in a combined oxidation absorption column. However, the additional flexibility provided by a separate oxidation cooling unit and the ability to minimize the amount of weak acid formed prior to absorption is considered advantageous by many producers.

Nitrogen Dioxide Absorption-- At near atmospheric pressures, oxidation and absorption rates are slow, and some earlier atmospheric and low-pressure plants used between five and ten

large, packed stoneware towers in which the partially oxidized gases were absorbed in a countercurrent stream of nitric acid of increasing concentration. Maximum strengths attainable were in the range of 42%-52% HNO_3 .

In order to reduce capital investment and to obtain increased operating efficiencies, absorption under pressure was developed, using various types of equipment, e.g., cascade coolers, packed columns, spray towers, and columns incorporating bubble plates, sieves, and such special devices as the Kuhlman tray.

Since acid concentrations are favored by low-temperature absorption, several different cooling methods have also been developed, e.g., by external units of the plate, drum, or cascade type; by water curtains outside the tower; and also by cooling coils strategically located inside the absorption column. In some plants using low-pressure ammonia oxidation, vaporization of the ammonia is used to precool the absorber feedwater and cooling water.

Modern pressure-absorption systems permit absorption efficiencies well over 99% to be obtained, together with acid concentrations in the range of 55%-65%. In some processes, concentrations of up to 70% HNO_3 are achieved by using high pressures and cooled water in conjunction with specially designed absorption columns. In some plants, excess air may be injected into either the cooler or absorption column to speed up the oxidation reaction. Process water for absorption systems must be very pure to reduce corrosion effects in the nitric acid plant and also in applications involving subsequent use of the acid. In particular, the chloride content must be very low. Hence, water from condensate sources or ion-exchange purification units is often used.

Acid Bleaching -- Acid produced in most absorber units is invariably yellow or brown in color, because of dissolved nitrogen dioxide. This is removed either in a separate small bleaching tower or in an additional, lower section of the main absorber column by means of compressed-air injection.

Tail-Gas Treatment -- Except for atmospheric units, exit gas from the absorber is normally preheated and expanded in a turbine to recover an appreciable amount of the energy used for compression purposes. This gas contains mainly nitrogen plus some water vapor, oxygen, and mixed nitric oxides.

In the 1960s typical concentrations of NO_x in the tail gas ranged from 1,500 to 3,000 ppm. In recent years concern about pollution control has led to laws and regulations that reduced permissible levels of NO_2 in tail gas from nitric acid plants (see chapter XXIII). For example, the maximum concentration in the United States is equivalent to 200 ppm of NO_x for new plants or 500 ppm for existing plants. (The level is stated in kg of NO_2 equivalent per ton of HNO_3).

To meet the requirements that authorities in various countries have set up, a variety of methods have been used. Some

countries may take the view that the NO_x output of nitric acid plants is only a small percentage of the total, since far greater quantities are discharged to the atmosphere from combustion engines. In such cases dispersion by tall stacks and /or dilution of tail gas by air to control ambient levels may be acceptable. However, most countries require reduction of the actual NO_x output below the levels of 1960's.

The principal methods employed to control the level of NO in tail gas are (1) extended absorption, (2) catalytic reduction with fuel such as methane or ammonia plant purge gas, (3) selective catalytic reduction with ammonia, (4) adsorption by silica gel or molecular sieves, or (5) scrubbing with alkalis or urea solutions.

There is a growing preference for "extended absorption" as a method of control of NO_x in tail gas. The method consists simply of increasing the efficiency of the absorption system by adding a second absorption tower, by adding more section to the absorption tower, or in some cases by reducing the temperature in the last absorption stages by cooling coils using chilled water or other coolant. One company uses refrigerated potassium carbonate solution as the coolant. These methods can be used with either new or existing plants; with new plants there is greater flexibility in selecting the economic optimum combination of parameters, including increased pressure. Several organizations, including Friedrich Udhe(Germany), Societe Chimique de Grande Paroisse (France) C&I Girdler (United States) and D.M. Weatherly and CO. (United States), offer nitric acid plant designs with extended absorption which will give tail gas NO_x concentrations below 200 ppm which is low enough to satisfy the present requirements of the United States or any European country. For countries where less stringent regulations are in effect, some savings in capital cost may be possible. The extended absorption method has the obvious advantage that recovery of nitrogen as nitric acid is increased by 1.0%-1.5% (as compared with former practice) which partially offsets the increased cost.

Tail gas reduction by fuel involves reduction of NO_x with natural gas, naphtha, or ammonia purge gas which contains H₂, NH₃, CH₄, and N₂. Illustrative reactions are:

1. $2\text{NO} + 2\text{H}_2 \rightarrow \text{N}_2 + 2\text{H}_2\text{O}$
2. $4\text{NO} + \text{CH}_4 \rightarrow 2\text{N}_2 + \text{CO}_2 + 2\text{H}_2\text{O}$
3. $4\text{NO}_2 + \text{CH}_4 \rightarrow 4\text{NO} + \text{CO}_2 + 2\text{H}_2\text{O}$
4. $6\text{NO}_2 + 4\text{NH}_3 \rightarrow 5\text{N}_2 + 6\text{H}_2\text{O}$
5. $2\text{NO}_2 + \text{CH}_4 \rightarrow \text{N}_2 + \text{CO}_2 + 2\text{H}_2\text{O}$
6. $2\text{NO}_2 + 4\text{H}_2 \rightarrow \text{N}_2 + 4\text{H}_2\text{O}$
7. $6\text{NO}_2 + 8\text{NH}_3 \rightarrow 7\text{N}_2 + 12\text{H}_2\text{O}$

The tail gas contains about 3.5% oxygen which also reacts with the added fuel. When a deficiency of fuel is used such as to reduce the O₂ content of the tail gas from 3.5% to 2.5%, for

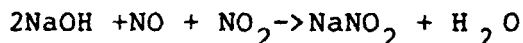
example, the NO₂ in the tail gas is reduced to NO as in reaction 3 above. This "decolorizes" the tail gas since NO is colorless while NO₂ has a yellow-to-brown color. In some countries decolorization of tail gas is acceptable although it does not lower the total NOx output.

For complete reduction of NOx enough fuel gas must be added to consume all of the oxygen in the tail gas. This method generates much heat and requires two or more catalyst beds in a series with intercooling to prevent excessive temperatures. The heat is recovered as steam. This method is likely to generate other pollutants in the tail gas. If the fuel is methane or any other hydrocarbon, appreciable amounts of CO and HCN are formed; with ammonia purge gas, some ammonia may remain in the tail gas.

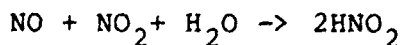
Selective reduction of NO by ammonia according to reactions 4 and 7 is a method that has been used successfully in several commercial plants in Japan, the United States, and Europe. Commercial processes are offered by Gulf Oil Chemicals, Inc. (United States); Mitsubishi (Japan); and BASF (Germany). Various catalysts are used, and the reaction takes place at temperatures ranging from 250°C to 450°C depending on the catalyst. The reduction unit may be located between the tail gas expander and the stack where the pressure is near atmospheric, or it may be located at some point between the absorption tower and the expander where the gas temperature is in a suitable range. The method is effective in reducing the tail gas NO concentration well below 100 ppm.

Adsorption by silica gel or molecular sieves is possible; the process requires regeneration of the adsorbent and permits return of the NOx to the process. One disadvantage is that water vapor in the tail gas must be removed for efficient adsorption.

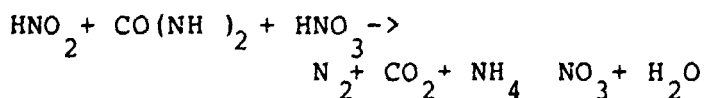
Scrubbing with alkali solution is effective only when the gas contains NO₂: NO mole ratios of 1:1 or more. Using NaOH as an example, the reaction is:



Utilization of the alkali nitrite may be a problem. Norsk Hydro has developed a scrubbing process in which the scrubbing medium is an aqueous solution of urea and nitric acid (30). The oxides of nitrogen react with water to form nitrous acid.



The nitrous acid then reacts with urea and nitric acid according to the reaction:

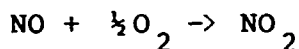


The intermediate reactions are believed to involve formation of nitrous acid (HNO₂) which reacts with urea to form HCNO and N₂; the HCNO reacts with HNO₃ and H₂O forming NH₄NO₃ and CO₂. The loss of fixed nitrogen in the process is a disadvantage.

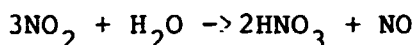
In the Goodpasture process (United States), the tail gas is scrubbed with ammonium nitrate solution with addition of ammonia in the scrubbing unit under controlled temperature and pH conditions. Part of the NOx may be recovered as ammonium nitrate, and part may be reduced to nitrogen.

An interesting version of the scrubbing principle is the COFAZ process (38).

The tail gas is scrubbed with water or weak nitric acid, in contact with activated carbon. The NO adsorbed on the carbon, reacts with the oxygen present in tail gas:



All the adsorbed NO₂ reacts with water to produce nitric acid and NO,



The nitric acid remains in solution in water, and can be recovered in the absorber unit; nitric oxide is removed with the gaseous effluent. This process doesn't need thermal regeneration and remove more than 80% of the NO present in the gas.

Various other scrubbing systems have been proposed or are under development, but, in general, the "extended absorption" method seems to be the most popular.

Energy Recovery-- Except in older plants operating at atmospheric pressure throughout and in very small medium-and high-pressure installations, most or all of the energy needed to drive the air compressor can be recovered in the form of steam and hot tail gas. In some instances, a small amount of surplus steam is generated.

This is made possible by the availability of highly efficient machines, which comprise a compressor, steam turbine, and tail-gas expander built in the form of a single, in-line unit. In dual-pressure processes, a compressor for raising the pressure of nitrogen oxides, prior to absorption, is also included. Occasionally, an electric motor is also added to the power unit for startup or emergency purposes, if sufficient steam is not always available. Electrical requirements for pumps and ancillary purposes are usually drawn from the main factory power supply.

Platinum Recovery-- Platinum passes into the gas stream in the form of very fine particles, and its loss can represent an increase of several percent in production costs. Therefore, recovery units are installed in many plants, and the fine dust reclaimed is returned with spent gauzes to the precious metal refinery. Several types of recovery units are in use; the more common incorporate filters of glass wool or silica fibers (31). One device uses calcium oxide as a filter medium, and the retained platinum dust is recovered by slurring with water and dissolving in nitric acid, followed by filtration. Recoveries should be of the order of at least 50% for dry filters and may be as high as 80% for the lime type of unit, according to the permeability of the filter media used and the type of process. Degussa's "getter" process uses Pd-Au (20% Au) gauzes placed immediately below catalyst. The entrained oxide vapors decompose at the surface maintained at high temperature and the noble metal diffuses into the "getter". Recovery of 45-60% is possible especially in high and medium pressure plants.

The unavoidable gold and palladium losses and the reprocessing costs amount to 40% of the original metal value. Also Engelhard can provide a similar process using palladium gauzes. Attempts to increase platinum recovery by using finer filter media may result in greater operating costs; hence, an optimum balance between these two factors must be adopted.

Technical and Economic Comparisons

The availability of low-, medium-, and high pressure techniques for oxidation and absorption offers a variety of alternative combinations by which nitric acid can be manufactured, and this has led to the development of numerous commercial processes differing largely in accordance with the combination selected (32). In general, high-pressure operation permits smaller plant units to be used for a given output and helps to reduce capital cost. High pressures also favor NO₂ absorption. However, high-pressure ammonia oxidation induces greater catalyst losses and also increases power requirements unless additional equipment is installed for power recovery. Because of recent emphasis on pollution control, the ability of high-pressure processes to attain acceptably low NO_x levels in the tail gas has favored their adoption. Therefore, most new plants use either mono-high-pressure or dual-pressure (medium-pressure combustion-high-pressure absorption) processes, although some mono-medium-pressure processes are used.

The advantages and disadvantages of the three types of processes can be summarized as follows:

	Mono-Medium Pressure 5/5 ^a	Dual-Medium-High Pressure 5/10 ^a	Mono-High Pressure 10/10 ^a
NH ₃ required, kg/ton HNO ₃	284	284	288
Pt loss, mg/ton HNO ₃ ^c	95	95	150
Electricity required kwh/ton HNO ₃	22	22	8
Steam credit, kg/ton HNO ₃	600	300	400
Relative capital cost	120	110	100
NOx in tail gas, ppm With abatement system	400	less than 200	less than 200

- a. Pressure in atmospheres in combustion and absorption, respectively.
- b. Typical values for extended absorption from various sources.
- c. Without any Pt recovery system.

The above values are intended to be illustrative only; actual values may vary widely depending on plant design and operating conditions. However, the tabulation illustrates the point that the high-pressure processes generally will have the lowest capital cost and highest operating cost because of higher platinum losses, less efficient NH₃ conversion, and lower steam recovery. The medium-pressure process will have the highest capital cost and lowest operating cost (assuming the NOx content of the tail gas is acceptable). The dual-pressure process represents a compromise. The choice may be influenced by local conditions.

A 1976 paper compared a dual-pressure process (COFAZ) operating at 3 and 10 atm with a single, high-pressure process (C&I Girdler) operating at 10 atm, both on a scale of 900 tpd and both with absorption efficiency sufficient to ensure tail gas NOx content of less than 200 ppm (24). Under U.S. conditions the capital costs were 13% higher for the dual-pressure process (\$13.8 versus \$12.2 million); under French conditions the cost differential was about 10%. Process requirements cover:

	Requirement per ton of HNO ₃	
	Dual Pressure	High Pressure
NH ₃ , Kg	282.1	286.6
Catalyst loss, mg	101	235
Electricity, kwh	4.7	7.5
Steam export, kg	341	456

The cost of production, with ammonia at \$121/ton, was estimated to be \$1.34/ton of HNO₃, lower for the dual-pressure process (\$34.28 versus \$35.84), not including capital charges. The authors concluded that, under the conditions assumed in the estimate, the saving in operating cost was not sufficient to justify the higher capital cost for U.S. conditions. However, changes in the cost of catalysts or in the value of steam could lead to a different conclusion. It was noted that the value of export steam would depend on what use could be made of it at the plant location.

Materials of Construction

The strongly oxidizing properties of nitric acid produce a passivating effect on certain metals, e.g., iron, steel, and aluminum, via the formation of complex oxides and nitride films. Hence, these metals can be employed for the construction of certain equipment items and storage vessels when used in conjunction with acids containing 55%-65% HNO₃ under mildly agitated or static conditions and not at elevated temperatures. For severe service, silicon-iron and some of the highly corrosion-resistant stainless steels are needed. Type 304 stainless steel is widely used for storage tanks. Dilute HNO₃ solutions, especially if agitated and heated, may also require the use of alloy steels, e.g., for the wetted parts of pumps, impellers, and distillation columns. For equipment used in handling hot, dry gases, mild steel is usually adequate. In some instances, plants built almost entirely of stainless steel are preferred since the saving in maintenance costs and the improved operating performance are said to justify the additional investment costs.

As regards nonmetallic materials, earlier plants used stoneware extensively for equipment construction. Industrial glassware has also been employed. Various fluorocarbon plastics in the form of lined and unlined piping, sheet and coatings, as well as gaskets and seals, are used to an increasing degree in nitric acid plants because of the inertness, flexibility, and convenience even though initial costs may be relatively greater than for steel or some ferrous alloys. Some of the latest proprietary fluorocarbon materials are said to be inert even to hot, fuming nitric acid.

Ammonium Nitrate

Ammonium nitrate is the most popular form of nitrogen fertilizer in most European countries and in some other temperate zone countries. It is popular in North America but not the most popular since that place is held by anhydrous ammonia. It is more readily available to crops than urea or ammonium sulfate; most crops take up nitrogen mainly in the nitrate form, thus ammoniacal nitrogen must be converted to nitrate in the soil before it becomes effective. While the nitrification process is rapid in warm soil, it is very slow in cool soil (10°C and below). Also urea is phytotoxic to some crops when placed near the seed while ammonium sulfate is strongly acid forming. For these and other reasons ammonium nitrate is the most popular nitrogen fertilizer in many temperate zone countries including most European countries. It is used as a straight material or

in mixtures with calcium carbonate, limestone, or dolomite called calcium ammonium nitrate (CAN) or ammonium nitrate limestone (ANL) or various trade names and in compound fertilizers including nitrophosphates. It is also a principal ingredient of most nitrogen solutions (chapter-X).

The main disadvantages of ammonium nitrate are: (1) it is quite hygroscopic, (2) there is some risk of fire or even explosion unless suitable precautions are taken, (3) it is reported to be less effective for flooded rice than urea or ammoniacal nitrogen fertilizers, and (4) it is more prone to leaching than ammoniacal products.

Increasing quantities of ammonium nitrate are used for blasting purposes in conjunction with fuel oil, and relatively small amounts are consumed by the brewing and chemical industries. The earlier "grained" type of ammonium nitrate, made by rolling the semi-molten salt in an open pan and coating with resin or waxes, has been largely superseded by prilled, granular and crystalline end-products.

Properties of Ammonium Nitrate

The more important properties of ammonium nitrate are given in table 5. The changes in crystal (Contd.....P/49..)

TABLE 5. PROPERTIES OF PURE AMMONIUM NITRATE (CRYSTALLINE FORM IV)

Color	White	
Molecular weight	80.04	
Nitrogen content	35.0%	
Density, 20°/4°C	1.725	
Melting point	170.4°C	
Solubility, g/100 g. of water		
Temperature (°C)		
0	118	
20	187	
40	297	
60	410	
80	576	
100	843	
Crystal states		
<u>Temperature (°C)</u>	<u>State</u>	<u>System</u>
169.6	Liquid	-
169.6 to 125.2	Cubic	1
125.2 to 84.2	Tetragonal	2
84.2 to 32.1	Rhombic	3
32.1 to -18	Rhombic	4
Below -18	Tetragonal	5
Critical relative humidities:		
20°C	63.3	
30°C	59.4	

state at 84.2°C and 32.1°C result in sudden expansion, which may cause particle degradation during processing and storage. The change in crystal form at 32.1°C can be particularly troublesome in climates where the ambient temperature often passes through this point; repeated cycling through this temperature can cause disintegration of prills or granules to a powder and lead to caking problems. However, methods of stabilizing the crystal form in the rhombic form IV have been developed and widely used. One of these methods developed and patented by Mississippi Chemical Corporation (United States) consists of adding a small proportion (about 1%) of a mixture of ammonium sulfate and diammonium phosphate called "Permalene." Magnesium nitrate is also used as stabilizer in some European countries. Another characteristic of ammonium nitrate is its negative heat of solution: 60 parts of salt will give a reduction in temperature from 13.6°C to -13.6°C when dissolved in 100 parts of water.

Hazard of Ammonium Nitrate

It is well known that ammonium nitrate can be used as an explosive. In fact, several plants were built during World Wars I and II to produce ammonium nitrate for use in bombs and other explosives. For this purpose it was usually mixed with more powerful explosives or detonators. A mixture of ammonium nitrate with about 6% fuel oil is widely used as a blasting agent in mining operations. Fertilizer-grade ammonium nitrate previously (in the 1940s) was conditioned with an organic coating (a mixture of paraffin, rosin and petrolatum), and some disastrous explosions occurred when shiploads of this material were detonated by fire and confinement. These disasters led to strict regulations governing the manufacture, transport, storage, and use of ammonium nitrate for fertilizer purposes. Some countries forbid the sale of straight ammonium nitrate as fertilizer. In these countries, the mixture of ammonium nitrate with calcium carbonate called CAN is permitted. Formerly CAN contained 20.5% N, corresponding to about 60% ammonium nitrate; at present, the most common grade is 26% N (75% AN).

In other countries (France, U.S.S.R., Romania, the United Kingdom, and the United States, to name a few) straight ammonium nitrate is commonly used as a fertilizer with strict regulations. For instance, the Fertilizer Institute (United States) has published a definition of ammonium nitrate fertilizer which follows:

"Ammonium Nitrate Fertilizer is defined as solid ammonium nitrate containing a minimum of 33.0% nitrogen, having a minimum pH of 4.0 in a 10% aqueous solution, 0.20% maximum carbon, 0.010% maximum elemental sulfur, 0.150% maximum chloride as Cl, or particulated elemental metals sufficient to release 4.60 ml, maximum, of hydrogen from 50.0-g sample and which will pass the detonation propagation test in section 2.0 and the burning test in section 4.0."

1501

The publication contains analytical and test procedures. In the detonation propagation test, ammonium nitrate is packed into a 6-ft (1.83-m) section of 3-in (7.6-cm) diameter iron pipe of specified quality, and a specified explosive charge is placed in the ammonium nitrate in the top of the pipe. When the explosive charge is detonated, the extent, if any, to which the ammonium nitrate is detonated is judged by the length of damaged pipe. Any material that propagates through the length of the pipe and leaves no undamaged pipe is considered unsafe.

The burning test is rather complicated, but in general it is designed to exclude formulations that may catalytically increase the decomposition rate of ammonium nitrate even though the catalytic substance is not excluded by the definition or detected by analytical procedures.

Further regulations cover precautions to be taken in storing, packaging, and transporting ammonium nitrate and in fighting fires where ammonium nitrate is present.

Some compound fertilizers containing ammonium nitrate and chloride, such as potassium chloride, are subject to propagated decomposition or "cigar burning" when ignited. The ignition temperature is about 200°C, but it may be lowered by certain sensitizing agents, such as copper salts. The range of composition of NPK and NK fertilizers that are subject to decomposition has been studied by Huyden and Perbal (33), TVA (34), and others. As little as 4% KCl (about 1.9% Cl) is sufficient to make some mixtures susceptible to cigar burning. The reaction is inhibited by ammonium phosphate; therefore, many NPK compositions containing ammonium nitrate and potassium chloride are free from this hazard. Figure 12, taken from Perbal (33), shows the area of cigar burning compositions in the system $\text{NH}_4\text{NO}_3\text{-KCl-NH}_4\text{H}_2\text{PO}_4$.

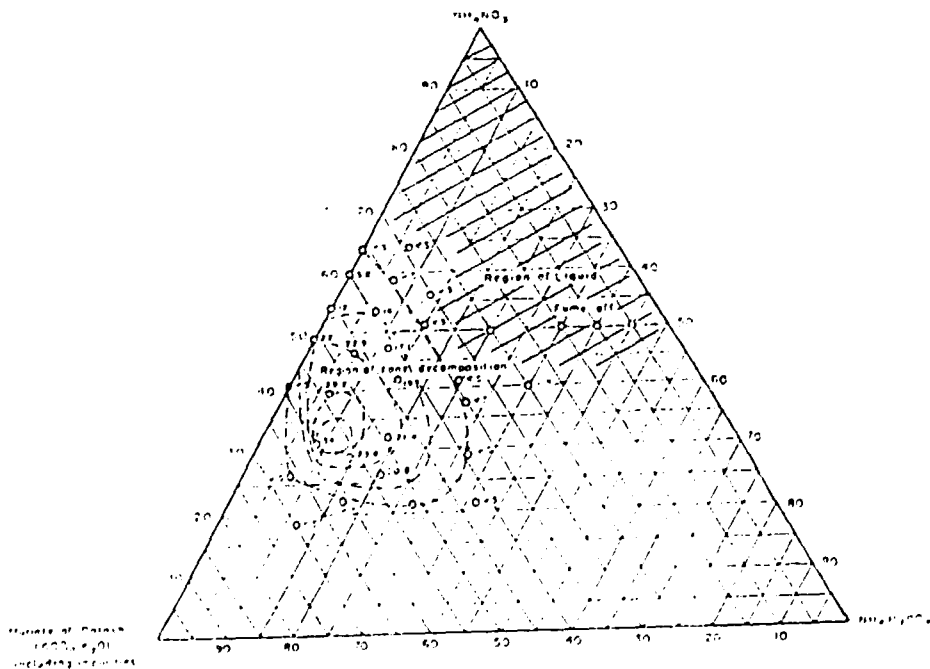
For materials that are susceptible to cigar burning, the reaction may be initiated by such accidental means as a piece of hot metal from a welding operation or an electric light bulb that becomes buried in the fertilizer or by overheating material caked on the flights of a dryer. Once initiated, the decomposition propagates through the mass of material at a rate that usually ranges from 5 to 50 cm/hr. The temperature in the decomposition zone usually is 300°-500°C. The exact nature of the reaction is not entirely clear, but it results in complete destruction of the ammonium nitrate and evolution of some of the chloride. Noxious red, white, yellow, or brown fumes are given off containing NH_4Cl , HCl , Cl_2 , NO_2 , and other oxides of nitrogen N_2 and H_2O . The fumes are toxic and have resulted in several fatalities in some incidents.

Since the reaction does not require oxygen, other than that present in ammonium nitrate, the fire cannot be extinguished by smothering. It can only be stopped by flooding with water. If a localized area of decomposition in a bin or pile is discovered early enough, the decomposing material may be removed from the building by a power shovel, for example, and extinguished by water, thereby saving the remainder of the material.

Since compound fertilizers may have a variety of formulations, it is not always possible to predict what composition will be in the cigar-burning class. TVA has developed a simple test; a 50-lb (23-kg) bag of the fertilizer to be tested is heated at one end with a blow torch until decomposition has started as evidenced by copious fumes. If the decomposition stops when the flame is removed, the material is not subject to propagated decomposition. If it continues to decompose the rate of progress of the decomposition zone can be measured by thermocouples inserted in the material at 10-cm intervals.

A more elaborate and precise method is described in a handbook titled Selected Methods of Test for the Thermal Stability of Compound Fertilizers Containing Ammonium Nitrate, which was issued jointly by IFA and APEA (first printing in 1970). The "zonal decomposition test" is carried out in an apparatus which consists of a trough 15 x 15 x 50 cm constructed of heavy wire mesh.

The trough is filled with the fertilizer to be tested, and a steel plate at one end of the trough is heated to a temperature between 400°C and 800°C, either with gas burners or an electric heating element. Heating is continued until decomposition of the fertilizer adjacent to the heated steel plate is well established or up to 1 hour. Then heating is discontinued and the position of the decomposition front is noted. If propagation of decomposition stops almost as soon as the heat source is turned off, the material does not show self-sustaining decomposition. If the decomposition zone continues through the entire trough, the fertilizer is capable of self-sustaining decomposition. If desired, the rate of progress of the zone may be timed. In some cases decomposition may continue some time after the heat is turned off but stops before it reaches the end of the trough. In this case the handbook suggests that the decomposition should be regarded as self-sustaining if it continues for a distance of 15 cm.



Note: Rates of Movement of Decomposition Zone Are Shown in cm/hr.

Figure 12. Area of Decomposition in the System $NH_4NO_3-NH_4H_2PO_4-NH_4H_2PO_4$.

The issuing organizations (IFA and APEA) disclaim responsibility for practical application of the test. However, some countries (mainly Scandinavian) prohibit the sale of fertilizers that are subject to self-sustaining decomposition, and the "trough test" described above is an accepted test method to identify such fertilizers.

The IFA/APEA handbook also contains test methods for determining explosibility (three methods), homogeneity, decomposition at elevated temperatures, self-heating of fertilizers, and oxidizing potential. Various agencies have worked out regulations for transport of potentially dangerous goods by rail, ship or barge, air, and truck.

Ammonium nitrate is generally regarded in most countries as posing no unacceptable hazard when suitable precautions are taken. "Fertilizer grade" ammonium nitrate (see definition above) cannot be exploded by impact. There are no records of explosions due to heat and fire alone. In several cases storage buildings and farm buildings containing ammonium nitrate have burned without explosion. In one case of a warehouse fire, a small amount of ammonium nitrate that had been contaminated by oil drippings from a power shovel exploded, but the rest of the ammonium nitrate did not explode. Some countries may prohibit straight ammonium nitrate from which it is relatively easy to make explosive devices.

The question is often asked "what maximum percentage of ammonium nitrate in fertilizer is nonexplodable?" There is no simple answer to this question; it depends on what materials the ammonium nitrate is mixed with, how much carbonaceous material is present, if any, how much detonator is used, and several other factors. As mentioned previously, pure ammonium nitrate is difficult to detonate, but it can be exploded if it is confined and primed with enough high explosive. Permal describes tests in which mixtures of ammonium nitrate and various other fertilizer materials were coated with 0.4% fuel oil. The mixtures were then tested for explosibility by two standard test procedures, both involving a standard detonating charge (33). As a result of these and other tests, the Dutch Government authorities have set the following maximum limits of ammonium nitrate in mixtures:

<u>Material Mixed with Ammonium Nitrate</u>	<u>Maximum Allowable % Ammonium Nitrate</u>
Chalk	80
$(\text{NH}_4)_2\text{SO}_4$	40-45
$(\text{NH}_4)_2\text{HPO}_4$	65-70
CaHPO_4	70
KCl	70
K_2SO_4	70

Perbal concludes that compound fertilizers in general may be regarded as safe from explosion hazard if they contain less than 70% NH_4NO_3 unless there is a high percentage of $(\text{NH}_4)_2\text{SO}_4$ or other reducible material in the mixture in which case the material should be tested (33).

Safety Aspects.

The EC's (European Community) recommendations regarding characteristics and limits for Ammonium Nitratesingle Nutrient Fertilizers with elevated Nitrogen content are as under:

1. Porosity (oil absorbency)

The absorbency of oil of the fertilizer must not exceed 4% wt. after two fold heating cycle at temperatures from 25 to 50°C.

2. Combustible Materials.

The weight portion of combustibles measured as C, must not exceed 0.2% if the nitrogen content of the fertilizer is higher than 31.5% wt, and must not exceed 0.4% if the nitrogen content is less than 31.5% wt, however, higher than 28% wt.

3. pH

A solution containing 10 g of the soluble portion of the fertilizer in 100 ml water show a pH-value of at least 4.5.

4. Particle size

A maximum of 5% wt of the fertilizer may pass a screen of 1 mm width of mesh, and a maximum of 3% wt may pass a screen of 0.5 mm width of mesh.

5. Chlorine

The chlorine content of the fertilizer must not exceed 0.02% wt.

6. Heavy Metals

The fertilizer must not contain any deliberately added heavy metals. As far as traces are present as a consequence of the production process, they must not exceed the limits fixed by the authorities.

Production Methods

Several proprietary processes for ammonium nitrate manufacture are available, using various combinations of different neutralization, evaporation, and drying and finishing methods.

Solid ammonium nitrate is produced in the form of prills, crystals, and granules, either alone or in combination with other materials. Large tonnages of ammonium nitrate are also made in the form of solutions having concentrations in the range of 80%-90% for use in granular compound fertilizers. The hot solution is shipped to granulation plants in insulated rail or road tankers, especially in the United Kingdom. The solution is also used to prepare nitrogen solution containing ammonia or urea for use in granulation plants or liquid fertilizer (see chapter X). The major unit operations used in ammonium nitrate manufacture are described below.

Neutralization-- When sufficient steam to operate the plant is readily available from byproduct or other low cost sources, the use of an atmospheric type of neutralizer may be preferable since such units are relatively low in capital costs and simple to operate. Alternatively, most or all of the steam needed to preheat the feeds and to concentrate the ammonium nitrate solution can be generated by neutralizing acids containing more than 50% HNO_3 in a unit of the pressure type. (By using a 64% acid, about 1 ton of steam can be produced for each ton of ammonia neutralized.) In some plants, especially those designed to make a crystalline product neutralization is performed under vacuum in equipment similar to that used for ammonium sulfate manufacture (35).

In pressure neutralizer processes, the neutralizer usually operates at 4-5 atm and 175°-180°C. Nitric acid is fed to the neutralizer at a usual concentration range of 50%-60%. In some cases it may be preheated with byproduct steam. Ammonia is fed to the neutralizer in gaseous form. If it is available in liquid form, it is vaporized in a heat exchanger by steam or air. If air is used the cooled air may be used to cool the prilled or granulate ammonium nitrate product. The neutralizer may be operated at a low pH (2-4) to avoid ammonia loss, and more ammonia may be added later to adjust the pH to 7. The concentration of the solution from the neutralizer usually is in the range of 80%-87% ammonium nitrate. It is evaporated further by use of steam from the neutralizer to a concentration of 94%-98%. In many plants, a final evaporator concentrator is used to bring the solution concentration up to 99.5%-99.8%.

In the case of atmospheric pressure neutralization, the temperature in the neutralizer is lower (about 145°C), and the steam generated is at a lower temperature and pressure. The waste steam can be used to vaporize ammonia or to evaporate the ammonium nitrate solution in a vacuum evaporator. Depending on the efficiency of utilization, the heat of reaction, the nitric acid concentration, and other factors, the net steam requirement may range from 0.0 to 0.5 ton/ton of AN; in some cases a small surplus of steam may be available for export.

Hydro Agri process for production of Ammonium nitrate is illustrated in fig 13. A large 3000 mtpd plant which operates for 350 days per year is in operation at sluiskil, Netherlands(40). In this process the neutralizer operates at 4.5 atm. abs. and 175-180°C with a combined natural/forced convection loop.

Nitric acid at 60% is preheated with vacuum process steam to 70-75 °C. Liquid ammonia is vaporized with vacuum steam and then superheated with low pressure process steam to 70-75 °C. The neutralizer is operated with a slight ammonia excess. The superheated process steam evolving during the reaction is scrubbed in a cocurrent flash column where it is neutralized with a metered nitric acid flow. This primary process steam is then used to concentrate the neutralizer solution to 95%. This solution is first flashed to nearly ambient pressure to recover further process steam.

The process steam condensate from the shell-side of the concentrator is cooled and exported as boiler feedwater after ion exchange guard. Extra utility steam (free of any process contamination) is generated in an auxiliary boiler in the forced convection loop, typically 0.20 ton steam (5 atm abs) per ton of 100 % AN solution. Residual vacuum process steam is condensed by air cooling. The resulting process condensates are acidified and recycled to the upstream nitric acid plant as process feed water.

A new method has been developed (Fig-14) by AZF (France) The neutralization takes place in a pipe line reactor where superheated ammonia is mixed with heated nitric acid.

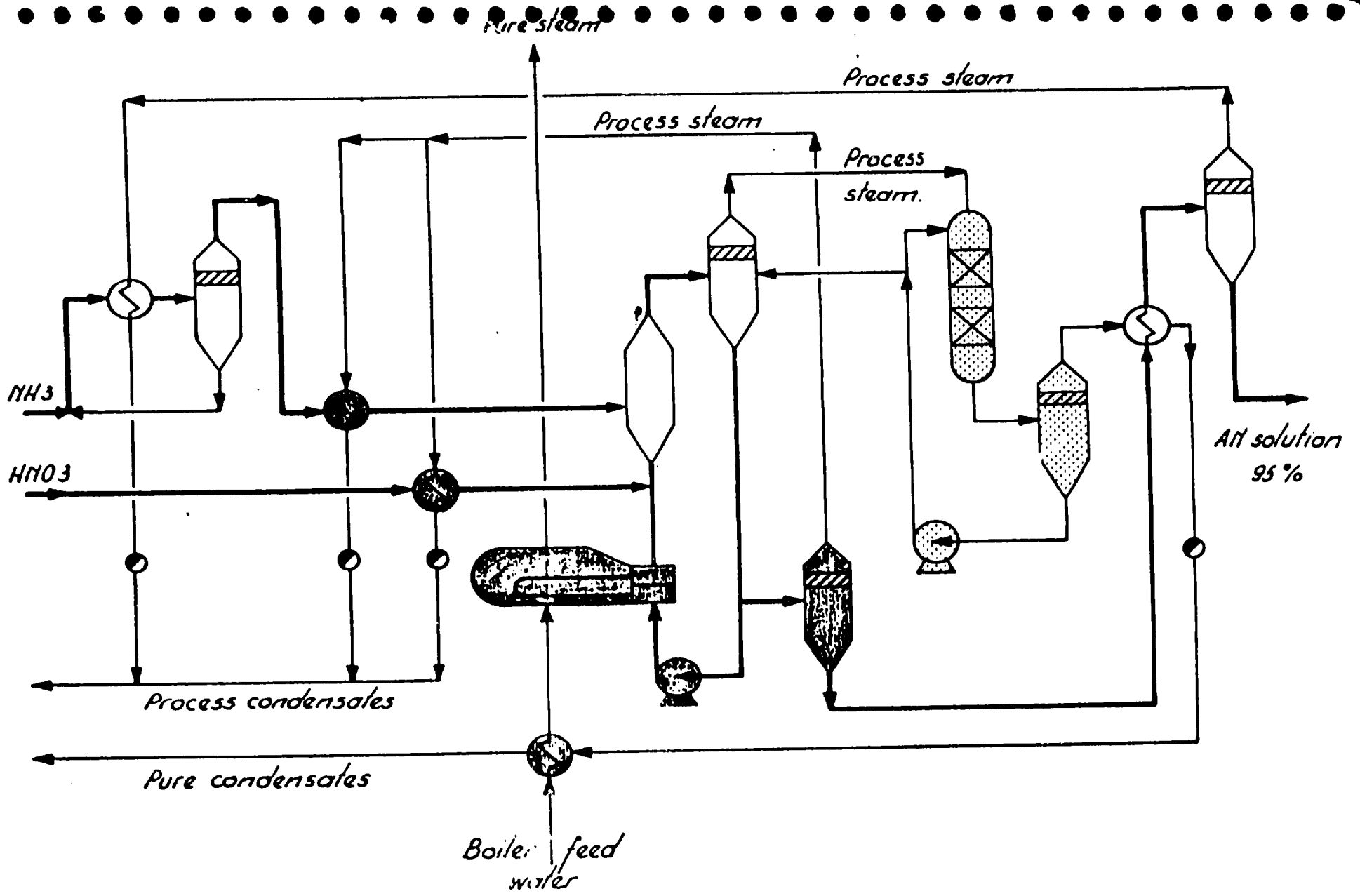
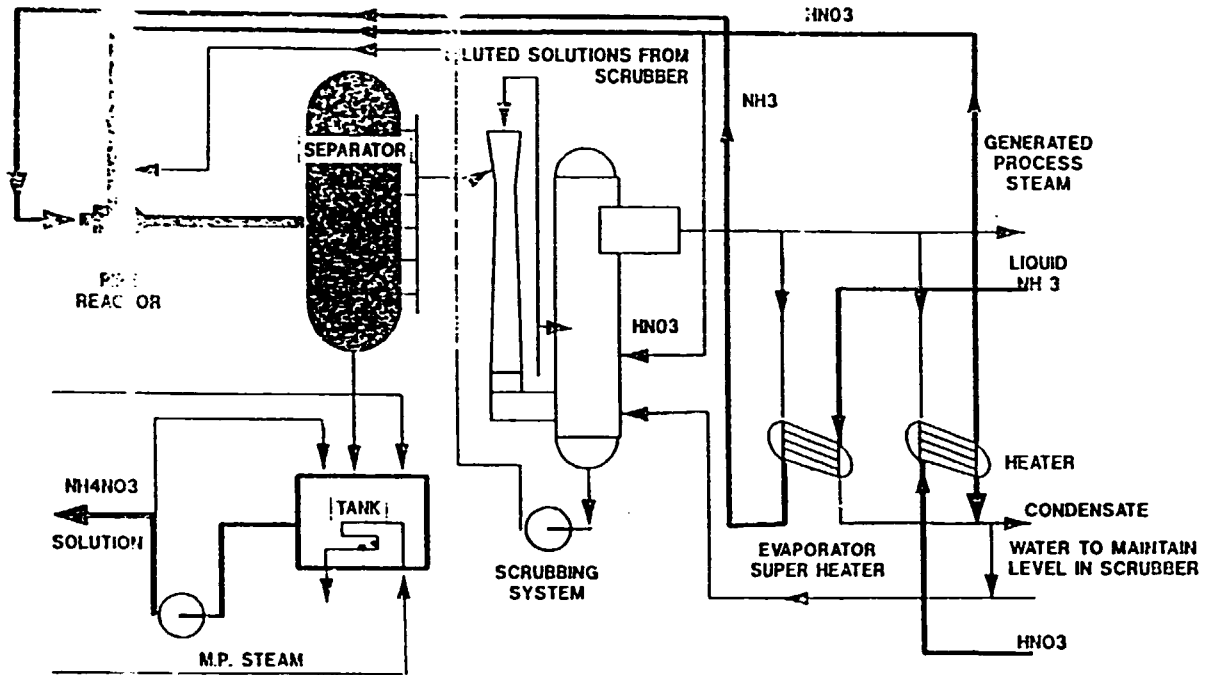


FIG. 13 HYDRO AGRI AMMONIUM NITRATE NEUTRALIZATION PROCESS.

Fig: 14 AMONIUM NITRATE SOLUTION
A ZF PIPE REACTOR PROCESS



under an atmospheric separator. Concentrated ammonia recovered in a tank is neutralized with a small amount of ammonia and stripped. From 58% nitric acid, it is possible, without any concentrator, to obtain directly a 92% solution.

This method allows a high production flexibility, and required low investment cost. It is a one stream process without recirculation (38).

Finishing Processes

In the past several finishing processes have been used including graining, flaking, granulation, crystallization, and "low-density" prilling. In low-density prilling, the ammonium nitrate solution is fed to the prill tower at about 95% concentration, and the resulting prills are dried and cooled. The prills are somewhat porous and may have an apparent specific gravity of 1.29 compared with 1.65 for high-density prills. Some of these methods are still in use, particularly for AN used as a blasting agent. A porous prill or granule that would absorb oil is preferred for this use.

For fertilizer use, the high-density prilling process, using 99% solution concentration, has been used in most new plants that make straight AN. Quite recently, however there has been a trend toward greater use of granulation processes that also use 99% solution. Granulation processes in commercial use are, a pan granulation process developed by Norsk Hydro (Norway) and a spray drum granulation ("Spherodizer") process developed in the United States by C&I Girdler, a subsidiary of Bechtel Corp.

Two new developments in this area are:

A fluid bed granulator developed by NSM (39). The granulator comprises several granulation chambers, followed by a cooling section (also several chambers) in which complete crystallization as well as some cooling is achieved. (Fig-15)

A 97% ammonium nitrate solution is sprayed upward in the first chambers into the layer of particles, which are gradually built up to granules by accretion.

After granulation the granules are transported to a screen, and after to a fluid bed cooler.

The solid recycle ratio is 0.4:1.

All grades between 26% N (CAN) and 34.5% N can be produced (39).

A Fluidized Drum Granulation (FDG) process, (40) has been developed by French company Kaltenbach-Thuring. It is a combination of drum granulation and fluidized-bed technology, in which the liquid layer acquired by the particles in the bottom of a granulation drum is solidified in a fluidized bed mounted inside the drum, onto which the particles drop from the lifting flights. By adjusting the

temperature of the fluidizing air, it is possible to set up a fluidized bed either to cool or to dry the circulating particles. Thus the FDG process is equally applicable for granulating materials fed in the molten condition, such as ammonium nitrate, urea or sulphur, or as a slurry, such as diammonium phosphate.

The process has a high granulation efficiency, with a recycle ratio of only 0.8/1 for ammonium nitrate or urea. On account of the granulation mechanism, with successive layer formation and cooling, granules are produced. Since granulation and drying are combined in the granulator, the evaporation of water occurs by layer, which not only gives the highest evaporation rate, but also very even, progressive drying, resulting in dry, dense granules. The granules are also very round and evenly sized. (Figure 16)

The advantages of the granulation processes over prilling are:

- (1) a wider choice of granule size including "forestry grade" (4-10 mm) and (2) less difficult collection of fume and dust to meet new, strict pollution control standards. The granulation processes are also applicable to urea and will be described further in chapter IX. Figure 17 is a process diagram of a high-dry prilling process including the neutralization and evaporation step.

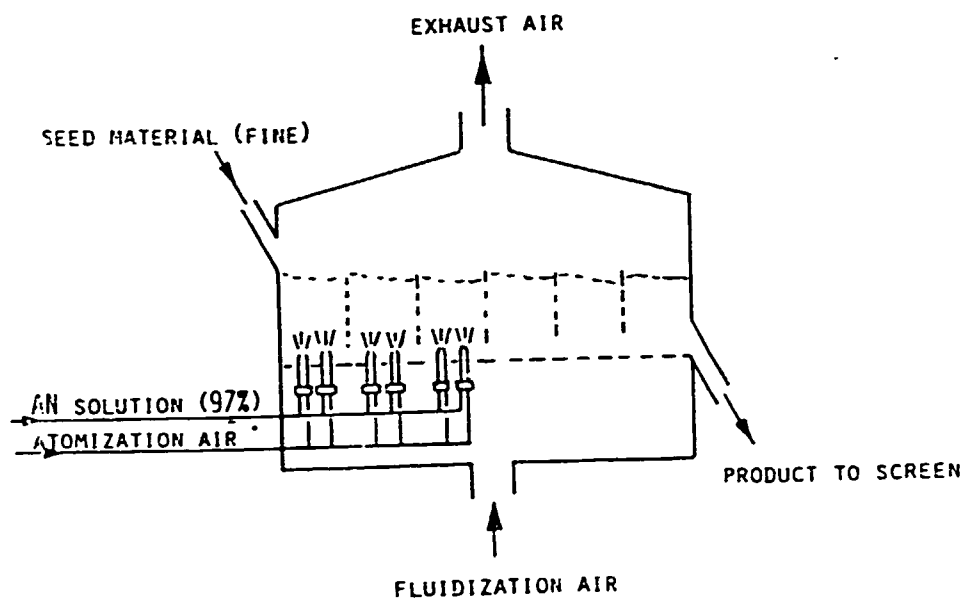


Figure 15 NSM fluid bed granulator. (Courtesy of Nederlandse Sticks-
stoff Maatschappij N.V.)

FLUID DRUM GRANULATOR

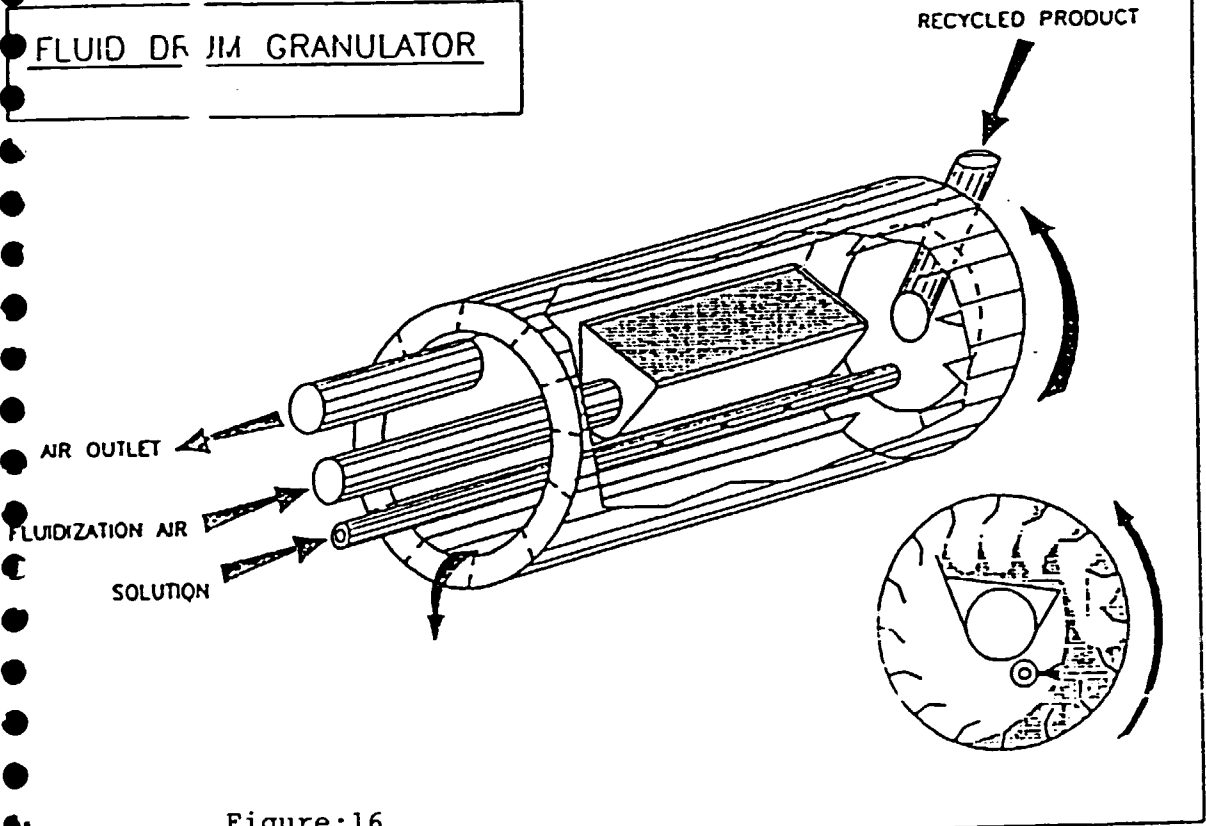


Figure:16

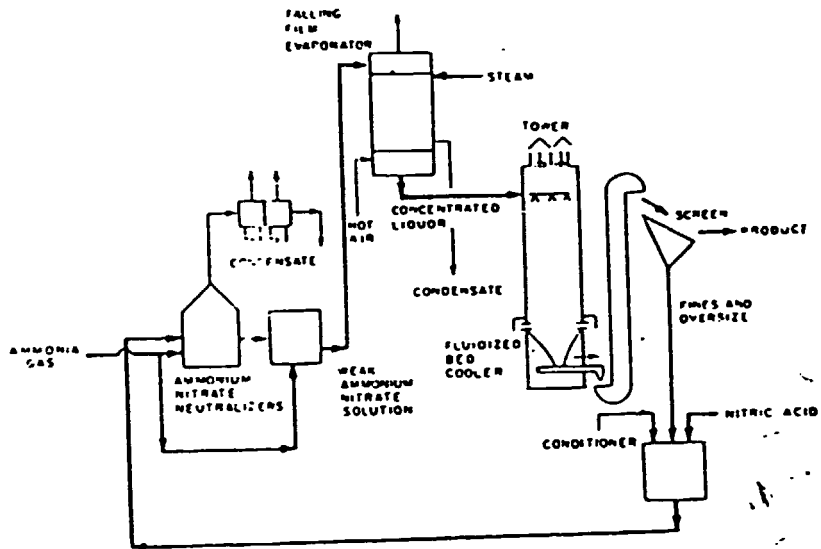
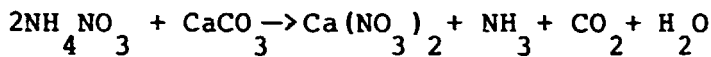


Figure 17 Ammonium Nitrate High-Density Prilling Process (ICI).

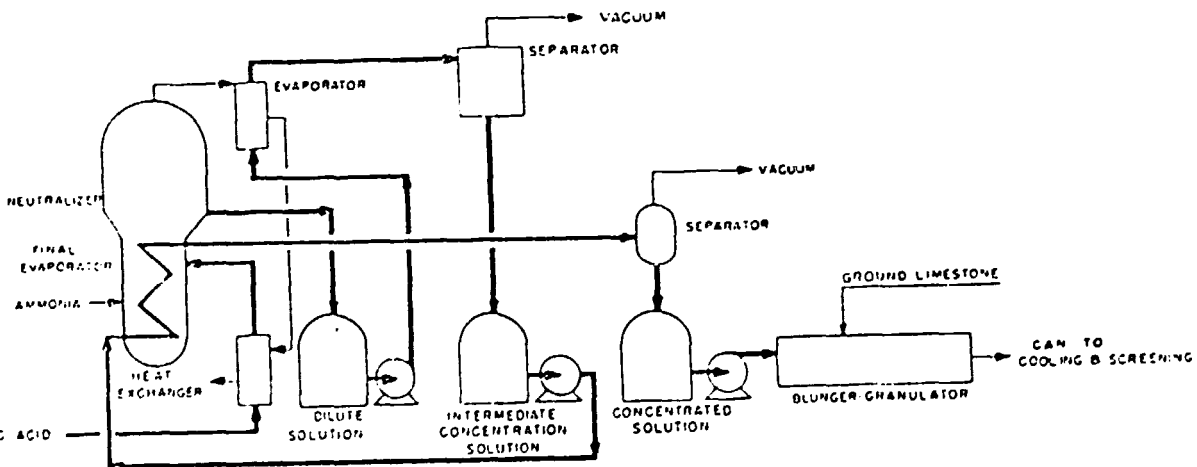
When the desired product is CAN, the usual choice is between prilling and granulation. Either rotary drum granulators, fluidized bed granulator or pan granulator are used. The concentrated ammonium nitrate solution is mixed with ground calcitic or dolomitic limestone, chalk, marl, or precipitated calcium carbonate (a byproduct of some nitrophosphate processes, see chapter XV). The mixing should be done quickly to limit ammonia loss by the reaction:



A soft or chalky limestone is preferred in some granulation processes. Gypsum has been used instead of limestone experimentally with good results.

The usual grade of CAN was about 21% N in the early 1960s; this grade corresponds to 60% AN; the grade has been increased in most countries to 26% N (about 74% AN). As in the case of straight ammonium nitrate, there has been a tendency to use more concentrated AN solution so as to avoid a drying step. However, 98% or even lower concentrations can be used since the heat of crystallization is sufficient to dry the product to an acceptable level. Figure 18 shows a typical CAN process diagram.

In rotary drum fluidized bed, pan and FDG granulators, the production of granular CAN is much like that of compound fertilizers (see chapter XIX). The product is cooled and screened, and fines crushed oversize are recycled. A fluidized bed cooler is used in some plants. In some plants part of the ground chalk or limestone is reserved for coating the final production to improve its physical properties. In other plants a clay conditioner may be used.



8 Process Using Pressure Neutralization and Limestone Addition to Make Calcium Ammonium Nitrate (CAN) (Based on SBA Process).

In prilling CAN, the AN solution is premixed with the ground limestone immediately before prilling. A rotating, perforated bucket is the preferred type of drop-forming apparatus. Prill towers for both CAN and AN commonly are 46-56 m high, although shorter ones also are used. For high-density prilling using 99.7% solution, prilling towers that are 15-30 m tall may be used. Cooling may be carried out in a rotary cooler or in a fluidized bed either in the bottom of the prill tower or in a separate unit.

Prilled or granulated AN or CAN materials are often coated with a powdery conditioning agent such as china clay, kieselguhr, or calcined fullers earth, in amounts ranging from 1%-3%. Conditioned ammonium nitrates usually have a guaranteed N content of 33.5%-34.0%. In some climates, coating to prevent caking is not considered necessary, especially with stabilized, high-density prills of very low-moisture content. In this case the guaranteed N content is 34.0%-34.5%. As mentioned previously, stabilizers that prevent change in crystal form at 32°C have been developed and used. These stabilizers include magnesium nitrate (produced by dissolving magnesite in the nitric acid) and "Permalene," a combination of ammonium sulfate and diammonium phosphate.

Ammonium nitrate may be stored in bulk although in most climates controlled-humidity storage buildings are advisable. In most countries the product is distributed in bags which should be "moisture proof"; at least one ply should be impermeable to moisture. Plastic film bags or bags with plastic liners are suitable if properly constructed. In the United States, bulk shipment is common using covered, hopper-bottom rail cars.

Ammonia nitrate should not be stored where it can be affected by any source of heat or by combustible materials.

Ammonia nitrate should not be stored where it can be affected by any source of heat or by combustible materials.

It is important to prevent the possibility of ammonium nitrate being contaminated with combustible or reactive organic substances such as grains and flammable liquids, chlorates, nitrates, zinc, and copper salts.

Storage facilities should have adequate ventilation, or be a construction that is self-ventilating, so as to allow quick dispersion of heat and toxic gases in the event of a fire (39).

Fisons Ltd, (United Kingdom) now Norsk Hydro Fertilizers Ltd has developed a unique ammonium nitrate process called the "Nitro-Top" process in which the AN solution (99.7%) is prilled into a fluidized bed of dust. Figure 19 is a simplified diagram of the process. The dust bed is cooled by circulating cooling water through coils and plates in the dust bed to maintain a temperature of about 50°C. The dust may be clay or talc or other material smaller than 50 μm . Some of the dust adheres to the prills as a coating which improves the physical properties. The amount of dust that adheres depends on the material; by using a mixture of montmorillonite clay and talc or other combinations, the desired coating weight of about 3% is obtained. The fluidizing air passes through a cyclone and bag

filter before it is discharged to the atmosphere; the recovered dust is returned to the dust bed. The prills are discharged from the bottom of the tower countercurrent to an airstream that holds back the dust. The product then goes to a final deduster and then to screens where small amount of offsize material is separated.

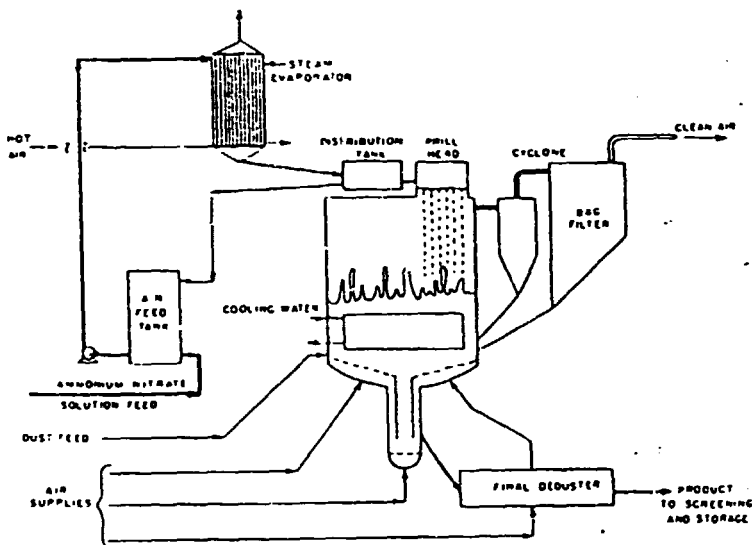


Figure 19 Ammonium Nitrate Dust Prilling Process (Fisons).

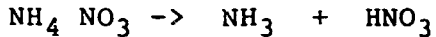
Advantages claimed for the process are:

1. The prill's size is uniform and can be larger than in air prilling, for example, 99% plus 2.4 minus 4.0-mm (mean diameter 2.6 mm). This size is a usual size for granular fertilizer in Europe and, therefore, can be applied by the same machinery without adjustment or used in bulk blends.
2. The prilling tower is only 7 m tall as compared with about 50 m for air prilling.
3. The same equipment combines the function of prilling, cooling, and coating.
4. There are no pollution control problems.

As an alternative to air, an oil or similar liquid may be used as the cooling medium in prilling process. This has the advantage that the improved heat transfer which is obtained enables the height of the prilling towers to be reduced to about 1 m. It is unlikely that it will be adopted for straight ammonium nitrate owing to the hazardous nature of oil-ammonium nitrate mixture (39).

Pollution Control

As in all industrial operations, pollution control requirements for AN and CAN plants have become more stringent in recent years. This has posed a difficult problem for high-density AN prilling because of the large volume of air exhausted from prill towers and because of the very small particle size of the fume in the air. Fuming is much more severe in high-density prilling because the AN melt to be prilled must be at a high temperature (about 180°C) to keep it from freezing. At this temperature there is an appreciable vapor pressure of $\text{NH}_3 + \text{HNO}_3$ resulting from dissociation of AN, according to the equation:



The dissociation products recombine in the cooler air to form a blue haze consisting of AN particles of submicron size. Particles of this size are difficult to collect, and they present a highly visible and stable haze or fog. The problem is much less serious with low density prilling because of lower AN solution temperatures. It is less serious in granulation processes because of much smaller volumes of air in contact with hot solution.

The amount of AN in exhaust gas from the high-density prill tower is likely to be only about 0.1% of total production including both dust and fume. Recovery of this amount is seldom justifiable by economics alone but is often necessary for environmental reasons. A wide range of gas cleaning equipment could be considered suitable for this duty, for example electrostatics precipitators, venturi scrubbers and other wet scrubbers and filters, and dry dedusting systems such as bag filters. (39)

Other solution to this difficult problem has been developed by the Co-Operative Farm Chemicals Association (CFCA) and is in use at its plants in Lawrence, Kansas, and at least 14 others plants in North America (36). The fume abatement system consists of installing a bell-shaped shroud around the spary head in the upper part of the prill tower to collect fume-laden air from that part of the tower where fume is formed due to contact of the air with hot AN solution or prills in the process of solidification. The air flow through this shroud is only about 25% of the total air flow through the tower; the remaining 75% is practically free of dust and fume and is discharged directly to the atmosphere. The air from the shroud is drawn through a scrubber and Brink high-efficiency mist eliminators. Fume and vapors from the neutralizer and evaporators are treated in the same scrubbing system. The scrubber solution is recirculated to build up its concentration and eventually recycled to the AN solution preparation step. The system recovers 3-7 kg of AN/ton of product from all sources (neutralizer, evaporator, and prill tower) which more than offsets the operating cost (excluding capital costs). From a pollution abatement viewpoint the system has met applicable

standards; atmospheric emissions less than 0.5 kg/ton of product and opacity of less than 10% have been attained (36).

Sodium Nitrate

General Information

Before the availability of synthetic ammonia and its derivatives, sodium nitrate of natural origin was the major source of nitric acid and chemical nitrogen for fertilizer purposes in many countries. Most of this nitrate originated in Chile, where it is principally found in a large ore body nearly 500 miles long and 10-50 miles wide on the eastern part of the Chilean coastal range. Nitrate production is still a major industry in Chile. Small deposits occur in other areas, e.g., Africa, Australia, Mexico, and Egypt. Substantial amounts of synthetic sodium nitrate were formerly made in Europe and the United States, but production has declined since World War II and now only insignificant amounts are produced from byproduct sources.

Principal Uses.

As a fertilizer, sodium nitrate has long been applied as a surface dressing for cotton, tobacco, and some vegetable crops. However, its use as a "straight" nitrogen fertilizer has declined considerably during the last century. For example, in the United Kingdom, some 20,000 tons of N was used in the form of sodium nitrate in 1899, whereas, relatively none is used today. As with other nitrates, sodium nitrate is prone to leaching in the soil, but it has the advantage of possessing a metallic cation. Unlike ammonia and its derivatives, including urea, sodium nitrate will not promote cation losses in the soil and lead to unsuspected soil acidity.

Industrial applications include meat preservation, heat treatment of metals, and use as a flux in the ceramic and metallurgical industries.

Properties of Sodium Nitrate

The properties of sodium nitrate are given in table-6.

TABLE 6. PROPERTIES OF PURE SODIUM NITRATE

Formula	NaNO ₃
Guaranteed analysis (typical)	
Nitrogen	16.48%
Sodium	27.05%
Appearance	White crystalline rhombohedra
Molecular weight	85.01
Melting point	308.3°C
Density, 20°/4°C	2.251
Solubility, g/100 g of water	
Temperature (°C)	
0	73
10	96
30	176
100	180
Bulk density	
Pellets	1,202 kg/m ³
Coarse material	1,282 kg/m ³
Fine powder	1,363 kg/m ³
Critical relative humidities	
20°C (68°F)	74.7
30°C (86°F)	73.7

Production Methods

From Natural Deposits-- In Chile, the nitrate ore or caliche is widely varying in composition and may range from 80% to virtually zero nitrate content although little high-grade material is available today. A typical analysis of run-of-mine ore might be the following (in percentages):

NaNO ₃	7-10
NaCl.....	4-10
Na ₂ SO ₄	10-30
Mg, Ca, K, Br, I ₂	2-7
H ₂ O	1-2
Remainder (Gangue)	41-76

These components are present in the form of complex, mixed sulfates, e.g., darapskite (NaNO₃.Na₂ SO₄.H₂O).

Early production methods were based on hand-picking the higher grade ore containing about 13% sodium nitrate and leaching it in directly heated open pans until saturation was reached. The solution was then piped to settling pans and cooled to produce sodium nitrate crystals, which were drained, dried in the sun, and bagged or shipped in bulk overseas. An improved version of this method known as the Shanks process, which was first used about 1890 and remained popular for about 50 years, is now virtually obsolete. Most current production is undertaken by the Guggenheim process, which permits ores containing under 10% nitrate to be profitably worked, thus extending the life of the Chilean nitrate industry by several decades.

In the Guggenheim method, caliche is mined by open-pit operations, using draglines and power shovels, and is crushed to about 80% between 3/4 and 3/8 in (1.9-0.95 cm). This product is leached at about 40°C with water in a series of vats, each having a capacity of some 10,000 tons of crushed ore. The underflow from each vat is heated before passing to the next since sodium nitrate has a negative heat of solution. After extraction and washing are complete, the residue is removed from the vats by grabs and is hauled to a waste dump.

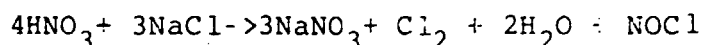
Fine material from the crushers is pulped in a separate system, and the gangue is removed by means of Moore filters. The filtrates are combined with liquor from the leach tanks and are chilled in shell-and-tube units to precipitate crystalline sodium nitrate. Initial cooling is effected by heat-exchange with in-process leach liquor and final chilling by ammonia. The sodium nitrate slurry is dewatered and washed in batch centrifuges to yield a crystalline product substantially 48-mesh in size and containing approximately 3.5% of free moisture. When a grained or prill-type product is required, the centrifuged salt is melted at about 400°C in reverberatory

furnaces, spary dried in large towers, cooled by heat exchange with mother liquor in shell-and-tube units and screened to yield pellets in the 10- to 20-mesh range cotaining about 98% sodium nitrate and 0.2%-0.3% free moisture.

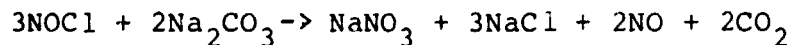
Iodine salts which are present in the caliche accumulate in the recycling mother liquor and are reduced to iodine in a separate process; this production amounts to some 2,000 tons annually. In addition, it has been found that salts which are insoluble in recycling leach solutions can be extracted from the caliche by fresh water and recovered by solar evaporation and selective crystallization to yield substantial tonnages of additional sodium nitrate, as well as potassium nitrate, various iodates, borates, and sulfates. These associated salts may be of future significane to the Chilean nitrate industry.

Synthetic Sodium Nitrate-- The dependence of the United States and other countries on natural Chilean sodium nitrate during the early part of the 20th century led to the development of several chemical processes for its manufacture. All these methods produce a sodium nitrate solution wich is concentrated, crystallized, and centrifuged. In some cases, the dewatered and washed salt is dried in a rotary drier prior to screening, storage, and bagging; alternatively, it may be melted and grained or prilled.

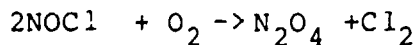
Appreciable quantities of sodium nitrate have also been made in the United States by the salt process developed by the Allied Chemical Corporation. In this method (which is believed not to be currently in operation), nitric acid and sodium chloride are reacted to yield sodium nitrate, chlorine, nitrosyl chloride and water, e.g.:



The nitrosyl chloride can be used as an intermediate for other derivatives, or it can be reacted with sodium carbonate to yield additional sodium nitrate, sodium chloride, nitric oxide, and carbon dioxide:



The salts produced can be redigested and the nitric oxide used to make additional sodium nitrate (or nitric acid). Alternatively, the nitrosyl chloride can be oxidized to yield dinitrogen tetroxide and chlorine for futher use, e.g.:



Norsk Hydro in 1934-35 worked up a process to produce sodium nitrate from calcium nitrate (by-product of nitrophosphate plants). It is based upon ion exchange, using as exchanger zeolite. The ion exchange takes place between calcium nitrate in water solution and sodium chloride contained in sea water, used as regenerating agent. (39). Other methods used to produce sodium nitrate in minor quantities (sometimes as a byproduct) include reacting nitric acid with soda ash or caustic soda. Several double-decomposition reactions between

various nitrates and alkali salts, for example, ammonium nitrate and caustic soda or common salt, have either been proposed or tested on a small scale.

Sotrage

Sodium nitrate can be stored and shipped in bulk, under conditions of low humidity but should be packed in moisture-resistant bags when intended for use in damp or tropical climates. In some countries, it is regarded as a potential fire hazard and may necessitate special labeling, insurance, and other precautions as for ammonium nitrate and potassium nitrate. Such materials as bags or timber, subsequently allowed to dry after impregnation with sodium nitrate, may quickly ignite if exposed to elevated temperatures and should be destroyed or thoroughly washed and fireproofed.

Potassium Nitrate

The production, properties, and use of potassium nitrate will be covered in chapter XVIII (Potash Fertilizers).

Calcium Nitrate

General Information

Although simple methods are available for producing calcium nitrate, its use as a fertilizer is offset by extreme hygroscopicity even in moderately humid climates. As fertilizer, calcium nitrate has special advantages for use on saline soils since the calcium displaces the sodium that is absorbed by clay in soils. For this reason it may be preferred for use in areas with soil salinity problems, such as parts of Egypt and California. It also has the advantage of being nonacidforming. Other applications include explosives, pyrotechnics, and inorganic chemical operations.

Properties of Calcium Nitrate

The properties of calcium nitrate are given in table 7.

Production Methods

Most calcium nitrate comes from Europe, where it is produced in two principal ways. In one method a direct reaction between calcium carbonate and nitric acid is employed, and in the other the calcium nitrate formed as a coproduct in some nitrophosphate processes is separated by crystallization and filtration or centrifuging.

Direct Process -- In the direct process, crushed limestone is reacted with 50% nitric acid in towers lined with acid-resistant

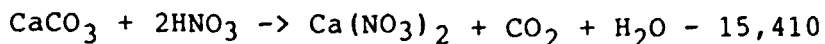
brick, and the residual acid is neutralized with lime.

The liquor which contains about 40% $\text{Ca}(\text{NO}_3)_2$ is clarified in settling tanks and brought to a concentration of 87% in a vacuum evaporator unit. Some 5% of ammonium nitrate is then added as a granulation aid to raise the nitrogen content to 15.5% prior to spray drying in a prilling tower. The granules or prills are cooled, screened and packed in moisture-resistant bags.

TABLE 7. PROPERTIES OF CALCIUM NITRATE

Formula	$\text{Ca}(\text{NO}_3)_2$
Appearance	White, crystalline
Molecular weight	164.10
Melting point	555.7°C
Density, 20°/4°C	2.36 (anhydride)
Solubility, g/100 g of water	
Temperature (°C)	
0	102
100	364
Approximate analysis (fertilizer grade)	
Nitrogen	15.5%
Calcium	36.0%
Critical relative humidities	
20°C	54.8
30°C	46.5

The above reaction, which is exothermic, is represented by:



Nitrophosphate/Calcium Nitrate Production--The production of by product calcium nitrate in nitrophosphate processes is discussed in chapter XV.

Nitrophosphate processes can be divided into two categories, namely, those in which calcium nitrate is separated from the nitrophosphate liquor and those wherein calcium nitrate is

converted to less hygroscopic compounds, e.g., ammonium nitrate, and no separation is undertaken (10).

Most processes in the first category are variations of the original Norwegian "Odda" method in which 1.0 part of ground phosphate rock is digested with about 1.5 parts of nitric acid at 55°-70°C in a continuous reaction system. The reaction liquor is then chilled by brine in heat exchangers to precipitate calcium nitrate tetrahydrate, which is separated and washed by means of centrifuges or rotary vacuum filters. The crystals are melted at 42°C, clarified, neutralized with ammonia gas, prilled, cooled, and bagged. In some plants, ammonium nitrate is added prior to crystallization to yield the double salt, $5\text{Ca}(\text{NO}_3)_2 \cdot \text{NH}_4\text{NO}_3 \cdot 10\text{H}_2\text{O}$.

A special process has been developed in the Netherlands and used there and in other countries. It consists of prilling the product into an oil bath rather than air. Since the oil contains about 10% paraffin wax which forms a coating on the prills, the rate of moisture absorption is retarded (37). The prills are separated from the oil by settling and centrifuging. They are stored in bulk for a few weeks while the oil remaining on the prills is about 1%. The decahydrate salt, $5\text{Ca}(\text{NO}_3)_2 \cdot \text{NH}_4\text{NO}_3 \cdot 10\text{H}_2\text{O}$ will rapidly absorb water when the relative humidity exceeds 50% and will deliquesce; whereas, the anhydrous salt, $\text{Ca}(\text{NO}_3)_2$ although more hygroscopic, will absorb about 40% of its own weight of water before incipient liquefaction occurs. Both products are promptly packed in moisture-resistant bags to minimize storage and handling problems during shipment.

In recent years Norks Hydro pan granulation and Kaltenbach FDG processes have been applied to calcium nitrate finishing.

Storage

Except in very dry climates, calcium nitrate is likely to deliquesce, and storage in moisture-proof bags is usually mandatory. As with other nitrate fertilizer salts, precautions should be taken to avoid impregnation of organic material with calcium nitrate to reduce possible conflagration from a source of heat in the vicinity. For this reason, special storage and shipping regulations may apply in certain countries.

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