

# Nitrogenous Fertilizer Plants

## Industry Description and Practices

This document addresses the production of ammonia, urea, ammonium sulfate, ammonium nitrate (AN), calcium ammonium nitrate (CAN), and ammonium sulfate nitrate (ASN). The manufacture of nitric acid used to produce nitrogenous fertilizers typically occurs on site and is therefore included here.

### *Ammonia*

Ammonia (NH<sub>3</sub>) is produced from atmospheric nitrogen and hydrogen from a hydrocarbon source. Natural gas is the most commonly used hydrocarbon feedstock for new plants; other feedstocks that have been used include naphtha, oil, and gasified coal. Natural gas is favored over the other feedstocks from an environmental perspective.

Ammonia production from natural gas includes the following processes: desulfurization of the feedstock; primary and secondary reforming; carbon monoxide shift conversion and removal of carbon dioxide, which can be used for urea manufacture; methanation; and ammonia synthesis. Catalysts used in the process may include cobalt, molybdenum, nickel, iron oxide/chromium oxide, copper oxide/zinc oxide, and iron.

### *Urea*

Urea fertilizers are produced by a reaction of liquid ammonia with carbon dioxide. The process steps include solution synthesis, where ammonia and carbon dioxide react to form ammonium carbamate, which is dehydrated to form urea; solution concentration by vacuum, crystallization, or evaporation to produce a melt; forma-

tion of solids by prilling (pelletizing liquid droplets) or granulating; cooling and screening of solids; coating of the solids; and bagging or bulk loading. The carbon dioxide for urea manufacture is produced as a by-product from the ammonia plant reformer.

### *Ammonium Sulfate*

Ammonium sulfate is produced as a caprolactam by-product from the petrochemical industry, as a coke by-product, and synthetically through reaction of ammonia with sulfuric acid. Only the third process is covered in this document. The reaction between ammonia and sulfuric acid produces an ammonium sulfate solution that is continuously circulated through an evaporator to thicken the solution and to produce ammonium sulfate crystals. The crystals are separated from the liquor in a centrifuge, and the liquor is returned to the evaporator. The crystals are fed either to a fluidized bed or to a rotary drum dryer and are screened before bagging or bulk loading.

### *Ammonium Nitrate, Calcium Ammonium Nitrate, and Ammonium Sulfate Nitrate*

Ammonium nitrate is made by neutralizing nitric acid with anhydrous ammonia. The resulting 80–90% solution of ammonium nitrate can be sold as is, or it may be further concentrated to a 95–99.5% solution (melt) and converted into prills or granules. The manufacturing steps include solution formation, solution concentration, solids formation, solids finishing, screening, coating, and bagging or bulk shipping. The processing steps depend on the desired finished product. Calcium ammonium nitrate is made by adding

calcite or dolomite to the ammonium nitrate melt before prilling or granulating. Ammonium sulfate nitrate is made by granulating a solution of ammonium nitrate and ammonium sulfate.

### Nitric Acid

The production stages for nitric acid manufacture include vaporizing the ammonia; mixing the vapor with air and burning the mixture over a platinum/rhodium catalyst; cooling the resultant nitric oxide (NO) and oxidizing it to nitrogen dioxide (NO<sub>2</sub>) with residual oxygen; and absorbing the nitrogen dioxide in water in an absorption column to produce nitric acid (HNO<sub>3</sub>).

Because of the large quantities of ammonia and other hazardous materials handled on site, an emergency preparedness and response plan is required.

## Waste Characteristics

### Air Emissions

Emissions to the atmosphere from *ammonia plants* include sulfur dioxide (SO<sub>2</sub>), nitrogen oxides (NO<sub>x</sub>), carbon monoxide (CO), carbon dioxide (CO<sub>2</sub>), hydrogen sulfide, volatile organic compounds (VOCs), particulates, methane, hydrogen cyanide, and ammonia. The two primary sources of pollutants, with typical reported values, in kilograms per ton (kg/t) for the important pollutants, are as follows:

- Flue gas from primary reformer
  - CO<sub>2</sub>: 500 kg/t NH<sub>3</sub>
  - NO<sub>x</sub>: 0.6–1.3 kg/t NH<sub>3</sub> as NO<sub>2</sub>
  - SO<sub>2</sub>: less than 0.1 kg/t
  - CO: less than 0.03 kg/t
- Carbon dioxide removal
  - CO<sub>2</sub>: 1,200 kg/t

Nitrogen oxide emissions depend on the process features. Nitrogen oxides are reduced, for example, when there is low excess oxygen, with steam injection; when postcombustion measures are in place; and when low-NO<sub>x</sub> burners are in use. Other measures will also reduce the total amount of nitrogen oxides emitted. Concentrations of sulfur dioxide in the flue gas from the reformer can be expected to be significantly

higher if a fuel other than natural gas is used. Energy consumption ranges from 29 to 36 gigajoules per metric ton (GJ/t) of ammonia. Process condensate discharged is about 1.5 cubic meters per metric ton (m<sup>3</sup>/t) of ammonia. Ammonia tank farms can release upward of 10 kg of ammonia per ton of ammonia produced. Emissions of ammonia from the process have been reported in the range of less than 0.04 to 2 kg/t of ammonia produced.

In a *urea plant*, ammonia and particulate matter are the emissions of concern. Ammonia emissions are reported as recovery absorption vent (0.1–0.5 kg/t), concentration absorption vent (0.1–0.2 kg/t), urea prilling (0.5–2.2 kg/t), and granulation (0.2–0.7 kg/t). The prill tower is a source of urea dust (0.5–2.2 kg/t), as is the granulator (0.1–0.5 kg/t).

Particulates are the principal air pollutant emitted from *ammonium sulfate plants*. Most of the particulates are found in the gaseous exhaust of the dryers. Uncontrolled discharges of particulates may be of the order of 23 kg/t from rotary dryers and 109 kg/t from fluidized bed dryers. Ammonia storage tanks can release ammonia, and there may be fugitive losses of ammonia from process equipment.

The production of *ammonium nitrate* yields emissions of particulate matter (ammonium nitrate and coating materials), ammonia, and nitric acid. The emission sources of primary importance are the prilling tower and the granulator. Total quantities of nitrogen discharged are in the range of 0.01–18.4 kg/t of product. Values reported for *calcium ammonium nitrate* are in the range of 0.1–3.3 kg nitrogen per ton of product.

*Nitric acid plants* emit nitric oxide, nitrogen dioxide (the visible emissions), and trace amounts of nitric acid mist. Most of the nitrogen oxides are found in the tail gases of the absorption tower. Depending on the process, emissions in the tail gases can range from 215 to 4,300 milligrams per cubic meter (mg/m<sup>3</sup>) for nitrogen oxides. Flow may be of the order of 3,200 m<sup>3</sup> per ton of 100% nitric acid. Nitrogen oxide values will be in the low range when high-pressure absorption is used; medium-pressure absorption yields nitrogen oxide emissions at the high end of the range. These values are prior to the addition of any abatement hardware.

### *Liquid Effluents*

Ammonia plant effluents may contain up to 1 kg of ammonia and up to 1 kg of methanol per cubic meter prior to stripping. Effluent from urea plants may discharge from less than 0.1 kg to 2.6 kg nitrogen per ton product. Effluents from ammonium nitrate plants have been reported to discharge 0.7–6.5 kg nitrogen per ton product. Comparable values for CAN plants are 0–10 kg nitrogen per ton of product. Nitric acid plants may have nitrogen in the effluent of the order of 0.1–1.7 kg nitrogen per ton of nitric acid.

### *Solid Wastes*

Solid wastes are principally spent catalysts that originate in ammonia production and in the nitric acid plant. Other solid wastes are not normally of environmental concern.

## **Pollution Prevention and Control**

### *Ammonia Plant*

The following pollution prevention measures are recommended:

- Where possible, use natural gas as the feedstock for the ammonia plant, to minimize air emissions.
- Use hot process gas from the secondary reformer to heat the primary reformer tubes (the exchanger-reformer concept), thus reducing the need for natural gas
- Direct hydrogen cyanide (HCN) gas in a fuel oil gasification plant to a combustion unit to prevent its release.
- Consider using purge gases from the synthesis process to fire the reformer; strip condensates to reduce ammonia and methanol.
- Use carbon dioxide removal processes that do not release toxics to the environment. When monoethanolamine (MEA) or other processes, such as hot potassium carbonate, are used in carbon dioxide removal, proper operation and maintenance procedures should be followed to minimize releases to the environment.

### *Urea Plant*

Use total recycle processes in the synthesis process; reduce microprill formation and carryover of fines in prilling towers.

### *Ammonium Nitrate Plant*

The following pollution prevention measures are recommended:

- *Prill tower*: reduce microprill formation and reduce carryover of fines through entrainment.
- *Granulators*: reduce dust emissions from the disintegration of granules.
- *Materials handling*: where feasible use covers and hoods on conveyors and transition points. Good cleanup practices must be in place to minimize contamination of stormwater runoff from the plant property.

It is important to note that hot ammonium nitrate, whether in solid or in concentrated form, carries the risk of decomposition and may even detonate under certain circumstances. Suitable precautions are therefore required in its manufacture.

### *Ammonium Sulfate Plant*

Ammonium sulfate plants are normally fitted with fabric filters or scrubbers as part of the process.

## **Target Pollution Loads**

Implementation of cleaner production processes and pollution prevention measures can yield both economic and environmental benefits. The following production-related targets can be achieved by measures such as those described above. The numbers relate to the production processes before the addition of pollution control measures.

### *Ammonia Plant*

New ammonia plants should set as a target the achievement of nitrogen oxide emissions of not more than 0.5 kg/t of product (expressed as NO<sub>2</sub>

at 3% O<sub>2</sub>). Ammonia releases in liquid effluents can be controlled to 0.1 kg/t of product. Condensates from ammonia production should be re-used.

#### *Nitric Acid Plant*

Nitrogen oxide levels should be controlled to a maximum of 1.6 kg/t of 100% nitric acid.

### **Treatment Technologies**

In *urea plants*, wet scrubbers or fabric filters are used to control fugitive emissions from prilling towers; fabric filters are used to control dust emissions from bagging operations. These devices are an integral part of the operations, to retain product. New urea plants should achieve levels of particulate matter in air emissions of less than 0.5 kg/t of product for both urea and ammonia.

In *ammonium sulfate plants*, use of fabric filters, with injection of absorbent as necessary, is the preferred means of control. Discharges of not more than 0.1 kg/t of product should be attainable for particulate matter.

In *ammonium nitrate plants*, wet scrubbers can be considered for prill towers and the granulation plant. Particulate emissions of 0.5 kg/t of product for the prill tower and 0.25 kg/t of product for granulation should be the target. Similar loads for ammonia are appropriate.

In *nitric acid plants*, extended absorption and technologies such as nonselective catalytic reduction (NSCR) and selective catalytic reduction (SCR) are used to control nitrogen oxides in tail gases. To attain a level of 150 parts per million by volume (ppmv) of nitrogen oxides in the tail gases, the following approaches should be considered:

- High-pressure, single-pressure process with absorbing efficiency high enough to avoid additional abatement facilities
- Dual-absorption process with an absorption efficiency high enough to avoid additional treatment facilities
- Dual-pressure process with SCR
- Medium-pressure, single-pressure process with SCR.

Other effluents that originate in a nitrogenous fertilizer complex include boiler blowdown, wa-

ter treatment plant backwash, and cooling tower blowdown from the ammonia and nitric acid plants. They may require pH adjustment and settling. These effluents should preferably be recycled or reused.

Spent catalysts are sent for regeneration or disposed of in a secure landfill.

Modern plants using good industrial practices are able to achieve the pollutant loads described below.

### **Emissions Guidelines**

Emissions levels for the design and operation of each project must be established through the environmental assessment (EA) process on the basis of country legislation and the *Pollution Prevention and Abatement Handbook*, as applied to local conditions. The emissions levels selected must be justified in the EA and acceptable to the World Bank Group.

The guidelines given below present emissions levels normally acceptable to the World Bank Group in making decisions regarding provision of World Bank Group assistance. Any deviations from these levels must be described in the World Bank Group project documentation. The emissions levels given here can be consistently achieved by well-designed, well-operated, and well-maintained pollution control systems.

The guidelines are expressed as concentrations to facilitate monitoring. Dilution of air emissions or effluents to achieve these guidelines is unacceptable.

All of the maximum levels should be achieved for at least 95% of the time that the plant or unit is operating, to be calculated as a proportion of annual operating hours.

#### *Air Emissions*

The emissions levels presented in Table 1 should be achieved.

#### *Liquid Effluents*

The effluent levels presented in Table 2 should be achieved.

**Table 1. Air Emissions from Nitrogenous Fertilizer Plants***(milligrams per normal cubic meter)*

<i>Parameter</i>	<i>Maximum value</i>
Nitrogen oxides (as NO <sub>2</sub> )	300
Urea	50
Ammonia (NH <sub>3</sub> )	50
PM	50

**Table 2. Effluents from Nitrogenous Fertilizer Plants***(milligrams per liter, except for pH and temperature)*

<i>Parameter</i>	<i>Maximum value</i>
pH	6–9
TSS	50
Ammonia (as nitrogen)	10
Urea	1
Temperature increase	< 3°C <sup>a</sup>

*Note:* Effluent requirements are for direct discharge to surface waters.

a. The effluent should result in a temperature increase of no more than 3°C at the edge of the zone where initial mixing and dilution take place. Where the zone is not defined, use 100 meters from the point of discharge.

### Ambient Noise

Noise abatement measures should achieve either the levels given below or a maximum increase in background levels of 3 decibels (measured on the A scale) [dB(A)]. Measurements are to be taken at noise receptors located outside the project property boundary.

<i>Receptor</i>	<i>Maximum allowable log equivalent (hourly measurements), in dB(A)</i>	
	<i>Day</i>	<i>Night</i>
	<i>(07:00–22:00)</i>	<i>(22:00–07:00)</i>
Residential, institutional, educational	55	45
Industrial, commercial	70	70

### Monitoring and Reporting

Frequent sampling may be required during start-up and upset conditions. Once a record of con-

sistent performance has been established, sampling for the parameters listed in this document should be as described below.

Air emissions should be monitored annually, except for nitrate acid plants, where nitrogen oxides should be monitored continuously. Effluents should be monitored continuously for pH and monthly for other parameters.

Monitoring data should be analyzed and reviewed at regular intervals and compared with the operating standards so that any necessary corrective actions can be taken. Records of monitoring results should be kept in an acceptable format. The results should be reported to the responsible authorities and relevant parties, as required.

### Key Issues

The key production and control practices that will lead to compliance with emissions requirements can be summarized as follows:

- Choose natural gas, where possible, as feedstock for the ammonia plant.
- Give preference to high-pressure processes or absorption process in combination with catalytic reduction units.
- Use low-dust-forming processes for solids formation.
- Reuse condensates and other wastewaters.
- Maximize product recovery and minimize air emissions by appropriate maintenance and operation of scrubbers and baghouses.

### Sources

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