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 the nitrogenous fertilizers typically occurs on-site, and is therefore, included in this document.

Ammonia

The feedstock for ammonia is derived from nitrogen in the air and hydrogen from a hydrocarbon source. Natural gas is the most commonly used hydrocarbon feedstock for new plants, however, other feedstocks that have been used include naphtha, oil, and gasified coal. Natural gas is favored over 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 reacting 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; solids formation by prilling or granulating; solids cooling and screening; coating of the solids; and bagging and/or bulk loading. The carbon dioxide for urea manufacture is produced as a byproduct from the ammonia plant reformer.

Ammonium Sulfate (AS)

AS is produced as a caprolactam byproduct from the petrochemical industry, as a coke by-product, and synthetically from reacting ammonia with sulfuric acid. Only the latter is covered in this document. The reaction between ammonia and sulfuric acid produces an AS solution which 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 to either a fluidized bed or rotary drum dryer and are screened before bagging and/or bulk loading.

Ammonium Nitrate (AN), Calcium Ammonium Nitrate (CAN), Ammonium Sulfate Nitrate (ASN)

AN is made by neutralizing nitric acid with anhydrous ammonia. The resulting 80-90 percent solution of AN can be sold as is or it may be further concentrated to a 95 to 99.5 percent solution (melt) and converted into prills or granules. The manufacturing steps include: solution formation, solution concentration, solids formation, solids finishing, screening, coating, bagging and/or bulk shipping. The processing steps will depend on the desired
Nitrogenous Fertilizer Plants

finished product. CAN is made by adding calcite or dolomite to the AN melt before prilling or granulating, while ASN is made by granulating a solution of AN and AS.

**Nitric Acid**

The production stages for nitric acid manufacture include: ammonia vaporization followed by mixing with air and burning the mixture over a platinum/rhodium catalyst; cooling the resultant nitric oxide (NO) and oxidizing it to nitrogen dioxide (NO₂) with residual oxygen; and absorbing the (NO₂) in water in an absorption column to produce nitric acid (HNO₃).

Note: 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 atmosphere from *ammonia plants* include: sulfur dioxide (SO₂), nitrogen oxides (NOₓ), and carbon dioxide (CO₂); hydrogen sulfide; volatile organic compounds (VOCs); particulates; methane; hydrogen cyanide; and ammonia. The two primary sources of pollutants, with typical reported values for the important pollutants, are as follows:

- **Flue gas from primary reformer**
  - CO₂ - 500 kg/t NH₃
  - NOₓ - 0.6-1.3 kg/t NH₃ as NO₂
  - SO₂ - <0.1 kg/t
  - CO - <0.03 kg/t
- **CO₂ removal**
  - CO₂ - 1200 kg/t

NOₓ emissions depend on the process features — NOₓ is reduced, for example, when there is low excess oxygen, with steam injection, where post combustion measures are in place, and where low NOₓ burners are in use. Other measures will also reduce the total amount of NOₓ emitted. The SO₂ concentration 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 29-36 giga Joules per metric ton (GJ/t) of ammonia (NH₃). And process condensate discharged is about 1.5 cubic meters per metric ton (m³/t) of NH₃. Ammonia tank farms can release upwards of 10 kg of ammonia per ton of ammonia produced. Emissions of ammonia from the process have been reported in the range of <0.04-2 kg/t 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 these are found in the gaseous exhaust of the dryers. Uncontrolled discharges of particulates may be in the order of 23 kg/t from rotary dryers and 109 kg/t from fluidized bed dryers. Ammonia storage tanks can release ammonia. In addition, there may be fugitive losses of ammonia from process equipment.

The production of *AN* results in 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 would be in the range of 0.01-18.4 kg N/t of product. Values reported for CAN are in the range of 0.1-3.3 kg N/t of product.

*Nitric acid plants* emit nitric oxide, nitrogen dioxide (the visible emissions), and trace amounts of nitric acid mist. The majority 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 215-4,300 milligrams per cubic meter (mg/m³) for NOₓ. Flow may be in the order of 3,200 m³/t 100% nitric acid. NOₓ values will be in the low range where high pressure absorption is used; medium pressure absorption yields NOₓ emissions in 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 m³ prior to stripping. Effluent from urea plants may discharge < 0.1-2.6 kg N/t product. Effluents from ammonium nitrate plants have been reported to discharge 0.7-6.5 kg N/t production while. Comparable values for CAN plants are 0-10 kg N/t production. Nitric acid plants may have nitrogen in the effluent in the order of 0.1-1.7 kg N/t acid.

**Solid Wastes**

Solid wastes are principally spent catalysts which 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**
- Where possible, natural gas should be the feedstock for the ammonia plant to minimize air emissions.
- Use hot process gas from the secondary reformer to heat the primary reformer tubes (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, and strip condensates to reduce ammonia and methanol.
- Use CO₂ removal processes which do not release toxics to the environment. Where monoethanolamine (MEA) or other processes (such as hot potassium carbonate) are used in the CO₂ 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 carry over 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.
- material handling—where feasible use covers and hoods on conveyors and transition points. Good clean-up practices are required to be in place in order to minimize contamination of storm water run-off from the plant property.

*Note: Hot ammonium nitrate, either 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 normally are fitted with fabric filters or scrubbers as part of the process.

**Target Pollution Loads**

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

**Ammonia Plant**

New ammonia plants should target on achieving NOₓ emissions of not more than 0.5 kg/t of product (expressed as NO₂ at 3% O₂). Ammonia releases in liquid effluents can be controlled to 0.1 kg/t of product. Condensates from ammonia production should be reused.

**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 the ammonium sulfate plant, 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 the nitric acid plant extended absorption and the use of technologies such as non-selective catalytic reduction (NSCR) and selective catalytic reduction (SCR) are used to control NO\textsubscript{x} in tail gases. To attain a level of 150 parts per million parts by volume (ppmv) of NO\textsubscript{x} 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 with SCR

Other effluents originate in a nitrogenous fertilizer complex. These include: boiler blowdown, water 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/reused.

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

Modern plants using good industrial practices are able to achieve the following in terms of pollutant loads:

Emissions Guidelines

Emission levels for the design and operation of each project must be established through the Environmental Assessment (EA) process, based on country legislation and the Pollution Prevention and Abatement Handbook as applied to local conditions. The emission levels selected must be justified in the EA and acceptable to MIGA.

The following guidelines present emission levels normally acceptable to the World Bank Group in making decisions regarding provision of World Bank Group assistance, including MIGA guarantees; any deviations from these levels must be described in the project documentation.

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

Air Emissions

The following emissions levels should be achieved:

Air Emissions from Nitrogenous Fertilizer Complexes

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Maximum value in milligrams per normal cubic meter (mg/Nm\textsuperscript{3})</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO\textsubscript{x} (as NO\textsubscript{2})</td>
<td>300</td>
</tr>
<tr>
<td>Urea</td>
<td>50</td>
</tr>
<tr>
<td>NH\textsubscript{3}</td>
<td>50</td>
</tr>
<tr>
<td>Particulates</td>
<td>50</td>
</tr>
</tbody>
</table>
**Liquid Effluents**

The following effluent levels should be achieved:

### Effluents from Nitrogenous Fertilizer Complexes

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Maximum value</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>milligrams per liter (mg/L)</td>
</tr>
<tr>
<td>pH</td>
<td>6 - 9</td>
</tr>
<tr>
<td>Total suspended solids</td>
<td>50</td>
</tr>
<tr>
<td>Ammonia (as nitrogen)</td>
<td>10</td>
</tr>
<tr>
<td>Urea</td>
<td>1</td>
</tr>
<tr>
<td>Temperature increase</td>
<td>less than 3°C</td>
</tr>
</tbody>
</table>

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

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

### Ambient Noise

Noise abatement measures should achieve either the following levels or a maximum increase in background levels of 3 dB(A). Measurements are to be taken at noise receptors located outside the project property boundary.

<table>
<thead>
<tr>
<th>Receptor</th>
<th>Maximum Allowable L_{eq} (hourly), in dB(A)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Daytime 07:00 - 22:00</td>
</tr>
<tr>
<td>Residential; institutional; educational</td>
<td>55</td>
</tr>
<tr>
<td>Industrial; commercial</td>
<td>70</td>
</tr>
</tbody>
</table>

The emission requirements given here can be consistently achieved by well-designed, well-operated and well-maintained pollution control systems.

### Monitoring and Reporting

Frequent sampling may be required during start-up and upset conditions. Once a record of consistent performance has been established, sampling for the parameters listed above should be as detailed below.

Air emissions should be monitored annually, except for nitrate acid plants where NO_x 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. These should be reported to the responsible authorities and relevant parties, as required, and provided to MIGA if requested.

### Key Issues

The following box summarizes the key production and control practices that will lead to compliance with emission requirements:

- 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 waste waters.
- Maximize product recovery and minimize air emissions by appropriate maintenance and operation of scrubbers and baghouses.

### Further Information

The following are suggested as sources of additional information (these sources are provided for guidance and are not intended to be comprehensive):


Technical note on Best Available Technologies Not Entailing Excessive Costs for Ammonia Production, 1990, European Union