AMMONIA AND AMMONIA DERIVATIVES

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1.0 SCOPE

This document provides loss prevention recommendations for ammonia and ammonia derivatives (including nitric acid and urea) facilities. Other derivatives, such as melamine (from urea), ammonium nitrate (AN) or emulsions/AN fuel oil (ANFO) are not covered in this data sheet. For information on AN, see Data Sheet 7-89, *Ammonium Nitrate and Mixed Fertilizers Containing Ammonium Nitrate*.

Primary reformers used for the production of ammonia are briefly referred to in this document. For full guidance, refer to Data Sheet 7-72, *Reformer and Cracking Furnaces*.

1.1 Hazards

Ammonia and ammonia derivatives facilities are typically located in large chemical complexes. Process hazards include large vessels and piping operating at high temperatures and pressures, large rotating equipment (motors, compressors, turbines) with large quantities of ignitable liquid for lubrication. Additional hazards include process control systems, flammable gas, corrosive materials, and reactive process materials.

The main loss drivers in the occupancy are:

- Fire and explosion of fuel, syngas, and lube oils in the production units
- Rotating and pressure equipment breakdown

1.2 Changes

January 2023. Interim revision. Minor editorial changes were made.

2.0 LOSS PREVENTION RECOMMENDATIONS

2.1 Construction and Location

2.1.1 Locate critical control and electrical equipment buildings in accordance with a facility siting study, with adequate space separation or blast-resistant construction. Use noncombustible construction and follow the construction and location guidance in the following data sheets as applicable:

- Data Sheet 7-14, *Fire Protection for Chemical Plants*
- Data Sheet 7-72, *Reformer and Cracking Furnaces*
- Data Sheet 7-95, *Compressors*
- Data Sheet 7-101, *Fire Protection for Steam Turbines and Electric Generators*

2.2 Process Safety

2.2.1 Establish a formal and comprehensive process safety program, with all elements in place and applied at a high level, in accordance with Data Sheet 7-43, *Process Safety*.

2.2.2 Establish an interlock bypass procedure. Conduct technical management reviews when critical interlock bypasses are being considered.

2.3 Protection

2.3.1 General

2.3.1.1 Install automatic sprinkler protection over combustible conveyors, bucket elevators, or conveyors with combustible belts (rubber belts), according to Data Sheet 7-11, *Conveyors*.

2.3.1.2 Provide passive or active steel protection according to Data Sheet 7-14, *Fire Protection for Chemical Plants*, on the main structural steel and equipment supports (load-bearing members) for process areas with the potential for a 3D spill, jet-fire, long-duration pool, or spray fire to occur. Ensure all the following is included:

- Support legs for reformers.
- Pipe rack supports or columns within the ammonia process area where Syngas is present.

2.3.1.3 Provide hydrant and monitor protection for ammonia storage tanks. See Data Sheet 7-14, *Fire Protection for Chemical Plants*, for additional information.

2.3.2 Turbines and Compressors

2.3.2.1 Provide sprinkler protection for equipment with lubricating oil systems located indoors, according to Data Sheets 7-95, *Compressors* with additional guidance in 7-101, *Fire Protection for Steam Turbines and Electric Generators*.

Where compressors and their drivers are located outdoors, utilize a deluge system with additional guidance from Data Sheet 7-14, *Fire Protection for Chemical Plants*.

2.3.3 Urea Plant

2.3.3.1 Provide sprinkler protection for the ammonia and/or carbamate (precursor to urea) pumps or other equipment that may have lube oil systems, according to Data Sheet 7-14, *Fire Protection for Chemical Plants*.

2.3.3.2 Install automatic sprinkler protection in the bagging/packaging area according to Data Sheet 3-26, *Fire Protection for Nonstorage Occupancies*.

2.4 Equipment and Processes

2.4.1 Ammonia

2.4.1.1 General

2.4.1.1.1 Install fail-safe type controls and instruments that regulate the flows and monitor critical parameters (i.e. reaction temperatures, pressure, etc.), during feed flow, steam, air, and/or electric power failures.

2.4.1.1.2 Provide safety controls, alarms and interlocks for processes or equipment that have been identify by a Process Hazard Analysis (PHA) to require specific controls to prevent damages or undesired events.

2.4.1.1.3 Provide gas analyzers to ensure a continuous checking of the composition of the synthesis gas flowing to the synthesis gas compressor, and the gas being circulated through the synthesis loop.

2.4.1.2 Fuel Fired Equipment (Startup Heaters/Reformers).

2.4.1.2.1 Protect startup heaters, auxiliary boilers and reformers with combustion safeguards and operational interlocks according to Data Sheets 6-10, *Process Furnaces* and 7-72, *Reformer and Cracking Furnaces*.

2.4.1.2.2 For safe light-off operations, follow the guidance in Data Sheet 6-10, *Process Furnaces*.

2.4.1.2.3 Prevent overheating on secondary reformers by installing a flow or pressure switch interlock on the air supply to supplement the high temperature interlock. Locate the flow switch downstream of the secondary reformer.

2.4.1.3 Rotating Equipment

2.4.1.3.1 Steam Turbines

2.4.1.3.1.1 Provide protective devices, alarms, and trips for steam turbines according to Data Sheets 13-3, *Steam Turbines*.

2.4.1.3.1.2 Conduct an oil fire hazard assessment (OFHA) according to Data Sheet 7-101, *Fire Protection for Steam Turbines and Electric Generators*. Ensure an emergency shutdown system is provided to allow the turbine and associated fluids to be shut down promptly and safely in emergency situations (e.g. lube oil gravity run-down tank).

2.4.1.3.2 Gas Turbines

2.4.1.3.2.1 For operations with gas turbines follow the protection guidelines in Data Sheet 7-79, *Fire Protection for Gas Turbines and Electric Generators*.

2.4.1.3.3 Compressors

2.4.1.3.3.1 For operations with compressors follow the guidelines in Data Sheet 7-95, *Compressors*.

2.4.1.3.3.2 Provide compressors with an online vibration monitoring/trip interlock system.

2.4.1.3.3.3 Install an automatic shutoff system for the compressor lube oil pump to be actuated in case of leakages or oil discharges.

2.4.1.3.3.4 Provide oil spray shields on high pressure (>50 psi) lube oil flanges.

2.4.2 Nitric Acid

2.4.2.1 Design and arrange equipment process to avoid any interconnection points where liquid nitric acid could enter to pipe or equipment that normally handled acid vapor phase only. If this is not practical, then protect any interconnection points with safety controls and alarms to prevent liquid nitric acid from entering upstream equipment sections. See Data Sheet 7-45, *Safety Controls, Alarms, and Interlocks* for additional information

2.4.3 Urea

2.4.3.1 Provide urea-ammonium nitrate (UAN) pumps with high temperature interlocks to prevent decomposition from prolonged churning.

2.4.3.2 Provide urea reactors with an automatic weep detection system. To provide a more reliable leak detection, the weep points may be connected to the detector via tubes.

2.5 Operation and Maintenance

2.5.1 Establish an asset integrity monitoring program in accordance with Data Sheet 9-0, *Asset Integrity*.

2.5.2 Inspect, test, and maintain safety controls, alarms, and interlocks in accordance with Data Sheet 7-45, *Safety Controls, Alarms, and Interlocks*.

2.6 Utilities

2.6.1 Compressed Air/Electrical Power

2.6.1.1 In addition to the main air supply, provide a reliable emergency source of compressed air and/or electrical power to ensure services in case of electric power or air compressor failure. In the event of air failure, apply all the recommended actions in Table 1.

Table 1. Actions for Air Failure Events

Valve Type	*Action*
Feed gas control valve	Close
Steam control valve	Open (to flood reformers tubes and compressed air line)
Air control valves	Open the vent valve to prevent surging in centrifugal compressor. Close the control valve for air supply line to process.
Fuel control valve	Close

3.0 SUPPORT FOR RECOMMENDATIONS

3.1 Loss History

Figure 1 provides a summary of the FM losses by peril in this industry between 2000 and 2019.

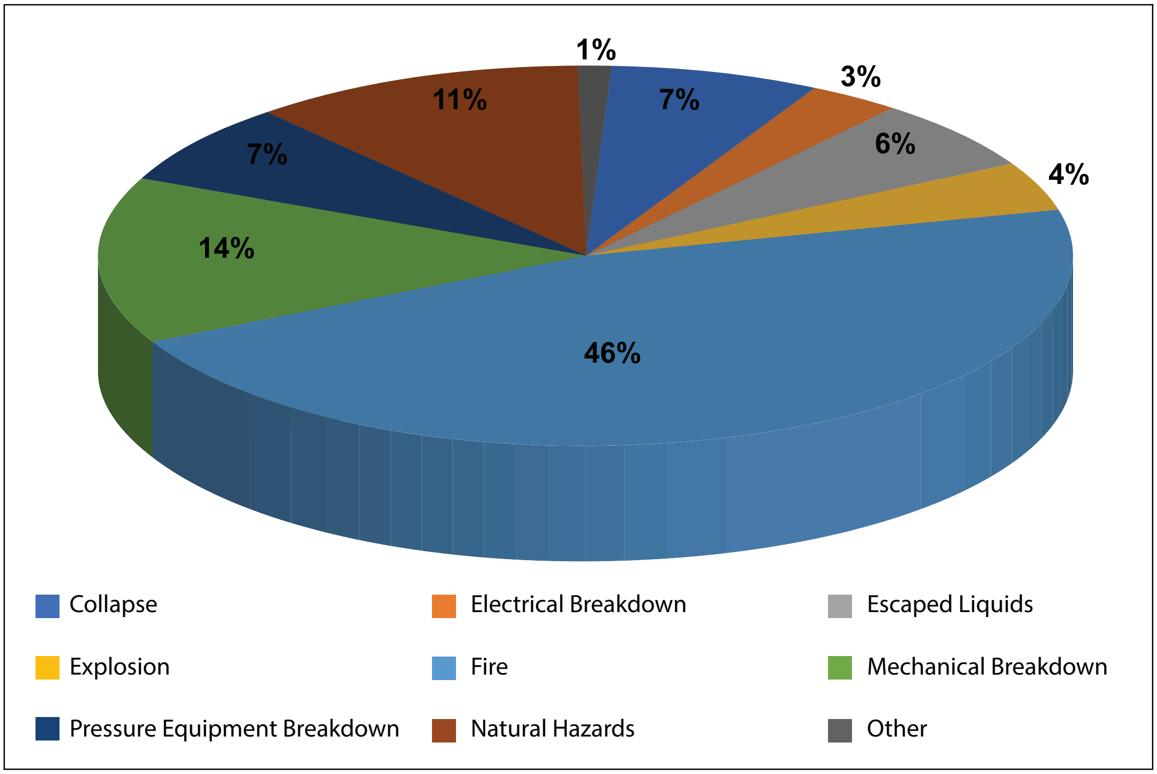

Fig. 1. Losses by peril, 2000-2019

Figure 2 provides a summary of the FM losses by equipment in this industry between 2000 and 2019.

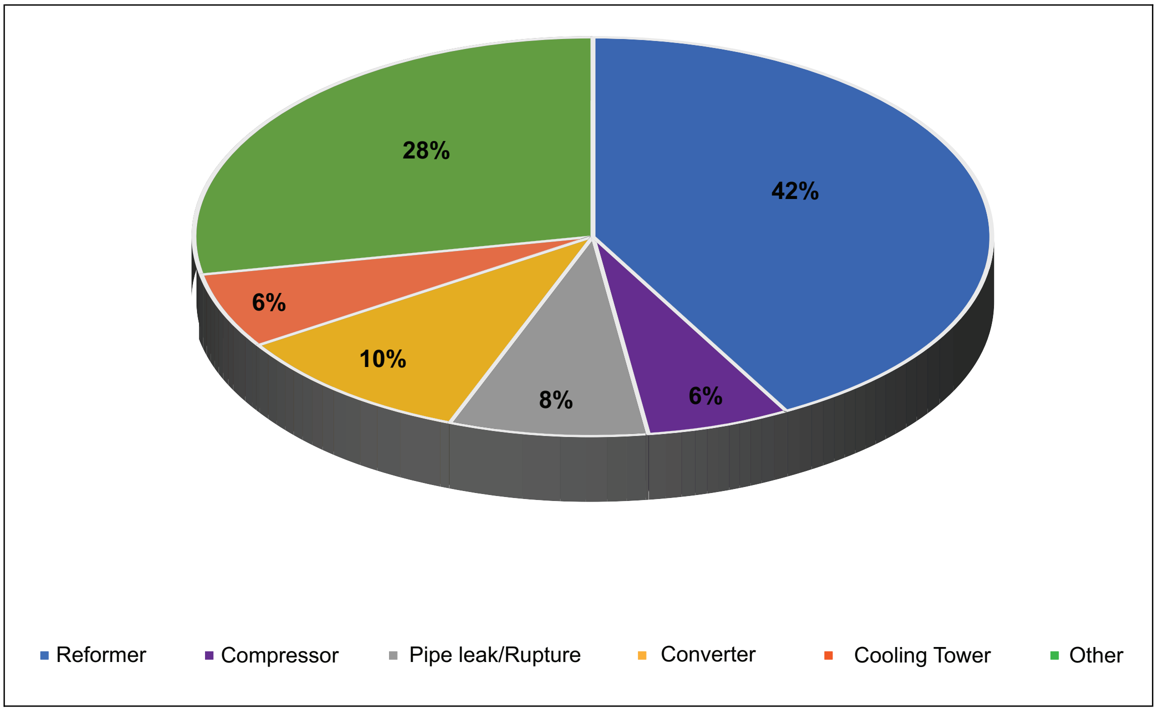

Fig. 2. Losses by equipment, 2000-2019

The most frequent causes of loss in this type of industry have been fire, mechanical breakdown, and natural hazards. Reformers have seen the highest number of losses.

3.2 Process Overview

Ammonia is produced in large volumes around the world, with some plants producing more than 3,000 tpd, mainly for the manufacturing of fertilizers which accounts for about 80% of the total ammonia production. The remainder is used mostly for the production of nitric acid, fibers, elastomers, plastics, resins, explosives, etc. Also, some commercial and industrial refrigeration units use ammonia as a refrigerant media.

Generally, ammonia plants are also designed to have onsite process areas for the manufacturing of nitric acid, ammonium nitrate (AN), calcium ammonium nitrate (CAN), and urea as shown in Figure 3.

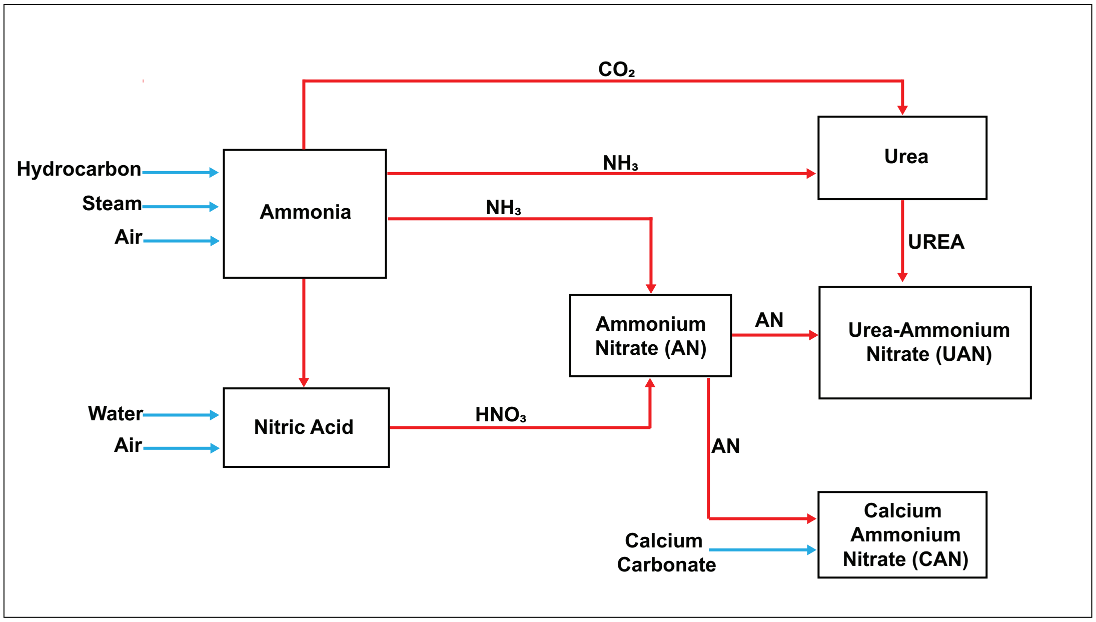

Fig. 3. Production flow for integrated ammonia/nitric acid/AN plant with urea/UAN

3.2.1 Ammonia Synthesis from Natural Gas

Ammonia is a molecule consisting of nitrogen (N) and hydrogen (H). About 85% of world ammonia production is based on the steam reforming process (see Figure 4). Ammonia is produced via syngas, created from steam reforming of methane. The syngas is mixed with nitrogen (from air) and converted under high pressure into ammonia. The primary byproduct in this process is carbon dioxide (CO_2). It is common to have a urea plant to consume this carbon dioxide, or to have a carbon dioxide plant next door to collect and sell CO_2.

The process begins with a desulfurization of methane gas to protect the catalysis in further steps. Sulfur is mainly present as carbonyl sulfide (COS) and hydrogen sulfide (H_2S).

The steam and gas mixture are heated to between 930°F and 1100°F (500°C and 600°C) in the primary reformer. As this is a highly endothermic reaction, additional heat up to 1500°F (830°C) is needed.

Only 30%-40% of the hydrocarbon reacts in the primary reformer. This mixture enters the secondary reformer to additional yield of hydrogen gas. The reaction produces carbon monoxide that needs to be removed. The gas passes through a bed of iron oxide/chromium oxide catalyst at around 750°F (400°C) (high-temperature shift conversion). This is an exothermic reaction in which process heat is used for steam production. This steam is critical for plant operation, and startup depends on having steam available for process steam as well as to operate steam turbines and provide heating where needed. An auxiliary boiler is usually present, and a startup heater supplements the needed heat to start. Carbon dioxide and water are removed by absorption in aqueous ethanolamine or other absorption solutions.

Methanation is the process by which the remaining carbon monoxide and dioxide are removed by conversion to methane using a nickel catalyst (this prevents downstream catalyst poisoning).

The ammonia converter operates at high pressure and moderate temperature. Ammonia synthesis is moderately exothermic, with temperatures handled via pressure interlocks. There is no decomposition or runaway potential in this reaction.

Hydrogen is catalytically reacted with nitrogen from process air to form anhydrous liquid ammonia. Centrifugal compressors are used at high pressure to increase the rate of reaction.

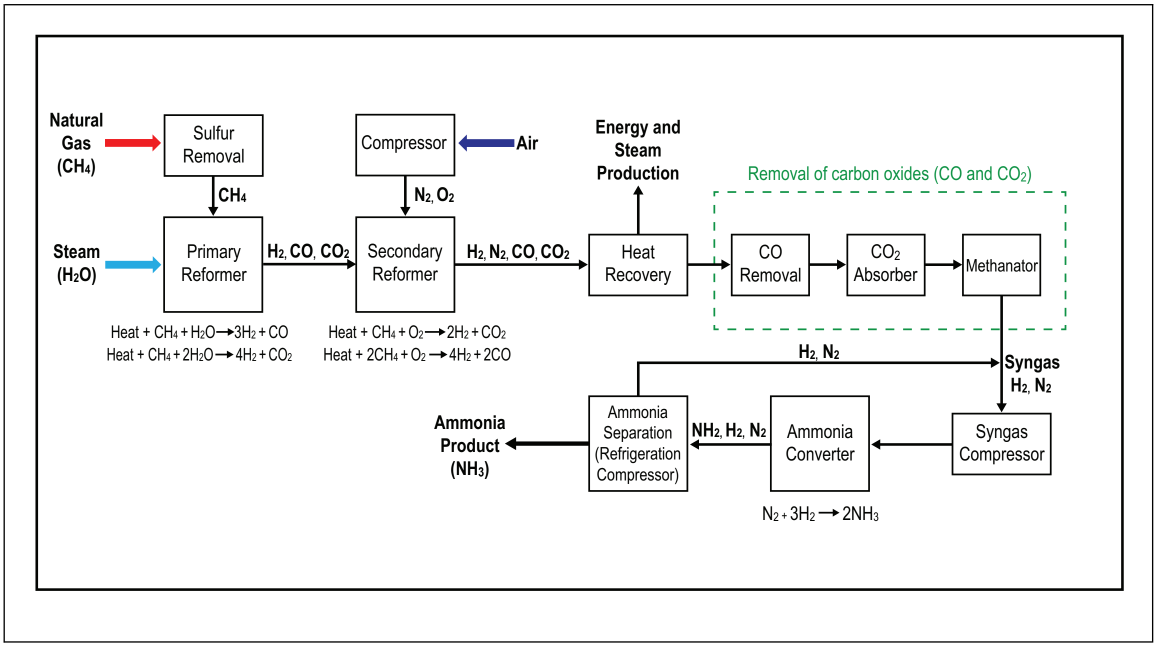

Fig. 4. Ammonia process diagram

3.2.2 Urea Manufacturing

Typical technology is the Stamicarbon process. This uses high pressure and moderate temperature. Urea is corrosive. Urea is made from 2 moles of NH_3 per 1 mole of CO_2.

The process consists of two main equilibrium reactions, with incomplete conversion of the reactants. The first is carbamate formation, which is a fast exothermic reaction of liquid ammonia with gaseous carbon dioxide (CO_2) at high temperature and pressure to form ammonium carbamate (NH_2COONH_4):

$2NH_3 + CO_2 \quad NH_2COONH_4$

The second is urea conversion, which is a slower endothermic decomposition of ammonium carbamate into urea and water:

$NH_2COONH_4 \quad NH_2CONH_2 + H_2O$

The overall conversion of NH_3 and CO_2 to urea is exothermic, the reaction heat from the first reaction driving the second. To allow the slow urea formation reaction time to reach equilibrium, a large reaction space is needed, so the synthesis reactor in a large urea plant tends to be a massive pressure vessel.

Because the urea conversion is incomplete, the product must be separated from unchanged ammonium carbamate. This may be accomplished by depressurizing the reaction solution in stages and passing it at each stage through a steam-heated carbamate decomposer, then recombining the resultant carbon dioxide and ammonia in a falling-film carbamate condenser and pumping the carbamate solution into the previous stage.

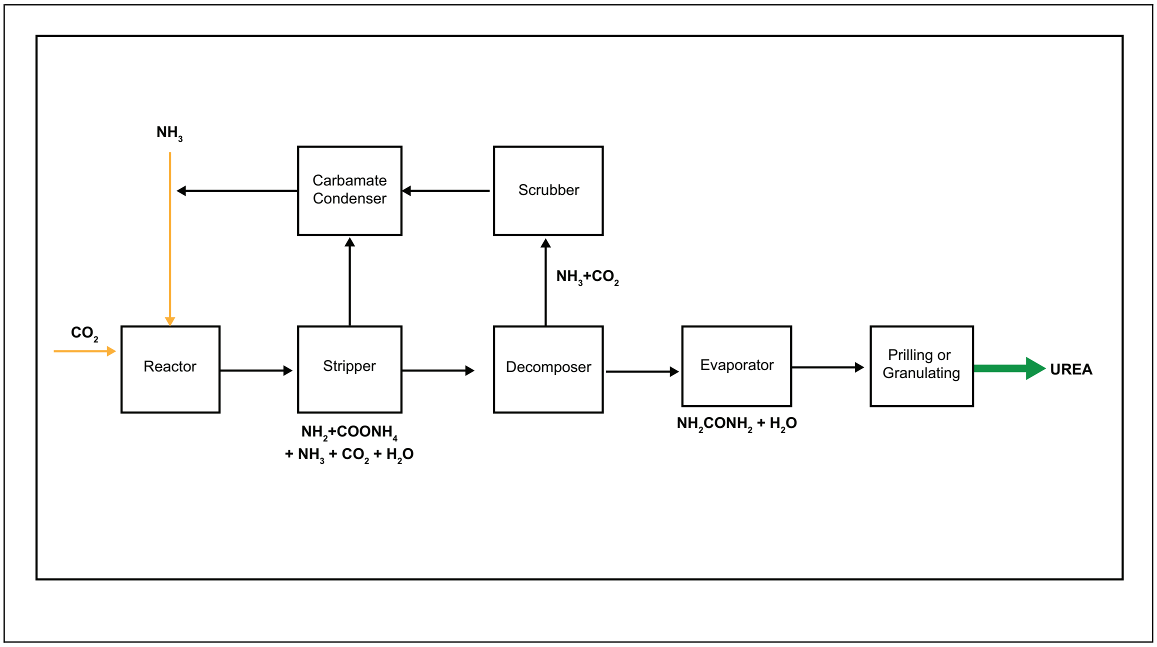

Fig. 5. Urea process diagram

3.2.3 Nitric Acid Manufacturing

Filtered air (from a large process air compressor) and liquid ammonia enter a burner and gas distribution system. Over a platinum catalyst gauze, the ammonia is combusted to nitrogen oxide. The gas is cooled and condensed, forming a weak nitric acid. This is separated from the process gas and sent to the absorption tower. Compression of the gas is used for heating the tail gas. In the absorption tower, the NOx gases are absorbed in water to form nitric acid. Heat generated is generally used for steam production and/or power supply for the site.

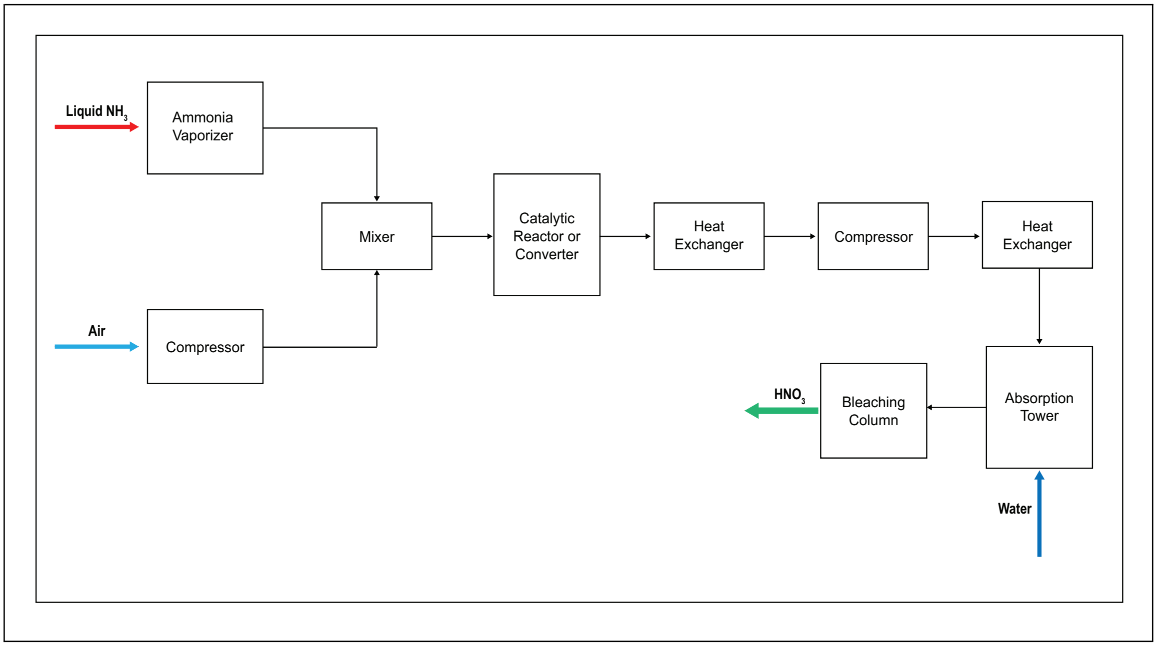

Fig. 6. Nitric acid process diagram

4.0 REFERENCES

4.1 FM

Data Sheet 3-26, *Fire Protection for Nonstorage Occupancies*
Data Sheet 6-10, *Process Furnaces*
Data Sheet 7-14, *Fire Protection for Chemical Plants*
Data Sheet 7-11, *Conveyors*
Data Sheet 7-43, *Process Safety*
Data Sheet 7-45, *Safety Controls, Alarms, and Interlocks*
Data Sheet 7-72, *Reformer and Cracking Furnaces*
Data Sheet 7-79, *Fire Protection for Gas Turbines and Electric Generators*
Data Sheet 7-95, *Compressors*
Data Sheet 7-101, *Fire Protection for Steam Turbines and Electric Generators*
Data Sheet 9-0, *Asset Integrity*
Data Sheet 13-3, *Steam Turbines*
Data Sheet 13-17, *Gas Turbines*

APPENDIX A GLOSSARY OF TERMS

Absorber: Uses amine solution to remove carbon dioxide from syngas.

Ammonia converter: High-pressure layered vessel, partially catalyst-filled, that reacts nitrogen and hydrogen into ammonia.

Carbamate: Intermediate salt in making urea.

Methantor: Changes carbon dioxide/monoxide back into methane (to prevent downstream catalyst fouling).

Reformer: Gas-fired furnace filled with catalyst-filled tubes to convert steam and methane into hydrogen and carbon dioxide/monoxide (syngas).

Secondary reformer: Introduces air to syngas stream from reformer; adds nitrogen for later use in making ammonia, and adds oxygen to continue reformer reaction.

Shift converter: Changes carbon monoxide to carbon dioxide.

Syngas: Synthesis gas, a flammable mixture of hydrogen and carbon monoxide/dioxide.

Urea reactor: High-pressure layered vessel that reacts ammonia and carbon dioxide into carbamate.

APPENDIX B DOCUMENT REVISION HISTORY

The purpose of this appendix is to capture the changes that were made to this document each time it was published. Please note that section numbers refer specifically to those in the version published on the date shown (i.e., the section numbers are not always the same from version to version).

January 2023. Interim revision. Minor editorial changes were made.

January 2022. Interim revision. Minor editorial changes were made, including the following:

A. Clarification to 2.4.1.2.3, to include that this recommendation applies specifically for the air supply system.

October 2020. This is the first publication of this document.