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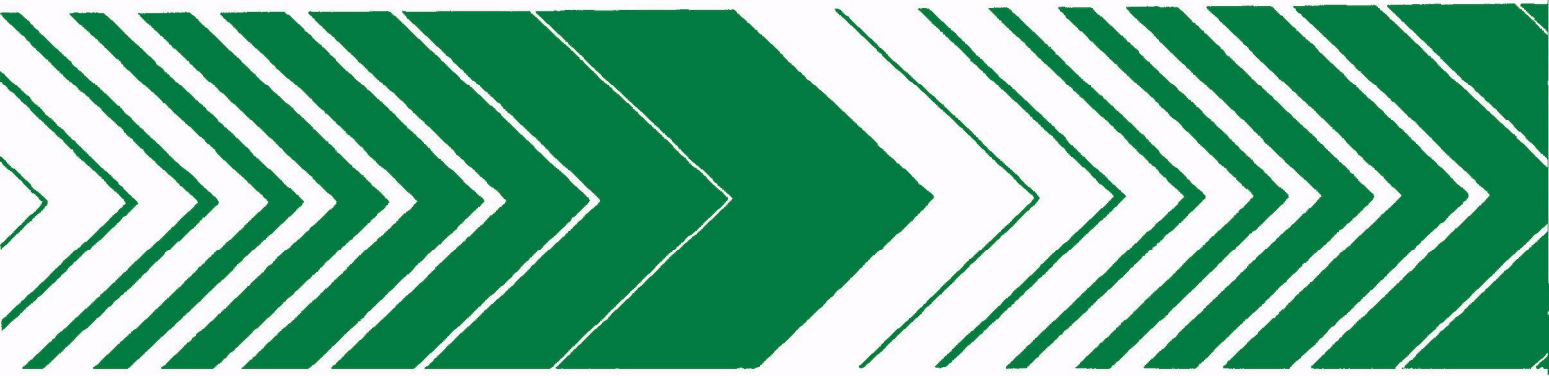
An Evaluation of Control Needs for the Nitrogen Fertilizer Industry

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This report has been assigned to the ENVIRONMENTAL PROTECTION TECHNOLOGY series. This series describes research performed to develop and demonstrate instrumentation, equipment, and methodology to repair or prevent environmental degradation from point and non-point sources of pollution. This work provides the new or improved technology required for the control and treatment of pollution sources to meet environmental quality standards.

EPA REVIEW NOTICE

An Evaluation of Control Needs
for the Nitrogen Fertilizer Industry

by

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ABSTRACT

This report evaluates the pollution control needs of the nitrogen fertilizer industry. It includes a description of ammonia, ammonium nitrate and urea manufacturing processes and an evaluation of existing pollution control equipment. In addition, this report evaluates the pollution reduction potential of alternative pollution control techniques, processes and feedstocks. Both air emission and water effluent control techniques are examined for each industry and its unit operations.

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FIGURES

FIGURES (continued)

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1.0 INTRODUCTION

The Industrial Environmental Research Laboratory (IERL) of the Environmental Protection Agency (EPA) has the responsibility of insuring that pollution control technology is available for stationary sources. If control technology is unavailable, inadequate, and/or uneconomical, IERL may help develop the needed control technique. Approaches to control include: process and equipment modifications, feedstock alternatives, add-on control devices, and complete process substitution.

This evaluation of the control needs of the nitrogen fertilizer industry is based largely upon the results of previous EPA-sponsored source assessment (SA) studies of the industry, and its objectives are to examine the various processes that create the pollutants and to evaluate control technologies that may reduce emissions to acceptable levels. Production processes are described, emission and effluent sources are identified, present and potential control technology are reviewed, and recommendations are made, as appropriate, for further work to define emission rates and/or evaluate process and control alternatives.

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2.0 CONCLUSIONS AND RECOMMENDATIONS

2.1 CONCLUSIONS

The two major emission problems associated with the nitrogen fertilizer industry are (1) oxides of nitrogen resulting from the addition of purge gas and overhead to primary reformer firing in ammonia synthesis and (2) particulates from prilling towers in urea and ammonium nitrate production. Apart from these two problems other emission sources within the industry are amendable to available control techniques. Tables 1, 2, and 3 summarize present and potential emission and effluent control techniques for ammonia, ammonium nitrate, and urea production, respectively. The following are more detailed conclusions:

1. Because the future of the United States ammonia industry is highly dependent upon energy costs, it is important that, insofar as practicable, the energy penalties associated with the installation of emission controls be minimized. Hence, long-term pollution control solutions must be considered along with those providing immediate emission reductions.

2. Natural gas feedstock for the production of ammonia is desulfurized by either an activated carbon bed or a zinc oxide bed. Steam regeneration of the former can result in air emissions of HC, CO, and SO_2. Controls have not been required on this unit by regulatory agencies; however, a few producers have installed thermal incinerators despite the added cost. The trend in desulfurization is an increased utilization of zinc oxide beds. The primary reason for this trend is that zinc oxide beds are not regenerated which results in energy savings.

3. In the primary reformer, natural gas reacts with steam to form carbon monoxide and hydrogen under high pressure and temperature. The heat for the reaction is supplied by firing the primary reformer with natural gas or fuel oil yielding typical combustion products (HC, CO, CO_2, SO_x, NO_x, and particulates). Many ammonia producers are now adding purge gas from the ammonia synthesis loop and overhead from the condensate stripper to the primary stack reformer, but while reducing emissions from these sources,

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TABLE 1. PRESENT AND POTENTIAL TECHNIQUES TO ABATE AMMONIA PLANT EMISSIONS

Source	Emissions	Present controls	Controls/modifications trends	Potential alternative controls/processes	Testing/R&D needs
Desulfurization					
• Activated carbon bed (95% of producers)	HC, CO, CO_2	None	(1) Thermal incineration (2) Zinc oxide bed (5% of ammonia producers – no air emissions)		• Testing carbon bed emissions • Testing thermal incineration of carbon bed emissions
Primary reformer					
• Natural gas/ fuel oil	NO_x, SO_x, CO, HC, particulates	None	(1) Combustion modifications	(1) NO_x reduction by ammonia injection	• Testing and evaluation of reduction processes
• Natural gas or fuel oil and purge gas	Combustion products plus high NO_x levels	None	(1) Cryogenic recovery of purge gas		• Testing primary reformer stack
• Natural gas or fuel oil and purge gas and condensate stripper overhead	Combustion products plus high NO_x levels and ammonia and methanol	None	(1) Ljungstron wheel (air preheater) decreasing overhead decomposition		• Testing primary reformer stack • Locate a higher temperature injection point for more efficient decomposition
• Vaporized fuel oil (VFO)	NO_x, SO_x, CO, HC, particulates	None	(1) Fuel conversion process		• Testing primary reformer stack
Carbon dioxide removal	NH_3, CO, CO_2, HC, MEA	None	(1) Hot potassium carbonate system		• Stack test data needed
Condensate stripper	(Air, ammonia methanol, carbon dioxide) (Water, ammonia, methanol)	• Overhead injection primary reformer stack • Overhead incineration • Condensate recycled as boiler feed water	(1) Overhead cryogenic recovery of ammonia (2) Modified reflux and production recovery 100% recycle (3) Natural gas saturation		• Examine the potential of cryogenic recovery of ammonia from the overhead
Alternative feedstocks for ammonia production					
• Coal	Combustion products	None	(1) Lurgi (2) Koppers-Totzek (3) Winker		• Extensive evaluation of pollution problems of each alternative feedstock process
• Heavy hydrocarbons	Combustion products	None			
• Naphtha	Combustion products	None			

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TABLE 2. PRESENT AND POTENTIAL TECHNIQUES TO ABATE AMMONIUM NITRATE PLANT EMISSIONS

Source	Emissions	Present controls	Controls/modification trends	Potential alternative controls/processes	R&D needs
Neutralization	NH_3, (HNO_3) NH_4NO_3 particulates	pH control wet scrubbers mist eliminators condensation	1) Close process control (MCC)	None	*
Solution Concentration	NH_3, (HNO_3), NH_4NO_3 particulates	Scrubbers mist eliminators	None	None	*
Solid Formation					
Prilling	NH_4NO_3 particulates, H_2O, NH_3	Wet scrubbers, mesh pads	1) CFCA/Monsanto cone collection 2) Esso spray head redesign	Formation of low density product by process other than prilling	Further modification of prill tower design and testing*
Drum granulation	NH_4NO_3 particulates, NH_3	Scrubbers	1) Foster-Wheeler evaporative scrubbers		*
Graining	NH_4NO_3 particulates, NH_3				*
Stengel reactor/Sandvik belt	NH_4NO_3 particulates, NH_3				*
Product Finishing					
Drying	NH_3	Wet scrubbers	None	None	*
Cooling		Wet scrubbers			*
Additives	Coating material				*
Handling and shipping	NH_4NO_3 fines				Improved handling techniques to avoid dust*

*Generally emissions from all process steps appear to be inadequately defined under varying operating conditions.

TABLE 3. PRESENT AND POTENTIAL TECHNIQUES TO ABATE UREA PLANT EMISSIONS

Source	Emissions	Present controls	Controls/modification trends	Potential alternative controls/processes	R&D needs
Solution Formation					
Ammonium carbamate synthesis	NH_3,CO_2, inerts	Scrubbers Recycling	None	None	÷
Urea formation	NH_3,CO_2, urea		None	None	÷
Solution Concentration					
Crystallization	NH_3,CO_2, urea	Condensation, wet scrubbers, demisters	None	None	÷
Evaporation	NH_3,CO_2, urea	Recycling	None	None	÷
Solid Formation*	Formaldehyde, particulates	Wet scrubbers, modification of production rates	Pan granulation, Foster-Wheeler evaporative scrubbers, centrifugal scrubbers	Vistron control system	Evaluation of pan granulation for production of low density product
Product Finishing*					

*These processes and these problems are very similar to those for ammonium nitrate (see Table 2).

†Generally, emissions from all process steps appear to be inadequately quantized under varying operating conditions; in particular levels of any escaping formaldehyde additive need further quantization.

a substantial increase in NO_x emissions from the primary reformer stack results. A promising applicable add-on control system for NO_x abatement is the ammonia injection technique. Several Japanese processes appear to be applicable to the primary reformer operation. A viable alternative to firing the reformer with purge gas for NO_x reduction is a cryogenic recovery system.

4. Many ammonium nitrate producers expressed difficulty in controlling neutralizer pH. High pH results in excess ammonia losses.

5. Prill towers for the production of solid NH_4NO_3 are a source of particulate emissions. For the most part, pollution control equipment is available to meet state emission requirements, and emissions from ammonium nitrate production can be lowered as the application of control technology increases.

6. Solid product urea is produced using equipment and procedures similar to those used in the ammonium nitrate industry. The addition of pollution control equipment to the industry has been very slow compared to the ammonium nitrate industry.

7. Emissions from the urea solution concentration process evaporator may be controlled to recover ammonia and/or urea to meet state emissions regulations. Approximately 40 percent of the urea evaporators are controlled by condensation, 10 percent by wet scrubbing and 5 percent by demisters. The remainder are operating without controls.

8. Prill towers are the major urea particulate emission source. Opacity limits are presently violated because a major fraction of particulate emissions from prill towers are extremely small particles (fume).

2.2 RECOMMENDATIONS

In order to further our understanding of the environmental impact of the nitrogen fertilizer industry, the following studies are recommended to EPA:

1. Additional research is needed to determine the pollution problems associated with each alternative feedstock, such as coal, naptha, etc. to natural gas for ammonia synthesis.

2. In view of its essential nature, high energy-intensive character, and vulnerability to foreign competition, a careful examination should be made, in light of probably increasing energy costs, of how much regulation our domestic nitrogen fertilizer industry can tolerate yet remain viable, including the economic impact of regulation, combined with energy costs, on the industry.

3. Additional testing is needed to determine the true severity of emissions from the steam regeneration of activated carbon ammonia

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production natural gas feedstock desulfurization beds. A more definitive evaluation is needed of zinc oxide beds versus activated carbon beds plus incineration in terms of costs, energy consumption and environmental impact (including solid waste disposal as well as air pollution).

4. In-depth research and development in the form of testing and pilot plants are still needed in order to determine NO_x reduction efficiencies, the proper ammonia injection point, catalyst life, and operation stability of the ammonia production primary reformer as applied to the process and cost of the available techniques. Several processes developed by the Japanese applicable to primary reformer operation should be examined as well as cryogenic recovery studies. Additional research and testing programs are needed to determine the efficiency of overhead decomposition in the primary stack and to evaluate injection at higher temperature locations. Other systems to abate condensate stripper overhead which should be evaluated are reflux incineration, modified reflux and product recovery, and natural gas saturation.

5. Because of insufficient data, the evaluation of emerging process modifications and pollution control equipment for the formation of ammonium nitrate by neutralization has been limited. Such data are necessary for formulating research and development needs for pollution control in the industry. Emissions from the ammonium nitrate industry are now being measured for the purpose of developing New Source Performance Standards (NSPS). This NSPS program will effectively fill many of the existing gaps.

6. An in-depth evaluation of pH controls and monitoring systems for ammonium nitrate production by neutralization is needed to determine what Best Available Control Technology (BACT) equipment is applicable to neutralizer pH control. Mississippi Chemical Corporation (MCC) has developed a two-stage neutralizer in which emissions are reduced by process design and close pH monitoring. Some ammonium nitrate producers use either total or partial condensation systems. Other methods used are mist eliminators and wet scrubbers. These approaches should be subjected to comparative evaluation.

7. A research and development program is needed to develop a means of producing low density ammonium nitrate solids in a granulator. This would provide an alternative to prill towers. The elimination of prill towers as process equipment is desirable because of their associated particulate pollution problem. Until such an alternative process can be developed, conventional control equipment will have to be used on existing prill towers. Approximately 50 percent of ammonium nitrate prill towers operate without emission control equipment, 2 to 5 percent use the Cooperative Farm Chemical Association (CFCA) cone/Monsanto high energy (HE) system, 15 percent use wet scrubbers and the remainder use mesh pads or similar devices. A program should be conducted to

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evaluate the collection efficiency of the CFCA cone as a function of airflow and cost. The shrouded spray head developed by Esso Chemical Canada also looks promising and the Foster-Wheeler evaporator scrubbing system for reducing particulates from prilling and granulation should be thoroughly examined and evaluated for BACT regarding air and water pollution.

8. Because of insufficient process and emissions data for urea production, the evaluation of emerging process modifications and pollution control equipment has been limited. Effort is needed to obtain such information; however, as in the case of ammonium nitrate production, work now being conducted by EPA to establish NSPS should fill many existing data gaps.

9. Controlled and uncontrolled urea concentrators should be tested to determine emission concentrations and control efficiencies.

10. The Foster-Wheeler system should be evaluated for urea as well as NH_4NO_3. C & I Girdler has developed a system to abate wastewater effluents as well as particulate emissions. Some problems have been experienced with the system; for example, difficulty has been experienced in removing the smaller particulates. However, additional research and development may elevate this system to BACT.

11. Urea production emission data are not sufficient to evaluate pollution control research and development needs of the urea industry. These data are essential to develop recommendations leading to research and development programs for improving pollution control for the nitrogen fertilizer industry.

3.0 THE NITROGEN FERTILIZER INDUSTRY

Modern agricultural technology, sometimes called "The Green Revolution,"
is based upon three practices:

1. the massive application of artificial fertilizers,

2. the massive application of synthetic pesticides, and

3. the use of fewer but higher yield crop genetic strains

and each of these three practices has great potential of adverse environmental
impact:

1. pollution from manufacture and field run-off of fertilizers,

2. pollution from manufacture and field run-off of pesticides, and

3. increased likelihood of catastrophic crop yield reduction by

    plant diesease and pest vectors

The three essential nutrient elements supplied by artificial fertilizers are
potassium, phosphorus, and nitrogen. The United States/Canada region is second
only to Europe in the intensive per capita use of these fertilizers with the
undeveloped countries lagging far behind. Artificial fertilizer production
is highly energy intensive and as energy costs rise, the situation of the de-
veloping countries will worsen.[1] As for the United States, as early as 1974
it was forewarned that unless we can find supplies of cheap gas we will go
from an exporter to a progressively larger importer of nitrogen products.[2]

The basic nitrogenous fertilizer chemicals are ammonia (NH_3), urea
($CO(NH_2)_2$), and ammonium nitrate (NH_4NO_3). Urea and ammonium nitrate are made

from ammonia. There are many other nitrogen fertilizers produced, however these are formed by combinations and/or additions to these three compounds.

In 1977, 3.6 million metric tons of anhydrous ammonia were produced in the United States.[3] Based upon historical consumption trends, anhydrous ammonia production may reach 4.5 million metric tons by 1988 (Table 4). However, imports may slow or reverse this trend. Approximately 85 percent of the ammonia produced is used as fertilizer and in the production of urea, ammonium nitrate, and ammonium phosphates. Other applications are the production of nonfertilizer products.

TABLE 4. ANNUAL U.S. PRODUCTION OF AMMONIA,
AMMONIUM NITRATE, AND UREA

	Annual production in million metric tons	
	1977	1988
Ammonia (NH_3)	3.6	4.5
Ammonium nitrate (NH_4NO_3)	6.8	8.5
Urea ($CO(NH_2)_2$)	4.0	5.0

The average capacity ammonia plant being built today is at least 900 metric ton/day. Ammonia plant production costs range from \$27 to \$36 per metric ton of ammonia produced.[4] Technological advances in the ammonia industry have been geared toward optimizing the energy requirements.

In 1977, preliminary figures indicate that the total U.S. production of ammonium nitrate was 6.76 million metric tons (100 percent ammonium nitrate).[3] Of this quantity, approximately 77 percent was intended for fertilizer and the remaining 23 percent for production of other products such as explosives and nitrous oxide. Approximately 50 percent of the ammonium nitrate produced for fertilizer use was in the solid form while the other 27 percent was sold as liquid fertilizer.

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Preliminary figures indicate that the total U.S. production of urea was 4.03 million metric tons in 1977.[3] Approximately 80 percent of the urea production was used in fertilizers; urea-formaldehyde resins and livestock feed are the other major uses. Urea fertilizer is produced in solid and liquid form. Forty-two percent of the urea produced was consumed in direct application as solid fertilizer, mostly in the form of granules. Livestock feed is generally produced as prills.

The production of fertilizer very often involves a complex of more or less integrated plants in which more than one fertilizer product is manufactured. To optimize production costs, many fertilizer companies may have an arrangement similar to that shown in Figure 1.[5] By plant integration and exchange of products or byproducts, costs normally incurred by external purchases, transportation, and energy become a savings for the company, thereby reducing overall production costs. Moreover, this arrangement appears advantageous relative to potential pollution problems. Advantages with respect to air and water pollution arise from recycling and reuse. The general use of a common outfall by integrated plants, where all process waters discharge into a single channel, is also advantageous from a control standpoint.

AMMONIA PRODUCT PLANT

AMMONIUM NITRATE PLANT

NATURAL GAS → FEEDSTOCK DESULFURIZATION

PURGE GAS
FUEL OIL → PRIMARY REFORMER

SECONDARY REFORMER

HIGH and LOW TEMPERATURE SHIFT

● PRIMARY REFORMER STACK
or
● CO_2 REGENERATION SYSTEM

PROCESS CONDENSATE

STEAM STRIPPER

STEAM

CONDENSATE USED BOILER FEED WATER

CO_2 ABSORBER

CO_2 EMISSION

CO_2 SOLUTION REGENERATION

METHANATION

PURGE GAS

AMMONIA SYNTHESIS

NH_3

HNO_3
NH_3 → NEUTRALIZER → EVAPORATOR CONCENTRATOR → SOLID FORMATION ● PRILLS ● GRANULATOR → DRYING COOLING SCREENING

PRODUCT PREPARATION

AN SOLUTION — AN SOLUTION

NH_3 → LIQUID BULK BLENDING

UREA

SOLID BULK BLENDING

CO_2
NH_3 → SOLUTION PRODUCTION → SOLUTION CONCENTRATOR ● VACUUM EVAPORATOR ● CRYSTALLIZATION ● REMELT → SOLID FORMATION ● PRILLS ● GRANULATOR → PRODUCT PREPARATION

UREA PLANT

SHIPMENT

Figure 1. Potential integration of a nitrogen fertilizer plant.

4.0 AMMONIA

4.1 PROCESS DESCRIPTION

Ninety-eight percent of the ammonia produced in the U.S. is by catalytic steam reforming of natural gas. The ammonia production process basically involves the production of hydrogen, synthesis gas purification, and ammonia synthesis.

Ammonia production by catalytic steam reforming involves seven processes:

1. Feedstock desulfurization,

2. Primary reformation,

3. Secondary reformation,

4. High and low temperature carbon monoxide shifts,

5. CO_2 absorption,

6. Methanation, and

7. Ammonia synthesis,

several of which are designed to remove impurities such as sulfur, carbon monoxide and carbon dioxide. Figure 2 shows a typical ammonia plant flow diagram with pollutants associated with each process.[6]

4.1.1 Feedstock Desulfurization

The reformer catalyst is poisoned by sulfur, therefore, the 229 to 915 $\mu g/m^3$ sulfur content, mostly hydrogen sulfide, of pipeline grade natural gas must be reduced to less than 280 $\mu g/m^3$.[6] For this purpose, approximately 90 percent of ammonia producers use activated carbon beds with a metallic additive (CuO) while the remainder use zinc oxide beds.[7]

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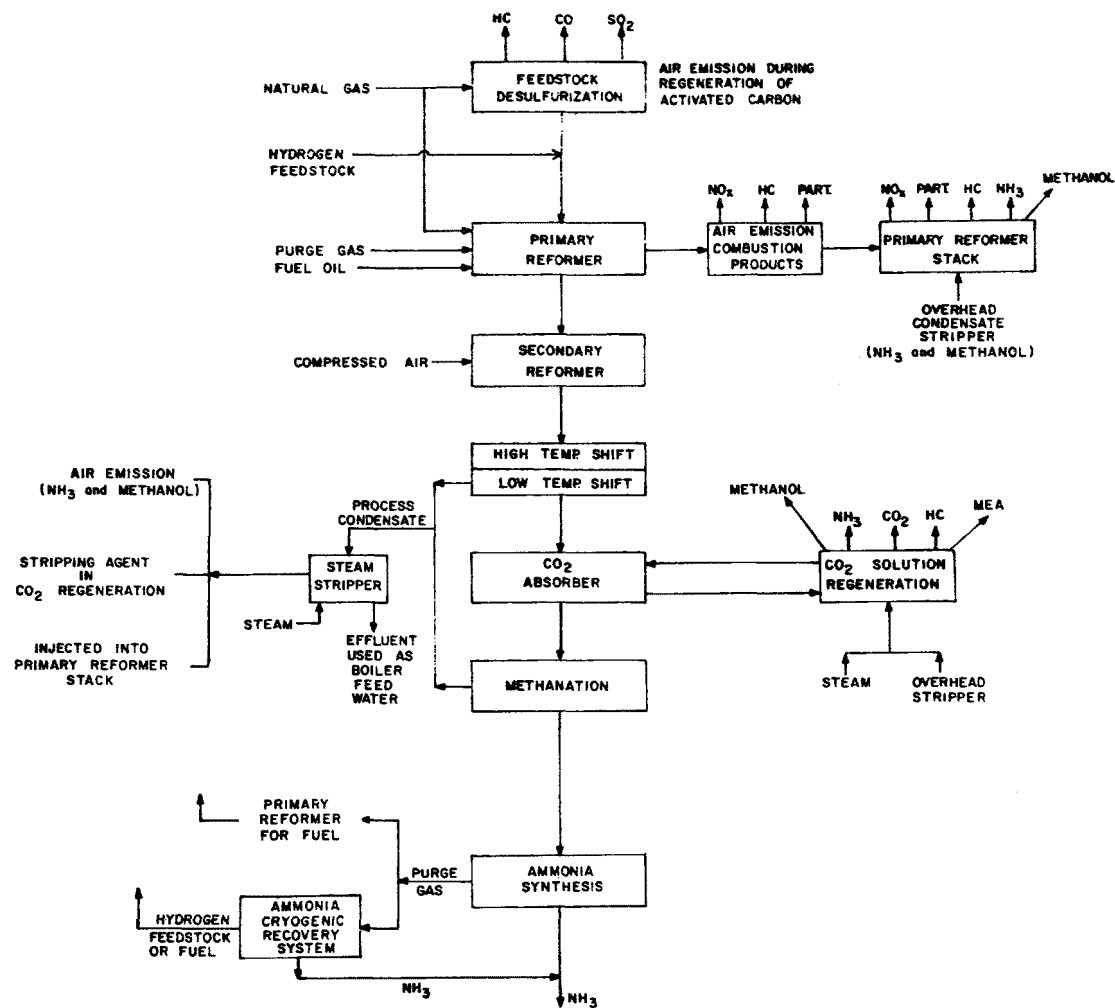
Figure 2. Process flow diagram for an ammonia plant with pollutants associated with each process.[6]

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$$CuO + H_2S \rightarrow CuS + H_2O \tag{1}$$

$$ZnO + H_2S \rightarrow ZnS + H_2O \tag{2}$$

When the feedstock sulfur concentration entering the reformer reaches approximately 0.2 ppm and/or elemental sulfur buildup in the carbon bed reaches 13 to 25 percent by weight of the carbon, the activated carbon bed is regenerated, typically every 20 days, by passing super-heated steam through the bed, and then maintaining a temperature of 230°C for 8 to 10 hours while additional air is added which reacts with the metal sulfide regenerating the metal oxide and elemental sulfur:

$$2\ CuS + O_2 \rightarrow 2\ CuO + 2S \tag{3}$$

Sulfur, carbon monoxide and hydrocarbons are released. Normally, ammonia producers will incorporate two desulfurizing units, with one unit operating while the other is being regenerated.

The zinc oxide catalyst absorbs sulfur up to approximately 18 to 20 percent by weight and is replaced about once a year rather than regenerated.

4.1.2 Primary Reformer

In the primary reformer, the desulfurized natural gas, consisting mostly of methane, is mixed with pretreated process steam in the presence of a nickel base catalyst to convert roughly 70 percent of the methane to carbon monoxide and hydrogen.

$$CH_4 + H_2O \xrightarrow{540°C} CO + 3H_2 \tag{4}$$
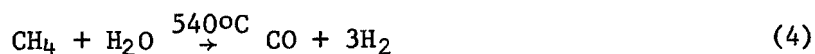
Figure 3 shows the primary reformer in synthesis gas production.[6] The heat (227 KJ/Mole) for the reforming reaction is supplied by firing natural gas or fuel oil and purge gas.
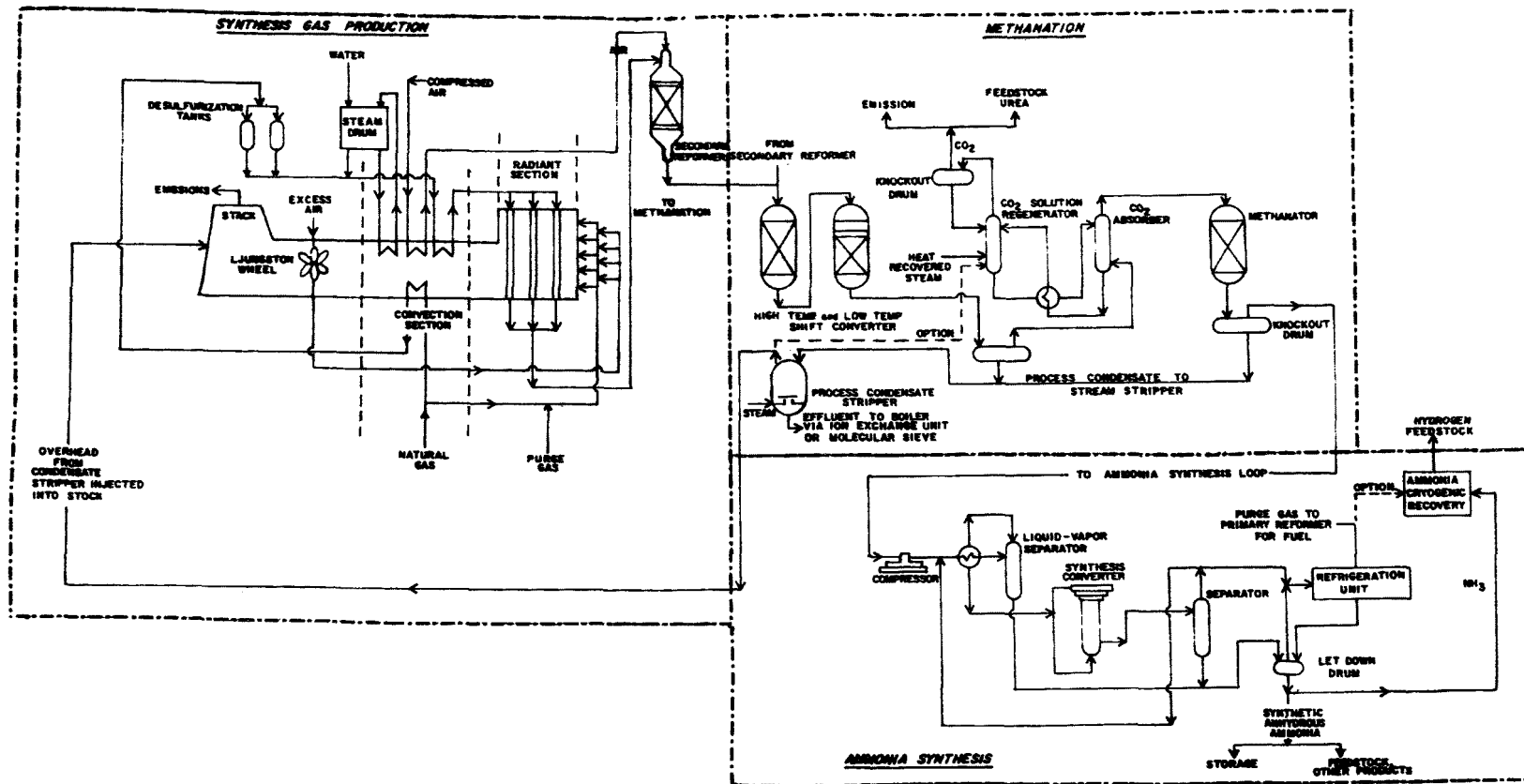
Figure 3. Flow diagram of an ammonia process.[6]

4.1.3 Secondary Reformer

The process gas is next introduced into the secondary reformer, where it is mixed with compressed air (3.4 MPa) preheated to a temperature of 540°C to give a hydrogen to nitrogen mole ratio of 3:1, corresponding to NH_3.

4.1.4 High and Low Carbon Monoxide Shifts

Cooled gas from the secondary reformer enters a high temperature CO shift converter (330 to 550°C) filled with an iron oxide-chromium oxide catalyst to remove carbon dioxide.

$$CO + H_2O \rightarrow CO_2 + H_2 \tag{5}$$

The gas stream is cooled to 200°C and passes into the low temperature shift converter for further CO removal. Unreacted steam is condensed and the condensate separated. Approximately 90 percent of the wastewater from ammonia production is from this process condensate. A 907 metric ton/day plant produces about 1,200 m^3 per day of condensate.[6] Components of wastewater condensate are ammonia, methanol, sodium, iron, copper, zinc, calcium and aluminum.

4.1.5 Carbon Dioxide Removal

Carbon dioxide next must be removed since it poisons the ammonia synthesis catalyst. About 80 percent of ammonia producers remove the CO_2 from the process gas by monoethanolamine scrubbing

$$\begin{array}{c} N_3C \\ \diagdown \\ H_3C \diagup \end{array} N - C_2H_5OH$$
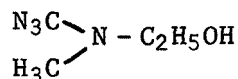
Monoethanolamine (MEA)

the others use hot carbonate scrubbing based on the reaction

$$CO_3^= + CO_2 + H_2O \rightleftharpoons 2HCO_3^- \tag{6}$$

Both scrubbing materials are regenerated by steam stripping.[7]

4.1.6 Methanation

Finally residual CO_2 is removed by conversion under pressure to methane using a nickel catalyst

$$CO_2 + 4H_2 \xrightleftharpoons{400-600^\circ C} CH_4 + 2H_2O \qquad (7)$$
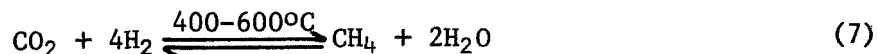
to yield purified synthesis gas with a 3:1 hydrogen to nitrogen mole ratio.

4.1.7 Ammonia Synthesis

Anhydrous ammonia is synthesized directly in two stages, first by compression and then by passing the purified synthesis gas over an iron oxide catalyst at elevated temperature and pressure.

$$N_2 + 3H_2 \rightleftharpoons 2NH_3 \qquad (8)$$

Liquid ammonia is collected from each stage for flashing to remove impurities such as argon. Anhydrous ammonia is either stored at a temperature of $-28^\circ C$ or piped to local plants to produce other products.

4.2 EMISSIONS AND EFFLUENT SOURCES

Table 5 summarizes major emission and effluent sources associated with the overall process steps in ammonia production (see also Figure 1) while Table 6 summarizes severities and pollution control requirements.

The source severity factor is used to evaluate the significance of an emission. Source severity is the ratio of the ground level concentration of each emission species to its corresponding ambient air quality standard (for criteria pollutants) or to a reduced Threshold Limit Value (TLV) for noncriteria emissions species. The TLV refers to the airborne concentration of a substance which represents conditions under which it is believed that nearly all workers may be repeatedly exposed day after day without adverse effect for a 7- or 8-hour workday and 40-hour workweek.

TABLE 5. SUMMARY OF AMMONIA PRODUCTION EMISSION AND EFFLUENT SOURCES

Process step	Air emissions (A) and water effluents (W)	
DESULFURIZATION		
Activated carbon bed regeneration	(A) Oxides of sulfur	
	(A) Free sulfur	$\Big\}$ 8.4 mg/kg NH_3*
	(A) Hydrogen sulfide	
	(A) Hydrocarbons	3.6 g/kg NH_3[†]
	(A) Carbon monoxide	6.9 g/kg NH_3[†]
PRIMARY REFORMER		
Natural gas combustion products	(A) Oxides of sulfur	0.0024 g/kg fuel[‡]
	(A) Oxides of nitrogen	2.7 k/kg fuel[‡]
	(A) Carbon monoxide	0.068 g/kg fuel[‡]
	(A) Hydrocarbons	0.012 g/kg fuel[‡]
	(A) Particulates	0.072 g/kg fuel[‡]
Fuel oil combustion products	(A) Oxides of sulfur	1.3 g/kg fuel[‡]
	(A) Oxides of nitrogen	2.7 g/kg fuel[‡]
	(A) Carbon monoxide	0.12 g/kg fuel[‡]
	(A) Hydrocarbons	0.15 g/kg fuel[‡]
	(A) Particulates	0.45 g/kg fuel[‡]
Fuel, purge gas and condensate stream combustion products	(A) Oxides of sulfur	
	(A) Oxides of nitrogen[§]	115–350 ppm
	(A) Carbon monoxide	
	(A) Hydrocarbons	
	(A) Particulates	
	(A) Ammonia[#]	
	(A) Methanol[#]	
CARBON MONOXIDE SHIFTS		
Condensate following low temperature shift	(W) Ammonia	0.57 kg/hr[§§]
	(W) Methanol	0.28 kg/hr[§§]
	(A) Carbon dioxide	127 kg/hr[§§]
	(W) Trace metals[‡‡]	
	(A) Ammonia	41.2 kg/hr[§§]
	(A) Methanol	22.7 kg/hr[§§]

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CARBON DIOXIDE ABSORPTION
    Regeneration of scrubbing
    solutions

(A) Carbon dioxide	1,220 g/kg NH_3[**]
(A) Methane	0.47 g/kg NH_3[**]
(A) Ammonia	1.0 g/kg NH_3[**]
(A) Carbon monoxide	1.0 g/kg NH_3[**]
(A) Methanol[†]	
(A) Monoethanolamine	0.05 g/kg NH_3[**]

FUGITIVE SOURCES - vents, leaky seals, compressors, pumps, storage, spillage,
                   etc.

[*] Monsanto Research Corporation, "worse case" estimate.

[†] Texas Sir Control Board estimate.

[‡] Reference 6.

[§] Adding the purge gas to the natural gas fuel may increase NO_x levels from approximately 35 ppmv to 115-350 ppmv. Adding overhead increases NO_x emissions in a worse case estimate over 50 percent (Reference 10).

[#] Overall plant NH_3 on CH_3OH emissions reduced to undetectable levels (based on a confidential information source). Other stack tests indicate only a 59 percent and 75 percent reduction of CH_3OH on NH_3 emissions respectively.

[**] Worse case estimate, Reference 6.

[††] If overhead from condensate stripper is used to strip regeneration.

[‡‡] Including Na, Fe, Cu, Zn, Ca, and Al.

[§§] Calculated (Reference 5) for a 1000 metric ton/day NH_3 plant.

TABLE 6. AIR POLLUTION CONTROL REQUIREMENTS[6]

| Source | Pollutant | Average plant | |
		Source severity	Required control percent*
Synthetic Ammonia Production			
Desulfurization tank	SO_2	0.05	0.0
	CO	0.30	94.4
	HC	32.4	99.85
Primary reformer (oil)	NO_x	4.1	98.78
	Part.	0.21	76.2
	HC	0.16	68.8
Carbon dioxide regenerator	NH_3	2.2	97.73
	CO_2	0.25	80.0
	HC	0.54	90.7
	MEA	0.33	84.9
Condensate stripper	NH_3	3.2	98.4
	Methanol	0.12	58.3

*To achieve a Source Severity factor of 0.05

Sources and pollutants were examined on the basis of source severity factors developed by Monsanto Research Corporation as a direct indication of a potential pollution problem.

Wastewater originates from three general sources at nitrogen fertilizer facilities:

● Process units

● Nonpoint sources such as leaks and spills

● General stormwater runoff

Table 7 summarizes effluent problems in the prodution of ammonia and other fertilizer industry products.

Source severity factors for major effluent sources in Table 7 indicate low impact of nitrogen fertilizer plant discharges on receiving waters.

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TABLE 7. POTENTIAL WATER POLLUTANT PROBLEMS IN
THE NITROGEN FERTILIZER INDUSTRY[6]

Product	Process	Effluent specie	Average source severity factor*	Effluent factor mg/kg product	Effluent concentration g/m^3
Ammonia	Condensate stripper	NH_3	0.2	15	12
		Methanol		7.5	6
Ammonium[†] nitrate	Neutralizer and evaporator condensate	Ammonia nitrogen $(NH_3 + NH_4)^*$	0.12‡	860	480
		Nitrate nitrogen	0.0004	470	120
Urea	Evaporator condensate	Ammonia nitrogen $(NH_3 + NH_4)^*$	0.09‡	760	120
	Crystallizer filtrate	Organic nitrogen	0.004	275	90

*Average for each plant weighted with respect to plant production.

†Effluent factors include minor contribution from ammonia plant.

‡Average for receiving water pH 9.

Process wastewater at modern plants originates primarily from condensation of vapor exhaust streams which would otherwise be exhausted to the atmosphere. Cooling tower and boiler water blowdown or wastage also contributes to process wastewater along with regenerate solution from ion exchange systems normally used at a plant to provide feed water. There may also be additions from wet scrubber air pollution control devices.

Nonpoint sources, generally intermittent and highly variable, result from accidential spills; valve and pump seal leaks; cooling tower blowdown, over-flows, and leaks; and plant washdowns. These wastewaters either enter the general plant wastewater treatment system for removal or recycling, or dis-charge to receiving ponds or water courses.

New plants generally use closed loop cooling towers with periodic wasting or blowdown, while some older plants still use once-through systems. Cooling water may contain NH_3 from absorption from ambient air (especially if cooling towers are downwind of ammonia emission points).[8] Slight leaks from process equipment may allow NH_3 or NO_3^- to contaminate cooling water, depending on de-gree of maintenance and inspection procedures applied at any particular plant. Both cooling tower and boiler blowdown usually contain corrosion inhibitors which are typical of any industrial process and include hexavalent chromium (10 mg/ℓ) and some copper and zinc. Many plants reduce hexavalent chromium to the less toxic trivalent species followed by lime precipitation prior to discharge.

Stormwater runoff can contain a significant quantity of nitrogeneous com-pounds, especially at plants with poor handling of dry product. Some state regulatory agencies address this potential problem by requiring containment and specifying discharge limitations for stormwater runoff from active plant areas.

The primary source of process wastewater in an ammonia plant is condensate from cracking of methane for hydrogen production. For a number of plants surveyed, process condensate averages about 1150 liters/metric ton of ammonia, containing about 870 mg/ℓ ammonia and 520 mg/ℓ methanol.[9]

4.3 PRESENT AND POTENTIAL CONTROL TECHNOLOGY

In general, most synthetic ammonia plant emissions are within current state compliance limitations and do not require air control equipment. The major reason for past reduction in air emissions in the ammonia industry is more efficient utilization of material and energy through process modification and advanced ammonia production technology development.

4.3.1 Desulfurization

During regeneration of an activated carbon bed, carbon monoxide, hydrocarbons, and steam are vented to the atmosphere. State air control agencies have not considered this source to be a problem because the emission only occurs from 10 to 20 hours once every 20 days. Hydrocarbon emission levels appear to be quite high during regeneration reaching 3.6 g/kg of product (measured as methane).[7] To date, the majority of ammonia producers do not have a control device on this source.

Emissions from regeneration of the activated carbon bed can be eliminated by incineration. Figure 4 illustrates how an incineration system may be utilized to burn various pollutant streams in a typical ammonia plant. Air emission from the desulfurization unit, overhead from the condensate stripper, relief valves and vents are all routed to the incinerator. In addition, this system allows all process condensate to be recycled.

Alternatively, the problem of regeneration emissions can be eliminated by the substitution of zinc oxide for activated carbon desulfurization beds. This

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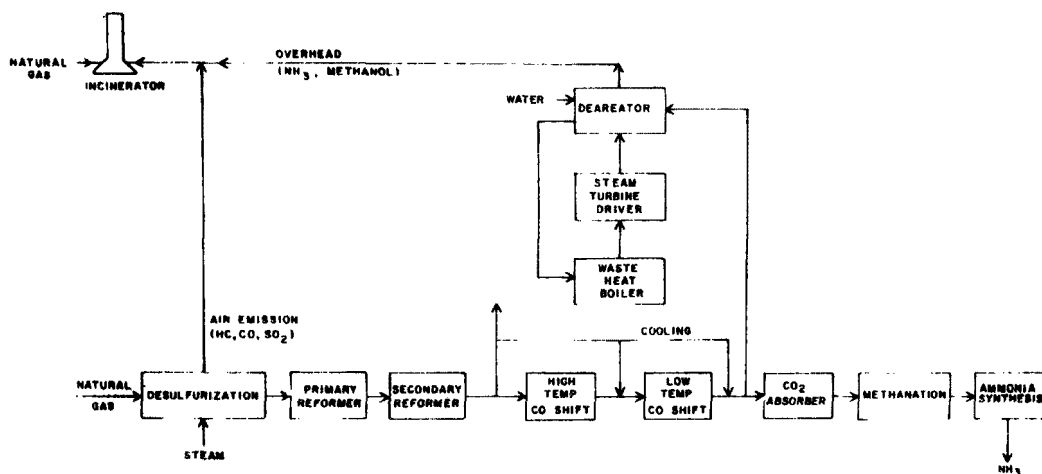
Figure 4. Incineration scheme of various air streams.

not only eliminates regeneration emissions but also saves energy and is a more

effective desulfurization technique.

Zinc oxide beds contain approximately 14 m^3 of zinc oxide. The normal

design life of a zinc oxide bed is 1 to 2 years depending upon the sulfur

concentration of the natural gas. The spent bed is disposed by landfill or

sale for recovery as zinc oxide.[10]

4.3.2 Primary Reformer

To date there are no pollution control devices used to control emissions

from the primary reformer. In the past, purge gas which was vented from the

synthesis process to prevent buildup of inerts was flared. Ammonia producers

now use purge gas for 15 to 20 percent of the energy input into the primary

reformer. Firing the reformer with purge gas results in a substantial increase

in NO_x concentrations (see above). If NO_x emission standards are made more

stringent, it may be difficult for ammonia producers to comply. There are

several approaches to the avoidance or abatement of this problem:

● cryogenic recovery instead of use of purge gas as fuel

● modification of combustion conditions

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- low nitrogen fuel use
- removal of NO$_x$ from flue gas

4.3.2.1 Cryogenic Recovery--

While most ammonia producers fire their reformers with natural gas and purge gas, a few ammonia producers are installing a cryogenic system for the separation of hydrogen and to maximize production. Cryogenic recovery instead of direct use of purge gas as fuel in the primary reformer reduces NO$_x$ emissions.[11]

Figure 5 shows a flow diagram of a cryogenic hydrogen unit at Vistron Corporation's (Cleveland, Ohio) 1360 metric ton/day ammonia plant.[12] Vistron's recovery unit costs less than $2 million with an expected system pay-back time of approximately 2-1/2 years. Figure 6 shows the rate of return with varying prices of ammonia and natural gas.

Vistron's recovery unit uses waste fuel-gas for molecular-sieve regeneration
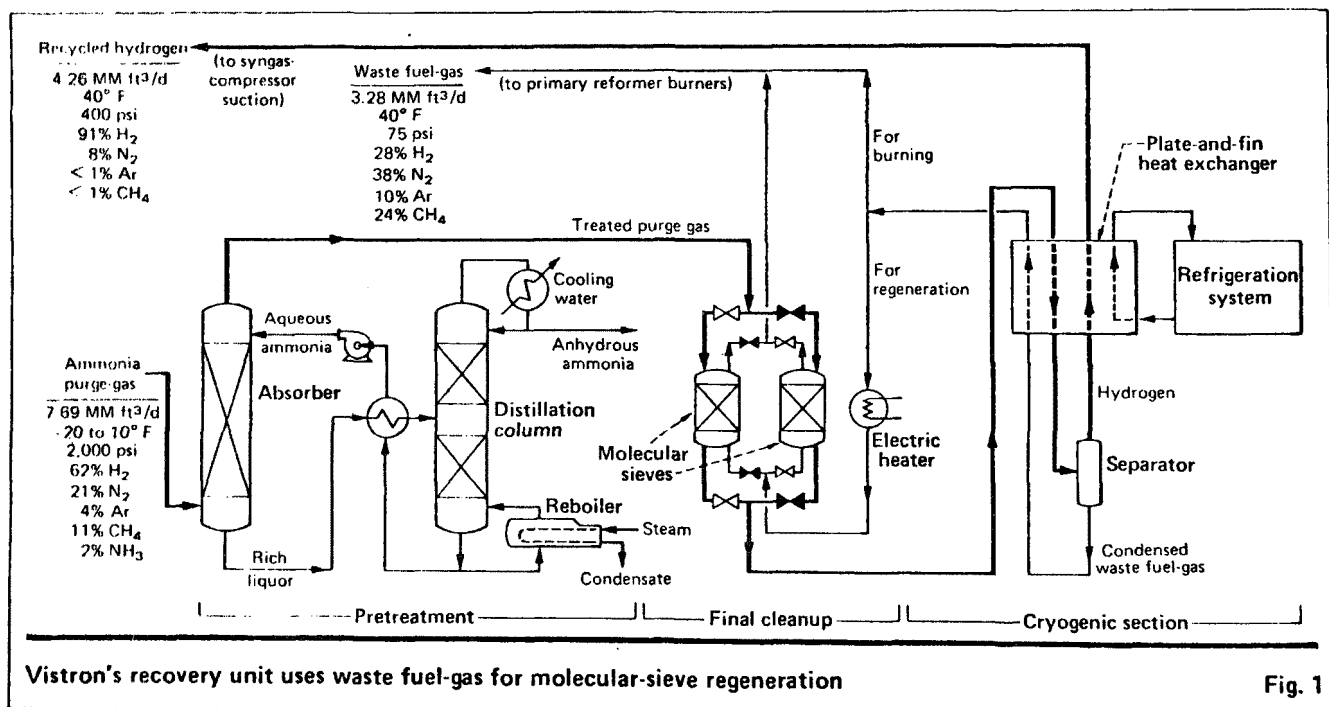
Fig. 1

Figure 5. Vistron's cryogenic recovery system.[12]
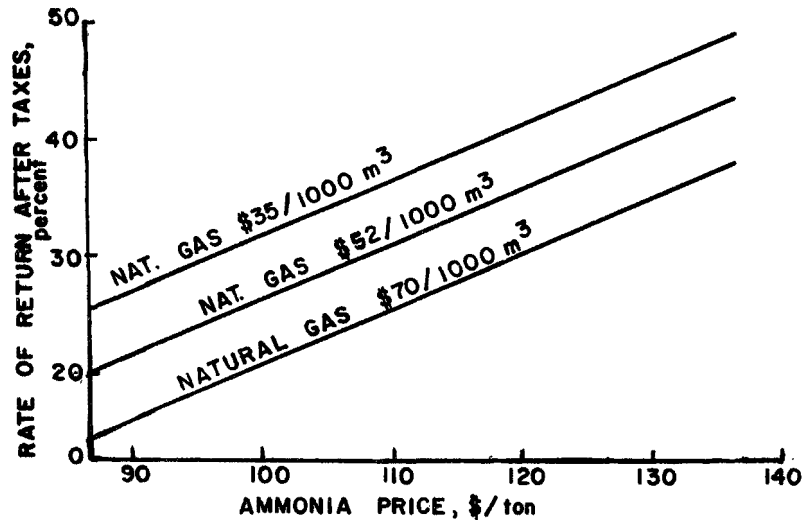
Figure 6. Percent return of a cryogenic system versus price of ammonia at various natural gas prices.[12]

4.3.2.2 Modification of Combustion Conditions--

Combustion modifications through changes in operating conditions and burner redesign are NO_x control techniques that have been successfully demonstrated on utility boilers and other stationary combustion sources. The formation of NO_x from fuel combustion takes place by two mechanism. The first mechanism, termed thermal fixation, involves the reaction of atmospheric oxygen and nitrogen. The second mechanism involves the oxidation of nitrogen contained in the fuel. Reduction in the oxygen content by use of low excess air or staged combustion reduces emissions of both fuel and thermal NO_x whereas reductions in flame zone temperature produce significant reductions only in thermal NO_x. Methods used to reduce temperature include water injection, reduced air preheating and extraction of heat from the flame zone by burner modification.

The primary reformer combustion unit of most ammonia produces operates at relatively low excess air levels (10 to 20 percent). A reduction of NO_x emissions by further reduction of excess air levels does not appear practical. Ammonia producers feel that the only means of reducing NO_x levels is through

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burner redesign.[13] However, the significance of achievable reductions will be lowered by use of purge gas as a reformer unit fuel and the injection of the stripper overhead into the reformer stack.

Burner modifications to reduce NO_x have been classified into the following categories: (1) mixing; (2) divided flame; (3) self-recirculation; and (4) staged combustion.

Good mixing qualities may be achieved by burner modification by the continuous injection of air into a cylindrical stream mixing with jets of fuel injected radially outward through shaped ports. In addition, the air and fuel mixing process is aided by a deflector plate (Figure 7). The homogenous mixture of air and fuel produces a radial conial flame thin and flat for maximum heat radiation and dissipation.[14] The shape of the flame ensures an extremely short nitrogen oxygen reaction time, thus reducing the production of thermal NO_x.
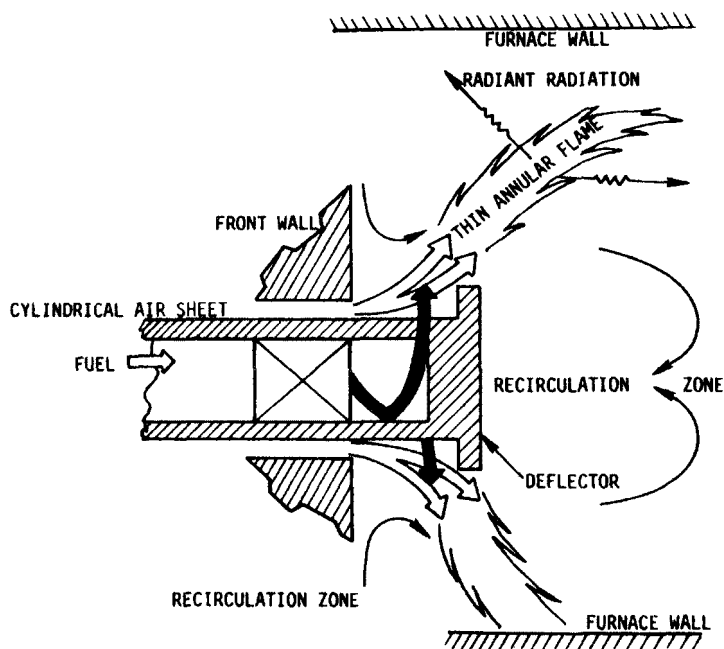
FURNACE WALL
RADIANT RADIATION
THIN ANNULAR FLAME
FRONT WALL
CYLINDRICAL AIR SHEET
FUEL
RECIRCULATION ZONE
DEFLECTOR
RECIRCULATION ZONE
FURNACE WALL

Figure 7. NFK-TRW burner flame reaction.[14]

Another method for reducing thermal NO_x is by exhaust recirculation. Personal communications with ammonia producers indicated that retrofitting an exhaust gas recirculation system to primary reformers would be impractical, and would increase energy demands. Figure 8 illustrates a self-recirculating gasification (SRG) burner which has been developed by Nippon Furnace Kogyo Corporation.[14]

There are two types of staged combustion burners: the two-staged combustion type and the off-stoicheometric combustion type. The two-stage combustion type burner is shown in Figure 9.[14] This type of burner is not yet used commercially because of flashback problems. However, it may be applicable as a combustion unit for the primary reformer and deserves further study.

The off-stoicheometric combustion type burner for gas firing features an atomizer with various size holes creating rich and lean regions of fuel under a uniform airflow. Because of easy installation and low cost, this burner is used widely in Japan. However, there is a tendency for the burner to increase soot emissions resulting from low excess air regions in the combustion zone.

Water and steam injection has been found to reduce effectively NO_x emissions. However, water and steam injection decreases thermal efficiency requiring additional heat input to produce an equivalent amount of ammonia, increases corrosion and causes undesirable operating conditions.

4.3.2.3 Use of Low Nitrogen Content Fuels—

Other methods of reducing NO_x are related to the nitrogen content of fuels. Normally, about 30 percent of the fuel nitrogen is converted into NO_x on combustion and is emitted along with thermal NO_x. Fuel NO_x emissions will decrease in the utilization of the following fuels in descending order: solid fuels (coal and coke), liquid fuels (petroleum) and gaseous fuels. At the

GASIFICATION GAS
CO, H2 RICH

RE-COMBUSTION GAS
$CO_2 \cdot H_2O \cdot N_2 \cdot O_2$

GASIFICATION REACTION

$C + O_2 \longrightarrow CO_2$

$CO_2 + C \rightleftharpoons 2CO$

$C + H_2O \rightleftharpoons CO + H_2$

$C_mH_n + mH_2O \rightleftharpoons mCO + \frac{2m+n}{2} H_2$

COMBUSTION PRODUCTS
$CO_2 \cdot H_2O \cdot N_2$
$O_2 \cdot$ OTHERS

SECONDARY AIR
$(O_2 \cdot N_2)$

FUEL
C_mH_n

Figure 8. Principle of SRG burner.[14]

GAS OR
GAS PREMIXED
WITH AIR

FIRST STAGE

SECOND STAGE
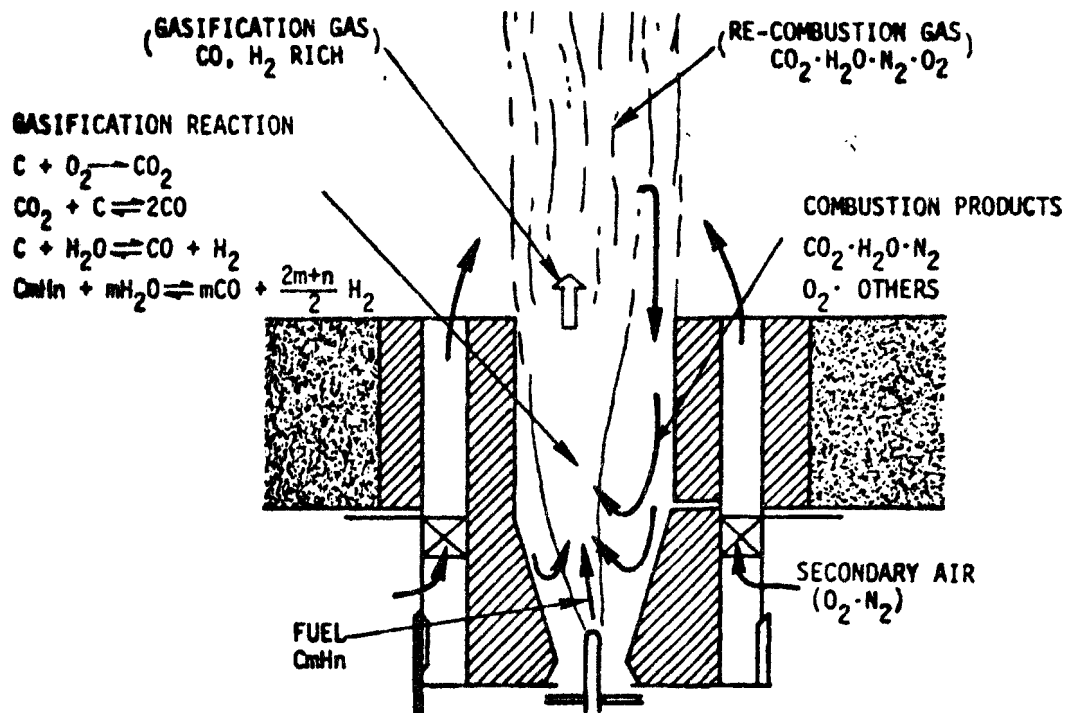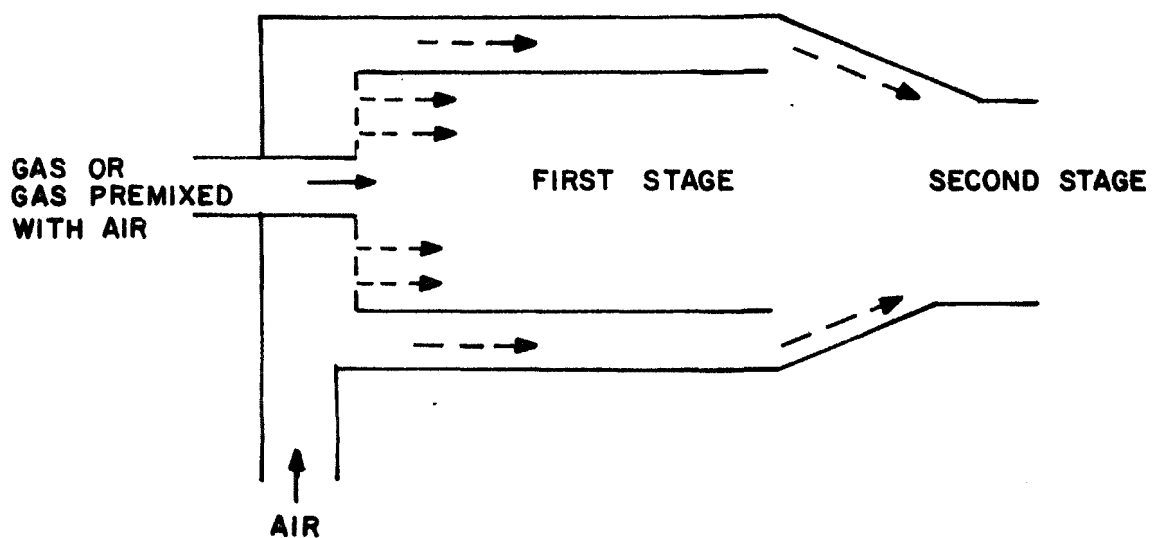
AIR

Figure 9. Low NO_x two-stage combustion burner.[14]

present time in the U.S., coal (~1.5 percent nitrogen by weight) is not used as a heat source in the primary reformer. Grade C heavy oil contains about 0.35 percent nitrogen by weight, Grade B, 0.08 percent, Grade A and kerosene 0.005 to 0.08 percent. Nitrogen content will be an important consideration in the development of alternative feed stocks (see Section 7.1).

4.3.2.4 Flue Gas Treatment to Reduce NO_x--

The Japanese are developing five techniques for denitrification of flue gas:

1. Selective catalytic reduction (SCR) with ammonia
2. Ammonia reduction (AR) without a catalyst
3. Electron beam radiation
4. Absorption (by molecular sieve, gelatinous materials, etc.)
5. Catalytic decomposition.

Only SCR and AR systems are being used commercially in a number of plants in Japan. The other three techniques are still in the R&D, pilot plant, and small scale production stages with very limited data available.[14]

The advantages of selective catalytic reduction are the consumption of less reducing gas than nonselective catalytic reduction, less plant space required, absence of troublesome byproducts, and no requirement of reheating of gases compared to wet NO_x denitrification. The disadvantages with SCR units vary with each system. Particulates can plug the catalyst and SO_x poison it.

The Sumitona Chemical Company in Japan has five commercial plants in operation using selective catalytic reduction of NO_x. One commercial plant is treating 200,000 m^3/hr of flue gas from a reformer burning LPG at Higashi Nikon Methanol Company (HNM). (Figure 10.)

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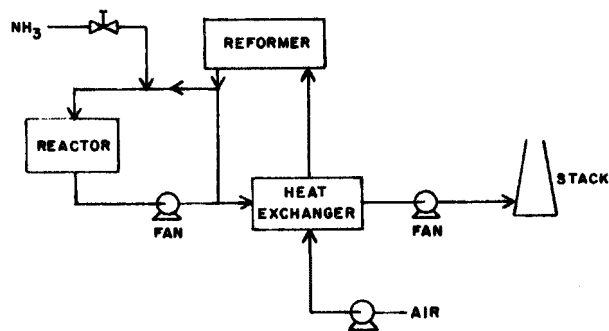
Figure 10. HNM plant denitrification process flowsheet.[14]

The advantages of HNM process are its simplicity, smooth operation, and very low NH_3 emissions. However, the cost for denitrifying is quite high, about $0.40/1000 m^3.

NO_x can be converted to N_2 by ammonia in the presence O_2. Tests by Exxon indicated that ammonia injected into flue gas at 960°C will convert approximately 70 percent of the NO to N_2,[15] tests on a full scale retrofit commercial combustion source conducted at the Kawasaki plant in Japan indicated a 60 percent conversion of NO to N_2, and tests on a denitrification process developed by Nippon Kokan indicated an 80 percent conversion of NO to N_2 with residual NH_3 in the treated gas less than 20 ppm. In large scale operations Nippon Kokan expects about 50 percent NO_x removal at an NH_3/NO mole ratio of 1.5 to 2.0.[16]

4.3.4 Carbon Monoxide Shift Condensate Stripper

Process condensate is formed while cooling synthesis gas. In order for ammonia producers to comply with effluent standards, most have incorporated a condensate stripper that reduces ammonia and methanol condensate by about 98 percent (Table 8) to levels in compliance with effluent standards for discharge into receiving streams.

TABLE 8. MASS BALANCE AROUND THE CONDENSATE STEAM
STRIPPER—RESULT OF 65 TEST MEASUREMENTS[9]

Stream	Stream flow rates (kg/hr)	Mass flow rate (Kg/hr)		
		Ammonia	Methanol	Carbon dioxide
Process condensate	80,500	39.2	21.1	1
Steam	7,980	0	0	0
Overhead	8,680	41.2	22.7	1
Effluent	81,200	0.57	0.28	0

Note: Mass entering the stripper does not exactly equal mass
exiting because these values are the averages from test
measurements.

An EPA-sponsored study developed effluent discharge factors for steam

strippers, shown in Tables 9 and 10.[9]

TABLE 9. EFFLUENT DISCHARGE FACTORS FOR A CONDENSATE
STEAM STRIPPER (mg/kg OF PRODUCT)[9]

Effluent species	Effluent discharge factor
Ammonia	15 ± 105%
Methanol	7.5 ± 97%

Note: Uncertainty values were calculated using
the "Student t" test for 95 percent
confidence limits.

TABLE 10. TRACE METAL EFFLUENT DISCHARGE FACTORS
FROM A CONDENSATE STEAM STRIPPER[9]

Metal	Average concentration (g/m^3)	Effluent discharge factor $(g/kg \text{ of product})$
Chromium	< 0.2	$< 4 \times 10^{-5}$
Copper	< 0.02	$< 4 \times 10^{-6}$
Iron	< 0.1	$< 2 \times 10^{-5}$
Nickel	< 0.2	$< 4 \times 10^{-5}$
Zinc	< 0.02	$< 4 \times 10^{-6}$

Stripping the ammonia from the water results in air emissions of ammonia and methanol, termed overhead. The overhead can be injected into the furnace inlet but this is uneconomical; for a 900 metric ton/day NH_3 plant an additional 2000 m^3/day of natural gas is required.[5]

Injecting the overhead into the primary reformer stack is the most widely used and economical abatement system. However, as discussed previously, while this reduces overall plant emissions of NH_3 and methoanol, NO_x emissions are significantly increased as shown in Table 11.[17]

TABLE 11. THEORETICAL CONVERSION OF AMMONIA IN
STRIPPER OVERHEAD OF A 900 METRIC TON/
DAY PLANT TO NO_x IN PRIMARY REFORMER
STACK[9]

Ammonia introduced		NO_x from stack	
mg/ℓ	kg/hr	ppm	kg/hr
4750	38	261	103
0	0	172	68

Some plants have installed a common incinerator for the thermal decomposition of emissions from vents, overhead and polluted streams. Figure 11 illustrates a flowsheet of a reflux incineration system. The refluxing system concentrate contaminants as an overhead vapor product which is incinerated or the ammonia can be recovered cryogenically. Stripper bottoms may be recycled as boiler feedwater or cooling tower makeup.[18] In the latter instance, nitrogen compounds may be eventually discharged with blowdown to water courses or treatment systems.

A system which has been used in conjunction with a carbon dioxide scrubbing system and low level heat is a modified overhead reflux and product recovery system. Figure 12 shows such a reflux condensate stripping system.[6]

Another scheme based on 100 percent condensate recycle utilizes a saturation tower to saturate natural gas feed to the primary reformer with untreated condensate (Figure 13).[18]

Hot water circulation supplies the heat required for vaporizing the condensate. This design utilizes the partial pressure of natural gas to facilitate saturation. All the condensate is vaporized and serves as feed for the reformer. This system does not require a condensate stripper. Figure 13 shows a natural gas saturation flow diagram. Natural gas saturation has the following advantages: (1) elimination of additional reforming steam, (2) reduction in boiler feedwater, and (3) complete elimination of condensate disposal.[8]

4.3.5 Carbon Dioxide Removal System

The composition of emissions from the carbon dioxide removal system is 98.5 percent carbon dioxide and 1 percent water. Industry has not been required to install air control devices on such units. Approximately 70 percent of ammonia producers use the carbon dioxide as a chemical feedstock in urea
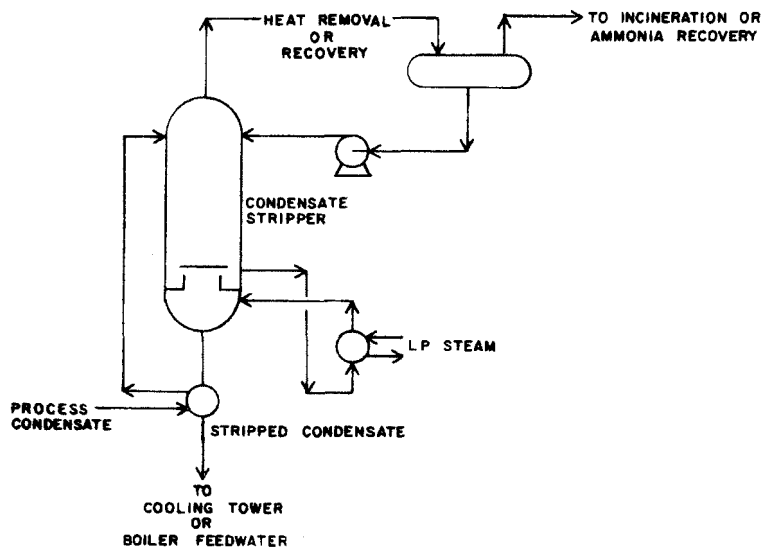
Figure 11.   Reflux incineration system.[18]
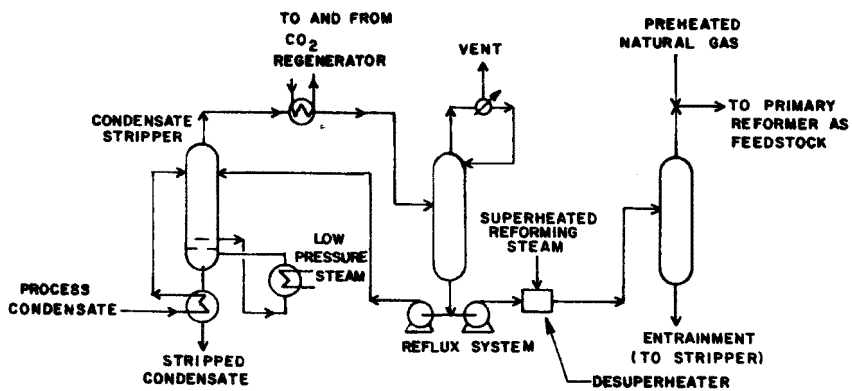
Figure 12.   Reflux condensate stripping system.[6]

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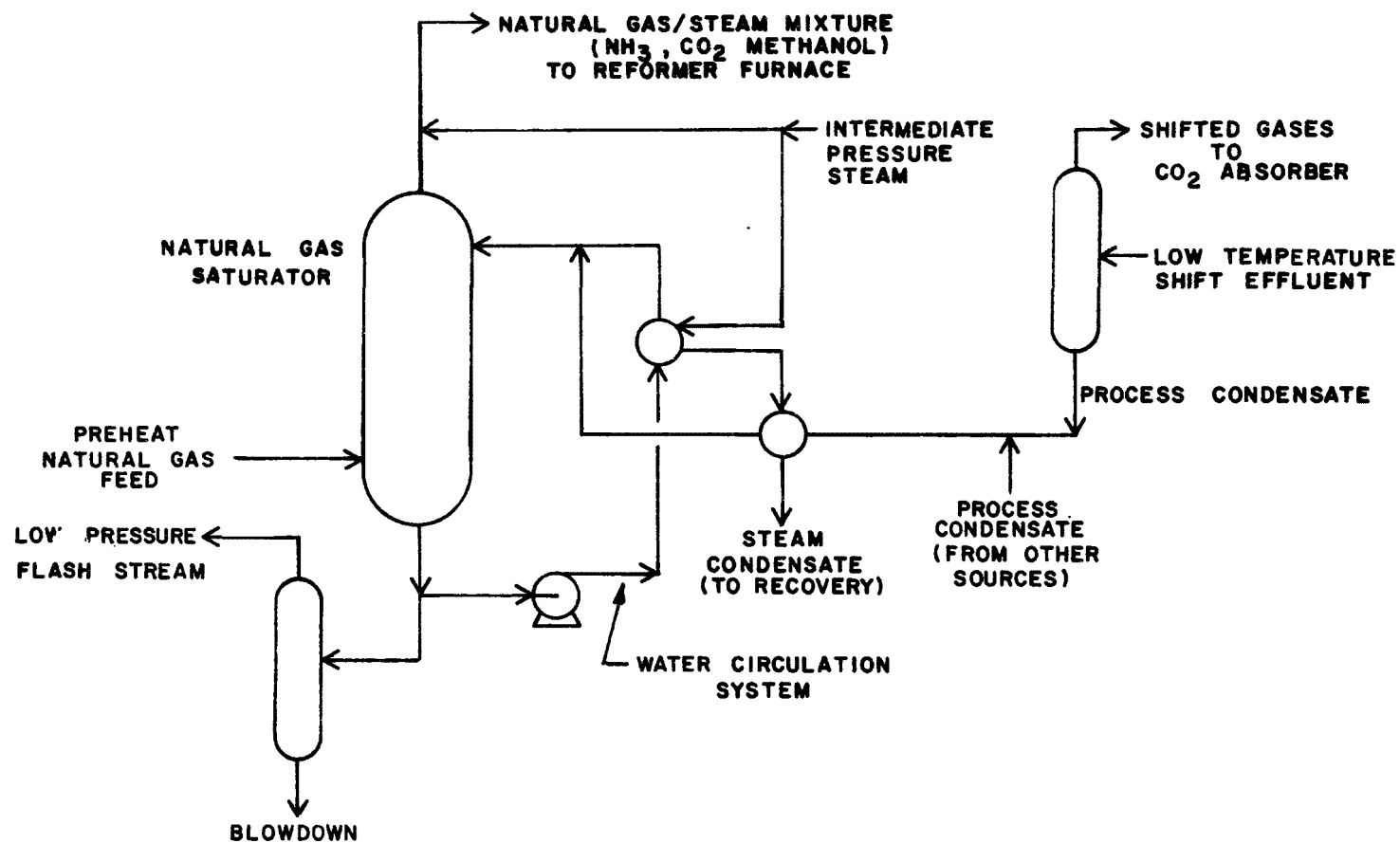
Figure 13. Process condensate natural gas saturation process flow diagram.[18]

production while the other 30 percent is used in other processes. In the past, most ammonia producers have used MEA carbon dioxide removal systems because of their low capital investment. However, the hot potassium carbonate system require 40 to 50 percent less energy for regeneration than the MEA system. In addition, after decades of research and development, capital costs for the hot potassium carbonate systems and MEA system are similar.[19] Therefore, the economic incentive from energy savings clearly favors an increase in hot potassium carbonate process utilization.

Still another method of treating stripper condensate is air stripping, an approach which has been considered in advanced municipal wastewater treatment. The technique is costly energy-wise and has other drawbacks. No air strippers are known to be operating or planned at nitrogen fertilizer facilities.

5.0 AMMONIUM NITRATE

5.1 PROCESS DESCRIPTION

Ammonium nitrate is presently produced at 57 plants located in 28 states. Present annual capacity is roughly 8.9×10^6 metric tons of ammonium nitrate solution in terms of 100 percent ammonium nitrate. The industry typically operates at 85 to 90 percent capacity. The average capacity of a low density ammonium nitrate plant is 550 metric ton/day. A large ammonium nitrate plant produces about 800 metric ton/day. The average high density plant produces 725 metric ton/day while a large high density plant has a capacity of about 1100 metric ton/day. Ammonium nitrate is produced by neutralizing nitric acid directly with ammonia:

$$NH_3 + HNO_3 \longrightarrow NH_4NO_3 \tag{9}$$
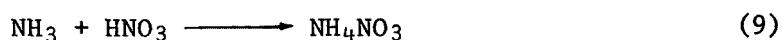
The reaction is exothermic, releasing roughly 112 KJ per gram mole of aqueous ammonium nitrate produced. This heat of reaction is used to drive off some of the water, concentrating the product stream.[20,21]

The overall manufacturing process can be broken down into the following operations:

1. solution formation
2. solution concentration
3. solids formation
4. solids drying and cooling
5. coating and/or additives

6.   screening

7.   bagging, storage and bulk shipping

5.1.1 Solution Formation

Approximately 90 percent of all the ammonium nitrate produced in the U.S. uses the same general solution formation steps. The other 10 percent is produced by the Stengel process and will be discussed later. During neutralization, the lower the pH, the lower the ammonia losses will be. Reaction pH is usually held either in the 1.5 to 2.5 or the 5.0 to 7.0 range.[5,21,22] Heat from the reaction concentrates the solution to the desired 83 percent.

5.1.2 Solution Concentration

Most plants producing solid ammonium nitrate rely on falling film evaporators to concentrate the ammonium nitrate to the levels required for subsequent prilling, granulation, etc. Typically, these units operate under a vacuum of 57 kPa. Most of these units are single stage, although two-stage evaporation is occasionally employed. Other evaporation equipment used are air-swept falling film heat exchangers, barometric condensors, and agitated tanks (e.g., calandrias).

5.1.3 Solid Formation

Approximately 60 percent of the ammonium nitrate produced in the United States is sold as a solid product. There are four methods of producing solid ammonium nitrate:

1.   prilling

2.   drum granulation

3.   grinding

4.   Stengel Reactor and Sandvik belt process

Eighty percent of the solid ammonium nitrate produced is by prilling; about another 10 percent by granulation, and remaining 10 percent by graining and Stengel and Sandvik belt processes.

In a prill tower, molten ammonium nitrate falls from the top of the tower countercurrent to an airflow. The airflow cools the falling droplets and allows their surfaces to crystallize before reaching the bottom of the tower.

Upon reaching the bottom of the tower, the solidified droplets or prills are either carried away on a conveyor or held temporarily at the bottom, fluidized by the entering air. The fluidized bed technique allows the prills to cool further with minimum caking or sticking before being removed.[7,23] Ammonium nitrate prill sizes typically fall in the range 1.5 to 4.0 mm.[23] Low density prills contain 95 to 96 percent NH_4NO_3, high density prills 99 percent. The former is used for fertilizer and explosives, the latter fertilizer.

In the granulation technique, particles are built up to granules by accretion. The particles produced are larger with greater abrasion resistance and two to three times the crushing strength of standard prills. These properties result in less crushing, dust formation and caking upon handling.[22,24,25]

Graining is a costly operation, accounting for less than 2 percent of the country's ammonium nitrate production. Ammonium nitrate grains are produced by discharging 98 percent melt into large jacketed kettles equipped with plows for stirring the molten material. The rate of cooling is controlled by steam and cooling coils in the kettle jacket. The material cools and "fudges," and then is broken up into grains by the plow. The resulting pellets are cooled, screened, and coated.[20,21]

Although the Stengel reactor process is actually a solution formation step, it is examined here because it is normally employed in conjunction with

a Sandvik belt to combine solution formation, concentration, and solid formation steps.

Ammonia and 55 percent nitric acid are fed into a high temperature, high pressure reactor packed with steel Raschig rings. The product stream is expanded into a cyclone separator, and is further concentrated to about 99.8 percent before exiting from the separator by a stream of hot air which enters at the bottom of the cyclone.

The melt from the Stengel reactor and separator unit is spread onto a water-cooled stainless steel Sandvik belt. A doctor blade removes the crystalline product from the belt. The material is ground, screened, coated, and bagged.[11,17,26,27,28]

5.1.4 Product Finishing

Drying removes water from solids which have been formed with a high moisture content melt, (< 98 percent ammonium nitrate). Typically, this step is performed by two rotary drum dryers in series although fluidized bed coolers are beginning to gain some acceptance. It is common practice to use a coating and/or an additive to enhance shelf life and to suppress dust emissions from solid ammonium nitrate particles. Additives include magnesium oxide, calcium oxide, and magnesium nitrate.[20,29]

Product size is primarily controlled by screening. Oversize and undersize material is removed from the product solids and recycled.

In most plants, it is common for material to be transported by conveyor belt from one process step to another. Ammonium nitrate shipment is either by bag or bulk. The trend has been toward bulk handling of ammoinium nitrate solids (over 90 percent of product).[20,30]

5.2 EMISSIONS AND EFFLUENT SOURCES

Process steps responsible for air emissions in ammonium nitrate production are as follows: (1) neutralization; (2) evaporation and concentration; (3) prilling; and (4) cooling. Sources of wastewater effluent in ammonium nitrate manufacturing process are as follows: (1) neutralizer, (2) evaporator exhaust, and (3) solutions from air pollution control equipment used on the cooler and/or dryer. In addition, there is a potential for fugitive air emissions and water effluent from vents, leaky seals, compressors, pumps, storage facilities, relief valves and ammonia spillage. Table 12 shows pollutants, source severity factors (see Section 5.2), and control equipment for various processes.[5,20]

Point sources of wastewater from ammonium nitrate manufacturing include condensate from neutralizer and evaporator exhausts and solution from wet scrubber air pollution equipment. Roughly one-half of ammonium nitrate plants condense process exhaust, and about one-half of these plants either recycle material to process units or combine it with fertilizer solutions. Thus, only about 25 percent of all plants release process condensate to treatment units or receiving waters.

EPA evaluated effluent parameters by surveying the industry prior to setting effluent standards. Ammonia nitrogen and nitrate nitrogen were the primary pollutants of ammonium process wastewater as summarized in Table 13.

5.2.1 Neutralizer

The vapor stream off the top of the neutralization reactor is primarily steam with some ammonia and NH_4NO_3 particulates present. The lower the pH (excess of nitric acid), the lower the ammonia emissions while the higher the pressure the higher the ammonia emissions. Uncontrolled particulates for

TABLE 12. AIR AND WATER POLLUTANTS AND CONTROL REQUIREMENTS
FOR AMMONIUM NITRATE PRODUCTION[5,20]

| Source | Pollutant | Average plant | |
		Source severity	Required control* percent
Air			
Ammonium nitrate			
Neutralizer	Particulate	2.07	97.6
Evaporator/Concentrator	Particulate	0.70	92.9
Prilling tower	Particulate	0.17	70.6
Granulator drum	Particulate	ND	ND
Cooler	Particulate	0.06	7.0
Water			
Ammonium nitrate* (including nitric acid and ammonia)	$NH_3 - N$	0.089	43.8
	$NH_4 - N$	0.0043	0
	$NO_3 - N$	0.0004	0

*To achieve a source severity = 0.05. Sources are not
identified. Data are for combined plant effluent.

Note: ND = No Data.

TABLE 13. AVERAGE EFFLUENT PARAMETERS FOR
NITROGEN FERTILIZER PLANTS[10]

Parameter	Ammonium nitrate	Urea
Wastewater effluent flow rate, m^3/s	0.0346	0.03
Effluent factor, g/kg of product		
Ammonia nitrogen ($NH_3 + NH_4^+$)	0.862	0.7
Nitrate nitrogen	0.471	
Organic nitrogen	0	0.2
Effluent concentration, g/m^3:		
Ammonia nitrogen ($NH_3 + NH_4^+$)	482	1
Nitrate nitrogen	121	
Organic nitrogen	0	

conventional neutralizers usually fall in the range Of 0.25 to 3.7 kg/metric ton of 100 percent ammonium nitrate. A typical uncontrolled emission rate for ammonia losses from a neutralizer is 1.5 kg/metric ton of NH_3.

5.2.2 Evaporator/Concentrator

Approximately 75 percent of the industry utilizes film-type evaporators. Ammonia emissions should not be a problem because of the pH range of 5.2 to 5.4. Ammonium nitrate particulate emissions in the vapor streams off the evaporators generally fall in the range of 0.1 to 1.0 kg/metric ton of ammonium nitrate.[20]

5.2.3 Prill Towers

The prilling process, which involves prills falling through a counter-current airstream, is highly conducive to particulate entrainment. The smaller particulates in the submicron range, referred to as "fume," resulting from the evaporation and subsequent condensation and solidification of the material being prilled, is particularly difficult to control. The quantity of fume produced has been found to be temperature dependent; to minimize fume formation, melt temperature should be kept as low as possible and melt composition carefully controlled.[28,31] Typical emissions from an ammonium nitrate prilling tower fall in the range 0.2 to 1.5 kg of ammonium nitrate particulates per metric ton of ammonium nitrate product.

5.2.4 Granulator

Because of the limited use of drum granulators in the ammonium nitrate industry, there is a scarcity of data regarding emissions from this source. A reasonable estimate for particulate emissions can be made by assuming emissions similar to those for urea. This assumption leads to an estimate of a range of 0.05 to 1.0 kg of particulate emitted per metric ton of ammonium nitrate produced for a granulator equipped with a scrubber. Note that this range is not for uncontrolled emissions as a scrubber is considered as an integral part of the process.

5.2.5 Dryers, Coolers, Additives, Coating, and Screening

Uncontrolled emissions from dryers and coolers range from 1 to 10 kg/metric ton of product, but are readily reduced by scrubbers. Pollutants from additive operations can be considered negligible. Emissions from coating operations are fugitive emissions. Based on the estimate of 10 percent loss of coating material during coating operations, there is an emission of 3 kg/metric ton of ammonium nitrate (for a coating level of 3 percent). Most of the material actually settles to the floor and only a small percentage of this material escapes to the atmosphere.[20] Only a small quantity of particulates escape as fugitive emissions from the building in which the screening is performed.

5.2.6 Product Handling

One source of emissions of airborne fines is the series of transfer points often by conveyor belt, in the process. The severity of this emission source will depend on the characteristics of the material.

Approximately 90 percent of all ammonium nitrate solids are handled in bulk. Because of the small quantities of fines present in the ammonium nitrate solid, particulate entrainment is low in these operations. One estimate is that less than 0.1 kg of particluates per metric ton of ammonium nitrate product is entrained in bulk handling.[20]

5.3 PRESENT AND POTENTIAL CONTROL TECHNIQUES

Particulates and ammonia are emphasized in this section. NO_x emission data was not available from the industry sources and equipment vendors contacted during this study. Because there is no standard test method for ammonium nitrate particulates, and the physical and chemical properties of ammonium nitrate can affect sampling results when the standard EPA Method 5 is used, there is also a paucity of information relative to the control of emissions of this material.

5.3.1 Neutralizer

The neutralization reaction is exothermic and produces quantities of steam which may contain particulates, ammonia, and/or nitric acid. During normal plant operations emissions can be eliminated by total condensation. However, even with total condensation it is necessary to vent steam during startup, shutdown, or upset conditions. Little information is available on the factors affecting other control methods. Emission rates after control, as shown in Table 14, range from 0.17 to 0.5 g/kg. Condensation, wet scrubbing, and Monsanto high efficiency mist eliminators should be effective for ammonia.

TABLE 14. SUMMARY OF NEUTRALIZATION
EMISSION DATA[17]

Emission control method	Emissions	
	g/m³*	g/kg of product
HV mist eliminator	0.50	0.42
Partial condensation	1.23	0.50
Mississippi Chemical unit	0.36	0.17

*Grams per wet standard cubic meter.

Mississippi Chemical Corporation (MCC) has developed and patented a neutralizer which reduces particulates and fumes and ammonia emissions to a fraction of those emitted from most conventional neutralizers. By process design and by close pH monitoring, particulate emissions from conventional neutralizers typically run about 1.07 to 1.92 kg/metric ton of ammonium nitrate while MCC neutralizers have been found to generate 0.074 to 0.247 kg/metric ton and < 2 kg of ammonia per metric ton of ammonium nitrate produced.

The MCC neutralizer (Figure 14) has two reaction zones: (1) a nitric acid aqueous reaction zone and (2) an ammonia aqueous reaction zone. Nitric acid circulates into the ammonia reaction zone in such a way that the acid entering

VAPOR
OUTLET

DEFLECTS SOLUTION
DOWNWARD INTO FIRST
REACTION ZONE

OUTLET

OVERFLOW
AMMONIUM
NITRATE

SPARGER

NITRIC ACID

NITRIC ACID
REACTION ZONE

AMMONIA REACTION ZONE

MESH SCREEN

INLET TO
AMMONIA
REACTION ZONE

AMMONIA
ENTERS REACTION
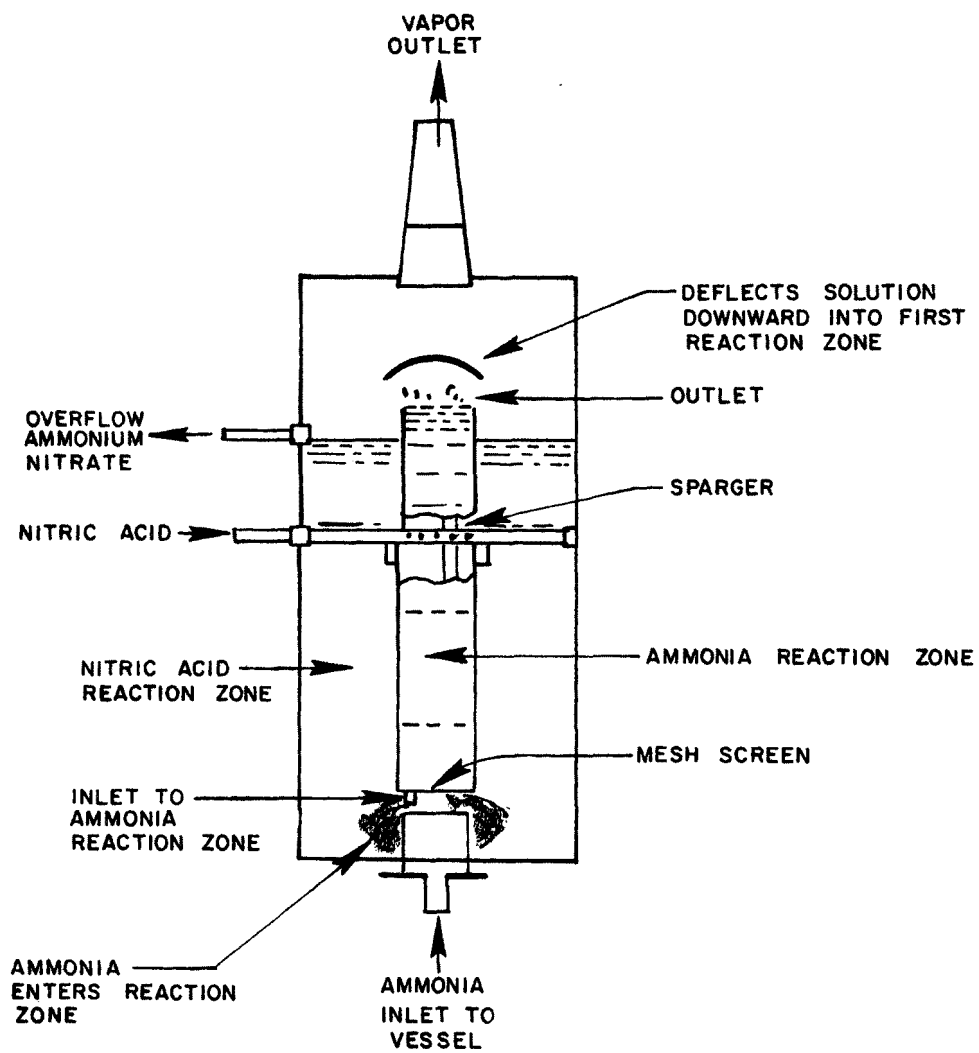ZONE

AMMONIA
INLET TO
VESSEL

Figure 14. A schematic view of MCC neutralizer.[32,33]

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the zone has been diluted to less than 5 percent by weight.[32,33] Figure 14

shows a schematic view of an MCC neutralizer.[32,33] Existing neutralizers can

be modified at moderate costs to incorporate these features.

5.3.2 Evaporator/Concentrator

About 70 percent of particulate emissions from the neutralizer, evaporator/

concentrator and prill tower are less than 3 µm in size. Emissions from the

evaporator/concentrator are commonly controlled by a high efficiency scrubber

(99 percent) or a medium efficiency scrubber (85 percent).

In a few plants, the neutralizer and the evaporator/concentrator are ducted

to a Monsanto HE mist eliminator. Figure 15 illustrates a Monsanto HE collec-

tion unit.[34] Test data indicated an efficiency of 98.6 percent cleanup on a

stream containing neutralizer evaporator/concentrator and prill tower (with a

Cooperative Farmers Chemical Association (CFCA) cone emissions. Figure 16

illustrates a CFCA cone with a Monsanto HE mist eliminator.

5.3.3 Prill Towers

Approximately 50 percent of ammonium nitrate prill towers operate without

emission control equipment, 2 to 5 percent use the CFCA cone/Monsanto HE system,

15 percent use wet scrubbers and the remainder uses mesh pads or similar devices.

Tests for uncontrolled ammonium nitrate prill towers indicated an emission rate

of 0.455 g/kg of product, at a concentration of 0.071 g/m^3. The overall CFCA/

Monsanto HE system appears to reduce emissions to below 20 percent opacity.

The CFCA cone collection efficiency was 76.9 percent (0.55 g/kg) of a

total uncontrolled emissions of 0.715 g/kg of product.[17] In addition, the

Monsanto HE unit with a CFCA cone achieved a control efficiency of 96 percent

(0.02 g/kg).[34] The overall control efficiency for the Monsanto HE unit alone

was only 68 percent. Tests for three different CFCA cone/Monsanto HE units

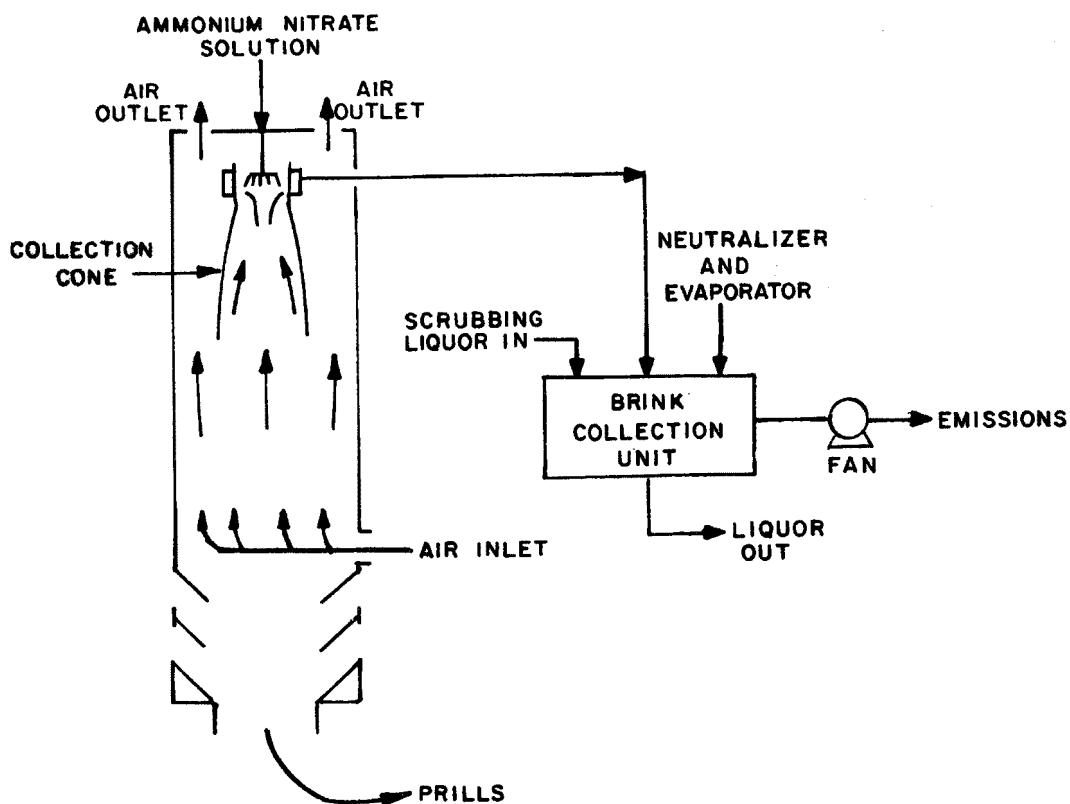indicated an emission of 0.285 to 0.55 g/kg of product.[17,34]
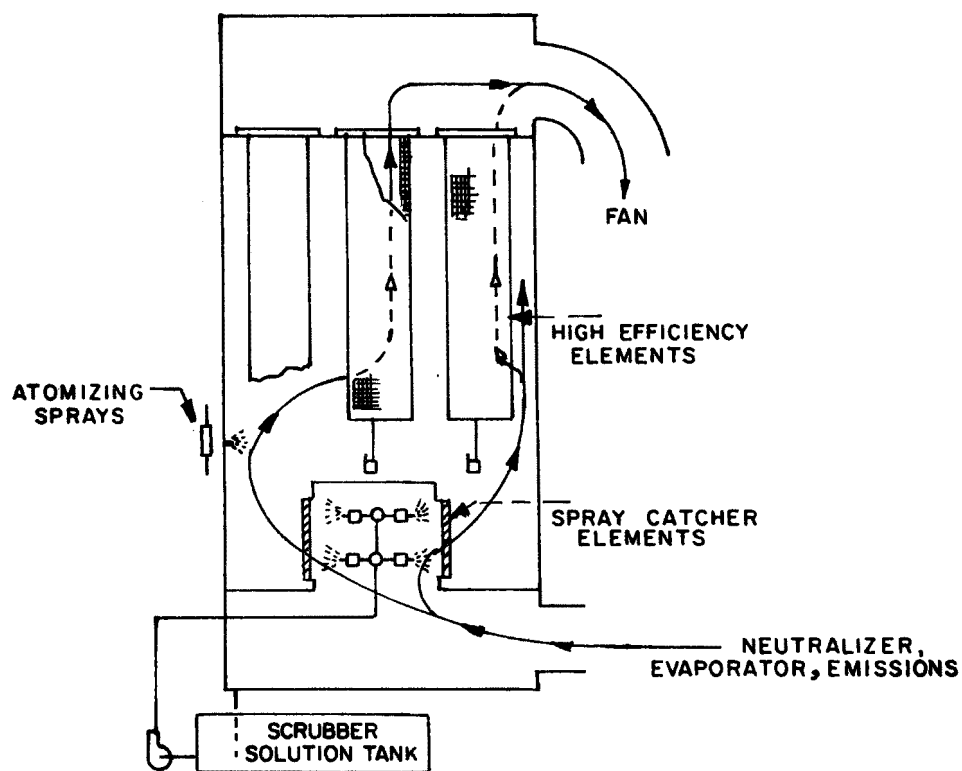
Figure 15. Brink collection unit.[34]

Figure 16. CFCA collection cone and Brink scrubbing unit.[34]

The performance of wet scrubbers is especially sensitive to the particulate size distribution. Particulate size distribution for a typical prill tower is as follows:

- 30 percent by weight: > 3 μm

- 20 percent by weight: 1 to 3 μm

- 35 percent by weight: 0.5 to 1 μm

- 15 percent by weight: < 0.5 μm

The large fraction below 1.0 μm creates a difficult control problem and a high opacity even at low concentrations.[20] A low energy scrubber reduces emissions to 0.625 g/kg at a concentration of 0.098 g/m^3.[17]

By replacing the 64 prill tower spray heads with two metal shroud enclosed spray heads, thereby creating a quiescent zone which decreases fume and micro-prill formation, ESSD Chemical, Canada, has achieved significant reductions in ammonia and ammonium nitrate emissions (Table 15) at a cost of $25,000.[35]

TABLE 15. EMISSIONS FROM ESSO CHEMICAL CANADA SPRAY HEAD WITH SHROUD PRILL TOWER MODIFICATION[35]

Condition	Ammonium nitrate kg/metric ton product	Ammonia kg/metric ton product	Gas velocity (m/sec)	Gas volume (m^3/min)
Before modification	6.5	0.18	2.04	7,500
After modification	1.2	0.10	4.24	15,500

5.3.4 Granulation

Drum granulation equipment is typically controlled by a Joy Turbulaire scrubber. Figure 17 illustrates a Type D Joy Turbulaire impingement scrubber and C&I Girdler granulation process.[36] Emission rates typically quoted in the
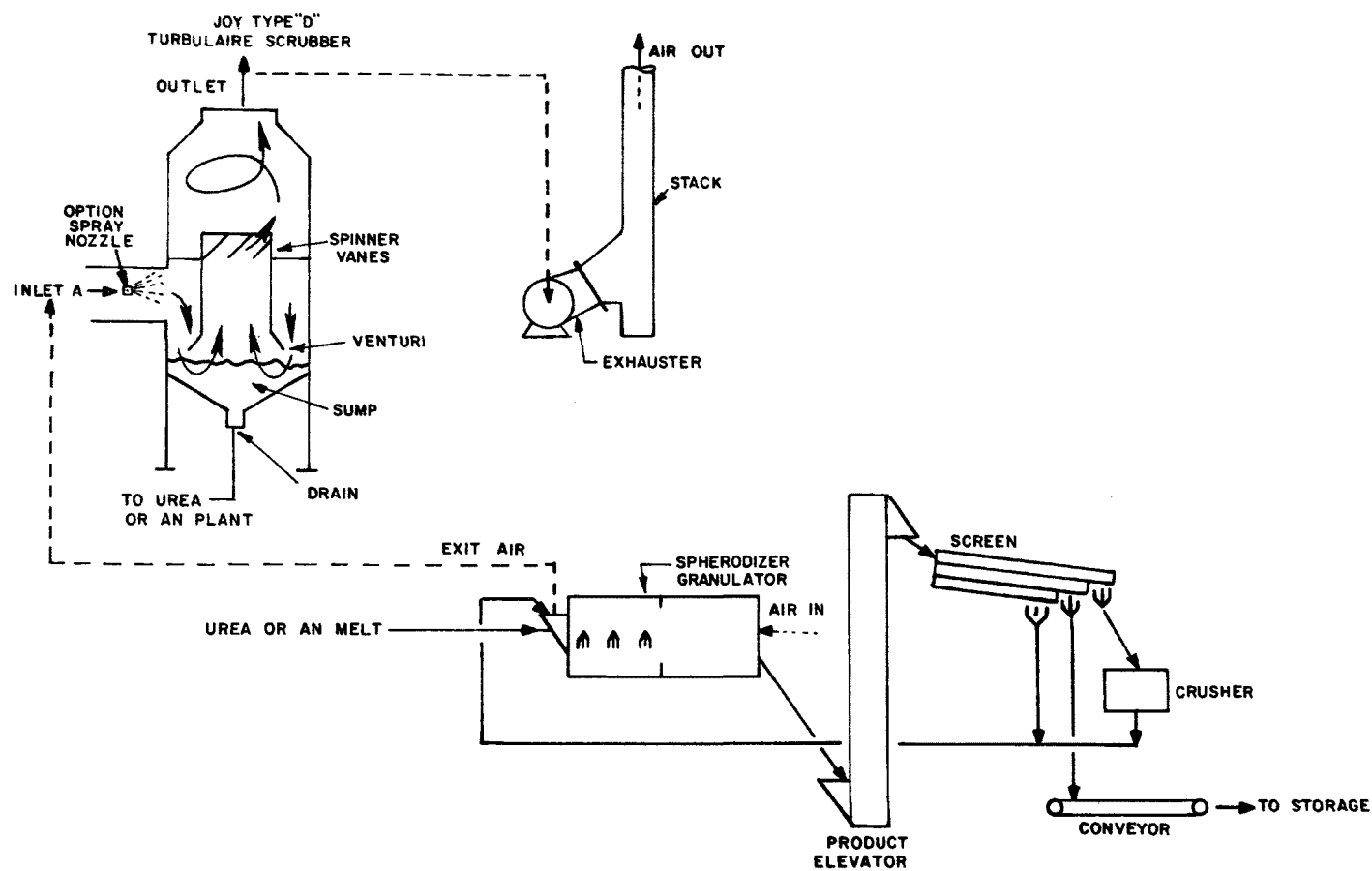
Figure 17. Joy Type D Turbulaire impingment scrubber and C&I Girdler granulation process.[36]

industry range from 0.05 to 0.5 g/kg of product. A high collection efficiency is achieved because particulate size is largely greater than 10 μm.[37]

Foster-Wheeler developed an evaporative scrubber system (Figure 18) to reduce or eliminate the particulate matter in the effluent airstream associated with the production of ammonium nitrate prills or granules and to eliminate the process condensate.[38] In addition, this system makes fertilizer recovery from effluent streams econimically viable. One disadvantage is that this type of scrubbing does not remove the "fume" from a high density ammonium nitrate plant, however, if high efficiency particulate removal systems are incorporated, such as those mentioned earlier, submicron particles could be eliminated.

5.3.5 Predryers, Dryers, Coolers and Product Handling

Predryers, dryers and coolers are usually very similar except that warm air is used for predryers/dryers and cold air is used for coolers. Wet scrubbers are practically the only type of equipment used to control emissions from predryers, dryers and coolers. Emission rates for low energy scrubbers controlling predryers, dryers and coolers range from 0.02 to 0.145 g/kg of product. Emissions from product handling, as discussed in Section 5.2.6, are negligible.
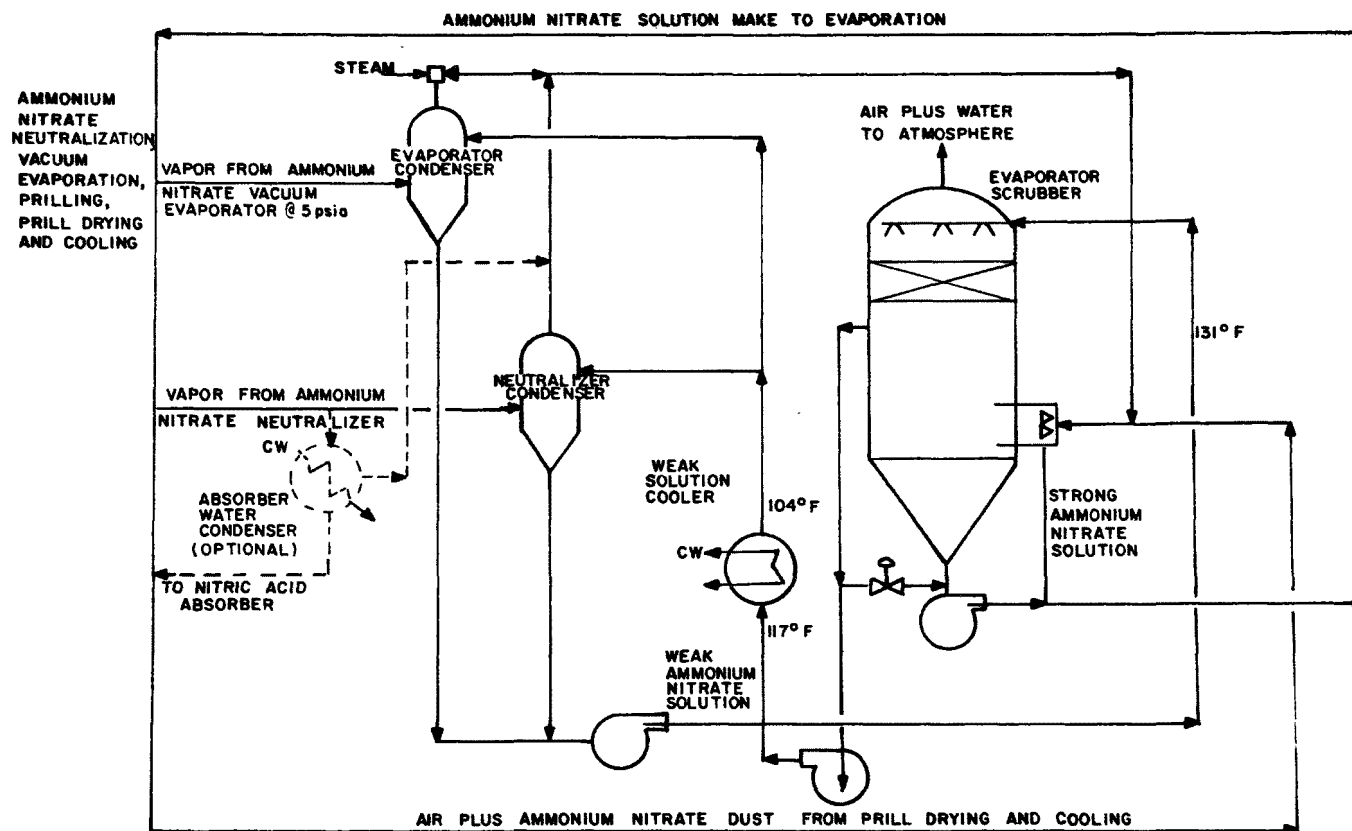
Figure 18. Evaporative scrubbing system for low density ammonium nitrate prills.[38]

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6.0 UREA

6.1 PROCESS DESCRIPTION FOR UREA PRODUCTION

Urea is presently being produced at 44 plants located in 23 states. Present annual capacity (340 days/year at maximum daily capacity) is approximately 5.7×10^6 short tons of urea solution in terms of 100 percent urea. The industry typically operates between 80 and 90 percent capacity.

Urea is produced by reacting ammonia (NH_3) and carbon dioxide (CO_2) to form ammonium carbamate ($NH_4CO_2NH_2$). The carbamate is then dehydrated to yield urea. The reactions can be represented as follows:

$$2NH_3 + CO_2 \rightleftharpoons NH_4CO_2NH_2 \tag{10}$$

$$NH_4CO_2NH_2 \rightleftharpoons NH_2CONH_2 + H_2O \tag{11}$$
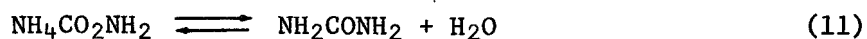
The final product is distributed as either a urea solution having a concentration of 70 to 75 percent urea, or a solid.[39]

The overall urea manufacturing process can be broken down into the following steps:

1. solution formation

2. solution concentration

3. solids formation

4. solids cooling

5. coating and/or additives

6. screening

7. bagging, storage, bulk shipping

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6.1.1 Solution Formation

There are three methods for producing urea: (1) once-through processes, (2) partial recycle processes, and (3) total recycle processes. The most important of these three classes is the total recycle process. The Snamprogetti process and the Stamicarbon CO_2 stripping process appear to be the best candidates for new plants. A less popular method is the Mitsui Toatsu D improvement upon the Toyo-Koatsu process, a version of conventional total recycle process. Additional improvements could make this process competitive with the Snamprogetti and Stamicarbon process. Figure 19 is a schematic diagram of a typical Stamicarbon CO_2 stripping process, Figure 20 of the Snamprogetti process, Figure 21 of the Toyo-Koatsu process, and Figure 22 of the Stamicarbon total recycle process for urea solution production.

6.1.2 Solution Concentration

There are two methods of concentrating urea solution prior to solid formation: crystallization and evaporation. The method chosen depends on the acceptable biuret ($H_2NCONHCONH_2$) level, and impurity formed by a side reaction. To obtain technical grade urea (< 0.4 percent biuret), more expensive crystallation is necessary.[39]

Crystallization is performed in a tank equipped with a heat exchanger to maintain a solution temperature of 57°C, evaporation in one or two (in series) falling film heat exchangers operated under vacuum.

6.1.3 Solids Formation

There are essentially three methods of producing solid urea: prill towers, drum granulators, and pan granulators. About 18 drum granulators are in operation in the United Stated. Drum granulation accounts for roughly 50 percent of the solid urea produced.[40] The remaining 50 percent is produced mainly by

prilling with only a small percentage produced by pan granulation. Pan

granulation is a recent development and its overall cost is somewhat less than

drum granulation.

Urea prilling and drum granulation processes are similar to those for

ammonium nitrate described above in Section 5.1.3. The pan granulator consists

of a tilted, rotating, circular pan. Feed material deposited at the top falls

through a fine spray of liquid urea and the larger granules thus formed spill

over the lower edge of the pan onto a conveyor belt. TVA has developed a low

temperature (100 to 107°C) and Norsk-Kydro a high temperature (113 to 121°C)

process. Cooling is typically accomplished in a rotary drum cooler.

6.1.4 Product Finishing and Handling

The principal means of product size control is screening. Oversize and

under size material is removed from the product size solids and recycled.

The primary purpose of coatings and additives is to reduce caking and dust

formation. The most common additives are formaldehyde and phosphate-based com-

pounds. In most plants, material commonly is transported by conveyors from one

process step to another. Urea shipment is either by bag or bulk. The trend

has been toward bulk handling. Solution bulk shipment of urea is in tank cars.

6.2 EMISSIONS AND EFFLUENT SOURCES

Process steps responsible for air emissions in urea production are:

(1) solution formation; (2) concentration; (3) prilling; and (4) granulation.

Sources of wastewater effluent in urea manufacturing are evaporator exhaust and

filtrate from the concentration of urea solution when a crystallizer is used.

In addition, there is a potential for fugitive air emissions and water effluents

from vents, seals, compressors, storage facilities, relief valves and spills.

Table 16 shows air and water pollutants and control requirements to reach the

acceptable severity factor of 0.05 for various process operations.
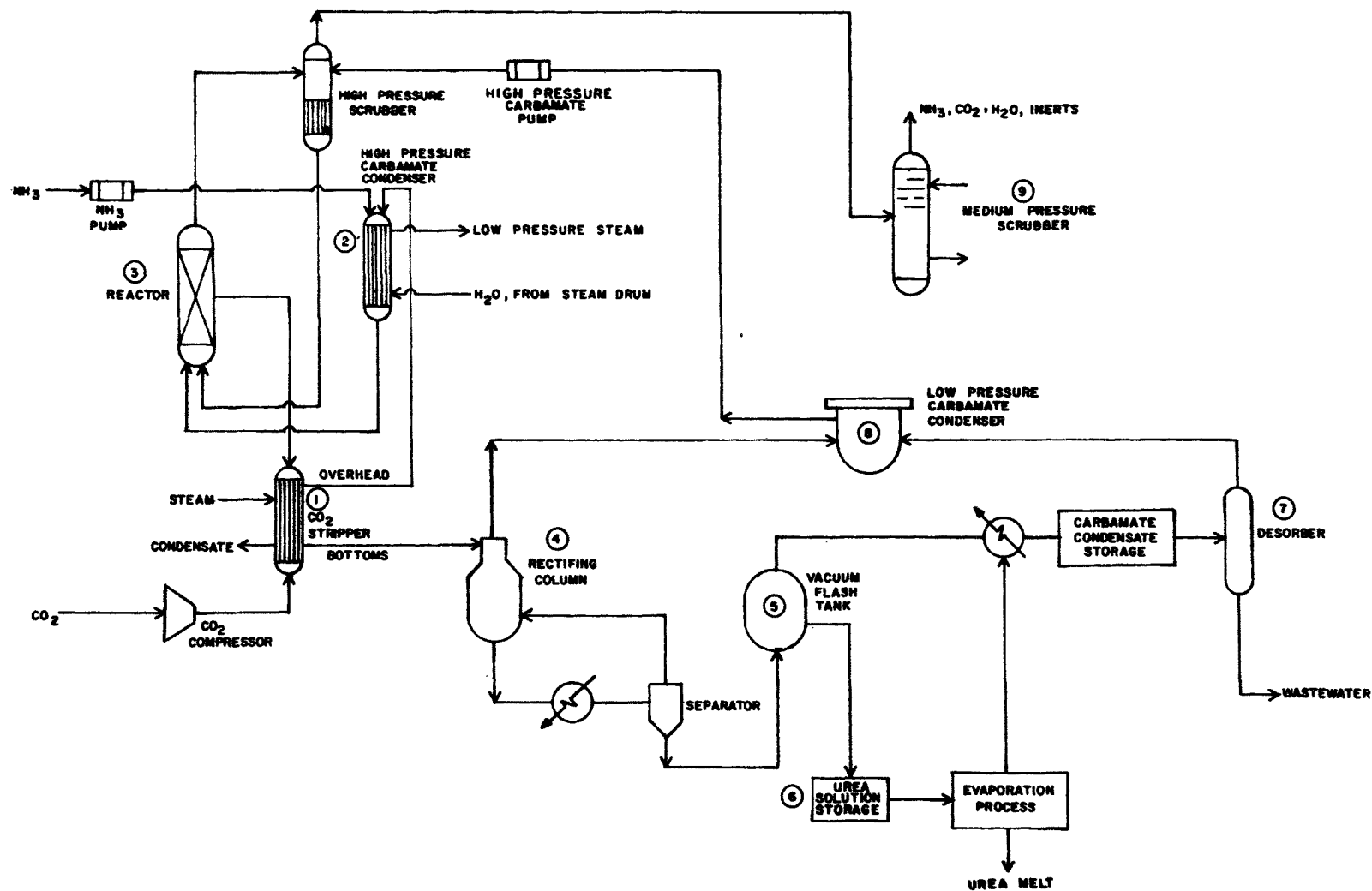
Figure 19. Stamicarbon CO_2 stripping process for urea production.
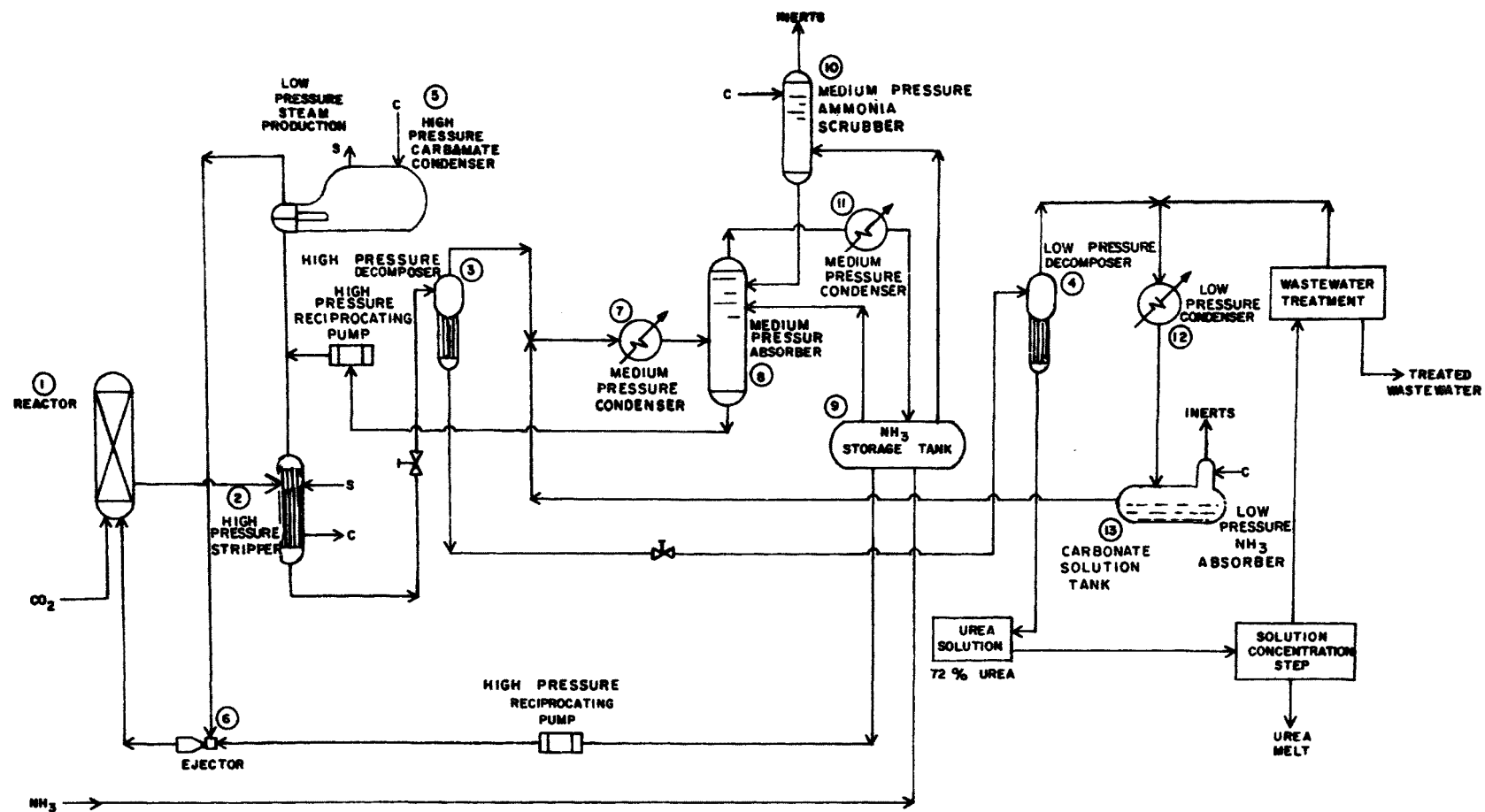
Figure 20. Snamprogetti process for urea production.
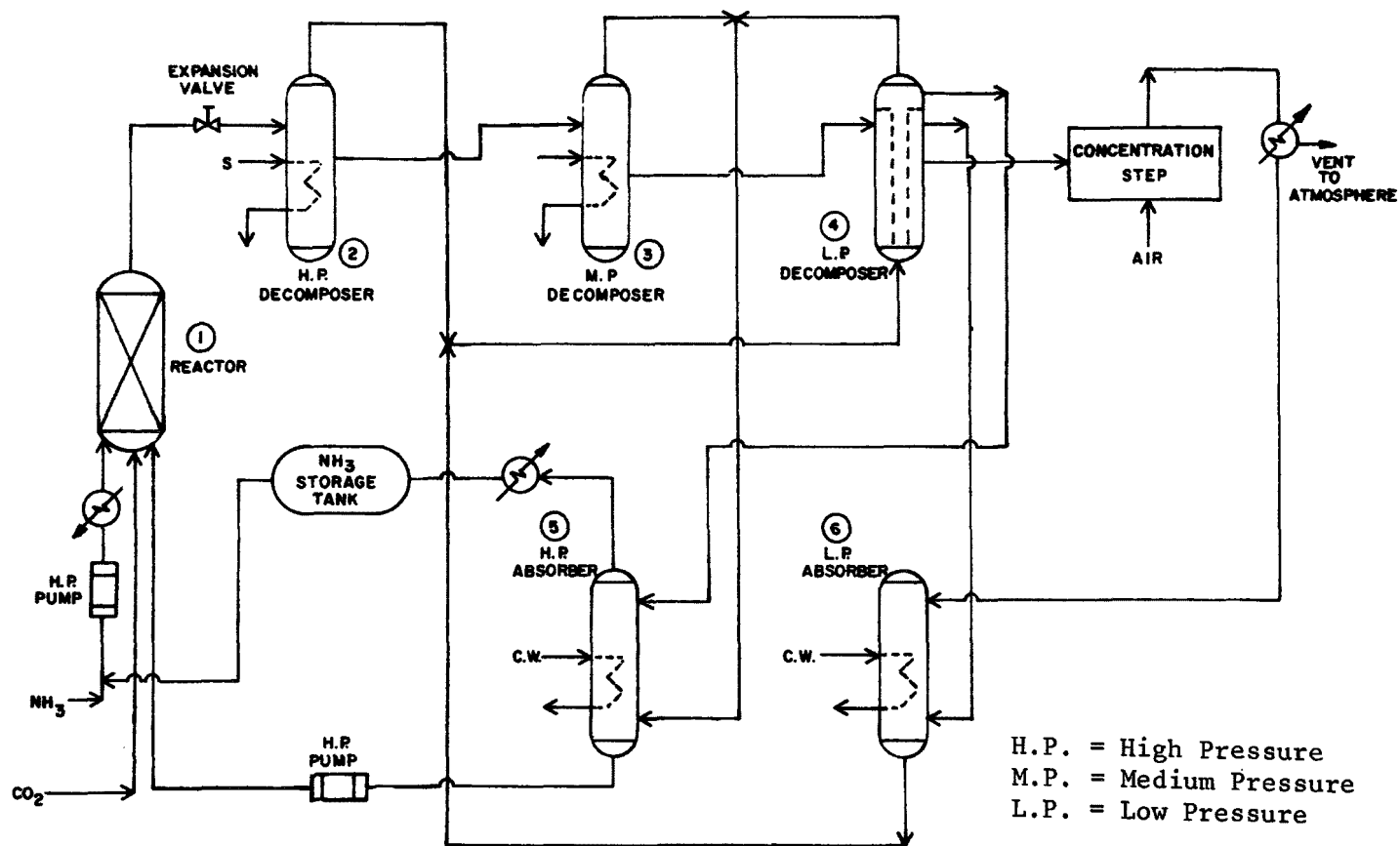
Figure 21. Toyo-Koatsu method in urea production.
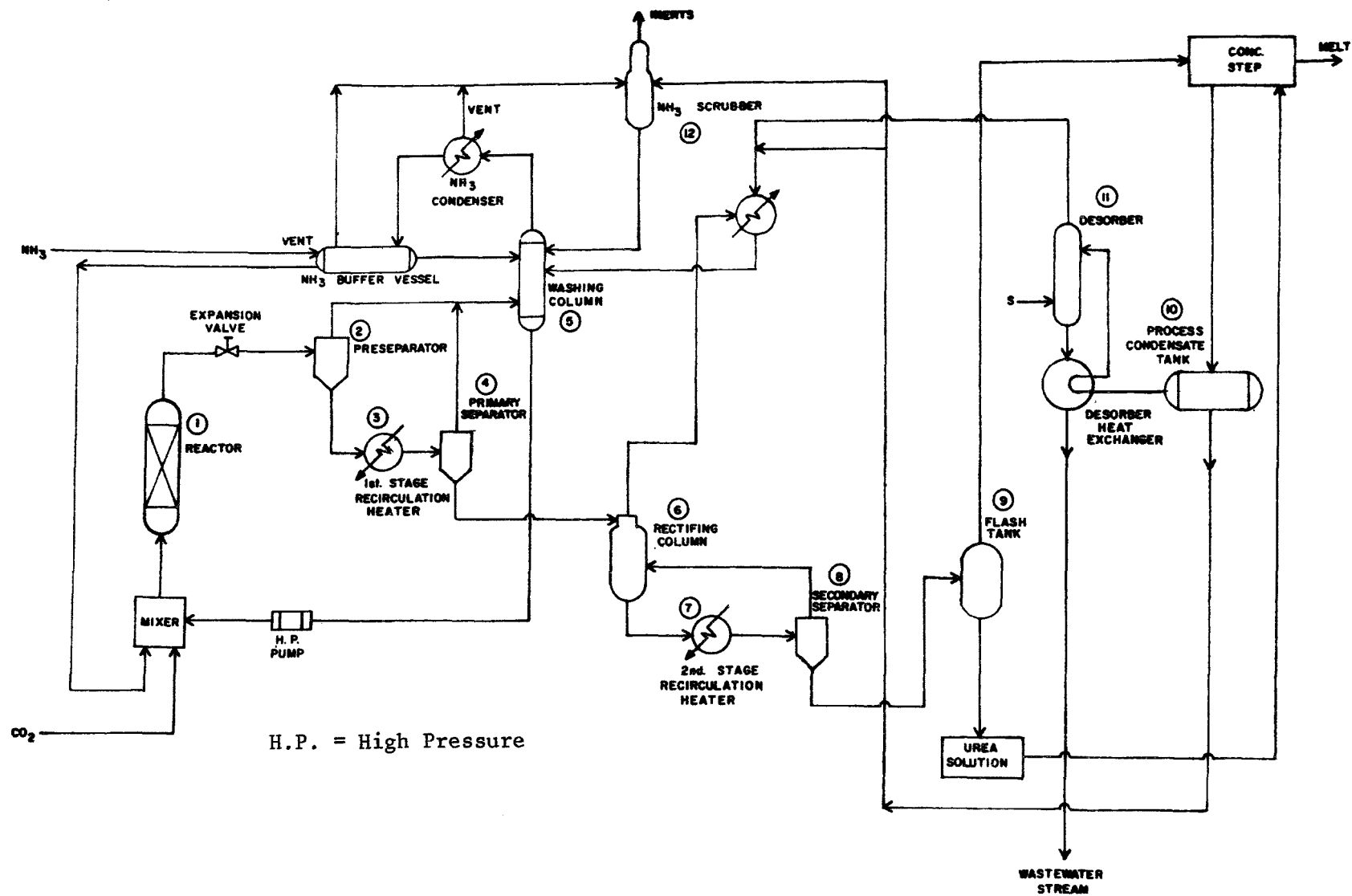
Figure 22.   Stamicarbon total recycle.

H.P. = High Pressure

TABLE 16. AIR AND WATER POLLUTANTS AND
CONTROL REQUIREMENTS FOR UREA
PRODUCTION[5,20]

Source urea	Pollutants	Average plant	
		Source severity	Required control percent*
Air sources			
Evaporator	NH_3	8.8	99.43
	Part.	0.12	58.3
Prill tower	NH_3	0.51	90.2
	Part.	0.94	94.7
Granulator	NH_3	1.27	96.1
	Part.	0.1 to 0.24	50 to 80
Water sources			
Including ammonia†	NH_3-N	0.161	69.0
	$NH_4^+ -N$	0.0083	–
	ORG-N	0.0025	–

*To achieve source severity = 0.05

†Sources are not identified. Data are for combined
plant effluent.

6.2.1 Solution Formation

Figure 19 is a schematic of a Stamicarbon CO_2 stripping process for urea production. The major emission sources of the Stamicarbon CO_2 stripping process are (1) the airstream from the medium pressure scrubber, (2) the wastewater stream from the desorber, and (3) the scrubbing fluid leaving the medium pressure scrubber. The air emissions and water effluents contain NH_3 and CO_2. In addition, the water effluent contains urea.

The emission sources of the Snamprogetti process are two airstreams, each treated by a water scrubber and one wastewater stream leaving the water treatment section. The primary emissions in the airstream are NH_3, CO_2, and urea.

The primary emissions from the Toyo-Koatsu Process are NH_3, CO_2, and urea.

Major emission sources in the Stamicarbon total recycle process are (1) gases vented through the NH_3 scrubber containing NH_3 and excess CO_2, and (2) wastewater stream containing NH_3, CO_2, and urea.

In summary, most solution processes have emission sources where inerts such as unreacted N_2 and H_2 are vented. Usually, these are extremely minor emission sources - low airflow and low NH_3 concentration. The solution formation step is not one of the major sources of air contamination in this industry.[4]

6.2.2 Solution Concentration

Crystallization under vacuum is maintained by a steam ejector on an overhead vent. The system has a minor emission source which contains NH_3, CO_2, and water vapor. In addition, wastewater effluent from the ejector contains NH_3, CO_2, and urea.

Typically, the evaporators are also operated under a vacuum; again steam

ejectors being a common method of applying vacuum. Emissions are the same as

those previously mentioned for the crystallizer. In the case of atmospheric

evaporators, the vapor stream exiting the exchanger contains NH_3 and CO_2.

This stream is usually recycled to the solution formation process. The air-

swept evaporators produce an airstream contaminated with NH_3, CO_2, and urea

particulates which is also usually returned to the process.

6.2.3 Solid Formation

Prilling of urea has emissions analagous to the prilling of NH_4NO_3 (see

above) with the fume being particularly difficult to eliminate.[41] Emissions of

NH_3 can result from urea decomposition. Uncontrolled emissions are typically

1.0 to 2.0 kg/metric ton of urea product for particulates and roughly 0.7 to

1.0 kg/metric ton urea for ammonia emissions.[39]

The cooling air passing through the drum granulator entrains 15 to 20

percent of the product, but this airstream is smaller (approximately one-third

the airflow used in prill towers) and easier to treat than corresponding prill

tower airflows.[25] Scrubbers are an integral part of the process. Drum granu-

lator emissions are relatively low, generally in the range of 0.05 to 0.50 kg/

metric ton product. Ammonia emissions are 0.1 t0 0.4 kg/metric ton product.[23]

Emissions from pan granulators are reportedly very low. Treatment is

standard procedure. Overall emissions, therefore, are comparable to those from

drum granulators, that is to say, 15 to 20 percent of the urea melt ends up as

potential particulate emissions.[22,23,42]

6.2.4 Product Finishing

Urea product finishing covers cooling, screening, incorporation of addi-

tives, and coating. As the cooling drum rotates, particulates are entrained

However, this exhaust stream from the cooling drum is typically treated. Particulate emissions from this unit can be expected to be lower than from a drum granulator.

Emissions from screening are difficult to assess but are believed to be generally of a fugitive nature and low.

6.2.5 Product Handling

It is also somewhat difficult to predict or determine emissions from urea product handling activities. A value of 0.12 kg NH_3/metric ton 100 percent urea upon loading into tank cars has been estimated on the basis of the equilibrium vapor pressure NH_3 over 70 percent urea solution.[43] For bagging operations, a "worst case" value of 0.15 kg particulates/metric ton of urea handled had been calculated on the basis of the fraction of fines.[39]

6.3 PRESENT AND POTENTIAL CONTROL TECHNIQUES

The major emission point from urea production is in the solid formation step. Generally speaking, controls have not been applied because no state standards are violated. However, the above examination of source severity factors for air emissions and water effluents for urea indicates a need for pollution control.

6.3.1 Solution Formation Process

Process vents from the solution formation process are often scrubbed to recover ammonia and other chemicals. There are no data available regarding the control or even the occurrence of particulate emissions from the solution production process, and Monsanto Research Corporation appears to conclude that there are no particulate emissions from the solution production process.[39]

6.3.2 Solution Concentration Process

In the solution concentration process, evaporator emissions may be controlled to recover ammonia and/or urea to meet state emission regultions.

Data collected as part of this study indicate that about 40 percent of the urea evaporators are controlled by condensation, 10 percent by wet scrubbing, and 5 percent by demisting. The remaining 35 percent of the urea evaporators are currently operating without control equipment.

Some evaporators are controlled by Venturi scrubbers. Available data show a particulates emissions rate, after such control, of 0.24 g/kg.[17] The exhaust from a wet-scrubber-controlled evaporator may be recycled in some instances, thus eliminating both particulate and ammonia emissions. The literature for a Wet scrubber-controlled evaporators show ammonia emission rates reduced to 1.7 g/kg.

6.3.3 Prill Towers

Approximately 45 to 50 percent of the plants use wet scrubbers for particulate emission control for urea prill towers. The other plants modify production rates to meet state regulations. Many facilities can meet existing mass emission rate regulations but have difficulty with opacity standards because of the relatively large fraction of fine particles.

Available emission data for wet scrubber-controlled urea prill towers are presented in Table 17. For "uncontrolled" towers, data show a typical emission rate of 1.6 g/kg.[17] The ammonia emission factor for prill towers is 0.4 g/kg. Many facilities add 0.4 g of formaldehyde per kilogram of urea to the melt before prilling. No data on formaldehyde emissions from prill towers are available.

6.3.5 Granulator

Emissions from drum and pan granulators are controlled by wet scrubbers. Approximately 10 to 20 percent of the feed would be lost if the scrubber were not used, so the scrubber may be considered as process as well as pollution

TABLE 17. SUMMARY OF EMISSION DATA FOR
PRILL TOWER CONTROLLED BY
WET SCRUBBERS*[17]

Facility	Emissions		
	g/kg product	g/m^3	g/sec
C	0.058	0.0071	0.18
D[†]	0.43	0.032	4.5
D[‡]	0.375	0.020	4.2
E	0.425	0.048	3.2

*Test data not yet validated.

[†]Fertilizer grade urea.

[‡]Feed grade urea.

control equipment. Emission rates from granulators are 0.25 g NH_3/kg and 2 g particulates/kg.

The primary purpose of the Foster-Wheeler evaporative system (Figure 23) is to eliminate particulate matter from prilling and granulation production processes and to eliminate the discharge of nitrogen bearing process condensate into receiving waters. Similarly the Vistron urea pollution control system (Figure 24) is also designed to abate both air and water pollution.

The pan granulator is more amenable to effective particulate emission control than prill towers and Figure 25 shows such a system incorporating a hood to collect fume and a centrifugal scrubber.[44]

Urea plant process condensate can be treated by urea hydrolysis. This reconverts the urea back to NH_3 and CO_2 which can be vented to the atmosphere or, preferably, recycled.

Several hydrolysis stripper units are commercially available and operating in domestic urea plants. The Technip SD unit is designed for influent concentrations up to 15 percent ammonia and 3 percent urea (by weight) with effluents
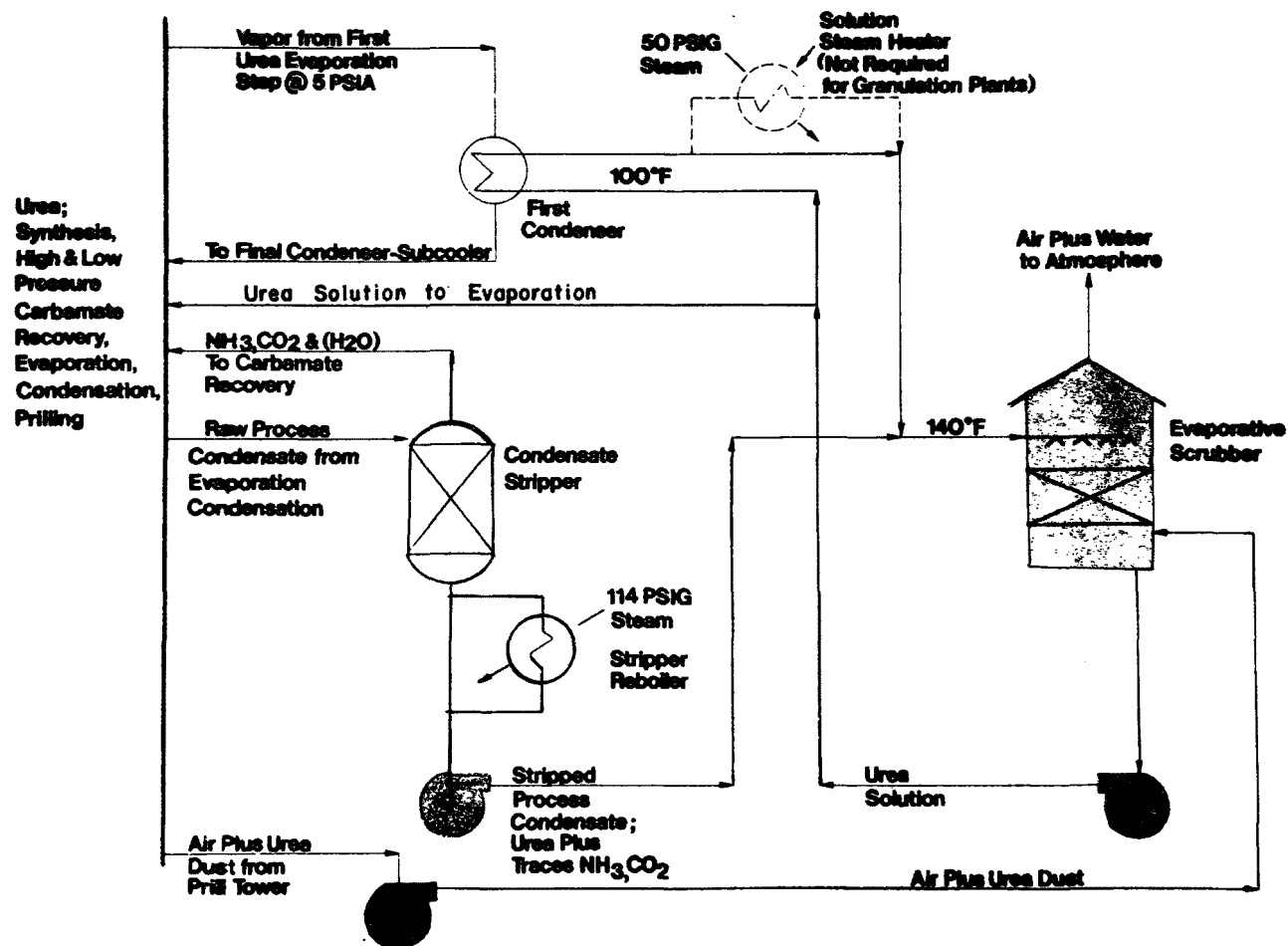
Figure 23. Evaporative scrubbing system, urea plant, prills or granules.[38]

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Urea Prill Tower
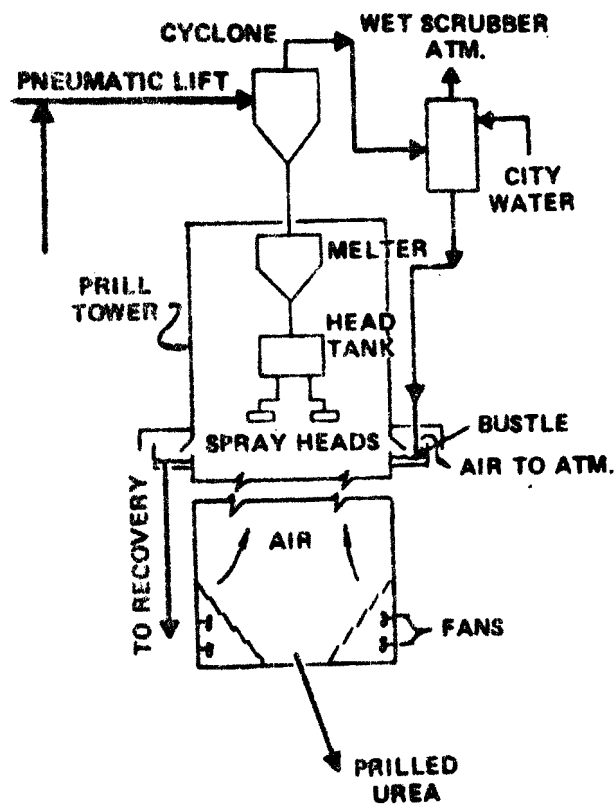
Figure 24. Vistron pollution control system.[43]

95 PERCENT SOLUTION

FUME HOOD

GRANULATED FERTILIZER

PAN GRANULATOR

FUME DUCT

MAKE-UP WATER

SURGE TANK

EFFLUENT CONCENTRATED IN SCRUBBERS FOR REUSE

STACK

C

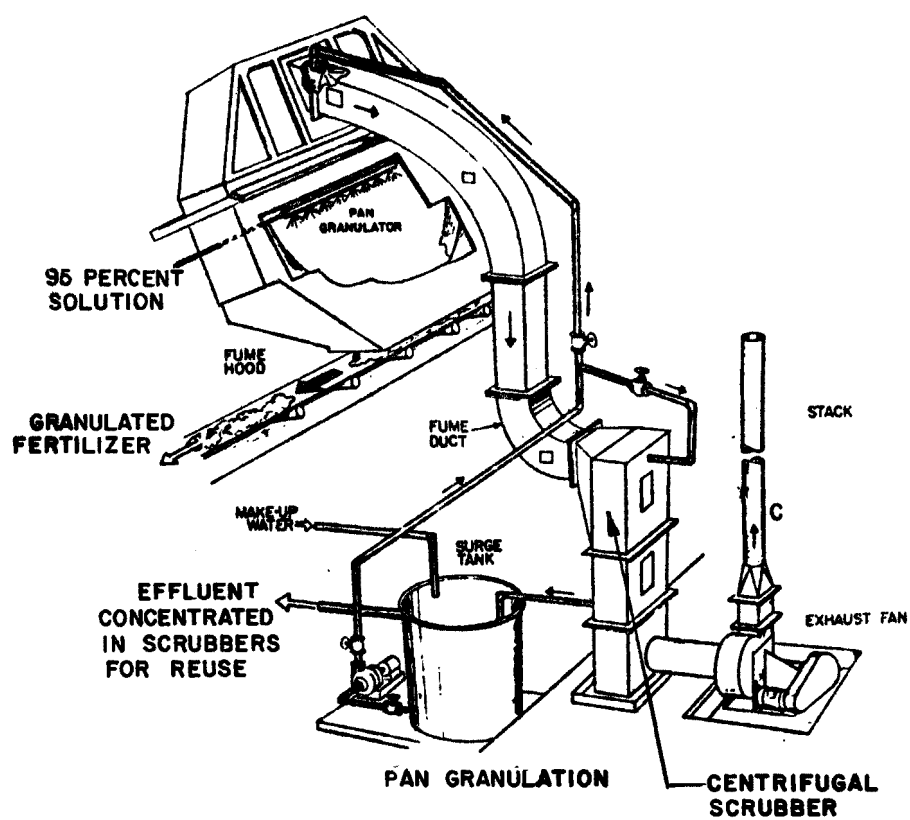EXHAUST FAN

PAN GRANULATION

CENTRIFUGAL SCRUBBER

Figure 25. Emission control system.[44]

of 30 g/m^3 (ammonia and urea combined).[45] Vistron, also has several operating units designed for comparable influent concentrations and effluents of 60 g/m^3 urea and 30 g/m^3 NH$_3$. This system was also discussed in Section 6.3.6.

Certain approaches to abatement of water pollution are applicable or of potential applicability to the fertilizer industry generally as well as to urea production.

6.3.5 Predryers, Dryers, Coolers, and Product Handling

As discussed in Section 5.3.5, emission from these operations are extremely low.

6.3.6 Other Water Effluent Treatment Approaches

Conversions of nitrogeneous compounds to nitrogen gas via biological nitrification/denitrification has been investigated and applied to some extent to municipal and industrial wastewaters.

Biological treatment can also reduce the methanol content of ammonia plant wastewaters. Some plants only apply nitrification in conjunction with oxidation of methanol and other organic matter. In this case, ammonia is converted to nitrates and nitrites which are much less toxic to receiving waters. Typical performance of this type of aeration lagoon is shown in Table 18.

TABLE 18. PLANT TREATMENT OF AMMONIA PLANT
PROCESS CONDENSATE[8]

Component	Process condensate bio-pond influent mg/ℓ	Bio-pond effluent mg/ℓ
Ammonia	800 – 1100	100 – 650
COD	2200 – 2800	100 – 400
BOD	1600 – 2800	150 – 250
pH	8 – 9	8 – 8.5

A continuous ion exchange process marketed by Chemical Separations Corporation (CHEM-SEPS) is currently in use at 10 or more plants for ammonium nitrate bearing wastes. A cation exchange unit removes ammonium ions and anion exchanger unit the nitrate ions. Typical waste effluents and treated water discharge are shown in Table 19.

It is technically feasible to remove nitrogeneous compounds from plant wastewater by breakpoint chlorination or by reverse osmosis, but these systems are not used due to high costs relative to other available treatment processes. Total nitrogen removal for these systems is on the order of 80 to 95 percent.

When faced with stringent effluent standards, most new and existing nitrogen fertilizer plants first minimize the quantity of wastewater requiring treatment commonly by recycling. In some cases, effluents may be recycled to an adjacent plant as illustrated in Figure 26, showing recylce of condensed neutralizer exhaust from an ammonium nitrate plant to a nitric acid facility.

TABLE 19. REPRESENTATIVE WASTE AND ION EXCHANGE
TREATED WATER ANALYSIS[46]

Component	Influent (g/m^3)	Effluent (g/m^3)
Ammonia (NH_3)	340	2 to 3
Magnesium (Mg^{++})	4.8	–
Calcium (Ca^{++})	60	–
Sodium (Na^+)	0	–
Nitrate (NO_3^-)	1,240	7 to 11
Chloride (Cl^-)	53	–
Sulfate ($SO_4^=$)	72	–
pH	5 to 9	5.9 to 6.4
Silica (SiO_2)	15	15

Ammonium nitrate removal is 99.4%

TO VENT SCRUBBER

MAKE UP ACID
FOR
NITRIC ACID

TAILGAS

COOLING WATER

CONDENSER

COOLING WATER

ABSORPTION
COLUMN

NITRIC ACID

CONDENSED
REACTOR VAPOR
WATER
PROCESS
RECYCLE

AMMONIA

SURGE
TANK

COOLING
WATER
FOR ABSORBER
TRAYS

REACTOR

TO CONCENTRATOR

GAS FROM CONVERTER
AND HEAT EXCHANGERS

PRODUCT
NITRIC ACID

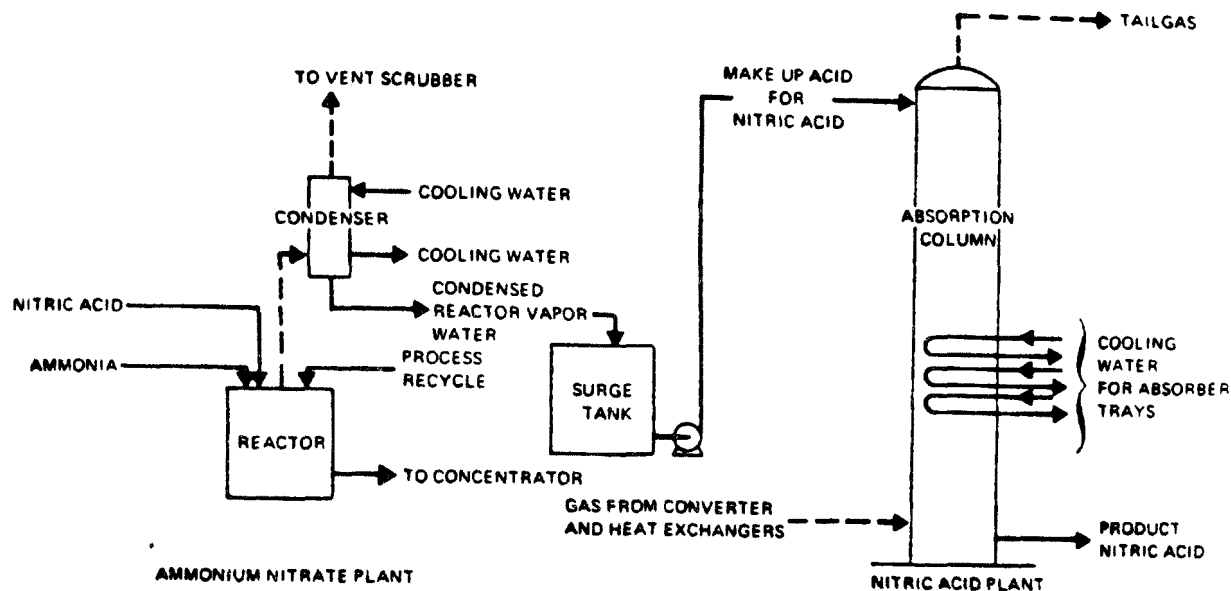AMMONIUM NITRATE PLANT

NITRIC ACID PLANT

Figure 26. Ammonium nitrate effluent utilization.[18]

Finally, such obvious abatement precautions for preventing the escape of washdown, storm run-off, and flushing of railcars and tank trucks waters off the site as constructing curbs, drains and storage facilities to contain these wastewaters for either treatment or recycle to scrubber or process solutions should be mentioned.

A review of effluent data on file at State water pollution control agencies in Louisiana and Texas (which accounts for about 50 percent of domestic nitrogen fertilizer facilities) to identify plant effluent control techniques was of limited usefulness because many plants are located within a manufacturing complex combining wastewater from a number of different plants and the uniqueness in individual plant design. At least one-half of the plants in Texas disposed wastewaters by either deep well injection or sale as farm irrigation water. Several plants in both states sent wastewaters to a biological treatment pond in conjunction with wastes from other manufacturing processes.

7.0 MEETING EFFLUENT GUIDELINES

Effluent guidelines for existing urea and ammonium nitrate plants and standards of performance for new plants were promulgated by EPA on April 26, 1978.[47] Based on a survey of about 80 percent of all ammonium nitrate and urea plants, effluent levels achievable by best conventional pollutant control technology (BCT) and best available technology economically available (BAT) were identified. The BCT guidelines were first promulgated on April 8, 1974, but were modified in 1978 to reflect industry comments and incorporate additional data. Under the Clean Water Act of 1977, industrial point sources must achieve effluent levels corresponding to BCT by 1 July 1977 and BAT by 1 July 1984. These effluent guidelines and also standards for new sources are summarized in Table 20.

Nitrogen fertilizer plants, equipment vendors, industry trade associations and research groups were contacted to discuss the need for improved control technology to meet the effluent guidelines. Some contacts inevitably felt the 1984 BAT guidelines were too stringent. EPA's position and response to these comments is addressed in the effluent guidelines of April 26, 1978, in the Federal Register.[47] Standards were relaxed somewhate from those originally proposed in 1974.[9] A few sources felt ion exchange technology for meeting ammonium nitrate BAT provisions in 1984 was not feasible for solids-producing plants because of disposal problems for resin regenerate solution. This issue was also addressed by EPA in promulgating the 1978 guidelines, indicating feasibility of concentrating regenerate for recycle to the process.

TABLE 20. EFFLUENT GUIDELINES AND STANDARDS OF APRIL 26, 1978[47]

Type plant	Effluent parameter	Effluent limitations kg/1000 kg product*	
		Maximum daily	Maximum for average of daily values for 30 consecutive days
BCT (1977)	Urea-solutions:[†] Ammonia-N	0.95	0.48
	Organic-N	0.61	0.33
	pH	6.0 - 9.0	6.0 - 9.0
	Urea solids: Ammonia-N	1.18	0.59
	Organic-N	1.48	0.80
	pH	6.0 - 9.0	6.0 - 9.0
BAT (1984)	Urea-solutions: Ammonia-N	0.58	0.27
	Organic-N	0.45	0.24
	Urea-solids: Ammonia-N	0.53	0.27
	Organic-N	0.85	0.48
New sources	Urea-solutions: Ammonia-N	0.53	0.27
	Organic-N	0.45	0.24
	pH	6.0 - 9.0	6.0 - 9.0
	Urea-solids: Ammonia-N	0.53	0.27
	Organic-N	0.86	0.46
	pH	6.0 - 9.0	6.0 - 9.0
BCT (1977)	Ammonium nitrate:[‡] Ammonia-N	0.73	0.39
	Nitrate-N	0.67	0.37
	pH	6.0 - 9.0	6.0 - 9.0
BAT (1984) and New sources	Ammonium nitrate:[‡] Ammonia-N	0.08	0.04
	Nitrate-N	0.12	0.07

*Based on 100 percent product.

[†]Urea guidelines do not include discharges from shipping losses, precipitation runoff outside of battery limits and cooling tower blowdown.

[‡]Applies to both solids and solution plants, but excludes shipping losses, precipitation runoff from outside of plant battery limits, cooling tower blowdown and plants which totally condense neutralizer overheads.

Several sources commented on problems of pH control (also addressed by EPA) and disposal of cooling tower/boiler blowdown and regenerate solution from feedwater ion exchange units. These latter problems are not specific to nitrogen fertilizer facilities, but rather confront industry in general.

Overall the ability to meet EPA effluent guidelines has been demonstrated by the plants selected as the basis for setting the standards.

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16. ABSTRACT The report gives results of an evaluation of pollution control needs for the nitrogen fertilizer industry. It includes descriptions of ammonia, ammonium nitrate, and urea manufacturing processes and evaluations of existing processes, pollution control techniques, and emissions. It also evaluates existing and potential pollution control techniques. processes, and alternative feedstocks as they apply to manufacturing ammonia, ammonium nitrate, and urea for additional pollution control and emission reduction. Air emission and water effluent controls were examined for each process. Source severity factors were used to evaluate the environmental significance of emission sources. The most significant emission problems associated with the industry are: (1) oxides of nitrogen from the addition of purge gas and overhead to primary reformer firing in ammonia synthesis, and (2) particulates from prilling towers in ammonium nitrate and urea production. Further work is needed to develop adequate control techniques for these pollutant sources. All other pollutant sources for this industry can be adequately controlled by existing technology.

17. KEY WORDS AND DOCUMENT ANALYSIS

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