

Control and Pollution Prevention Options for Ammonia Emissions

CONTROL TECHNOLOGY CENTER

Sponsored by

Information Transfer and Program Integration Division
Office of Air Quality Planning and Standards
U.S. Environmental Protection Agency
Research Triangle Park, NC 27711

Air and Energy Engineering Laboratory
Office of Research and Development
U.S. Environmental Protection Agency
Research Triangle Park, NC 27711

April 1995

April 1995

Control and Pollution Prevention Options for Ammonia Emissions

Prepared by

Jennifer Phillips
ViGYAN Incorporated
1953 Gallows Road, Suite 320
Vienna, VA 22182-3934

EPA Contract No. 68-D1-0073
Work Assignment No. 3-39

Project Manager

Robert J. Blaszcak
Information Transfer and Program Integration Division
Office of Air Quality Planning and Standards
U.S. Environmental Protection Agency
Research Triangle Park, NC 27711

Prepared for

Control Technology Center
U.S. Environmental Protection Agency
Research Triangle Park, NC 27711

EPA REVIEW NOTICE

This report has been reviewed by the Control Technology Center (CTC) established by the Office of Research and Development (ORD) and the Office of Air Quality Planning and Standards (OAQPS) of the U.S. Environmental Protection Agency (EPA), and has been approved for publication. Approval does not signify that the comments necessarily reflect the view and policies of EPA, nor does mention of trade names, organization names, or commercial products constitute endorsement or recommendation for use.

This document is available to the public through the National Technical Information Service, Springfield, Virginia, 22161, (800) 553-6847.

ACKNOWLEDGEMENTS

Funding for this project was provided by the Control Technology Center. This report does not necessarily reflect the views of this organization and no official endorsement should be inferred. This project was managed by Bob Blaszcak, Control Technology Center, United States Environmental Protection Agency (U.S. EPA). The cooperation of State Air Pollution Control Agencies and control equipment manufacturers aided in the development of this document, through the use of U.S. EPA Contract Number 68-D1-0073, Work Assignment No. 3-39.

PREFACE

The Control Technology Center was established by the U.S. Environmental Protection Agency's (EPA's) Office of Research and Development (ORD) to provide technical assistance to State and local air pollution agencies. Several levels of assistance can be provided when appropriate. These include the following:

- **CTC HOTLINE** provides quick access to EPA expertise, information, and assistance on matters relating to control technology (919/541-0800).
- **Engineering Assistance Projects** provide more in-depth assistance to State and local agencies when needed to address a specific pollution problem or source.
- **Technical Guidance Projects** address problems or source categories of regional or national interest by developing technical guidance documents, computer software, or presentation of workshops on control technology issues.
- **Federal Small Business Assistance Program (SBAP)** coordinates efforts among EPA centers participating in the Federal Small Business Assistance Program to assist State SBAPs.
- **International Technical Information Center for Global Greenhouse Gases** provides information on global greenhouse gas emissions and available prevention, mitigation, and control technologies and strategies.
- **RACT/BACT/LAER Clearinghouse (RBLC)** bulletin board system (BBS) provides access to more than 3,100 pollution prevention (P2) and control technology determinations addressing over 200 pollutants. Select the RBLC from the technical BBS menu on the OAQPS Technology Transfer Center (TTN) BBS (919/541-5742).
- **CTC BBS** on the OAQPS TTN provides around-the-clock access to all CTC services, including downloadable copies of many CTC products. Select CTC from the TTN BBS Technical BBS menu (919/541-5742).
- **CTC NEWS** is a quarterly newsletter published by the CTC. It contains updates on all CTC activities including the RBLC and Federal SBAP. Call or write the CTC to get on the CTC NEWS mailing list.

This CTC project was undertaken as a result of requests for guidance concerning technologies available for the control and prevention of ammonia emissions. This study included a search of technical literature and a review of available information on current and potential methods for ammonia emissions control. Both pollution prevention (P2) methods and control devices were identified.

TABLE OF CONTENTS

Item	Page
EPA Review Notice	iii
Acknowledgements	iv
Preface	v
List of Figures	viii
List of Tables	viii
Executive Summary	ix
Abbreviations	x
Chapter 1 Ammonia	1
Chapter 2 Fertilizer Industry	3
Chapter 3 Coke Manufacture	21
Chapter 4 Fossil Fuel Combustion	31
Chapter 5 Livestock Management	39
Chapter 6 Refrigeration	43
Chapter 7 Control Techniques Applied to Ammonia Emissions	45
Chapter 8 Conclusions	51
References	R-1

LIST OF FIGURES

Figures	Page
Figure 1: Ammonia Plant Process Flow Diagram	4
Figure 2: Urea Plant Process Flow Diagram	9
Figure 3: Typical Once-Through Urea Process	11
Figure 4: Typical Partial-Recycle Urea Process	12
Figure 5: Typical Ammonium Nitrate Manufacturing Operations	15
Figure 6: Ammonium Phosphate Process Flow Diagram	18
Figure 7: Typical Layout for a By-Production Coke Oven Battery	22
Figure 8: Ammonia Destruction Process	26

LIST OF TABLES

Tables	Page
Table 1: Stable Operating Parameters for the Ammonia Destruction System [9]	29
Table 2: Nitrogen Oxide Reduction Using Ammonia and Urea	36
Table 3: Control Efficiencies for Wet Scrubbers Applied to Livestock Facilities	40
Table 4: Capital Cost Figures for a Monsanto Wet Scrubber Package	47

EXECUTIVE SUMMARY

In response to requests for guidance concerning technologies available for the control and prevention of ammonia emissions, the Control Technology Center (CTC) initiated a review of current and potential methods for ammonia emissions control. A review of various industries has identified significant sources of ammonia to be fertilizer production, coke production using the by-product recovery method, fossil fuel combustion, livestock management, and refrigeration using ammonia as a refrigerant. Control methods implemented by these sources include wet scrubbers, condensate strippers, recovery and recycle of exhaust streams, capture systems, and good maintenance practices.

The fertilizer industry implements wet scrubbers, condensate strippers, and recovery and recycle methods to control ammonia emissions. Coke manufacturers use scrubbers and capture devices to collect and treat ammonia emissions. Livestock management facilities use wet scrubbers and good maintenance procedures to reduce emissions from animal manure. Facilities using ammonia as a refrigerant use capture devices and good management practices to safeguard against potential hazards due to leaks and spills of ammonia. Unlike other sources, emission of ammonia from fossil fuel combustion sources results from the implementation of post-combustion controls using ammonia or urea to decrease nitrogen oxide emissions. In this process unreacted ammonia exits the source in the effluent, representing a condition known as ammonia slip. Using good operating practices, the level of ammonia slip can be reduced.

This report discusses each industry process identified above, concentrating on the sources of ammonia emissions and the controls and pollution prevention (P2) methods applied. Only these industries are presented because they have demonstrated successful implementation of control or P2 methods to reduce ammonia emissions. Other industries may have minor ammonia emissions, but they are not addressed in this report because neither control technologies nor P2 methods are applied.

ABBREVIATIONS

acfm:	actual cubic feet per minute
atm:	atmospheres
cfm:	cubic feet per minute
°F:	degrees Fahrenheit
ft ² :	square feet
ft ³ :	cubic feet
gpm:	gallons per minute
gr:	grains
hr:	hour
lb:	pound
mg:	milligram
ppm:	parts per million
ppmv:	parts per million, volume
psi:	pounds per square inch
psig:	pounds per square inch, gauge
scf:	standard cubic feet
scfd:	standard cubic feet per day
tpd:	tons per day

CHAPTER 1

AMMONIA

A. INTRODUCTION

As a result of inquiries made by industry concerning available techniques for controlling or preventing emissions of ammonia, the United States Environmental Protection Agency (U.S. EPA) Control Technology Center (CTC) undertook a project to review successful applications of ammonia control methods.

Ammonia is a colorless gas with a pungent odor that is noticeable at concentrations above 50 ppm. It is poisonous if inhaled in great quantities and is irritating to the eyes, nose, and throat in lesser amounts. At normal atmospheric pressure, ammonia has a boiling point of -28°F and a freezing point of -107.86°F . It is highly soluble in water, with one volume of water absorbing 1.148 volumes of ammonia at 32°F . [1, 2]

The danger associated with ammonia is that it is explosive when mixed with air in certain proportions, approximately one volume of ammonia to two volumes of air, and is much more so when mixed with oxygen.

B. INDUSTRIES EMITTING AMMONIA

Various industries were identified as emitters of ammonia. These include the fertilizer manufacture industry, coke manufacture, fossil fuel combustion, livestock management, and refrigeration methods. Most of the ammonia emitted is generated from livestock waste management and fertilizer production, comprising about 90% of total ammonia emissions.

Fossil fuel combustion is different from the other industries identified in that ammonia is not emitted from the process itself, but from the control technology applied to the source in order to control nitrogen oxide (NO_x) emissions. Selective catalytic reduction and selective non-catalytic reduction are two technologies used to control nitrogen oxides in the post-combustion gases exhausting from combustion sources. These methods reduce nitrogen oxides by injecting urea or ammonia into the exhaust gas to react with the nitrogen oxides, with or without a catalyst present, depending on the method selected. If the reaction is not complete, a portion of the ammonia may exit the system in the effluent. This condition is known as ammonia slip. [3]

C. CONTROL TECHNIQUES

The various control technologies available to control ammonia emissions include both add-on control devices and pollution prevention techniques. The wet scrubber, specifically the packed tower scrubber, has been successfully used to control ammonia emissions, demonstrating control efficiencies up to 99%. Condensers are also used to remove ammonia by converting the gas to a liquid. Many times the condensate is returned to the process for reuse. Ammonia recycle, in which the ammonia is retrieved from the exhaust gas stream and returned to the process, is a common pollution prevention method. The recycling method is often used in the manufacture of fertilizers, where ammonia is a feedstock and the implementation of recycling benefits the process in addition to controlling emissions. In the case of fossil fuel combustion where ammonia is emitted as a result of the controls implemented to reduce nitrogen oxide emissions, careful application of the nitrogen oxide control method will limit the amount of ammonia that will slip through the process. With regards to ammonia leakage, good management practices can reduce the amount of ammonia that escapes. For those leaks that cannot be prevented, capture devices such as hoods may be used to collect the ammonia gas, which is then conveyed to a control device for treatment. [5, 6, 13, 15]

In evaluating control methods for ammonia, it was discovered that these basic types of controls are used in the variety of industries emitting ammonia. Where the cost of add-on controls are not warranted, ammonia emissions may be limited by applying good management practices.

CHAPTER 2

FERTILIZER INDUSTRY

The manufacture of fertilizers accounts for approximately 27% of the ammonia emissions generated in the United States. Fertilizer production is divided into two categories: nitrogen fertilizers and phosphate fertilizers. The nitrogen fertilizer industry encompasses ammonia, urea, ammonium nitrate, and nitric acid manufacture, while the phosphate fertilizer industry consists of ammonium phosphate, normal superphosphate, and triple superphosphate production. [3]

Since this document addresses ammonia emissions and associated control techniques, the sections of this chapter only discuss ammonia, urea, ammonium nitrate, and ammonium phosphate plants. Nitric acid, normal superphosphate, and triple superphosphate plants are not addressed because they do not emit ammonia. The pollutants of concern from the production of these fertilizers are nitrogen oxides from nitric acid plants and particulate matter and fluoride from both normal and triple superphosphate plants. [4, 5]

A. NITROGEN FERTILIZER PRODUCTION

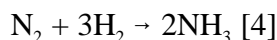
This section discusses the production of ammonia, urea, and ammonium nitrate, outlining the process steps involved in the manufacture operations and the subsequent sources and control of ammonia.

1. Ammonia Plants

Ammonia is the primary element used in the production of nitrogen fertilizers. Ammonia is either applied as a fertilizer directly or is used as a feedstock in the manufacture of urea, ammonium nitrate, or nitric acid. [4]

a. Process Description

Ammonia (NH₃) is formed by reacting hydrogen (H₂) and nitrogen (N₂), as shown by the following chemical equation:



The production of ammonia is achieved through the following steps: (1) feedstock desulfurization; (2) primary reforming with steam; (3) secondary reforming with air; (4) high and low temperature carbon monoxide (CO) shifts; (5) carbon dioxide (CO₂) absorption; (6) methanation; (7) ammonia synthesis; and (8) product storage and handling. [6] Steps 1, 4, 5, and 6 remove impurities from feedstock and synthesis gas streams, steps 2 and 3 generate hydrogen and add nitrogen, step 7 manufactures anhydrous ammonia

from synthetic gas, and step 8 pertains to the handling of the final product. These eight steps are the basic processes performed at all plants, though operating conditions, such as pressure, temperature, and feedstock amount vary. [3] Figure 1 illustrates the process steps for a typical ammonia production plant.

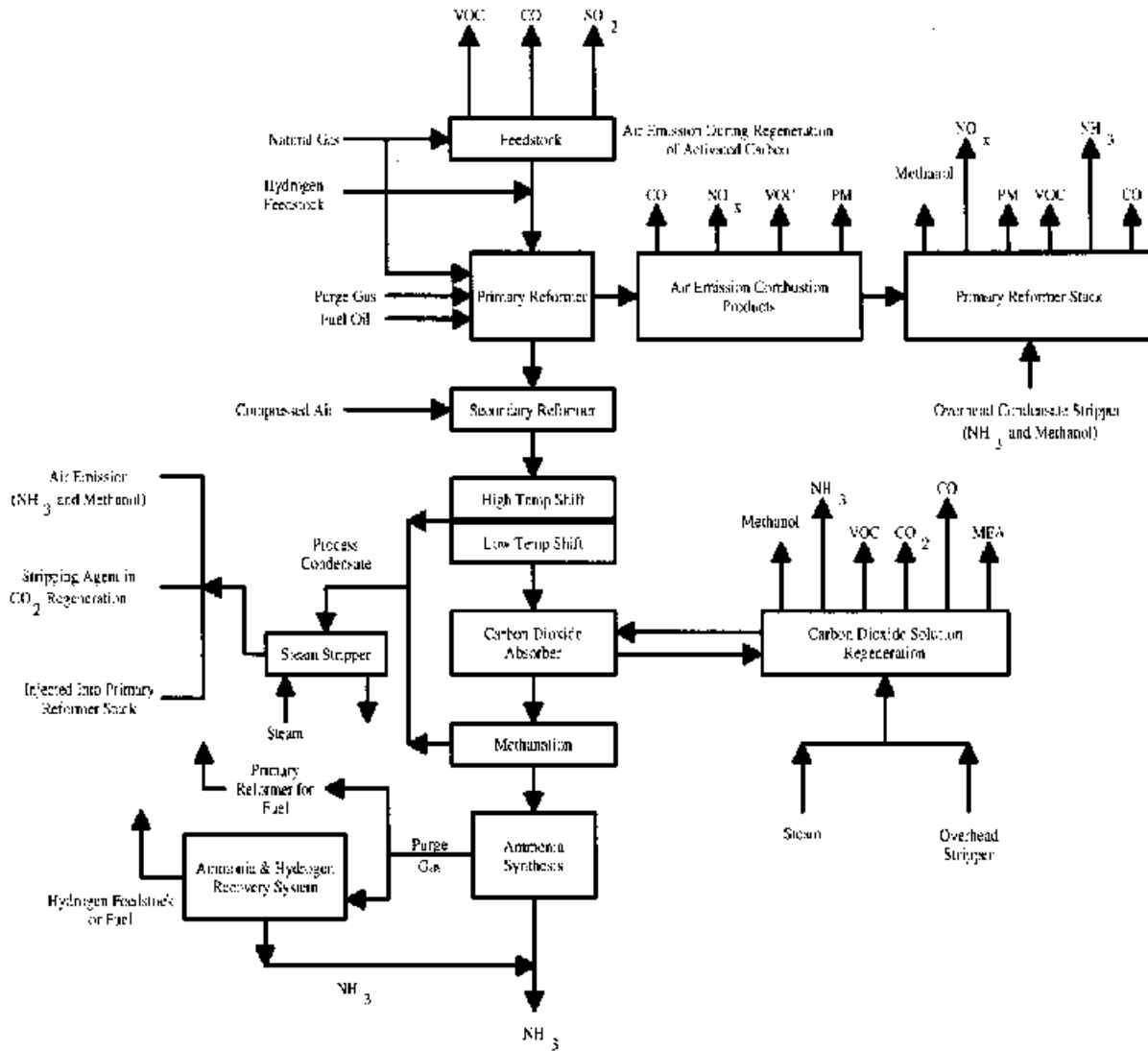


Figure 1: Ammonia Plant Process Flow Diagram [6]

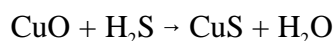
The following sections delineate the eight process steps used in the production of ammonia.

1. *Desulfurization (Process Step 1)*

Various feedstocks are available, but most of the ammonia plants in the United States use natural gas to supply hydrogen. The use of alternate feedstocks, such as naphtha, fuel oil, and coal has been evaluated, but natural gas is the most economical. [7]

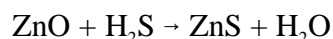
Desulfurization of the feedstock is the first step in the ammonia manufacturing process. The sulfur concentration is reduced to below 0.5 ppmv since concentrations higher than this can adversely affect the performance of the reformer catalyst. Desulfurization is performed using either activated carbon beds or zinc oxide (ZnO) beds. Older plants often use activated carbon beds containing cuprous oxide (CuO), while new plants typically employ zinc oxide beds.

When desulfurization is performed using activated carbon beds, the cuprous oxide reacts with the hydrogen sulfide (H₂S) to yield water and copper sulfide (CuS), as represented in the following equation:



Activated carbon must be regenerated approximately every 30 days to remove adsorbed pollutants, thereby renewing spent carbon. Pollutants accumulated on the activated carbon may be removed by passing air through the bed at a temperature of 450°F for 8 to 10 hours.

When zinc oxide beds are used, the zinc oxide reacts with the hydrogen sulfide to yield zinc sulfide (ZnS) and water, as shown by the equation below:



This method absorbs up to 20% sulfur by weight. Since spent zinc oxide is replaced, not regenerated, the energy outlay is lower for this method than the expenditure associated with the use of activated carbon bed adsorbers. [6]

2. *Primary and Secondary Reformer (Process Steps 2 and 3)*

After desulfurization is performed, the feed gas enters the primary reformer where it reacts with steam to yield hydrogen and carbon monoxide. This reaction is performed at a high temperature and pressure. Air is then supplied to the secondary reformer to provide nitrogen. [6]

3. *High and Low Temperature Carbon Monoxide Shifts (Process Step 4)*

This step of the process employs a two stage shift converter. Cooled gas exiting the secondary reformer enters the high-temperature shift converter, where the carbon monoxide present in the gas reacts with steam, thereby producing carbon dioxide and hydrogen. The stream is then cooled to 392°F and enters

the low-temperature shift converter where additional carbon monoxide is removed. Most of the unreacted steam is removed as process condensate. [6]

4. *Carbon Dioxide Absorption (Process Step 5)*

Since carbon dioxide adversely affects the catalyst used in ammonia synthesis, it is removed from the gas stream through scrubbing with monoethanolamine or hot potassium carbonate solution, with most of the production facilities using monoethanolamine as the scrubbing liquor. The liquor is regenerated using steam stripping. [3, 6, 8]

5. *Methanation (Process Step 6)*

Methane is formed by a reaction between hydrogen and trace amounts of carbon monoxide and carbon dioxide present in the gas, with the reaction occurring in the presence of a nickel catalyst. This is done to remove residual carbon monoxide and carbon dioxide. The purified gas is comprised of hydrogen, nitrogen, and small quantities of methane, argon, and helium. This gas is then compressed and routed to the synthesis operation. [6]

6. *Ammonia Synthesis (Process Step 7)*

The compressed gas enters the ammonia converter, where ammonia is synthesized by reacting hydrogen and nitrogen in the presence of an iron catalyst. The converters usually operate at temperatures ranging from 550 - 700°F. For small plants (< 600 tpd), the pressure condition in the converter lies in the range of 130 - 680 atm (1,930 - 10,100 psig), while converters at larger plants (\geq 600 tpd) operate at lower pressures. In order to attain high pressures, small plants use reciprocating compressors, while larger plants implement centrifugal machines for gas compression.

Only 10 - 20% of the gas is converted to ammonia through the synthesis of nitrogen and hydrogen. As a result, ammonia refrigerant is used to cool a large portion of the reaction gas to remove ammonia through condensation. Since unreacted gas, such as methane and argon, often accrues in this portion of the process, some of the gas is purged to decrease the concentration of inert gases. The remaining gas is then recompressed and mixed with make-up gas and subsequently reheated and recycled to the converter. [4, 6]

7. *Product Storage and Loading (Process Step 8)*

The ammonia product is stored in large atmospheric tanks at a temperature of -28°F or in large spheres maintained at pressures up to 20 atm (300 psig) at ambient temperatures. [4, 6]

b. *Ammonia Emission Sources and Controls*

The production of ammonia, using natural gas as a feedstock, generates few environmental problems. [4] Most air emission sources at synthetic ammonia plants comply with environmental

regulations, without the use of add-on control equipment, by implementing the methods of recycling and reuse of process water. This limits the amount of wastewater effluent requiring treatment and attains compliance with effluent guidelines. [6]

The following sections describe the techniques used by ammonia plants to control ammonia emissions. Only those steps in the manufacturing process that emit ammonia are discussed.

1. *Primary and Secondary Reformer*

The primary reformer emits the combustion products of nitrogen oxides, carbon monoxide, and particulate matter, with nitrogen oxides being emitted in the greatest quantity. In addition, the stripper overhead generated later in the ammonia production process during the carbon monoxide shifts is reinjected into the primary reformer stack. Stripper overhead contains the pollutants collected from the gas stream being treated and exits the stripper tower as the waste stream. The stripper overhead is the waste stream containing the pollutants that exits the stripper. This stream contains ammonia and methanol. Currently, control devices are not required to control air emissions from the primary reformer. However, various methods are available to control nitrogen oxide emissions. Those methods involving ammonia emissions are described below.

Ammonia and Hydrogen Recovery: Hydrogen present in the fuel gas stream increases the flame temperature, which in turn increases the production of thermal nitrogen oxides. A cryogenic or permeation system may be used to recover the hydrogen from the purge gas, while water scrubbing is used to remove ammonia. This method removes a great source of nitrogen oxide emissions from the furnace and increases production. The cost of a cryogenic system is recovered within two to three years, depending upon the price of ammonia and the feedstock used, which is usually natural gas.

Post-combustion Nitrogen Oxide Control: Two methods available for post-combustion nitrogen oxide control include selective catalytic reduction (SCR) and selective non-catalytic reduction (SNCR), with most of these technologies being implemented in the utility industry. With these two processes there are several areas of concern, including ammonia slip, which is the presence of ammonia in the effluent, and the potential formation of ammonium sulfate and ammonium bisulfate as a result of this ammonia slip. These technologies and the possible generation of ammonia as a byproduct are discussed in detail in Chapter 4 of this document.

2. *High and Low Temperature Carbon Monoxide Shifts*

Process condensate is formed when the synthesis gas is cooled after the low temperature carbon dioxide shift conversion. The condensate contains ammonia, carbon dioxide, methanol, and trace metals. Most plants implement condensate strippers to remove ammonia and methanol from this condensate. Traditionally, the overhead was introduced into the furnace inlet, but the economic infeasibility of this method has been realized since extra fuel is needed to reform the gas stream. Another common method is

the introduction of the overhead stream into the primary reformer stack. Although the amount of ammonia and methanol emitted are decreased, the nitrogen oxide emissions are greatly increased.

The M. W. Kellogg Company has developed a closed system, consisting of a stripper and ion exchange unit, that recovers and treats process condensate. The stripper removes ammonia, carbon dioxide, and methanol from the process condensate leaving concentration levels of approximately 20, 40, and 50 ppm in the gas, respectively. The stripper overhead is then condensed to retrieve the aqueous ammonia. The process condensate is recycled to the ammonia unit and therefore is not contributing to effluent discharge. Since the recycled condensate is used as feedwater for the high pressure steam system, the amount of water needed to be demineralized is reduced, subsequently decreasing the amount of effluent discharged from the demineralizer. Although this stripper system has been favorable in its demonstrated control, certain disadvantages are associated with its operation, such as the entire amount of condensate is not reused, a great amount of steam is required, and air pollutant emissions are not eliminated entirely.

Due to these drawbacks, modern plants use a high pressure stripper that is similar to the low pressure system, except that the system operates at the same pressure level as that of the reforming steam. The process and stripped condensates are heated prior to entering the top of the condensate stripper, while high pressure steam is sent through the bottom of the stripper to contact the condensate in the packed column. The steam removes the impurities from the condensate and the overhead steam vapor is recycled for use as reforming steam. This process eliminates the vapor emissions from the condensate stripper and recovers the steam vapor with a minimal energy loss.

The process condensate may also be recycled by using a feed gas saturator coil in the reformer convection section, which vaporizes the process condensate into process feed gas. This improves the heat recovery from the reformer, reduces the liquid effluent, and lessens the requirement for process steam generation. [6]

3. *Carbon Dioxide Absorption*

The scrubbing solution, either monoethanolamine or hot potassium carbonate solution, is regenerated using steam. [3] The gas vented from the carbon dioxide absorption system is predominantly carbon dioxide (99%), with trace amounts of ammonia, carbon monoxide, water, and methanol. The gas stream is vented directly to the environment, unless the carbon dioxide is supplied as a feedstock to a urea or other plant. At this time, emission controls are not required on the carbon dioxide absorption system. [6]

4. *Product Storage and Loading*

Ammonia leaks often occur when the product is being handled. Such leaks happen when the product is being loaded into trucks or railroad cars. Since these leaks occur at identified locations, the emissions can be easily controlled through capture and treatment by wet scrubbers. In order to control ammonia emissions from fugitive leaks, good maintenance is required. Since fugitive ammonia emissions

are often low concentrations and are not hazardous, they do not warrant the implementation of control methods. [4]

2. Urea Plants

Urea ($\text{CO}[\text{NH}_2]_2$), also known as carbamide or carbonyl diamide, is a major source of nitrogen fertilizer.

a. Process Description

Seven different operations are performed in the production of urea: (1) solution synthesis; (2) solution concentration; (3) solids formation; (4) solids cooling; (5) solids screening; (6) solids coating; and (7) bagging and/or bulk shipping. The combination of these operations is decided based on the product form desired. For the production of urea solutions, only solution synthesis, solution concentration, and bulk shipping operations are performed. For solid urea production, all seven operations are executed. [6] Figure 2 illustrates process operations at a typical urea plant.

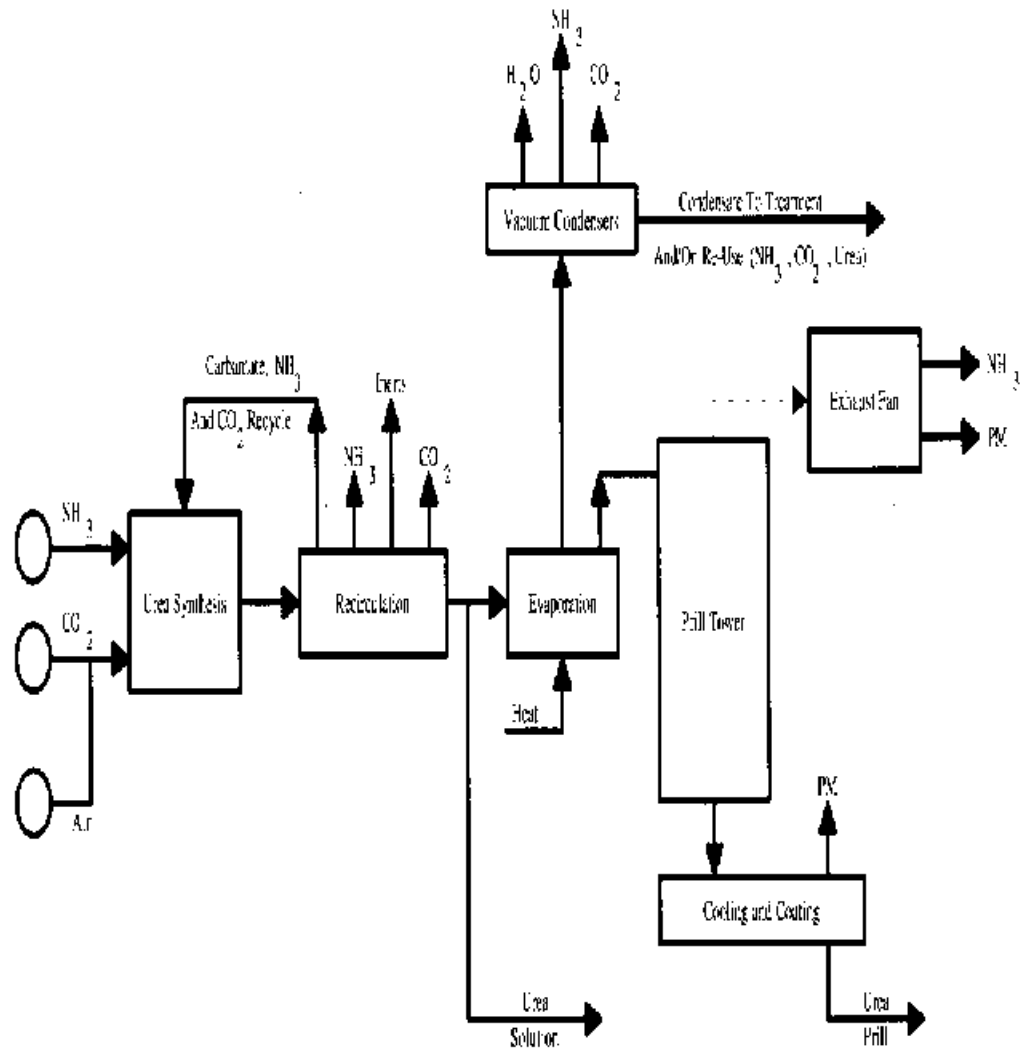


Figure 2: Urea Plant Process Flow Diagram [6]

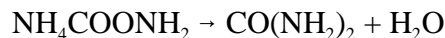
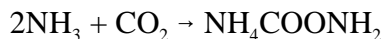
The following sections delineate the seven process steps used in the production of urea.

1. Solution Synthesis (Process Step 1)

Carbon dioxide is reacted with ammonia to form urea. The reaction occurs at a pressure ranging from 128-148 atm (1885-2175 psi) and a temperature ranging from 340-370°F. Since ammonia is a primary feedstock for the production of urea, the urea plant is usually located next to an ammonia plant of comparable size. The ammonia plant supplies necessary ammonia and high purity carbon dioxide, which is generated as a by-product of ammonia production. [6]

The reaction is comprised of two basic steps; ammonium carbamate is formed and then dehydrated. [4] Over fifteen types of basic production methods are available to perform these reactions, though conditions vary from plant to plant, such as vessel design, operating conditions, and type and amount of unreacted material recycled. [3]

An ammonia pump and carbon dioxide compressor feed the liquid ammonia and gaseous carbon dioxide to the high pressure condenser at reaction pressure, while a recycle gas stream of unreacted ammonia and carbon dioxide retrieved from the system is fed simultaneously. The combined new and recycled gas streams are partially condensed to form ammonium carbamate ($\text{CO}_2[\text{NH}_3]_2$), which then breaks down into urea and water. After the stream is separated into ammonium carbamate and unreacted ammonia and carbon dioxide, the resulting solution will contain approximately 70-80% urea. The solution can be transformed into a prilled or granulated solid to suit market demands. [6] The following chemical equations illustrate this reaction:



Three different synthesis process methods are used to produce urea: once-through, partial-recycle, and total-recycle. The methods differ in the way the unreacted ammonia and carbon dioxide are treated. Newer plants usually implement the total-recycle process.

Once-Through Process: The once-through process is the simplest of the three types. Liquid ammonia and carbon dioxide are sent to the reactor which is maintained at a pressure of 200 atm (2940 psi) and a temperature of approximately 365°F by controlling the amount of excess, or added, ammonia. Approximately 100% excess ammonia is needed, with about 35% of the ammonia and 75% of the carbon dioxide being converted to urea. The carbamate strippers steam heat the effluent to remove unreacted ammonia and carbon dioxide, with the stripped effluent containing approximately 80% urea.

This process generates a large amount of off-gas ammonia which is used to produce fertilizer products like ammonium nitrate, ammonium phosphate, nitric acid, or ammonium sulfate. [4, 5]

Figure 3 illustrates the operations for a typical once-through application.

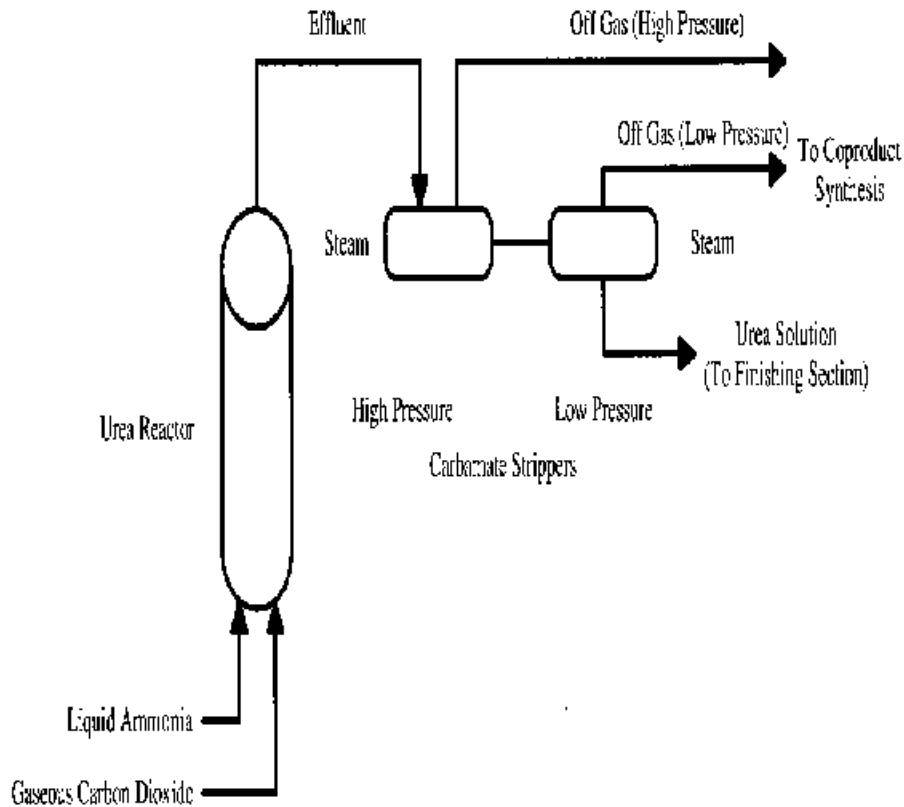


Figure 3:
T y p i c a l
O n c e -
T h r o u g h
U r e a P r o c e s s [5]

Partial-Recycle Process: The partial-recycle method recycles back to the urea reactor a portion of the unreacted ammonia and carbon dioxide present in the off-gas. Recycling reduces the amount of input ammonia required and may be performed by absorbing the gases from three different streams: the recycle stream of stripped urea effluent, the process-steam condensate, or the liquid from the crystallization finishing process. With this method, the amount of unreacted ammonia that must be used in another process is about 15% of that generated by the once-through process.

As in the once-through process, the ammonia and carbon dioxide are injected into the urea reactor at 200 atm (2940 psi), with the reactor temperature being maintained at about 365°F by controlling

the amount of excess ammonia and carbamate solution recycled. Approximately 100-110% excess ammonia is added, with approximately 70% ammonia and 87% carbon dioxide being converted to urea. The effluent from the reactor contains approximately 80% urea, with 30% ammonia requiring recycling.

Unreacted ammonia and carbon dioxide are removed in the high-pressure separator and several steam-heated carbamate strippers are operated at lower pressures. The high-pressure absorber collects the off-gas from the separator and first stripper using reactor effluent from the high pressure separator. In order to increase the absorption capability, a portion of the liquid ammonia feedstock is added to remove the heat generated in the absorber reaction. After condensation, ammonia gas from the absorber is returned to the reactor. The solubility of ammonium carbamate prevents the absorbing liquor from removing the entire amount present, so a portion of the ammonia and carbon dioxide cannot be returned to the process. The excess gases are used at a plant manufacturing a coproduct nitrogen material, with the plant operation being coordinated with the urea plant. [5] Figure 4 illustrates the operations for a typical partial-recycle application.

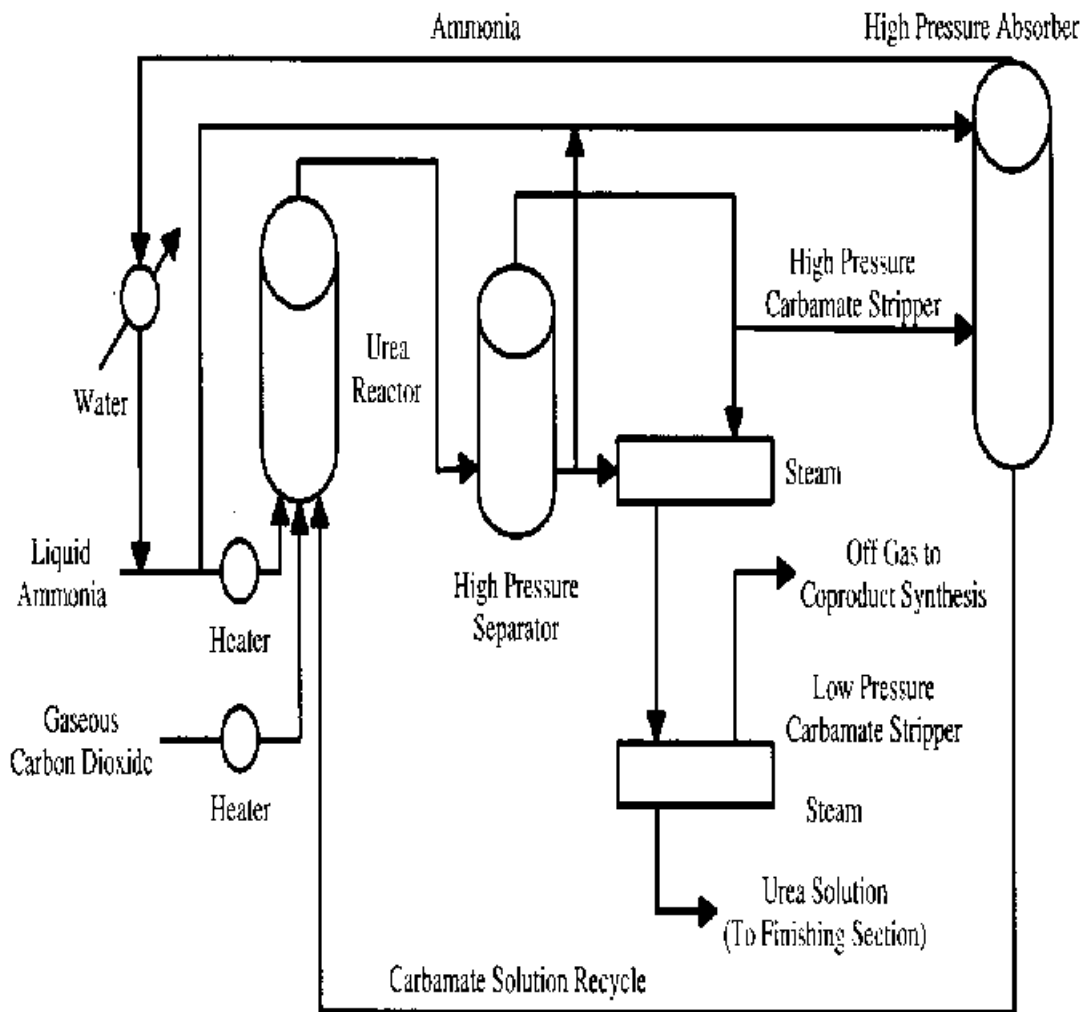


Figure 4 :
Typical Partial-Recycle Urea Process [5]

Total-Recycle Process: In the total recycle process, the unreacted ammonia and carbon dioxide from the off-gas are returned to the urea reactor. No coproduct plants are required since there is no excess material. This process can be separated into five divisions: hot-gas mixture recycle, separated-gas recycle, slurry recycle, carbamate-solution recycle, and stripping. The first four employ similar procedures for carbamate decomposition as those for the once-through and partial-recycle process, though the fifth step differs.

The operating conditions are consistent for each of these total-recycle methods. The reactor is kept at a temperature of 365°F and a pressure of 200 atm. An ammonia to carbon dioxide mole ratio of 4:1 is maintained in the synthesis loop and a 65-65% conversion of urea is achieved for each loop through the reactor, with the conversion of ammonia to urea being at least 99%. The pressure of the reactor effluent is lowered, after which the solution travels through two or three levels of decomposition, in the presence of heat, at succeeding lower pressures. The gas is condensed in each stage and sent back through the system to the reactor. Excess ammonia obtained from the original reactor feed is sent through absorbers and recycled to the reactor. At the recycle stage of the process, the solution contains quantities of ammonia and carbon dioxide, with urea amounts of approximately 75%. [4, 5]

2. *Solution Concentration (Process Step 2)*

After synthesis is performed, the solution is concentrated to 99+% by evaporation in a vacuum that is sustained by a steam ejector. This stage yields an urea solution that can then be used to produce liquid nitrogen fertilizers. If a liquid form of urea is desired, the urea solution is stabilized at room temperature and then shipped in bulk. [6]

3. *Solids Formation and Cooling (Process Steps 3 and 4)*

If a solid fertilizer is desired, the urea solution is processed further as described in steps 3 through 7. Depending on the desired form of the end product, the urea enters the top of a prilling tower or is sent to a granulation plant. The prilling process is the most common used to prepare the solution for use in fertilizer. The solution is evaporated and prilled in a drop-forming device, such as a spray system or rotating perforated bucket. The formed droplets cool and solidify as they descend through an upward airstream.

Granular urea is formed in either a rotary drum granulator or spouted-bed granulator. The molten urea is sprayed onto a moving bed of fines, from which the desired size of urea is removed, cooled, and subsequently stored. The small and large sized granules are recycled to the granulator where the process is repeated.

The granular form of urea is stronger than the prilled form, which is why new plants often use the granulation method. In addition, existing plants using prilling are beginning to add granulation equipment. [5]

4. *Solids Finishing Process (Process Steps 5, 6, and 7)*

The final procedure in the process is product finishing and handling. Screening is used to achieve size control by removing very large and very small material and returning it to the process. Coatings and additives are applied to limit the amount of caking and dust formation, with the most used additives being formaldehyde and phosphate compounds. Often conveyors are used to transfer the material within the process finishing system. Urea is shipped in either bags or bulk quantities. [6]

b. Ammonia Emissions and Controls

Emissions from urea production are ammonia and solid urea particles. [3] Fugitive emissions may occur from vents, seals, compressors, storage facilities, relief valves, and spills. [6] The following sections describe the techniques used by urea plants to control ammonia emissions. Only those steps in the manufacturing process that emit ammonia are discussed.

1. Solution Synthesis

Emissions control is intrinsic in the recovery and recycle process of carbamate. The emissions are typically unreacted gases from ammonium carbamate decomposers and separators. These are often minor emission sources of ammonia and carbon dioxide, with low airflow. These emissions are generally combined with the solution concentration process and vented to the atmosphere through a common stack. Control provisions are not often made for the synthesis and concentration processes, except concerning the recovery and recycle of ammonia. Ammonia can be recovered from process vents through scrubbing. The hydrolyzer/desorption system, which treats the process condensate to recover ammonia, is also used to treat the scrubber effluent. [5, 6]

2. Solution Concentration

The crystallizer is a minor source of ammonia, carbon dioxide, and water vapor and the ejector wastewater effluent contains ammonia, carbon dioxide, and urea. The evaporator generates emissions of ammonia, carbon dioxide, and urea particulates which often require control.

Ammonia and urea are recovered from evaporator emissions through condensation, wet scrubbing, and demisting. A survey of urea plants located in the United States revealed the following distribution for the use of these controls: condensation (50%), wet scrubbing (10%), and demisting (5%), no controls (35%).

In newer plants, overhead condensers are used to control evaporator vents, after which the condenser gases are sent to a scrubber before exiting to the environment. The hydrolyzer/desorption system treats the effluent from the condensers and scrubber to recover ammonia, carbon dioxide, and urea. [6]

3. Solids Formation

The decomposition of urea can result in ammonia emissions. Significant amounts of particulate matter are emitted from prilling towers, with the associated fume being hard to eradicate. The treatment of airflows from prill towers is difficult.

At about half of the urea plants located in the United States, wet scrubbers are used to control particulate emissions from prill towers. The scrubbers also reduce ammonia emissions, though they are not installed for this purpose. Wet scrubbers are used to control particulate emissions from various types of

granulators, such as fluid bed, drum, and pan. If a scrubber was not used, about 4 to 20% of the feed would be lost. Therefore, the scrubber is important to the process as well as being a control device. [6]

3. Ammonium Nitrate

a. Process Description

As in the manufacture of urea, the production of ammonium nitrate can consist of up to seven different operations, depending on the desired end product as a solution or a solid: (1) solution formation; (2) solution concentration; (3) solids formation; (4) solids finishing; (5) solids screening; (6) solids coating; and (7) bagging, and/or bulk shipping. For the production of liquid ammonium nitrate, only the solution formation and bulk shipping operations are performed. To make a granular product, all processes may be employed. An aqueous ammonium nitrate solution (83% by weight) is produced, which is sold as a fertilizer directly or concentrated for use in the formation of solid ammonium nitrate. Figure 5 illustrates the manufacturing operations at a typical ammonium nitrate plant. [5]

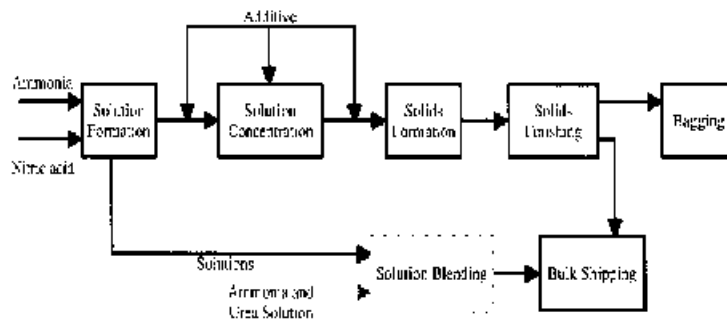


Figure 5: Typical Ammonium Nitrate Manufacturing Operations [5]

The following sections delineate the seven process steps used in the production of ammonium nitrate.

1. Solution Formation (Process Step 1)

Liquid ammonium nitrate (NH_4NO_3) is produced by mixing nitric acid and ammonia in a reactor or neutralizer. The reaction is performed at atmospheric pressure or pressures up to 410 kPa (45 psig) and temperatures ranging from 270 - 365°F. If a liquid product is desired, the ammonium nitrate solution is then blended and shipped in bulk. [5]

2. *Solution Concentration (Process Step 2)*

In order to form a solid product, an evaporator or concentrator is used to dehydrate the ammonium nitrate solution. The resulting material is a melt, containing 95 to 99.8% ammonium nitrate at approximately 300°F.

3. *Solids Formation (Process Step 3)*

The melt is then transformed into solid ammonium nitrate products using the finishing processes described below.

4. *Solids Finishing (Process Steps 4, 5, 6, and 7)*

The finishing processes often used in the past included graining, flaking, granulation, crystallization, and low-density prilling. Although some of these methods are still in use, newer plants often use high-density prilling in which a 99+% concentration is used. Granulation using a 99+% solution has also become popular. Screening is performed to retrieve the desired material size.

The prilled or granulated product is then coated with a conditioning agent to prevent caking, but if additives are injected into the melt before prilling, coating may not be needed. In addition, some climates may not require the use of coatings.

The product is then stored in bulk, sometimes in controlled-humidity containers. Plants in the United States often ship the product in bulk, using covered, hopper-bottom rail cars. [3, 5]

b. *Ammonia Emissions and Controls*

Ammonium nitrate production plants emit ammonia, particulate matter (ammonium nitrate), and nitric acid. [3, 5] The following sections describe the techniques used by ammonium nitrate plants to control ammonia emissions. Only those steps in the manufacturing process that emit ammonia are discussed.

1. *Solution Formation and Concentration*

The neutralizers and evaporators emit ammonia and nitric acid. However, the emissions vary depending on the type of reactant used in the neutralizer. Most plants use ammonia in excess, although nitric acid in excess may also be used. Wet scrubbers are used to control particulate matter. Although no controls are specifically identified for ammonia, wet scrubbers are effective in the control of ammonia. [5]

2. *Solids Formation*

This process emits ammonia and particulate matter. The specific sources are the prill towers and the granulators, and their associated dryers and coolers. For high-density prill production, a fume abatement system made of a bell-shaped cover on the spray head located at the top of the prill tower may be used to control particulate matter. The collected vapors are then sent to the scrubber used by the neutralizers and evaporators. Although no controls are specifically identified for ammonia, wet scrubbers are effective in the control of ammonia. [5]

B. AMMONIUM PHOSPHATES

Most of the ammonium phosphate, which is usually produced as monoammonium phosphate (MAP) or diammonium phosphate (DAP), is used as a component of fertilizer, with DAP being the most common.

1. Process Description

Phosphoric acid is reacted with anhydrous ammonia to generate ammonium phosphate, which is used to manufacture both liquid and solid forms of ammonium phosphate fertilizers. Subsequent to ammoniation, the molten material is subjected to one of two processes, depending upon the desired form of the finished product. To create liquid fertilizers, the molten matter is dissolved in aqua ammonia and for solid fertilizers, the material is solidified using a granulation process that either implements a pug-mill mixer or a rotary drum granulator. Most of the solid ammonium phosphates produced (95%) in the United States are done so using a rotary drum granulation process patented by the Tennessee Valley Authority (TVA).

With this process, an acid surge tank is used to mix the phosphoric acid with 93-98% sulfuric acid, as well as recycle streams and acid from wet scrubbers. A tank-type or pipe reactor is then used to partially neutralize the mixture with liquid or gaseous anhydrous ammonia.

A rotary-drum granulator is comprised of an open-end rotary cylinder, positioned at a slight angle, with retaining rings at each end. The inside of the drum shell houses either a scraper or cutter and sustains a rolling bed of recycled solids.

Slurry from the reactor is spread on or in the bed, while the rest of the ammonia ($\approx 30\%$) is sprayed underneath the bed. Granulation is performed in the rotating drum, where the particles are mixed with slurry and agglomerated. From here the granules are sent to a rotary dryer and subsequently to a cooler for cooling. The granules may be cooled before or after screening. This is typically performed by a double-deck screen to separate out large and small particles from the target particle size. The oversized particles are then ground and combined with the finer material and reentered into the drum granulator. Most of the final product is shipped to market in bulk, although a small amount is bagged. [5]

Figure 6 illustrates the operations performed at a typical ammonium phosphate plant.

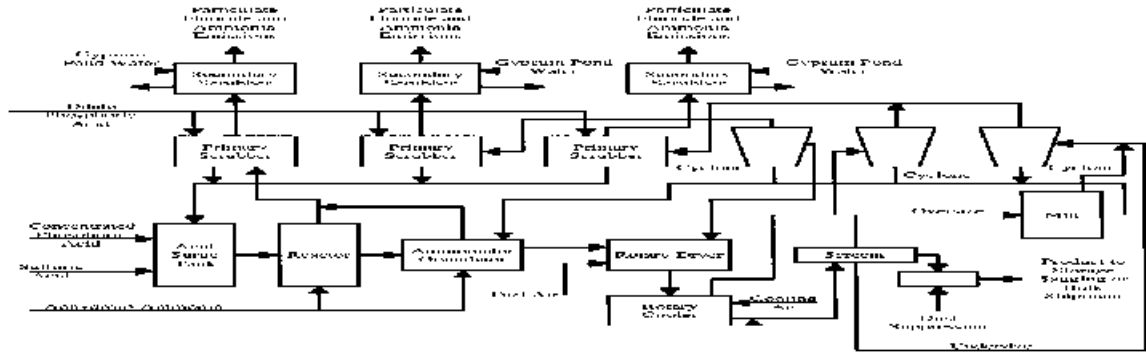


Figure 6: Ammonium Phosphate Process Flow Diagram [5]

2. Ammonia Emissions and Controls

Ammonium phosphate production plants using the ammoniation-granulation method emit ammonia, particulate matter, and fluorides. [3, 5] The following sections describe the techniques used by ammonium phosphate plants to control ammonia emissions. Only those steps in the manufacturing process that emit ammonia are discussed.

a. Reactor and Ammonia Granulator

The gas streams from the reactor and the ammoniator granulator are often combined and treated by primary and secondary scrubbers prior to discharge to the atmosphere. The primary scrubber uses phosphoric acid to recover ammonia and particulate matter, while fluoride emissions are controlled using secondary scrubbers employing gypsum pond water as the scrubbing liquor. [3, 5]

b. Dryer and Cooler

The gas streams from the dryer and cooler are typically combined and sent through cyclones and primary and secondary wet scrubbers in series prior to exhausting to the atmosphere. [3, 5]

c. Product-sizing and Material-transfer

Emissions from the product-sizing and material-transfer process are also controlled using cyclones and primary and secondary wet scrubbers, though levels of ammonia are low for this operation. The gas stream first enters the cyclones to remove particulate matter, and then enters the primary scrubbers. The secondary scrubbers use gypsum pond water to remove fluoride. The matter collected by the cyclone and primary scrubbers is recycled to the process, and the secondary scrubber effluent is recycled to the gypsum pond. [3, 5]

d. Control Specifications

Primary controls used to recover ammonia consist of venturi and cyclonic spray towers, while the secondary controls used to control fluoride include cyclonic spray towers, impingement scrubber, and spray-cross-flow or vertical packed-bed scrubbers. The scrubbing liquor often used in primary scrubbers to control ammonia is phosphoric acid with 20-30% P_2O_5 , while gypsum pond water is used in secondary scrubbers to control fluoride. However, the types of liquor used in the controls varies across the industry.

Existing plants have ammonia-recovery scrubbers installed on the reactor, ammonia granulator, and dryer, with reported control efficiencies of 94-99%. Particulate controls exist on the dryer and the cooler, with reported efficiencies of 75-99.8%. Scrubbers to control fluoride emissions are often used, but not

typical, with reported efficiencies of 74-94%. An United States Environmental Protection Agency (U.S. EPA) survey identified the use of spray-cross-flow packed-bed scrubbers or similar controls for fluoride control on 15-20% of plants contacted. [3, 5]

CHAPTER 3

COKE MANUFACTURE

Metallurgical coke, comprised of elemental carbon and minerals, is made by heating high quality bituminous coal to approximately 1925°F in the absence of oxygen. Furnace coke and foundry coke are the two major types of metallurgical coke produced. Furnace coke is produced for use in steel mill blast furnaces and foundry coke is made for foundry cupolas. The same process equipment may be used to produce both of these types of coke, though the coals and operating conditions for each end product are different. The main contrast is that foundry coke is made from lower volatility coals, is heated for a longer time period, and is larger in size than furnace coke. In the early 1990's, most of the coke produced in the United States was furnace coke.

Coke is produced by one of two methods: by-product manufacture and nonrecovery manufacture. The by-product method is the most common, with only one facility in the United States employing the nonrecovery method. In the by-product process, the volatiles are removed from the coal and processed in the by-product plant. This yields clean coke, tar, sulfur, ammonium sulfate, and light oil. A portion of the coke oven gas, 33-40%, heats the battery, while the remaining gas is used as fuel in other plants. In the nonrecovery method, by-product plants are not required since the battery drives off all the volatiles and combusts them within the oven to supply heat for carbonization. Controls for this process involve removing sulfur dioxide and particulate matter from the gas stream before discharge through the waste stack. [3, 5] As the by-product method is the most common, this document will address this process only.

A. BY-PRODUCT COKE PRODUCTION

1. Process Description

The manufacturing of coke is accomplished by heating high quality bituminous coal to approximately 1925°F in the absence of oxygen.

The coke is produced in a battery which is a group of narrow, slot-type coking ovens made of silica brick. Depending on the production rate desired and the size of each oven, the battery may consist of between 35 to 100 ovens. Coke is pushed into the oven on the pusher side and exits from the oven on the opposite coke side. The coke side of the oven is somewhat larger than the pusher side, thereby allowing the coke to travel easily through the oven.

The walls of the ovens are comprised of a series of heating flues. Half the flues in a wall combust gas, while the other half transport the waste heat combustion products to the waste heat stack.

The process is reversed every 20 to 30 minutes to achieve a more uniform heating of the coke. During this reversal, the waste heat flues become combustion flues and vice-versa.

The battery may be fired with a variety of fuels, such as natural gas, coke oven gas, and blast furnace gas. However, coke oven gas is the most common since the coking process produces this fuel in abundance. A typical battery consists of over 2000 flues, with one to four burners for each flue. Nozzles are located on each burner and must remain clean. The proper heat distribution must be maintained to ensure efficient operation. Several factors influence the heating of the battery: the type, moisture content, and density of the coal, the amount of the coal charged, changes in the production schedule, the openings on the oven coke side are wider than those on the pusher side, and the order of charging and pushing of the ovens. Figure 7 illustrates the typical layout of a coke oven battery. [3, 5]

Figure 7: Typical Layout for a By-Production Coke Oven Battery [5]

a. Coke Oven

The coking process volatilizes approximately one-fourth of the coal charged, for removal as gas. The collection, cleaning, and distribution of this gas is a prime part of emissions control for coke

manufacture. The ovens are connected to a collector main using offtake piping assemblies that span the length of the battery. The gas in the collector main is transferred to the by-product recovery plant. Here the gas is processed into clean gas and by-products such as tar, light oil, naphthalene, ammonia, and sulfur. [5]

b. Coal Handling

In order to keep the quality and coking time of the coke consistent, coal of a consistent blend, moisture content, and density is selected. Quality control at the mine is critical to ensure good operations at the coke facility. [5]

c. Charging

The larry car runs across top of the battery, providing pulverized coal to the ovens through the ports. The ovens are put at a slightly negative pressure using steam or liquor aspiration and the coal is supplied until the oven is full. A bar then levels the charge to aid the filling of the oven. After filling, the bar is returned to the leveler door, the oven ports are sealed, and the steam and liquor aspiration ceases. The off-take piping is set so that the generated gas is sent to the collector main. [5]

d. Coking

Gas combustion in the flues provides heat to the ovens. Formation of the coke begins at the walls of the ovens and then moves towards the center, with the process taking 16-20 hours. In this time volatile matter is removed from the coke and converted to gas, which is sent to the collector main through the off-take piping. [5]

e. Pushing

The oven selected for pushing is then secluded using dampers to prevent the gas from exiting the oven to the environment during the pushing process. The doors on each side of the oven are removed and a ram moves the coke from the pusher side to exit the coke side of the oven and deposit into a quench car. The car is mounted on rails and conveys the coke to the quench tower. [5]

f. Quenching

The coke exiting the ovens is approximately 1922°F and will burn if oxygen contacts the surface. To prevent this, water in the quench tower cools the coke to below its ignition point. This targeted temperature ranges from 120 to 400°F. The coke is dried and then separated according to size. [5]

2. Ammonia Emissions and Controls

Ammonia is emitted from oven leaks during the coking process, charging, pushing, and quenching operations, with the quenching process emitting the most ammonia of all these sources. [3] The following sections describe the techniques used in by-product coke plants to control ammonia emissions. Only those steps in the manufacturing process that emit ammonia are discussed.

a. Coke Oven Doors

Leaks ensue when there are gaps between the coke door and jamb, or the jamb and the oven brickwork. Since the oven is operated at a slight positive pressure during coking, imperfections in the seals will allow the leakage of gas that is volatilized during the process.

U.S. EPA classifies door leaks as coke oven emissions which have been identified as a hazardous air pollutant (HAP) under Section 112 of the Clean Air Act. The leaks are uncleaned coke oven gas and ammonia is one of the constituents in the emitted gas.

In order to control emissions from the oven doors, the gaps must be minimized. This is accomplished by keeping close tolerances on the seal between the door and jamb. The tars in the escaping gas that remain between the door and jamb will condense to seal the opening.

The efforts to minimize these gaps are complicated by the warping of the jambs and door frames over time. To reduce leaks, doors and jambs may be replaced, the sealant may be adjusted to fit a crooked jamb, and sealants like sodium silicate may be used to fill gaps. Using these methods, the immediate result is decreased leakage, but the performance is not long-lived. Use of sodium silicate is effective at first, but it merely masks the problem of incorrect sealing.

The emissions also may be captured using door hoods or coke side sheds and subsequently vented to a control device. Door hoods are not as effective since the amount of emissions leaking from the ovens is small compared to the distance between the oven and the hood. Therefore, the gas may be diverted from the hood. Coke side sheds are effective in capturing almost all coke side door leaks, which are the hardest leaks to control.

Work practices are vital to controlling emissions from coke oven doors. These include jamb and brickwork maintenance, door maintenance, door adjusting, door cleaning, sodium silicate sealing, battery back-pressure optimization, and door removal and installation, spotting, and latching. [5]

b. Coke Oven Lids

The lids of the ovens remain closed, except when charging or pushing is being performed. The emissions from these sources are similar to those from the coke oven doors. Control of leaks from charging port lids can be accomplished through good management practices, which include cleaning and maintenance. [5]

c. Charging

The composition of emissions from the charging process is similar to those from the door and lid leaks and again are labeled as the hazardous air pollutant, coke oven emissions.

Several different methods are available to control emissions during charging. Almost all emissions from larry car charging are controlled through stage charging, in which steam aspiration at the connection of the off-take piping is used to develop a vacuum in the charged oven. Therefore, the material that would be given off is now transported to the collector main and sent to the by-product plant for cleaning. In order to maintain emissions removal at an optimum level, good work practices must be maintained. For example, the drop sleeves on the larry car must match the charging ports on the battery and the steam nozzles must be cleaned and properly sized.

In the past, scrubbers were attached to the cars, but weight limitations prevented the scrubbers from being powerful enough to sufficiently remove and clean the emissions generated. As a result, batteries are now controlled through stage charging, with only a few scrubber-equipped cars remaining as backups when the stage charging cars are removed for maintenance. To avoid the problems of mobile scrubbers, land based scrubbers were implemented with gases being vented to the control unit through a series of ductwork.

However, the stage charging has proven to be the simplest and most effective method for control of emissions from the charging process. [5]

d. Pushing

This process is the most difficult to control of all the coke manufacturing processes. As the hot coal exits the oven and enters the quenching car, it breaks up and exposes a larger surface area to the air. As a result, volatile material that has not yet been extracted during coking has a tendency to ignite. Both the ignition and falling of material generates the release of coke particles. The amount of emissions from this process varies, depending on the completeness of the coking process. These emissions are generally particulates, with the gases not considered to be air toxics. Therefore, pushing emissions are not included in the hazardous air pollutant labeled coke oven emissions.

To control emissions from the pushing step in the process, capture devices are used to collect and divert emissions to a control device, such as a venturi scrubber. Capture devices include sheds, traveling hoods, and indexing hoods. Sheds made of steel are placed over the battery to collect rising gas. The sheds are evacuated constantly, and depending on the size of the battery, the exit airflow may range from 154,000 to 600,000 acfm. Sheds are effective in capturing pushing emissions, as well as emissions generated from door leaks. Traveling hoods are attached to a duct spanning the length of the battery and are evacuated while in motion. The hood is designed to control airflows ranging from 6000 to 9000 acfm per ton of coke pushed and can control emissions from coke pushing as well as the quench car travel. Indexing hoods are

similar to travel hoods, except they cannot travel with the coke to the quenching tower because they are connected to a pollution control duct at fixed locations and can only be drained at these points. [5]

e. Quenching

Coke quenching is performed with water comprised of process waste and previous quenching streams. The contaminants in the solution evaporate and decompose through contact with the hot coke. The pollutants, which depend on the makeup of the quenching water, are discharged to the atmosphere with the water vapor. The most common control device is a baffle, which can reduce particulate emissions by at least 50%. [5]

B. CITIZENS GAS AND COKE UTILITY

This section presents information concerning control methods applied to an actual coke manufacture facility for the control of ammonia emissions.

1. Project History

Citizens Gas and Coke Utility is a public trust operating as the Department of Utilities for Indianapolis, Indiana. The manufacturing division, Indianapolis Coke, operates a by-product plant that produces foundry and blast furnace coke. Excess coke oven gas (COG) is combined with natural gas and sold. The facility operates three batteries that process 900,000 tons of coal per year.

In 1987, the ammonia treatment equipment had to be updated to conform with a new Categorical Pretreatment Standard applicable to wastewater containing ammonia. The division selected the ammonia destruction process as the replacement control. This process uses excess flushing liquor to scrub coke-oven gases. The generated ammonia water is preheated, steam stripped, and blown down as wastewater. The ammonia vapor, coke-oven gas, and air are mixed at the top of the destructor, which is kept at a temperature of 2100°F. Ammonia is dissociated, cooled, and recycled for use as battery underfire gas. Figure 8 illustrates the design of the ammonia destruction process. [9]

Figure 8: Ammonia Destruction Process [9]

2. Ammonia Destruction Process

The sections below describe the operation of the ammonia destruction system, providing the specifications of the system, as well as the problems encountered during start-up and the subsequent adjustments made to improve the functioning of the system. [9]

a. Coke-oven Gas Scrubbing

The temperature of the inlet gas must be lowered to achieve effective ammonia absorption. This is performed in the first section of the combined secondary cooler/ammonia scrubber tower, where the gas enters at 115 to 120°F and is subsequently cooled below 86°F [30°C] using 500 gpm of recycled liquor. The extracted heat is removed by an air surface wet cooler. Solids accumulation is restricted by the addition of an exchange liquor, while tar (3 to 10%) is added to collect naphthalene.

The ammonia portion of the tower has four beds of pall ring packing. The coke oven gas ascends to the top of the tower and is first scrubbed by 45 gpm of flushing liquor. This liquor has already been subjected to secondary decantation in the settling tank and cooling in the wet surface air cooler. The ammonia enters the remaining three sections of the tower where 90 gpm of stripped water from the free stripper is introduced to absorb the ammonia. The system has demonstrated ammonia outlet concentrations <3 gr/100 ft³. [9]

b. Stripping

The system is composed of two identical stripping columns operated in series. The columns are 4 ft-6 in x 42-ft, each with 17 valve trays. Each stripper is split into two sections, so each column is able to strip both free and fixed ammonia. The upper section contains five trays and functions as the free ammonia stripper, while the lower section contains 12 trays and operates as the fixed ammonia stripper.

The overhead vapors enter a common header and are then conveyed to a single partial condenser. The steam injected into the free and fixed columns is controlled separately. This limits the amount of free ammonia at the base of the free column to 200 ppm and the amount of wastewater ammonia to less than 100 ppm at the base of the fixed column.

Since these columns are interchangeable, one may be taken off-line for maintenance without compromising the quality of the wastewater. It has been demonstrated that all process control parameters can be preserved with only one column in operation. [9]

c. Dissociation

Temperature control in the partial condenser is used to modify the volume and composition of the stripping column vapors. By maintaining the temperature at 199°F, the steam carryover is diminished while the vapor purity is optimized. As the stream travels toward the destructor, the process computer monitors the vapor flow. Coke-oven gas and steam are added at a ratio of approximately 2.5:1 before the stream enters the destructor mixing chamber. This ratio is modified to maintain a top temperature of 2100°F in the destructor, based on the current operating conditions. A process air blower provides air to a concentric ring of the mixing chamber at a ratio about 4.2 times the coke-oven gas volume.

The destructor is a carbon steel vessel, lined with brick, having a diameter of 7 feet and a height of 29 feet. In the presence of a nickel catalyst, the ammonia and hydrocarbons react to separate from the stream and form a tail gas. The average composition by volume of the tail gas consists of the following constituents: 29% water vapor, 1.1% hydrogen sulfide, 3% carbon dioxide, 14% hydrogen, 0.2% oxygen, 51% nitrogen, 1.7% carbon monoxide, and 250 ppm ammonia.

The gas exiting the destructor is cooled to 450°F in an attached shell and tube heat exchanger, with boiler feedwater being added to the shell. The heat transfer generates 50-psig steam which is returned to the stripping columns, thereby reducing the need for fresh steam. The quencher lowers the temperature of the tail gas to 200°F by contact with wastewater exiting the plant. The gas is then sent back to the coke-oven gas piping to be used as an underfire gas. [9]

d. Ammonia Condensation

If the destructor is not operating, the ammonia gas exiting the stripping columns is automatically sent to the ammonia condenser. Operation of the recirculation pump commences and the cooling water control valve on the attendant plate and frame heat exchanger is opened. Strong ammonia liquor is formed from the condensation of ammonia and acid gases, and subsequently stored. Once the destructor is put back on line, this liquor is reprocessed. [9]

e. System Start-up

When the ammonia destruction system was first operated, the combination of breaking in new equipment and incorporating the system into the existing process caused instability in the stripping area. The scrubbing part of the system was shut down in order to stabilize the stripper-destructor.

Evaluation of the tail gas revealed ammonia concentrations that were higher than expected. Since adjustments to the air to gas ratio provided only limited improvement, the destructor was examined.

Significant corrosion had occurred on the 410 stainless steel mixing chamber tip so a 446 stainless steel burner was installed as a replacement. Additional catalyst was also added. These changes effected a great increase in the dissociation efficiency, resulting in an ammonia concentration of 250 ppmv in the tail gas. The destructor gas controls were modified to prevent combustion within the titanium piping that connects the partial condenser and destructor. This modification included an automatic shutdown provision for low vapor flow and changes in the pressure control valve operation.

It was also observed that the flushing liquor contained high amounts of chloride, which caused material changes in the heat exchangers used in the stripped water recycle system. A plate and flame heat exchanger made of 316 stainless steel was replaced with Hastelloy C. Another 316 stainless steel shell and tube heat exchanger was installed to lower the temperature to below 150°F. This was done to diminish the corrosion on the wet surface air cooler. Process air blower sizing was increased to provide control over the full range of operating load conditions.

The original valve trays were replaced with new trays having 50% smaller valves. This increase in the number of valves resulted in a 38% increase in the valve surface area per tray. The quality of wastewater from the new trays is similar to that from the original installation, yet at a lower pressure drop across the column.

After being taken off-line for investigation, the ammonia destruction system was put back on-line the next month after modifications were implemented. A performance test has illustrated that the system operates successfully at the average conditions given in Table 1 below. [9]

Table 1: Stable Operating Parameters for the Ammonia Destruction System [9]

Ammonia scrubbing

Coke-oven gas flow 26 million scfd
Gas temperature
 Inlet 117 °F
 Outlet 83 °F
Ammonia concentration
 Inlet 260 gr/scf (dry)
 Outlet 2.0 gr/scf (dry)
 Combined gas 3.0 gr/scf (dry)
 Stripped water (free) 200 mg/litre
Flushing liquor
 Total 6.6 g/litre
 Free 2.4 g/litre

Stripping

Flow 150 gpm
Ammonia concentration stripper feed
 Total 8.6 g/litre
 Free 5.5 g/litre
Wastewater 50 mg/litre
Steam
 Total stripping 14,500 lb/hr
 Live makeup 7500 lb/hr

Dissociation

Tail gas ammonia concentration 250 ppmv

CHAPTER 4

FOSSIL FUEL COMBUSTION

A. FOSSIL FUEL COMBUSTION

The Clean Air Act Amendments of 1990 have brought about more stringent standards for nitrogen oxide (NO_x) emissions. The concern over nitrogen oxides is generated from the fact that nitrogen oxides have been recognized as contributors to smog and acid rain. When fossil fuels, such as coal, fuel oil, and natural gas, are used to fuel combustion sources, high temperatures are generated which create thermal nitrogen oxides. Regulatory agencies are requiring lower nitrogen oxide emissions from these fossil fuel combustion sources. [10, 11]

With this new set of regulations, new technology development has been sparked in order to attain compliance. Nitrogen oxide emissions from fossil fuel power plants may be controlled using combustion modifications or post-combustion control methods. Post-combustion control methods include selective catalytic reduction (SCR) and selective non-catalytic reduction (SNCR) which use ammonia or urea to control nitrogen oxide emissions. With these post-combustion control technologies, the problem of ammonia in the effluent has become a concern. This condition is labeled "ammonia slip", which is caused by an addition of ammonia in excess of the amount required in the stoichiometric equation, or the formation of ammonia as a by-product in the reduction of nitrogen oxides charged by ammonia or urea. [11, 12, 13]

This report discusses SCR and SNCR post-combustion controls since they have the potential to emit ammonia emissions. The use of ammonia or urea, or any other nitrogenous compound to decrease nitrogen oxide emissions is relatively new, so the problem of ammonia present in combustion ash is just beginning to draw attention. Therefore, limited information is available for preventing such an occurrence. [12]

B. SELECTIVE CATALYTIC REDUCTION

Presently, the most common post-combustion nitrogen oxide control is selective catalytic reduction (SCR). The equipment necessary for this process is a reactor, catalyst, and an ammonia storage and injection system. In the reactor vessel, the nitrogen oxides react with ammonia in the presence of a catalyst to yield nitrogen gas and water. The ammonia injection point is usually upstream of the air heater, where the temperature window (550-750 °F) ideal for reduction reactions can be achieved. The catalyst is usually a mixture of titanium dioxide, vanadium pentoxide, and tungsten trioxide. Unreacted ammonia that passes through the system can form ammonium sulfate which may cause blockage in equipment downstream of the reactor, such as the air heater. Based on installations in Japan and Europe, the acceptable slip value is 5 ppmv. Demonstrated nitrogen oxide reductions range from 60-90%. The process is costly, with high initial and operating costs. [5, 13]

C. SELECTIVE NON-CATALYTIC REDUCTION

The SNCR method reacts nitrogen oxides with ammonia or urea to form nitrogen gas and water. The reaction occurs at temperatures ranging from 1,650 to 2,000°F in the presence of oxygen. Since the reaction takes place at a higher temperature, with a high activation energy, the need for a catalyst is eliminated. [13] The effectiveness of nitrogen oxide reduction using this method varies among the literature, though reductions in the range of 30-70% are expected. SNCR is still in the developmental stages.

This method is appealing for use at gas and oil fired power plants. The technology equipment costs are moderate since a catalyst is not needed. However, there are disadvantages associated with this process. The process functions over a restricted temperature range of 1600-1900°F. This makes a full-scale application difficult since the temperature window usually happens in the convective section, where there is limited access space, high gas velocities, and short residence times. As with the SCR process, there is a potential to emit ammonia as an unwanted byproduct. [11]

D. NEW POST-COMBUSTION TECHNOLOGIES

Several technologies have been developed, using SCR or SNCR, for the reduction of nitrogen oxides from post-combustion fuel gases. The systems vary in the type of reducing agent that is employed. This section presents a few of these patented control systems.

1. Fuel Tech NO_xOUT

In 1976, the Electric Power Research Institute (EPRI) began research concerning the use of urea to control nitrogen oxide emissions from combustion sources. An urea-based reduction process was then patented by the institute in which post-combustion flue gas was controlled using chemicals to reduce nitrogen oxides.

Fuel Tech began work to improve the use of this technology through modifications, including widening the temperature range appropriate for the reaction. This was accomplished by adding chemicals to enhance the performance of the urea, changing process conditions, and altering process control methods and injector design. The company patented this process, known as NO_xOUT.

The NO_xOUT process is designed to control nitrogen oxides from stationary sources using a variety of carbonaceous fuels. The process uses urea and/or chemical enhancers to lower nitrogen oxide emissions at temperatures ranging from 1,000 to 2,100°F. It can be used as a retrofit application and is adaptable to other controls. Commercial testing on boilers demonstrated nitrogen oxide control efficiencies up to 85%.

The NO_xOUT process involves the injection of a solution, made of urea and/or chemical enhancers, into the post-combustion flue gas. The components of the solution react with the nitrogen oxides present in the gas and form nitrogen gas, water, and carbon dioxide, as illustrated by the

following chemical equation: $\text{CO}(\text{NH}_2)_2 + 2\text{NO} + 1/2 \text{O}_2 \rightarrow 2\text{N}_2 + \text{CO}_2 + \text{H}_2\text{O}$

This equation shows that one mole of urea is needed to react with two moles of NO. However, actual tests show that greater quantities of urea are required to obtain the desired nitrogen oxide removal. The excess amount degrades to nitrogen, carbon dioxide, and small amounts of ammonia. The Normalized Stoichiometric Ratio (NSR) illustrates the amount of urea actually used as compared to the stoichiometric amount required.

$$\text{NSR} = \frac{\text{Actual Reagent Molar Ratio}}{\text{Stoichiometric Reagent Molar Ratio}}$$

In order for a urea reducing agent to effectively control nitrogen oxide emissions, the chemical must have high activity at the treatment temperature and be well mixed with the nitrogen oxide. Having met these two conditions, the use of urea in a circulating fluidized bed achieves over 85% reduction. The only dangerous byproduct generated is ammonia, which is controlled to less than 5 ppm by limiting the amount of urea used. Ammonia breakthrough occurs when the NSR is over 1.9. Testing showed that in addition to the first two conditions identified above, the appropriate amount of chemicals must be used in order to limit ammonia slip.

Enhancer chemicals are applied to widen the applicable temperature range of the process over which the solution is effective. If only urea is used, the temperature window ranges from 1,700 to 1,900°F. However, with the addition of enhancers, the effective temperature range expands to 1,500 to 2,100°F.

In order for the reaction to occur efficiently, the reduction chemicals must be thoroughly mixed with the nitrogen oxides. The use of a multiple level injection system, as illustrated in Figure 10, enhances this mixing and improves the nitrogen oxides reduction level, thereby decreasing ammonia emissions. This method allows for limiting the NSR.

This process has been demonstrated successfully on combustion sources using fuels including hard coal, brown coal, oil, gas, wood waste, and municipal solid waste. The types of boilers tested include front-fired, corner-fired, and circulating fluidized beds. Demonstrated reductions range from 50 to 60% in two European coal-fired boilers with a 5 ppm ammonia emission limit. With a 20 ppm ammonia limit, the reduction level was raised to 65 to 75%. Ammonia slip levels of 5 to 20 ppm are acceptable, depending on the locality. [13]

2. Fuel Tech, Incorporated Invention for the Reduction of Nitrogen Oxides in Flue Gases

William Epperly and James Sullivan of Fuel Tech, Incorporated developed a process designed to reduce nitrogen oxides generated from the combustion of carbonaceous fuels. The system injects a solution, comprised of ammonia and an enhancer, into the effluent. Acceptable enhancers for use with ammonia include hexamethylenetetramine, furfural, or low carbon alcohol among others. It has been demonstrated that the use of enhancers generates a nitrogen oxide reduction greater than if ammonia were used alone.

Ammonia can be used in its pure form, with the enhancer added to it, but solutions such as the aqueous ammonia solutions with enhancer are preferred because they are more economical and applicable to most conditions.

The ammonia is added at an ammonia to nitrogen oxide molar ratio ranging from 1:5 to 5:1, with a ratio of 1:2 to 2:1 being ideal. The range of the ratio of enhancer to ammonia is 1:5 to 4:1, with 1:3 to 3:1 being ideal. The ammonia-enhancer mixture is added to provide a molar ratio of nitrogen, in the ammonia and enhancer, to the amount of nitrogen oxides at a level of 1:5 to 6:1, with 1:2 to 2.5:1 being the best.

In order to ensure an efficient reaction, the ammonia-enhancer mixture is injected in the correct ammonia-enhancer proportion and at the appropriate effluent temperature, which ranges from 1300 to 1700°F.

Testing of this method has demonstrated lower ammonia slip levels than for other methods. The exact reason for this is not known, but probably occurs from a series of reactions between the ammonia, enhancer, and nitrogen oxide. This process better utilizes ammonia than other processes. [10]

3. Union Oil Company of California Invention for the Removal of Nitrogen Oxides From Flue Gases

The method of selective catalytic reduction using ammonia to convert nitrogen oxides to nitrogen gas and water is effective, but the danger of chemical spills occurring during the transfer of anhydrous ammonia has generated concern due to its volatile and corrosive nature. The other reducer commonly used, urea, also presents similar problems.

Donald Young of Union Oil Company of California has developed a technology that removes nitrogen oxides from gas streams, using liquid solutions that are safe and easy to handle. The reducer is a mixture of ammonia, urea, and water. This practically eliminates the problems associated with the use of ammonia or urea alone, while playing on the advantages of each compound. Mixtures comprised of ammonia, urea, and water are supplied as low volatility solutions that are stable during transportation of the liquid.

Both the urea and ammonia react with the nitrogen oxides. At high temperatures the urea is converted to ammonia. In addition, the urea acts catalytically to promote the reaction between nitrogen oxides and ammonia. Ultimately, this process is more effective for reduction and safer than using ammonia or urea alone.

Such solutions are effective in wider temperature and residence time ranges. The reaction temperature range is from room temperature to 1832°F. The reason for this is not clear. One possibility is that the urea acts as a catalyst between the ammonia and nitrogen oxides. At higher temperatures, urea can hydrolyze to yield ammonia and carbon dioxide. The production of ammonia from urea is increased

when ammonia is already present, which may be why the mixture is more effective than its components alone.

The use of the mixture can generate high rates of conversion for the nitrogen oxides to nitrogen and water, without problems associated with transporting anhydrous ammonia and solid urea. [14]

E. STUDIES EVALUATING POST-COMBUSTION CONTROL TECHNOLOGIES

Several studies have been conducted to evaluate the use of SCR and SNCR to control nitrogen oxide emissions from fossil fuel combustion sources. The results from a few of these studies are presented in the sections below.

1. Pacific Gas and Electric Company

The Pacific Gas and Electric Company and the Gas Research Institute participated in a study designed to evaluate the application of SNCR to utility boilers. The main objectives were to evaluate the nitrogen oxide removal efficiency and the emission of undesirable products, such as unreacted ammonia, carbon monoxide, and N_2O , using the SNCR process. The selected boiler, Morro Bay Power Plant Unit 3, was a Babcock and Wilcox opposed-fired system rated at 345 MW.

Several companies supply the SNCR process, including Noell, Incorporated, Exxon, and Nalco Fuel Tech. These products use pressure and pneumatic-assist atomizers, or jets of high-velocity carrier fluid, such as air, to combine the ammonia or urea with the nitrogen oxides present in the exhaust streams. The first two suppliers use the air-jet method, while Nalco Fuel Tech uses the atomizer principle.

The Noell high-energy SNCR process was chosen for use in this study. Since boiler cavities have a relatively short height, it is necessary to rapidly mix the reducing agent with the combustion products in the convective section of the cavity. The Noell system uses a high-velocity air carrier stream that supplies the energy for rapid mixing. Air-jet mixing blends the aqueous ammonia or urea with the nitrogen oxides in the flue gas. Both ammonia and urea were tested as nitrogen oxide reducing agents in the SNCR system. The following results were generated from this study.

- Ammonia slip levels were greater than originally estimated. This discrepancy was credited to the relatively short residence times (50 to 150 milliseconds (ms)) obtainable in the convective section cavities. Pilot studies conducted in a laboratory showed that residence times of 250 ms are required for a complete reaction.
- Ammonia slip levels were lower when aqueous ammonia was used as the reducing agent as opposed to those when urea was used, although actual levels were comparable.

- Ammonia slip levels increased as the nitrogen/nitrogen oxide ratio increased, and decreased as the nitrogen/nitrogen oxide ratio decreased. This testing demonstrated that nitrogen oxide emission reductions and ammonia slip are directly proportional to one another.
- Greater nitrogen oxide reductions are achieved when using ammonia as a reducing agent than for urea.

The main constraint for each reducing agent is the level of ammonia emissions allowed. Based on this value and the amount of nitrogen oxides exiting the source, the amount of ammonia injected into the process is determined. Using this method, the nitrogen oxide/ammonia ratio is monitored. [11] Table 2 illustrates the percent reduction of nitrogen oxides achieved using ammonia and urea, based on various ammonia slip limits.

Table 2: Nitrogen Oxide Reduction Using Ammonia and Urea

Allowable Ammonia (ppm)	Percent Nitrogen Oxide Reduction over the Boiler Load Range (%)	
	Aqueous ammonia	Urea
10	15-21	13-18
30	19-31	19-27
50	24-36	21-32

Industries are often required to limit ammonia emissions when using SCR or SNCR. Based on this limit and the amount of nitrogen oxides being generated, the amount of aqueous ammonia to be injected is decided. In this manner, the excess amount of aqueous ammonia is limited to minimize the amount of ammonia slip.

2. Air and Energy Engineering Research Laboratory

To evaluate the combined control of sulfur dioxides and nitrogen oxides using sorbent-reducing agents, the United States Environmental Protection Agency (U.S. EPA) began a Cooperative Research and Development Agreement with Nalco Fuel Tech to test their commercial reducing agents NO_xOUT A and NO_xOUT A+, coupled with sorbent injection. Testing was performed at the Air and Energy Engineering Research Laboratory (AEERL) 14,650 W pilot facility.

The main objective of this study was to measure the effectiveness of sulfur dioxide and nitrogen oxide removal using simultaneous injection of a calcium-based slurry and the Nalco urea-based reducing agent, while limiting ammonia slip.

The major environmental concern associated with the use of SNCR is the emission of ammonia, resulting from the incomplete reaction of the reducing agent. Ammonia slip can cause the formation of ammonium bisulfate at approximately 572 °F, which can deposit on air preheater surfaces and cause a

reduction in heat transfer and an increase in pressure drop. Ammonia slip can also cause the formation of ammonium sulfate (NH_4SO_4) at approximately 302°F and ammonium chloride (NH_4Cl) at approximately 212°F. The emission of ammonia is sensitive to the injection temperature. Attempts to expand the temperature window has been met with some success. The following results were generated from this study.

- With the use of calcium-based sorbent injection with SNCR technologies in a slurry injection process, sulfur dioxide and nitrogen oxide reduction was consistently demonstrated at 60-80%.
- The use of a modified urea-based solution greatly reduced levels of ammonia below levels previously reported for urea injection.
- As the injection temperature of the reducing agent increased, the amount of ammonia slip decreased.
- As the molar ratio of nitrogen/nitrogen oxide increased, the amount of ammonia slip increased. [15]

It is nearly impossible to eliminate ammonia slip entirely, though as shown by these study results, ammonia slip may be minimized by monitoring the injection temperature and limiting the amount of urea injected only to quantities required, thereby reducing the amount of excess reducing agent added. [16]

CHAPTER 5

LIVESTOCK MANAGEMENT

Livestock and poultry manure is a major source of ammonia emissions. Inorganic nitrogen in the waste is emitted through several mechanisms including ammonia volatilization, nitrification, denitrification, leaching, and runoff, with ammonia volatilization generating the highest total loss of this nitrogen. The two main sources of ammonia emissions within this category are livestock feedlots and cropland spreading.

A. LIVESTOCK FEEDLOTS

1. Process Description and Ammonia Sources

The livestock feedlots located in the United States hold cattle ranging in weight from 450 to 1200 pounds for each animal, with the average being 850 pounds. The fattening period ranges from 130 to 150 days, with manure being collected at an average of 1 dry ton per period, or 2 dry tons per year per animal.

Livestock facilities generate odors that can be offensive to neighboring residents, though these odors are not toxic. Citizen complaints have prompted livestock farmers to evaluate controls for the formation of such odorous compounds. Odors are generated from feed materials, such as food-processing wastes and fermented feeds, fresh manure, and decaying manure. The big concern has been over volatile compounds emitted from the storage and treatment of manure. Fresh manure emits large amounts of ammonia, but the most offensive odors are usually associated with decomposing manure. The odors depend on the biological reactions taking place and the type of storage or treatment unit implemented.

Closed buildings often have a high odor production potential, resulting from a high livestock density, a great amount of manure stored, and limited airflow. Open feedlots located in warm, humid areas or those with poor drainage systems or drying conditions are more likely to have odor problems than those in cooler, dry climates. Anaerobic decomposition is favored in large open feedlots that become wet, especially in warm weather.

The anaerobic decomposition of livestock manure generates ammonia, which sometimes results in odor problems. Studies have shown that the amount of ammonia in manure corresponds to the odor intensity, with the concentration of ammonia increasing greatly with an increase in temperature. Several states have regulations limiting the odor at the property line based on available measurement techniques. [3, 5]

2. Controls

In order to reduce odor emissions generated from livestock manure, the manure may be treated, the odorous gases may be captured and treated, or the odor may be dispersed.

a. Treatment of Manure

Anaerobic lagoons are often used to effectively control odors. However, they must be well designed with an adequate capacity to achieve low odor production. Frequent collection of the manure through flushing, scraping, or drainage is effective in absorbing odors and eliminating the anaerobic conditions prevalent in manure storage within closed buildings. [5]

b. Capture and Treatment of Odor

Industrial and food processing plants often use wet scrubbers to control odor emissions by spraying the exhaust air stream with water or oxidizing chemicals. Some studies have applied them to livestock buildings. The control efficiencies achieved are provided in the Table 3 below.

Table 3: Control Efficiencies for Wet Scrubbers Applied to Livestock Facilities [5]

Equipment	Percent Reduction	Problems Encountered
Wet scrubber on the exhaust emitted from a swine building	odor - 88%	Sludge created from collected dust caused difficulties in recirculating the scrubbing water
Wet scrubber	Not given	Problems with spray nozzles clogging when recycled water and biological treatment were used
A cross-flow packed-bed wet scrubber on a big containment building	ammonia - 8-38% odor - 82%	None identified
A packed-bed dry scrubber containing zeolite (clinoptilolite) used on a poultry house	ammonia - 45% at first, but then decreased to 15% in 18 days	None identified
Soil filter system on a swine confinement building	ammonia - 52-78% organic constituents - 86%	None identified
0.25-acre sand filter field for air scrubbing on a poultry manure composting operation	ammonia - 95-99% odor - 30-82%	None identified

Soil filter systems are effective for scrubbing odors from a process or building exhaust stream. When using a soil filter, a moderately fine soil, sufficient moisture, and pH control of 7 to 8.5 are required. On average, the land area requirement ranges from 2,500 to 4,600 ft² / 1000 cfm, based on the airflow rate.

c. Odor Dispersion

As the gases travel downwind of the facility, the odor intensity diminishes. It has been demonstrated that odors and ammonia travel a longer distance when manure is spread over crops than when it is stored on site. [5]

B. CROPLAND SPREADING

1. Process Description and Ammonia Emission Sources

Combined excrement from cattle and poultry feedlots are spread on cropland. The amount of ammonia emitted depends upon the soil type, excrement qualities, atmospheric conditions, and the application method implemented.

As the pH values increase in the soil and manure, the tendency for the ammonia to volatilize increases, thereby raising the ammonia emissions. The reaction between ammonia and the ammonium ion (NH₄⁺) becomes imbalanced as the pH level rises, resulting in greater ammonia emissions.

2. Controls

A soil with a high cation exchange capacity will suppress the amount of ammonia volatilized since the soil's capacity to adsorb and hold the ammonium ions increases as the cation exchange capacity increases.

Ammonia emissions are greater when spreading is done on a wet soil, than on a dry soil. Higher temperature and wind velocities also increase the amount of ammonia volatilized. Therefore to minimize the amount of ammonia emitted from this process, it is important to consider these factors. [3]

CHAPTER 6

REFRIGERATION

A. USES AND CONTROLS

Ammonia is the oldest used refrigerant, yet less than 2% of the ammonia manufactured is used as a refrigerant. [18] However, interest in ammonia as a refrigerant has arisen since existing refrigerants, such as chlorofluorocarbons (CFC) have come under attack due to their ozone depleting potentials and effect on global warming.

Ammonia is mostly used in large industrial plants, with packing house freezers often using ammonia as a refrigerant. A refrigeration unit with a large capacity is possible with small machines. Water-cooled units are commonly used to cool down the refrigerant. High pressures are used in the lines (125 to 200 psi) so heavy steel fittings are required due to the high pressures.

Since ammonia has a very noticeable odor, even a small leak can be detected by smell. Leaks in refrigeration units can also be detected using a number of scientific methods. The electronic detector is widely used in the manufacture and assembly of refrigeration equipment to detect refrigerant leaks. Ammonia leaks can also be detected by using a burning sulfur candle or litmus paper.

For plants using ammonia as a refrigerant, precautions should be taken to prevent ammonia leaks from process equipment. Since ammonia is a highly toxic chemical that can be explosive if mixed with air in the right proportions, it is necessary for facilities handling ammonia to apply safeguards. If leaks or spills do occur, precautionary methods will prevent anyone from being harmed. [17]

Refrigeration plants are a source of emissions resulting from leaking refrigerant. In order to control emissions, a newly proposed technology can detect and adsorb emissions from plants. The basic concept is to capture emissions from refrigerant leaks and convey the emissions to a common filter and/or detection device. Although this system was designed for CFCs, it can be applied to leaks of ammonia refrigerant. With this technology, suspected leak points are covered with plastic or fabric covers and sleeves. Each cover is connected to a manifold using a hose. The manifold is connected to a vacuum-pump or blower, depending on the size of the facility. Small installations use the vacuum-pump while larger installations use the blower. This makes the hoses and sleeves at subatmospheric pressure. Once collected by the capture devices, the emissions are conveyed to a filter which adsorbs the pollutants. The refrigerant may be removed from the filter and recycled, thereby allowing the ammonia to be used again. [19]

B. FLASH FREEZING PROCESS USED IN FISHERIES

Fish are frozen as a preservation technique to delay spoilage of the catch. The purpose is to deliver frozen fish that, when thawed, will be practically as fresh as newly caught fish. Quick freezing is performed at sea on the fishing boat, and is done by rapidly lowering the temperature of the fish and keeping it at frozen storage temperature.

Ammonia can be used as the refrigerant for deep freezing. [20] Conventional freezers may be used at sea, requiring little modification, however, the freezer and refrigeration system must conform to requirements. The use of ammonia in this application is not common since many countries do not allow ammonia to be used as a refrigerant since it is toxic and potentially explosive. [21]

CHAPTER 7

CONTROL TECHNIQUES APPLIED TO AMMONIA EMISSIONS

A review of various industries emitting ammonia has identified several techniques used to control ammonia emissions. These control methods include both add-on control equipment and pollution prevention techniques. Although the industries discussed are large sources, the methods of control may be downsized to accommodate smaller sources.

A. ADD-ON CONTROL EQUIPMENT

1. Wet Scrubbers

a. Description

The most common add-on control device used to control ammonia emissions is the wet scrubber which employs the method of absorption. Through absorption, gaseous material is collected through direct contact with a scrubbing liquid, which is usually water. The success of the scrubber is dependent on the solubility of a gas in the scrubbing liquor. Since ammonia is highly soluble in water, the wet scrubber is effective in controlling ammonia emissions. Control efficiencies up to 99% have been demonstrated in actual applications.

Ammonia gases are most effectively treated by packed column or cross-flow scrubbers, with a cross-flow scrubber merely being a packed column scrubber in which the gas flow is horizontal. Packed column scrubbers are continuous operating vertical columns filled with packing material having a large surface area. The countercurrent packed column is the most common unit employed for gaseous removal. In this unit, the gas stream ascends through the packing material in the column, while the scrubbing liquid moves downward, resulting in the highest efficiency possible. This high efficiency results from the decreasing solute concentration in the gas stream as it rises, thereby providing fresher solvent for contact. The cross-flow scrubber is a horizontal unit in which the gas stream moves horizontally through the packing material and the scrubbing liquor moves downward through the unit. Such units have a low water consumption and a high airflow capacity at a low pressure drop.

The advantages associated with using a wet scrubber include relatively small space requirements, ability to collect gases, ability to handle high-temperature and high-humidity gas streams, and a low capital cost if wastewater treatment is not required. Facilities may or may not be required to treat their scrubber effluent, depending on the locality. Some areas allow the discharge of such effluents directly to the wastewater treatment plant without requiring prior treatment of the water by the facility. Other areas on the otherhand require the facility to treat its own process water.

The disadvantages associated with the use of wet scrubbers include a possible water disposal problem, possibility of high pressure drop and horsepower requirements, and corrosion of the unit. Since the wet scrubber has a high corrosion potential, the unit is usually made of stainless steel or another corrosion-resistant material to prevent this from happening. Control efficiencies up to 99% have been demonstrated in actual applications. [5, 22]

b. Costs

Several vendors were contacted to obtain cost estimates for typical wet scrubber systems. The cost of a wet scrubber depends on the airflow (cfm) that will be treated by the system. As airflows increase, so does the cost of the control device. The cost values provided below are merely estimates since actual costs depend on the process being controlled and its corresponding operating conditions. The wet scrubber system must be designed for a specific facility and therefore will vary in actual application.

Operating costs for the system depend on the power required to run the pump and blower, chemicals added, and the water supply. Since these values will vary from plant to plant, the operating costs are determined by the specific application.

1. *Misonix Incorporated*

Misonix indicated that the capital cost for a wet scrubber unit ranging from 1-10,000 to 15,000 cfm will vary from \$8,000 - 50,000. A wet scrubber system may range from a basic system to a complete system. A basic system was described as including equipment such as a scrubber pump, blower, and resurge tank. The buyer is required to assemble and install this system. A complete system includes a turn key, blower, chemical addition, and control panels. This system contains all the necessary equipment and requires only to be hooked-up to the process equipment to be controlled. For an airflow of 1,000 cfm, the basic system was estimated at \$5,000, while the complete system costs around \$10,000. For an airflow of 50,000 cfm, a basic system was quoted at \$35,000, while a complete system costs around \$50,000.

The scrubber can be designed to achieve a desired efficiency, which depends on several factors including the rate of transfer, the liquid to gas ratio, the kinetic relationship versus time, and the type of packing material. Scrubbers can be designed to attain control efficiencies of up to 99%. Below a control efficiency of 90% the design is straightforward, but above 99% it is very difficult since the control efficiency fractions above 99% are the hardest to achieve.

With the use of wet scrubbers there is a concern over the treatment and disposal of effluents. If the locality of the plant using the scrubber has a good wastewater treatment system available, the industry can usually send the effluent directly to the treatment plant without adding chemicals. However, some industries add sulfuric acid to the effluent to react with the ammonia, thereby forming air ammonia salt. The effluent is then discharged to a drain or wastewater treatment plant.

The lifespan of the equipment is basically infinite since the unit has no moving parts. However, maintenance is required. Every one to two years the nozzles must be replaced since the holes get bigger over time, resulting in a less desirable spray flow. Pumps are usually replaced every five to six years, while blowers last for about ten years. The packing material may have to be replaced at some point, but this is unlikely.

Misonix sells wet scrubbers to both large and small companies, with approximately a 50 / 50 distribution. Unlike other companies, Misonix manufactures an ammonia scrubber that can handle a flow as low as 1 cfm. This is accomplished by downsizing the packing material. [23]

2. *Monsanto Enviro-Chem Systems Incorporated*

Monsanto provided cost figures for a wet scrubber package, considered to be an upgrade from a packed scrubber, that controls particulate matter as well as ammonia. The scrubber package includes pumps, interlocking ductwork, and control instrumentation, with the option of adding fans to the system. Since the scrubber package is a complete system, only a hook-up line is required to connect the scrubber to the process equipment requiring control. [24]

Table 4 provides the capital cost figures given by Monsanto for a typical scrubber package.

Table 4: Capital Cost Figures for a Monsanto Wet Scrubber Package [24]

Unit Airflow (acfm)	Scrubber Package Cost (\$)	Cost of Additional Fan (\$)
1,000 - 2,000	70,000	-
7,000	100,000	25,000 - 30,000
16,000	150,000	35,000 - 40,000
22,000	175,000	40,000

The cost of a packed tower scrubber designed only to control ammonia would be about 10 - 15% less than the prices quoted for the scrubber package.

The effluent is usually sent to a wastewater treatment plant since the stream is very treatable. Ammonium chloride may be added, though this depends on the scrubbing liquor used. [24]

2. **Condensation**

Condensation converts a gas to a liquid by removing heat or increasing the pressure. The former method is often applied since it is more economical and the system usually uses water or air to cool and condense the gas stream. Removal efficiencies of condensate strippers are not high for most gas pollutants since the unit does not lower temperatures below 100 °F.

Industry review indicated that condensate strippers are used to remove ammonia in the fertilizer industry. The process condensate formed is recycled back to the process. With this method, valuable feedstock is retrieved, and therefore the device is used as a control, as well as being important to the process. [5]

B. POLLUTION PREVENTION TECHNIQUES

1. Recycle

For operations that use ammonia as a feedstock, emissions control is intrinsic in the recovery and recycle process. The recycle method benefits the process in that process condensate is collected and reused so less ammonia feedstock is required. In addition, the ammonia emissions are prevented by returning them to the process. With this technique, excess material is reused instead of being wasted and the emissions remain within the system.

For smaller applications such as refrigeration systems, emissions of ammonia refrigerant may be collected and recycled back to the system for reuse. This decreases the amount of refrigerant that is lost through leakage and therefore reduces the amount of new refrigerant that must be purchased.

2. Limiting Ammonia Input

Ammonia is emitted from post-combustion control systems such as SCR and SNCR which use ammonia or urea to reduce nitrogen oxide emissions from the fossil fuel combustion sources. Although it is nearly impossible to prevent ammonia slip from occurring, the amount of slip can be minimized. This is accomplished by limiting the amount of reducing agent added to prevent ammonia in excess of the amount required to react with the nitrogen oxides. The amount of ammonia or urea added is determined based on the allowed level of ammonia slip and the amount of nitrogen oxides exiting the combustion source. The ammonia to nitrogen oxide ratio must be minimized to keep ammonia slip levels low. Studies have shown that enhancers decrease the amount of ammonia slip since the reaction with nitrogen oxides is more efficient. In addition, the use of ammonia has exhibited lower slip levels than those generated by the use of urea as the reducing agent. Since combustion sources are present at facilities within many different industries, the use of SCR or SNCR is an applicable control method for nitrogen oxides that may be adapted to the concerned stationary combustion source.

3. Capture Systems

In order to collect ammonia emissions, capture devices such as hoods may be used. These hoods are divided into three categories: enclosure, capture hood, or receiving hood. Enclosures, either partial or complete, encircle the emission source without interrupting the process and prevent emission releases from entering the atmosphere. Capture hoods, or exterior hoods, are placed on the outside of the process and use a powerful airstream to draw emissions into the hood after they are released to the atmosphere. Receiving hoods also capture emissions once they exit the process and are emitted to the atmosphere. These devices

use the momentum of certain exhaust streams to facilitate the collection of emissions. Once these streams are collected using capture systems, the streams are often vented to a control device for treatment. [5]

4. Maintenance Practices

Good maintenance practices may be applied by any source handling ammonia, even small sources. Ammonia leaks occurring from process equipment can be easily controlled by applying capture devices to collect the fugitive emissions. Since leaks often occur around equipment connections, the source of the leaks can be identified and targeted. In addition, there are several leak detection devices available that may be used to identify unknown leak points. After collection, the vapors may be conveyed to a control device such as a filter or wet scrubber for treatment. Ammonia adsorbed by the filter may be retrieved and reintroduced into the process which is economically beneficial. In addition, the equipment must be properly maintained to ensure that worn parts are replaced.

CHAPTER 8

CONCLUSIONS

The concern over the hazards of ammonia, including its potentially explosive nature and its toxicity, has resulted in the need to examine available methods for the control of ammonia emissions.

A review of various industries has identified the main sources of ammonia emissions to be fertilizer production, coke manufacture using the by-product recovery method, fossil fuel combustion through the control of nitrogen oxides, livestock management, and refrigeration. This report focuses on these industries since they are the only ones that have been identified as implementing controls to reduce the emissions of ammonia.

The various control technologies implemented by these industries include wet scrubbers, condensate strippers, recovery and recycle techniques, reducing agent limitation, capture systems, and good maintenance practices.

The wet scrubber and the condensate stripper are the two add-on control devices commonly used to control ammonia emissions. The wet scrubber is the most common of these two devices and has demonstrated control efficiencies up to 99%. Facilities in the fertilizer industry, livestock management industry, and coke by-product manufacture industry use the wet scrubber to control ammonia emissions.

Although larger sources often install such controls, this does not preclude smaller sources from implementing wet scrubbers. One vendor indicated the availability of a wet scrubber that is small enough to treat an airflow as low as 1 cfm.

Condensate strippers remove the ammonia from the gas stream by converting the gas to a liquid. The resulting process condensate is then recycled back to the process. Not only are these strippers used as control devices, they are intrinsic in the process operation. The fertilizer industry has demonstrated use of these controls to remove the ammonia and recycle it back to the system for use in the manufacture operations.

Pollution prevention techniques include recycle, limiting the amount of ammonia or urea used to control nitrogen oxides from combustion sources, capture devices, and implementing good maintenance practices.

The recycling of ammonia back to the process is not only a means of emissions control, but it is also beneficial to the process operation since the amount of raw input materials is reduced. Demonstrated use of the recycle process is exhibited in the fertilizer industry and refrigeration units, where ammonia is recovered from the process and returned to the system.

Post-combustion control technologies, such as selective catalytic reduction (SCR) and selective non-catalytic reduction (SNCR), are used to control nitrogen oxide emissions from fossil fuel combustion sources. Since either ammonia or urea is used as the reducing agent, there is the potential for ammonia to be in the effluent stream. This condition, known as ammonia slip, may be limited by properly operating the reduction technologies. This is accomplished by adding the appropriate amount of reducing agent, as determined by the amount of nitrogen oxides present and the level of ammonia slip allowed.

Capture systems, as used in coke by-product facilities and refrigeration systems, collect ammonia emissions using hoods. These hoods either enclose the process to prevent emissions from entering the atmosphere, or use airflows to collect the emissions from the surrounding environment once they exit the process. Often the collected emissions are conveyed to a control device for treatment.

In order to minimize leaks, good maintenance practices may be implemented by any source to ensure that equipment is maintained at a quality operational level. Where leaks are unavoidable, capture devices may be implemented to collect gases. Industries that demonstrate the use of good maintenance practices include coke manufacture and refrigeration systems.

Based on a review of available information, the controls methods identified in this report have demonstrated effective reduction of ammonia emissions.

REFERENCES

1. Refrigeration : Home and Commercial (Anderson and Rex Miller)
2. G. Eggen, "Ammonia Heat Pumps for Water Heating in Fish Farming Plants," *18th International Congress of Refrigeration*, (Canada, August 10-17, 1991)
3. David Misenheimer, Thomas Warn, and Sharon Zelmanowitz, *Ammonia Emission Factors for the NAPAP Emission Inventory*. Alliance Technologies Corporation, January 1987. EPA-600/7-87/001.
4. Marshall Sittig, *Fertilizer Industry - Processes, Pollution Control and Energy Conservation*. Noyes Data Corporation, (New Jersey, 1979).
5. Anthony J. Buonicore and Wayne T. Davis, *Air Pollution Engineering Manual*. Air and Waste Management Association, (New York, 1992).
6. Hassan M. Goma and David T. Cindric, "Environmental Control Measures for Ammonia and Urea Plants," 35th Annual Ammonia Symposium, 1991.
7. T. A. Czuppon and Leon J. Buividas, "Which Feedstock for Ammonia," *Hydrocarbon Processing* September 1979: 197-200.
8. Philip Hanceman and Peter Sparn, *An Evaluation of Control Needs for the Nitrogen Fertilizer Industry*, GCA Corporation, (Bedford, Massachusetts, August 1979).
9. Jeff H. Currey, "Ammonia Destruction at Citizens Gas and Coke Utility," *Iron Steel Engineering* 1991: 43-45.
10. William Epperly and James Sullivan, *Process for the Reduction of Nitrogen Oxides in Flue Gases*, (United States Patent, August 25, 1988).
11. Gas Research Institute, *Selective Noncatalytic Reduction (SNCR) Field Evaluation in Utility Natural Gas-Fired Boilers*, (June 1991 - March 1992).
12. Luther Wolfenden and Bryan Fisher, *Process for Reducing the Amount Ammonia Affixed to Fly Ashes from Combustion Processes*, (United States Patent, April 28, 1994).
13. W. R. Epperly and R. G. Broderick, "Control of Nitrogen Oxides Emissions from Stationary Sources," *American Power Conference Proceedings* 1988: 911-15.

14. Donald Young, *Process for Nitrogen Oxide Removal from Flue Gases*, (United States Patent, November 16, 1993)
15. Air and Energy Engineering Research Laboratory, *Evaluation of Simultaneous SO₂/NO_x Control Technology*. (September 1993). EPA-600/R-93-188.
16. Jeremy Peter Hoblyn, Linda Lin, William Sun, and John Hofmann, *Process for the Catalytic Reduction of Nitrogen Oxides*, (United States Patent, November 11, 1993).
17. W.F. Stoecker and J.W. Jones. *Refrigeration and Air Conditioning Technology*. McGraw-Hill, Incorporated. (New York, 1982)
18. S. M. Miner, "An Appraisal of Ammonia as an Alternative Refrigerant in Light of the CFC and GWP Situation," *18th International Congress of Refrigeration*, (Canada, August 10-17, 1991).
19. J. Paul, "A Simple Technology to Reduce and Avoid Emissions from Refrigeration Plants in Operation," *18th International Congress of Refrigeration*, (Canada, August 10-17, 1991).
20. G. Alefeld, W. Kern, J. Scharfe, Pl Riesch, and F. Ziegler, "Advanced Absorption Cycles for Environmental Protection," *18th International Congress of Refrigeration*, (Canada, August 10-17, 1991).
21. Food and Agriculture Organization of the United Nations, *Freezing in Fisheries*. (Rome, May 1977)
22. C. David Cooper and F.C. Alley, *Air Pollution Control, A Design Approach*, (United States, 1986).
23. Misonix Incorporated, (1995 Cost Data). Farmingdale, N.Y.
24. Monsanto Enviro-Chem Systems Incorporated, (1995 Cost Data). St. Louis, Missouri.