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UNITED NATIONS INDUSTRIAL DEVELOPMENT ORGANIZATION
Vienna International Centre, P.O. Box 300, 1400 Vienna, Austria
Tel: (+43-1) 26026-0 · www.unido.org · unido@unido.org

05657

Distr.
LIMITED

ID/WG.175/10
23 July 1974

ORIGINAL: ENGLISH

United Nations Industrial Development Organization

Expert Group Meeting on Minimizing Pollution from Fertilizer Plants

Helsinki, Finland, 26 - 31 August 1974

SOLUTIONS FOR MINIMUM POLLUTION IN NITROGEN FERTILIZER PLANTS[1]

E. C. Bingham*

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* UNIDO Consultant

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INTRODUCTION

The manufacture of nitrogen fertilizers has long led to serious pollution of all segments of the environment. The obnoxious consequences of nitrogenous poisoning of air and water has ranged from respiratory disorders in humans, plant life destruction, eutrophication of lakes, to toxicity to man and stream life. Ill effects have also resulted from disposal of solid wastes, noise from factory equipment and heat discharged into receiving waters by process cooling waters.

It is the purpose of this paper to present an in-depth study of solutions for achieving minimum pollution in water, air, solid waste, noise, and thermal - in nitrogen fertilizer manufacturing plants. The study, based largely on the personal experiences of the author from nearly ten years' activity as director of environmental affairs for a large manufacturer, includes evolution of pollution problem areas, recognition and definition of the problems, and development of a program for solution or avoidance of pollution by selective use of process designs. In-plant modifications which reduce the pollutional input to the environment are discussed, including the application of procedures such as product recovery and recycle as pollution control measures. Emphasis is placed on extensive research efforts employed to apply principles of physical, chemical and biological treatment to remove large quantities of nitrogenous compounds from plant waste discharges. The use of sophisticated systems such as ion exchange for concentrating contaminants and clarifying waste streams will be discussed, together with the stressing of water conservation and water reuse in manufacturing processes. Several systems are to be explored for the control of air pollution emanating from the production of nitric acid and ammonium nitrate including inquiry into adsorption by molecular sieves. Discussion of solid waste pollution solutions will include waste resulting from fertilizer processing.

I. NITROGEN FERTILIZERS

A. Nitrogen as plant nutrient

In Nature's plant life cycle, nitrogen is needed in larger quantities for good plant growth than any other nutrient. In the United States, as in most parts of the world, nitrogen consumption has exceeded both phosphate and potash on a tonnage basis. With the development of the Haber-Bosch process for ammonia production in the early 1900's, atmospheric nitrogen became the principal source of fertilizer nitrogen. The economic development of this process for production of ammonia from atmospheric nitrogen and hydrogen, principally from natural gas, has resulted in ammonia becoming the most important fertilizer material in the United States.

Not only is ammonia used on a very large scale as a fertilizer in the United States, but it also serves as a raw material for the manufacture of almost all other nitrogen-containing fertilizers. On a tonnage basis, the most important nitrogen fertilizers, in addition to ammonia, are ammonium nitrate, ammonium sulfate and urea, as well as direct application solutions containing the various nitrogen fertilizer elements. United States consumption of these basic materials in fertilizer applications is shown in Figure I. The data presented are for total consumption of each material and include tonnages used in direct application and in the preparation of mixed and solution fertilizers.

As can be seen from Figure I, ammonium sulfate consumption in the United States is fairly stable with no growth in production facilities indicated. By-product sources of ammonia (such as coke oven gas) and sulfuric acid (spent refinery acid) account for a large portion of the ammonium sulfate production. As a result, there are a large number of relatively small plants producing this fertilizer. Many of these are operated by steel companies to utilize the ammonia from coke oven gas. For these reasons, ammonium sulfate is not normally produced in conjunction with other nitrogen products in what has become known as nitrogen fertilizer manufacturing complexes.

B. Manufacturing processes

Following are brief descriptions of the processes by which the nitrogen fertilizers are usually manufactured. Ammonia is produced in four steps: (1) sulfur-free natural gas is reacted with steam over a nickel catalyst to form a mixture of hydrogen, carbon monoxide and carbon dioxide; (2) air is added and reacts, leaving a mixture of hydrogen, nitrogen, carbon monoxide and carbon dioxide; (3) the gas stream is again reacted with excess steam that converts the carbon monoxide to carbon dioxide and produces additional hydrogen (the carbon dioxide is removed for further use and trace carbon oxides are catalytically reacted with hydrogen to form methane); (4) under high pressure and temperature in the presence of an iron catalyst, the purified hydrogen and nitrogen are combined into ammonia. A typical flowsheet for ammonia production is shown in Figure II.

To produce ammonium nitrate, nitric acid of about 60 weight percent is needed. Ammonia is oxidized to oxides of nitrogen by heating with air in the presence of a platinum-rhodium catalyst. Nitric acid is formed by the absorption of the oxides in water. A typical flowsheet for nitric acid production is shown in Figure III.

Ammonium nitrate is produced by a straightforward neutralization reaction between anhydrous ammonia and nitric acid. Because the reaction is highly exothermic, much water is evaporated from the process leaving an intermediate solution of about 83 weight percent. Of the three major processes for preparing the solid product (prilling, crystallization, and flaking), prilling is the most widely used in the United States. To form prills, the ammonium nitrate solution is concentrated by heat to over 96 weight percent and sprayed through orifices into the top of a tall prill tower against a counter-current of air. The droplets reach the bottom of the tower as solid pellets of ammonium nitrate prills containing at least 33½ weight percent nitrogen. The prills, to qualify as fertilizer grade ammonium nitrate, are either self-coated by the introduction of an additive to the solution before prilling or coated with an inert material such as clay after prilling. A typical flowsheet for ammonium nitrate production is shown in Figure IV.

Urea is produced by the chemical reaction of ammonia and carbon dioxide (which may be recovered from the ammonia process). The reaction is carried out in a pressurized reactor to form a solution containing mainly ammonium carbamate, some urea, and water. The ammonium carbamate is dehydrated to form urea. The process product stream is a mixture of urea, ammonium carbamate, water, unreacted ammonia and carbon dioxide. The final steps in the urea process involve the decomposition of the ammonium carbamate, removal of the urea product in usable form, and disposal of the unreacted ammonia and carbon dioxide. There are three types of processes for urea production which differ primarily in the way in which the unreacted ammonia and carbon dioxide are handled. In the once-through process no attempt is made to recycle the unconverted reactants. Instead, the off-gas ammonia is used in the production of other fertilizer products such as ammonium nitrate. In the partial recycle process a portion of the unreacted ammonia is recovered and recycled while the carbon dioxide is used in other processes or is wasted. In the total recycle process both the unreacted ammonia and carbon dioxide are recovered and recycled to the urea reactor. Where the urea is used only in the production of nitrogen fertilizer solutions, it is handled as a solution of about 75 weight percent from the reactor. Where a solid product is desired the urea solution is concentrated and solidified by crystallization, prilling or crystallization followed by prilling, much the same as in making solid ammonium nitrate. A typical flowsheet for urea production is shown in Figure V.

Two types of nitrogen fertilizer solutions are made by blending the various liquid constituents. So-called direct application nitrogen solutions are produced by blending the intermediate ammonium nitrate and urea solutions. Ammoniating or manufacturing type nitrogen solutions are made by blending ammonium nitrate solution with anhydrous ammonia, and sometimes with urea solutions.

C. Typical nitrogen fertilizer manufacturing complex

A typical nitrogen fertilizer manufacturing complex would contain an ammonia plant of from 600 to 1500 tons per day capacity and one or more ammonia oxidation plants (AOP) nitric acid units of at least 500 tons per day capacity. The new large scale ammonia and acid plants feature new technology such as the use of centrifugal compressors, new and improved catalysts, and systems for efficient utilization of energy derived from waste heat. The newer ammonia plants have steam systems closely integrated with the process. Heat is recovered from the process and used for boiler feed water preheating, steam generation and superheating. The high pressure steam systems, over 1,000 psi, provide steam for driving pumps, compressors and are used in the process reactions. Such a steam system requires high purity boiler feed water that is usually provided by demineralization utilizing ion exchange. The modern nitric acid plant is of a compact single train design effecting high ammonia conversion, maximum power recovery by an expander turbine for compressor drive, and a means of stripping the residual nitrogen oxides out of the plant tail gas to an environmentally acceptable level.

The typical complex would also contain a 500 to 1000 ton per day ammonium nitrate neutralizer facility, together with concentrators and means to finish the product in flake, crystal or prill form and to produce solutions. Also included would be a urea plant of one of the three types with a capacity of 200 to 600 tons per day.

The typical complex would likewise contain a steam generation plant, process cooling water facilities, and a wastewater treatment plant.

II. WATER POLLUTION PROBLEMS

A. Water usage

A nitrogen fertilizer manufacturing complex such as that just described is a fairly heavy user of water. Ten to fifteen years ago water consumption in the industry was relatively high because of the use of once-through cooling. About 75 percent of all water used is for cooling purposes, but the bulk of this is now recycled.

Little specific information is available on water requirements for nitrogen fertilizer manufacture. A recent study has shown requirements to range from 56,000 to 188,000 US gallons per ton of ammonia, 3,000 to 35,000 US gallons per ton of ammonium nitrate and 20,000 to 90,000 US gallons per ton of urea. The wide ranges are due to a number of factors including processing alternatives, water availability and air pollution control which can require considerable water scrubbing of gas streams. In urea production the wide range in water requirements reflects the type of process used – whether once-through, partial recycle or total recycle. A reasonable estimate is that the wastewater discharge resulting from usual water usage in a typical complex would be approximately one million US gallons per day.

B. Pollution potential

As can be seen from the foregoing discussion of nitrogen fertilizer processes and water use, the water pollution potential is enormous. The specific operations in each process which generate wastewater streams will be identified and discussed. Definition of the compositions and volumes of the various wastewater streams is generally difficult. Minor process variations, water recycle, and operating philosophies can result in a wide range of waste stream volumes and compositions between different plants for a given product. It is significant to note that the principal pollutants found in nitrogen fertilizer plant effluents are inorganic materials. Except in a few instances, organic contaminants are relatively unimportant. Therefore, pollutional criteria such as BOD and COD are less important in evaluating nitrogen fertilizer plant waste streams than is the case with most industrial waste.

C. Sources of water pollution

Aqueous effluent streams generated in a typical nitrogen fertilizer manufacturing complex would be from three general sources: cooling water; steam condensate; and process effluents. As mentioned earlier, about 75% of all plant water usage is for cooling purposes. However, with today's widespread use of cooling towers, less than 5% of this water finds its way into the effluent as blowdown. This will be discussed in greater detail later. The remaining 25% of plant water usage is for process use and its effluent contains the bulk of the contaminants generated by the various processes. Process effluent can normally be divided into five general classes: (1) barometric condenser water; (2) equipment washdown water; (3) process spills; (4) solutions from gas scrubbers; and (5) by-product streams. All fertilizer processes will generate one or more of these streams.

Process wastewater from an ammonia plant results from spills and condensate. Spills include effluents which occur as a result of operating upsets or mechanical failures. Their occurrence is, of course, not predictable, and in a well-built and well-operated plant spills occur rarely if at all. The principal source of process wastewater is condensation of excess steam used in the vessel where steam is reacted with the natural gas, the primary reformer. This condensate contains sizeable quantities of ammonia which may originate from recycle of purge gas and from feed air containing ammonia. Ammonia is also formed inadvertently in the shift converter where carbon monoxide is converted to carbon dioxide. This ammonia enters the condensate stream here and the stream also becomes saturated with carbon dioxide. The condensate can contain small amounts of sodium, iron, copper, zinc, calcium, magnesium and silica, which impurities enter the process stream through contact with catalysts, internal refractory, vessel walls and piping. In some instances small amounts of the absorbent for carbon dioxide, monoethanolamine (MEA), are lost to the waste stream. Oil and grease also occur in the effluent as the result of drippings from pumps and high pressure compressors.

Other than wastewater from cooling tower and boiler blowdowns to be discussed later, the only sources of water pollution from nitric acid manufacturing are leaks and spills from the process.

In the urea plant, following the urea-forming reactions, the pressure is reduced to allow ammonia, carbon dioxide and ammomium carbamate to flash from the urea product. Water scrubbing of these flashed gases, along with the condensation of water vapor from the urea concentration step, results in a waste stream containing amounts of all of the above-mentioned materials. Dust particles from prill towers and crystallizers may also enter water collection systems via rainwater or wash water.

As discussed earlier, the neutralization reaction for the production of ammonium nitrate is highly exothermic and a large amount of water containing ammonia, nitric acid, ammonium nitrate and some nitrogen dioxide is evaporated. Air scrubbing of these contaminants results in their presence in the wastewaters. Also, scrubbing of stacks to evaporators used in the concentration step results in more ammonium nitrate contamination of aqueous effluent. As with urea, prilling or crystallization of the product results in dust particles entering water collection systems via rainwater or wash water. With both ammonium nitrate and urea, process spills and resultant cleanup can generate a significant waste stream. Solid spills, of course, should be recovered as solids rather than washed down. Liquid spills are usually washed to a sump or drainage system. In some instances the wash solutions cannot be returned to process because of the possibility of oil or grease contamination and its resultant hazard.

The major portion of the water used in fertilizer production is for cooling purposes, however, little of it enters the effluent because of the widespread use of closed loop cooling towers. Cooling water does become contaminated from at least four sources: leaks in process equipment and piping; the buildup of dissolved solids from the feed water; chemicals added to the cooling water to control biological growth, scale, and corrosion; and air emissions such as ammonia, nitrogen oxides, etc. that can be absorbed by noncontact cooling water at cooling towers. About 3% of cooling water used in cooling towers is blown down to control buildup of solids such as chlorides and silica that can cause damaging corrosion to high alloy steel equipment. In addition to these solids, the blowdown stream entering the plant effluent can contain lubricants from pump and compressor bearings and any of the materials present in the complex processes as feeds, intermediates, products, or by-products. The chemicals added to the cooling water and present in any blowdown can include both organics and inorganics. Chromates and phosphates are frequently added for corrosion control and organics for control of biological growth.

In addition to the waste streams discussed above, there are three other sources that must be considered and controlled. They are: rainwater runoff which picks up contaminants from air emission fallout, spills, leaks, etc.; blowdown to control solids buildup from numerous steam generating units and heat recovery boilers; and waste from the treatment of feed water for such steam production. The high pressure steam systems for modern fertilizer plants require high purity boiler feed water which is usually provided by ion exchange demineralizers. Regeneration of the resins by strong acid and caustic results in a waste stream containing the dissolved ions removed from the raw water plus the excess of regenerants.

III. WATER POLLUTION SOLUTIONS

A. General

The optimum pollution solution is the provision of a process plant that embodies process designs that will minimize pollution. However, one must be realistic and recognize that compromises in design are often encountered so that the newest plant most probably will not be "pollution-free." Consequently, in minimizing pollution in plants of any age similar techniques must be employed.

The first step in any pollution control study is to identify and define the problem areas and characterize the waste flow as to volume, composition and source. Once this is done, the process facilities need to be examined for means of reducing or removing nitrogen compounds before they might enter the waste streams. This will not only reduce the cost of treatment but will help offset the overall treatment economics due to product recovery. Major processes should be evaluated from the standpoint of the economics involved in the cost of modification or change-over versus the cost of treatment or product loss. In-plant modifications for the purpose of reduction of nitrogenous pollutional input to plant effluent are quite numerous and will be described in the discussions of treatment of specific nitrogen fertilizer effluents to follow. Other in-plant procedures to control pollution include, of course, good housekeeping, control of spills, immediate correction of leaks, reduction and control of start-up and shut-down operations, reuse of wastewater, salvage of by-products for sale, and control of runoff and seepage from lagoons.

"End-of-the-pipe" wastewater treatment schemes include sedimentation, flocculation, precipitation, filtration, neutralization, holding basins, lagoons, cooling towers, condensers, disposal of solids to land fill areas, continuous monitoring of cooling water, evaporation, steam or air stripping of ammonia, urea hydrolysis, ion exchange, and recycle. An in-depth study of an end-of-the-pipe treatment scheme for a nitrogen fertilizer manufacturing complex will be discussed below.

B. Ammonia production

The United States Environmental Protection Agency (EPA) considers the best practicable control technology currently available for ammonia plants to be stripping of the ammonia from the process condensate waste stream by air and/or steam. The EPA reports ammonia levels of 0.125 pounds NH_3 per 1,000 pounds of product have been achieved. Air stripping of an ammonia-laden waste stream can be easily effected by raising the pH to 10 or above with lime or caustic which releases the ammonia from solution and blowing it into the air by means of a stripper such as a modified cooling tower. The drawback to this process is that it amounts to a substitution of an air pollution problem for the water pollution. Steam stripping of ammonia from the process condensate is fairly easy to achieve and results in by-product recovery and water reuse with resultant reduction in plant effluent. A system is in use where the condensate stream which is normally discarded, is recovered, purified, and reused as boiler feed water. The system reduces the plant effluent in two ways. First, the process condensate is recovered and reused and second, the boiler feed water demineralizer effluent is reduced since the need for dimineralization of raw water is decreased. As shown in Figure VI, the system consists of a stripper and an ion exchange unit. The process condensate is fed to a steam heated stripping tower to remove the volatile ammonia and carbon dioxide. The stripper overhead is condensed to recover aqua ammonia. The stripper will reduce the ammonia and carbon dioxide concentrations to 20 and 40 ppm, respectively. The stripped water is sent to an ion exchanger where the heavy metal ions are removed and replaced with ammonium ions. The amount of ammonia added to the water is very small compared to the amount removed in the stripper. The ion exchange unit produces boiler feed water of comparable quality to the demineralizer with respect to heavy metals. The relatively infrequent regeneration of the resin is accomplished with an acid followed by ammonium hydroxide to convert the resin to the ammonia form. The water from the ion exchanger joins the fresh demineralized water and is used as boiler feed water. Another system of process condensate treatment has been employed that uses ion exchange only. The ammonia is removed from the condensate stream by passing it through a fixed bed of strong cationic resin. The carbon dioxide is kept in solution by maintaining an 80 psig pressure within the system. The resin is regenerated with dilute sulfuric acid resulting in a by-product ammonium sulfate. It is reported that this system has reduced ammonia in the effluent to less than one part per million. The author suggests that if nitric acid were used instead as the regenerant, the by-product ammonium nitrate would be more compatible with a nitrogen fertilizer manufacturing complex. An in-plant process modification is worthy of note here The aqua ammonia resulting from stripping and otherwise collected in older ammonia plants is sometimes stripped of ammonia gas for recycle. In some instances steam heated recovery units have been used. Such units have characteristically added ammonia-laden water to the plant wastewater. The substitution of gas-fired ammonia recovery reboilers has been found to overcome this problem. In such a reboiler, an external source of heat is provided for flashing out the ammonia. Not only does this increase recovery efficiency but no source of water is added to the system. As mentioned, oil and grease are a pollution source in ammonia plants. These can be controlled at the source by drip pans under pumps and compressors. Otherwise, oil and grease removal from waste streams can be accomplished by gravity type separators.

It is estimated that the best practicable control technology currently available for use in ammonia plants can be achieved at a cost of $1.11 per ton of product. Best available technology economically achieveable can be attained at an additional cost of $0.33 per ton of product.

C. Nitric acid plant

There is no discharge of process wastewater from the nitric acid manufacturing process. Best practicable control technology currently available therefore involves detection and containment of leaks and prevention of spills.

D. Ammonium nitrate manufacture

The US EPA considers the best practicable control technology currently available for ammonium nitrate plants to be ion exchange removal of ammonium and nitrate ions. The EPA reports ammonia and nitrate levels of 0.1 pounds per 1,000 pounds of product and 0.125 pounds per 1,000 pounds of product respectively can be achieved. The treated water may be reused within the plant as make-up boiler feed water, or as cooling tower make-up water, or may be recycled back to the raw water treatment unit. The regeneration of the ion exchange resins creates a concentrated ammonium nitrate solution which may be further concentrated and sold. This treatment will be discussed in more detail later. It is estimated that the best practicable control technology currently available for use in ammonium nitrate plants can be achieved at a cost of $3.70 per ton of product. Best available technology economically achievable can be attained at an additional cost of $2.20 per ton of product.

Ammonium nitrate plants, particularly older ones, present many opportunities for the application of in-plant process modifications to reduce the pollutional input to the effluent of a nitrogen fertilizer manufacturing complex. A few of such opportunities will be mentioned.

The use of calandria-type evaporator for concentration of the ammonium nitrate intermediate solution often results in the entrainment of ammonium nitrate in the evaporator condensate and carry-over into the effluent. Substitution of a falling-film type evaporator has been shown to not only provide more efficient concentration but eliminates any condensate. Process improvements toward the production of a high-density self-coated ammonium nitrate prill has been shown to eliminate pollutionally offending steps such as predrying, drying and clay coating. This has abated nitrogenous loading of the effluent from air emission fallout as well as eliminating an aggravating pollutional load caused by the clay. Other significant modifications include paving and diking of areas and sump collection of leaks, spills and runoff for process recycle.

E. Urea synthesis

The best practicable control technology currently available for use in a urea plant can be achieved by hydrolysis of urea in wastewater to ammonia and carbon dioxide. These gases can then either be returned to the urea manufacturing process or stripped to the atmosphere. EPA reports that the resultant effluent can achieve ammonia and organic nitrogen levels of 0.075 pounds per 1,000 pounds of product and 0.0375 pounds per 1,000 pounds of product respectively.

It is estimated that the best practicable control technology currently available for use in urea plants can be achieved at a cost of $1.70 per ton of product. Best available technology economically achievable can be attained at an additional cost of $0.60 per ton of product. Where end-of-the-pipe treatment results in water for reuse containing small amounts of urea, this urea may be satisfactorily destroyed by heat in boiler feed water and cooling tower use.

F. Cooling tower operation

Most nitrogen fertilizer manufacturing complexes now use cooling towers for the recycle of the large volumes of water required for process cooling. Since most process equipment is of stainless steel and is susceptible to corrosion from the buildup of chemicals in the water supply, corrosion inhibitors such as sodium chromate and dichromate and organo-phosphates are added. These treatment chemicals are present in significant quantities in blowdown from the cooling towers and in the plant effluent where they are highly objectionable for discharge to receiving waters. At least two successful treatments are available for the removal of chromates from waste streams: destruction and recovery. To destruct the chromates, the blowdown stream is first acidified to a pH of 2 or 3 and then the hexavalent chromium is reduced to the trivalent state by a reducing agent such as sulfur dioxide. The chromium is then precipitated as the hydroxide by treatment with lime or caustic and then removed from the stream and disposed of by land fill. A more attractive treatment results in the complete recovery of the chromates for recycle back into the cooling water system. This is accomplished by ion exchange whereby the chromate ion is picked up on a weak base anion resin of a special type. It is then stripped off upon regeneration with caustic as recovered sodium chromate and dichromate for reuse. The phosphates can also be removed by ion exchange using an alumina bed. Regeneration with dilute caustic produces by-product sodium phosphate. Other contaminants from the complex that are picked up by the cooling waters are treated by methods already discussed.

It should be noted that in water poor areas extensive use is now being made of air coolers and condensers in order to solve the water supply problem. Their use may aggravate air pollution control.

G. Boiler feed water treatment

The remaining waste stream from the typical nitrogen fertilizer manufacturing complex yet to be discussed is waste from boiler blowdown and from the treatment of water for use as boiler feed water. Boiler blowdown is usually treated along with the effluent from the plant in which it originates. Its alkalinity is sometimes useful in treatment schemes. Waste from boiler feed water treatment, especially heavy demineralization, sometimes presents a problem, but it is usually susceptible to concentration and land fill disposal.

H. Research on end-of-the-pipe treatment

Extensive research has been fairly recently conducted on physical, chemical, and biological means for treatment of the end-of-the-pipe effluent of a typical nitrogen fertilizer manufacturing complex. First, a comprehensive examination of the process facilities was made for means of reducing or removing pollutants before they could enter the waste streams, including many of the in-plant modifications mentioned above. The total waste stream was then characterized and found to have a volume of about 900,000 US gallons per day containing pollutants in concentrations as shown in Table 1.

Laboratory investigations were carried out and extended to pilot and full-scale field tests. Six different processes for removal of the high concentration of nitrogenous compounds from the wastewater were evaluated. Five of these were found to be limited by certain restraints:

(1) Microbial nitrification of ammonia - nitrogen over trickling filters - slow and inefficient.

(2) Biological denitrification of nitrate - nitrogen in anaerobic lagoons - inefficient and expensive.

(3) Air stripping of ammonia - promising but results in an air pollution trade-off.

(4) Precipitation of ammonia as magnesium ammonium phosphate - problem of removing all the phosphate that must be added to effect the reaction.

(5) Reverse osmosis for concentrating the pollutant for product recovery and clarifying wastewater for plant reuse - vendor's equipment was tried but membranes were not available to give good nitrate ion rejections. (Newer

membranes have been developed so that separation - concentration of ammonium and nitrate ions can now be accomplished by reverse osmosis with 85% rejection which is not considered by this author to be acceptable.)

The sixth process evaluated was that of concentrating the pollutant for product recovery and clarifying the water for plant reuse by continuous ion exchange. Of all wastewater treatment methods tried, only this one was considered to provide the ultimate of a closed process wastewater reuse system. This treatment process provides effluent water of adequate quality for reuse in plant processes, cooling, or steam generating; or discharge into receiving streams. Table 2 shows the effluent water quality as compared with the "raw" wastewater. The process provides for recovery of the collected contaminant ions as product, in this case ammonium nitrate, for recycle into production processes. In this particular plant the recovered product is recycled back into the production of nitrogen solutions. Table 3 shows the composition of the recovered product. The cost and consumption of the chemicals used to regenerate the ion exchange resins are low and all regenerants are recovered as product. The regenerant chemicals used, nitric acid and aqua ammonia, are co-products and intermediates in the complex. Table 4 shows the recovered product material balance. The wastewater treatment process provides real opportunities for cost savings through product recovery, water reuse, lowered costs for all types of water treatment chemicals, possible reductions in overall plant operation and maintenance costs.

As shown in Figure VII, the essential steps in the process are: collecting plant wastewaters, including runoff, in a large pond; contacting the wastewater with strong acid cation exchange resin that removes cation contaminants especially ammonium ion to less than 3 ppm; contacting the "decationated" water with a weak base resin in the hydroxide form that removes the anion contaminants to 7-11 ppm nitrate; regenerating cation resin with 22% nitric acid; regenerating anion resin with 7% ammonium hydroxide; combining the regenerant products and neutralizing excess acid with ammonia to form an 18% ammonium nitrate solution for recycle into nitrogen solution production. An optional step is provided for removal of accumulated silica by ion exchange before the demineralized water is recycled to cooling towers, boilers and process for reuse.

The ion exchange equipment required to treat one million US gallons of wastewater per day costs about $500,000. Gross operating costs have been found to be about $275,900 annually - equivalent to 84 cents per 1,000 US gallons of wastewater. Net treatment costs, after allowing a credit for the recovered ammonium nitrate, runs about $25,900 - equivalent to only 8 cents per 1,000 US gallons of wastewater or 8 cents per ton of ammonium nitrate capacity in the typical nitrogen fertilizer manufacturing complex.

IV. AIR POLLUTION PROBLEMS AND SOLUTIONS

A. General

The air pollution potential of a typical nitrogen fertilizer manufacturing complex is quite staggering. Pollutant emissions into the air can occur from each of the elements that make up the complex: steam generators; cooling towers; and ammonia, ammonium nitrate, urea, and nitric acid production units.

Particulate and gaseous pollution from steam generation can generally be minimized by the installation of modern "smokeless" equipment that burns "clean" fuel. The "energy crunch," of course, will result in compromises in these process decisions. Some provision should be made in the interest of fuel conservation for usefully converting collected waste oil into energy.

Cooling towers are not normally considered to be sources of air pollution, but they most certainly can be. As has been detailed above, cooling waters will contain volatile ammonia and carbon dioxide, along with dissolved solids such as ammonium nitrate in concentrations which may be heavy if there are numerous leaks in the equipment. If cooling towers are under-designed for capacity, the evaporation rate and drift from the towers will exceed normal expectations and result in a significant air pollution problem. The pollution solution here is proper basic design and minimizing of equipment leaks to cooling water.

B. Ammonia and urea synthesis

Ammonia plants are relatively air pollution free. There is some leakage and venting of ammonia, but it generally cannot be detected outside the boundaries of the complex. Since odor indicates loss of product, there should be good economic motivation to eliminate the emission as soon as possible. Where air stripping is used for treatment of the process condensate wastewater stream, the installation of a gas scrubber may be required by regulatory bodies.

Except for the total recycle plants, urea plants produce a significant volume of off-gas consisting of carbon dioxide, water and ammonia. This off-gas is run through the ammonium nitrate neutralizer where the ammonia is salvaged and used as feed stock.

Urea prill tower dust can be controlled by water scrubbers.

C. Ammonium nitrate manufacture

Of all nitrogen fertilizer manufacturing complex plants, the ammonium nitrate plant can be the worst air polluter. Emissions arise from the neutralizer, the evaporators, prill towers, and dust collectors.

The reaction in the neutralizer where ammonia and nitric acid are reacted is highly exothermic. Huge quantities of water vapor containing entrained contaminants are released along with unreacted materials that are added such as urea plant off-gas. The vent stream from the neutralizer contains significant quantities of carbon dioxide, water, ammonia and ammonium nitrate fines. High efficiency water spray-type scrubbers using an acidic weak ammonium nitrate scrubbing liquor have been quite successful in controlling these emissions. However, the carbon dioxide is discharged from the scrubber as a dense, sometimes objectionable plume. Only total condensation has been found to control this and it is deemed to be far too expensive. A side stream from the scrubbing liquor is recycled for product recovery.

The evaporators used to concentrate the 83% intermediate ammonium nitrate solution up to prilling strength are generally of two types: calandria for lower concentrations - may be operated under vacuum with discharge into water or vented to atmosphere; or falling film using air stream discharged to atmosphere. Both types result in severe air pollution, the control of which will be dealt with later.

Two types of ammonium nitrate prills are produced: high density and low density. Low density prills are those that are formed from a "melt" of concentrated ammonium nitrate containing about 4.5% moisture and the prills are made essentially anhydrous by subsequent stepwise moisture losses in the tower, rotary predryer, dryer and cooler. They are then coated with a clay conditioner. High density prills, on the other hand, are made by concentrating the "melt" to 99.8% before prilling. This eliminates the need for a dryer and predryer. Moreover, an additive is usually added to the melt so that the prill becomes self-coated, thereby eliminating the clay conditioning.

When prills are formed at the top of the prill tower by spraying the concentrated melt through an orifice, uniform globules are not continuously formed. Instead, the size varies considerably and for each regular-sized prill formed there is a small satellite prill formed. It is these satellite prills that are thought to create the fines problem in prilling. It has been found that when the spray plates are vibrated, uniform-sized prills will be continuously formed with no satellite prills.

In producing low density prills, emissions from the evaporators are minimized because of lower concentration of the melt and emissions from the prill tower are also at a minimum. Air pollution does result from dust picked up by the air stream through the dryer and predryer. Cleaning of this air stream by cyclones is generally ineffective.

In producing high density prills the drying dust problem is eliminated by the elimination of the dryers from the process. Heavy emissions are found at the evaporators in producing the stronger melt. In addition, a heavy blue smoke is emitted from the tower during prilling that generally results in an equivalent opacity of 3 measured on the Ringleman scale or 60% obscuration.

A speculation on the blue haze is that it results from decomposition of the ammonium nitrate at the high temperature (375°F) at which the melt is sprayed from the top of the tower. The decomposition of the ammonium nitrate is thought to be a direct function of the vapor pressure of the melt. Thus, lowering the temperature by 30°F would halve the vapor pressure and have a favorable effect on the blue haze. A process change to lower the temperature to just above the salting-out temperature of 340°F has reduced the blue haze.

At a number of nitrogen fertilizer manufacturing complexes, the ammonium nitrate air pollution problems have been rolled into one. All emissions – from neutralizers, evaporators and prill tower – have been collected and are cleaned in a single high energy venturi-type scrubber that effects significant product recovery for recycle. Particle size growth appears to result from the synergistic effect so that contaminant removal is highly efficient. Unfortunately, carbon dioxide still remains to cloud the stack. In most instances part of the process air used in the prill tower is recycled with a side stream taken off for cleaning.

D. Nitric acid plant nitrogen oxides

A paramount air pollution problem in a nitrogen fertilizer manufacturing complex is the control of NO_x emissions from the nitric acid plant(s). It will be recalled that in the synthesis of nitric acid, a mixture of ammonia and air at high temperature is passed over a platinum gauze catalyst to form nitric oxide (NO), a colorless gas. This is followed by oxidation to the dioxide (NO_2) of intense reddish-brown color and subsequent absorption in water to produce aqueous nitric acid. Nitrogen and small amounts of oxygen and unabsorbed oxides of nitrogen are discharged into the atmosphere as tail gas. This discharge represents the obnoxious air pollution from a nitric acid plant. The oxides of nitrogen (NO_x) concentrations in the tail gas of a plant without controls run about 0.1 to 0.4 percent by volume, or 1,000 to 4,000 ppm. This is equivalent to 2-3% of plant production.

Much information has been compiled by the US EPA on nitrogen oxides in the air. Scientific information was assembled to show the effects on human health and welfare. Long-term exposure to air containing 117 to 205 micrograms of NO_2 per cubic meter was indicated to have some adverse effects on human health. EPA has set the national ambient air standard for nitrogen dioxide at 100 micrograms per cubic meter of air (0.05 ppm) for the annual arithmetic mean value.

EPA has determined that industrial processes in the US were sources of about one percent of total NO_x emissions. Chemical processing may, however, be responsible for high but localized emissions. Allowable NO_x levels in tail gas have been set for US nitric acid plants: existing plants – 5.5 pounds NO_x, calculated as NO_2, per ton of 100% acid or 400 ppm; new plants – 3.0 pounds per ton or 200 ppm. Most states in the US have adopted similar standards.

There are a number of abatement processes that can be added to existing plants or engineered into new plants to meet the above air quality standards. These are: catalytic combustion; incineration; extended absorption; refrigeration; molecular sieve adsorption; adsorption on silica gel; and acid scrubbing. Only the more important processes will be discussed.

Scrubbing of the tail gas from a nitric acid plant with stripped nitric acid is known as the continuous catalytic absorption process. Essentially, the process removes and recovers the NO_x as nitric acid thus increasing the yield of the plant by 2-3%. The main elements of the process are an absorber using catalyst packing, a stripper and nitric acid as the absorption medium. To the author's knowledge this control process is not yet in use on a nitric acid plant.

Molecular sieves that are used as adsorbents are synthetically produced alumosilicates that possess high porosity. They have been activated for adsorption by removal of water of hydration. The pores (lattice vacancies) are of uniform size and essentially are of molecular dimensions. These materials adsorb small molecules only, are selective on molecular shape, and have a particular affinity for unsaturated and polar molecules.

A typical NO_x emission control system for a nitric acid plant using molecule sieve adsorption consists of two sieve beds - one for adsorption, one for regeneration. Tail gas from the acid plant absorber tower is passed through one bed. There the nitric oxide (NO) is catalytically converted to nitrogen dioxide (NO_2) in the presence of the 3% oxygen typically present in the tail gas stream. The NO_2 is then adsorbed on the molecular sieve as an equilibrium mixture of NO_2 and dinitrogen tetroxide (N_2O_4). The loaded sieve bed is regenerated by desorbing with water and heat which recycles the NO_x back to process resulting in a 2½% yield increase. The system, which is in limited use in Europe and the US, is considered to be capable of providing an NO_x effluent concentration of less than 10 ppm.

The extended absorption process is now being used successfully in both existing and new nitric acid plants. NO_x emission limits of 200 ppm are being met and plant capacity is reported to have been boosted as much as 5% in some cases. The process equipment consists of an oversized secondary absorber tower into which tail gas from the existing absorber tower, typically containing 1500-5000 ppm NO_x, is routed for "extended absorption" of the nitrogen oxides. The tail gas is contacted countercurrently with process water, and the additional acid produced in the secondary absorber is pumped back to the primary absorber. The advantages of this method would be the compatibility within existing nitric acid units and the lack of additional labor and expertise required for operation. Because of the additional pressure drop in the system, some decrease in power recovery occurs.

The most widely used process for the abatement of NO_x in nitric acid plant tail gas is catalytic combustion reduction. Not only can this process reduce NO_x emissions to the acceptable level of 200 ppm or less, but combustion of the oxygen in the tail gas provides power that is transmitted to the plant air compressor by way of a heat expander turbine. As shown in Figure III the combustor is located in the process train following the absorber and just ahead of the expander turbine. The combustor vessel is packed with a substrate of ceramic honeycomb or alumina pellets that have been impregnated with precious metal such as platinum or palladium. Fuel that is added for the reduction reaction may be hydrogen (usually as purge gas from an ammonia plant) or natural gas. The reactions occur almost sequentially: (1) decolorization by reducing the orange-colored NO_2 to colorless NO; (2) combustion of the oxygen to permit further reducing reactions; and (3) NO_x abatement by reduction of NO to nitrogen gas. These reactions are shown in Table 5. A principal concern in the operation of a catalytic reduction unit is the stabilization of catalyst activity. Frequently encountered problems include catalyst poisons, carbon deposits on the catalyst, and high intermittent temperatures in the catalyst bed. Poisoning of catalysts has occurred from sulfur, halogen and iron compounds. Improper control of reaction temperatures, excessive fuel to oxygen ratios and improper fuel mixing can cause carbon deposits on the catalyst. High temperatures in the catalyst bed sometimes occur during plant upsets which allow oxygen levels to exceed design recommendations. Good and careful operation of an abater-equipped acid plant is always necessary.

V. NOISE, THERMAL, AND SOLID WASTE POLLUTION PROBLEMS AND SOLUTIONS

A. Noise

The control of noise is now required from the standpoints of human health and welfare. Regulations increasingly specify the noise levels permitted in the environment. Occupational health rules are being established in most countries to regulate noise controls to protect workers' health. Industrial noise which pervades plant boundaries and violates the former rules must be abated. Industrial noise of the latter category should be abated but in any event the workers must be provided ear protection when required to work in areas where the noise level exceeds 85 decibels.

Excessive noise in a typical nitrogen fertilizer manufacturing complex is caused generally by centrifugal compressors, steam generators, and the venting of pressurized gases. As noted above, noise that escapes to the general environment such as the venting of gases must be abated. This can be accomplished by the installation of silencers or mufflers. Noise from steam generators and gas compressors can be controlled in some instances by the erection of sound absorbing barriers. Where noise levels cannot be reduced by such means to below 85 decibels, workers must be provided with ear protection and required to use it in the interest of preserving their health.

B. Thermal

In considering the effect on the environment of the operation of the typical nitrogen fertilizer manufacturing complex the aspect of thermal pollution must be considered. In most localities regulatory bodies place restrictions on the temperature of aqueous waste streams that may be discharged into receiving waters. Means must usually be provided for cooling any wastewater streams that exceed the prescribed limits. When cooling water is used on a once-through basis, or where other waste streams are especially warm, a cooling pond is usually provided for reducing the wastewater temperature prior to discharge to the receiving stream. The blowdown from recirculated cooling water systems is usually relatively cool and does not need additional cooling prior to discharge. The ultimate thermal pollution solution is, of course, complete water reuse. Also, the increased use of air coolers and condensers in place of water coolers suggests better use of natural resources.

C. Solid waste

In the well-operated nitrogen fertilizer manufacturing complex little solid waste usually results. That which does arise comes from off-specifications solid product, floor sweepings, and spill cleanup. Some solid wastes for disposal may result from the precipitation of chromic hydroxide in the cooling tower chromate destruction or concentration of ion exchange regenerant waste from boiler feed water treatment or polishing of treated wastewater for silica removal.

Laws that protect the farmer from being short-changed on fertilizer quality often forbid fertilizer producers from disposing of off-specification material or sweepings by any other means than to the "dump." Sensible revision of these laws is required so that such low quality material can at least partially fertilize crop land rather than fertilize land fills.

When a land fill must be used for the disposal of solid wastes from a nitrogen fertilizer manufacturing complex the disposal site must be selected, operated and maintained with care. Disposal sites should be selected so as to prevent horizontal and vertical migration of these contaminants to the ground or surface waters.

In nearly all cases land fills produce a leachate, or percolation of chemical elements out of their original form, with seepage of raw chemicals into surrounding ground. Should soil borings, examinations and tests indicate a poor degree of natural imperviousness, the land fill walls should be lined with clay or long lasting impervious membrane. In addition, monitoring wells must be dug and accurate testing and analysis of the composition of possible seepage carried out.

VI. CONCLUSION

It is apparent that serious pollution of all segments of the environment has resulted from the manufacture of nitrogen fertilizers. It is likewise obvious that the industry is exerting a strong effort toward the abatement of water, air, noise, thermal, and solid waste pollution. Economists predict that the nitrogen industry is expected to hold a more cooperative attitude toward pollution control than other segments of the fertilizer industry.

As this study has shown, the technology, at reasonable cost to the consumer, is currently available for controlling many of the pollutants resulting from nitrogen fertilizer manufacture. There are, however, certain problem areas where additional development effort is needed to provide possible waste treatment methods. Moreover, environmental quality criteria most certainly will become more restrictive in the future. Waste treatment methods which are adequate for meeting current criteria may not be satisfactory for meeting future standards. This means new waste treatment technology will have to be developed for these situations where existing technology may prove inadequate.

Much of the technology that has been discussed is still in some stage of development such as continuous ion exchange, advance urea hydrolysis, and high flow air and steam stripping of ammonia. However, progress to date shows that much of the remaining work deals with equipment modification, mechanical improvements and control instrumentation which should make each one of these processes completely functional.

There is no question but that there are solutions for minimizing pollution in nitrogen fertilizer plants.

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FIGURE I CONSUMPTION OF NITROGEN FERTILIZERS IN THE UNITED STATES
SOURCE: US EPA REPORT 12020 FPD 09/71

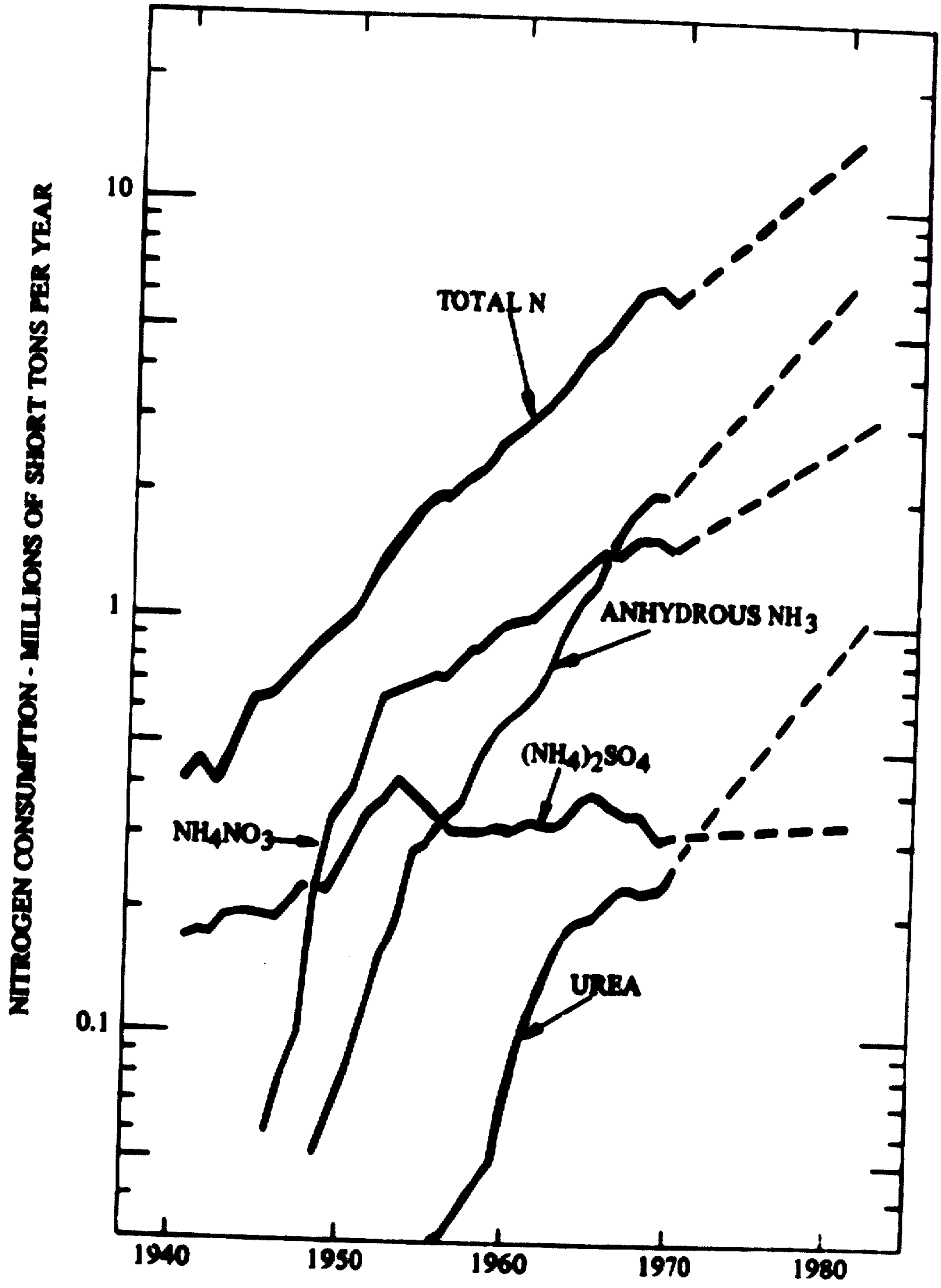


FIGURE II TYPICAL FLOWSHEET FOR AMMONIA PRODUCTION - SOURCE: US EPA REPORT 12020 FPD 09/71

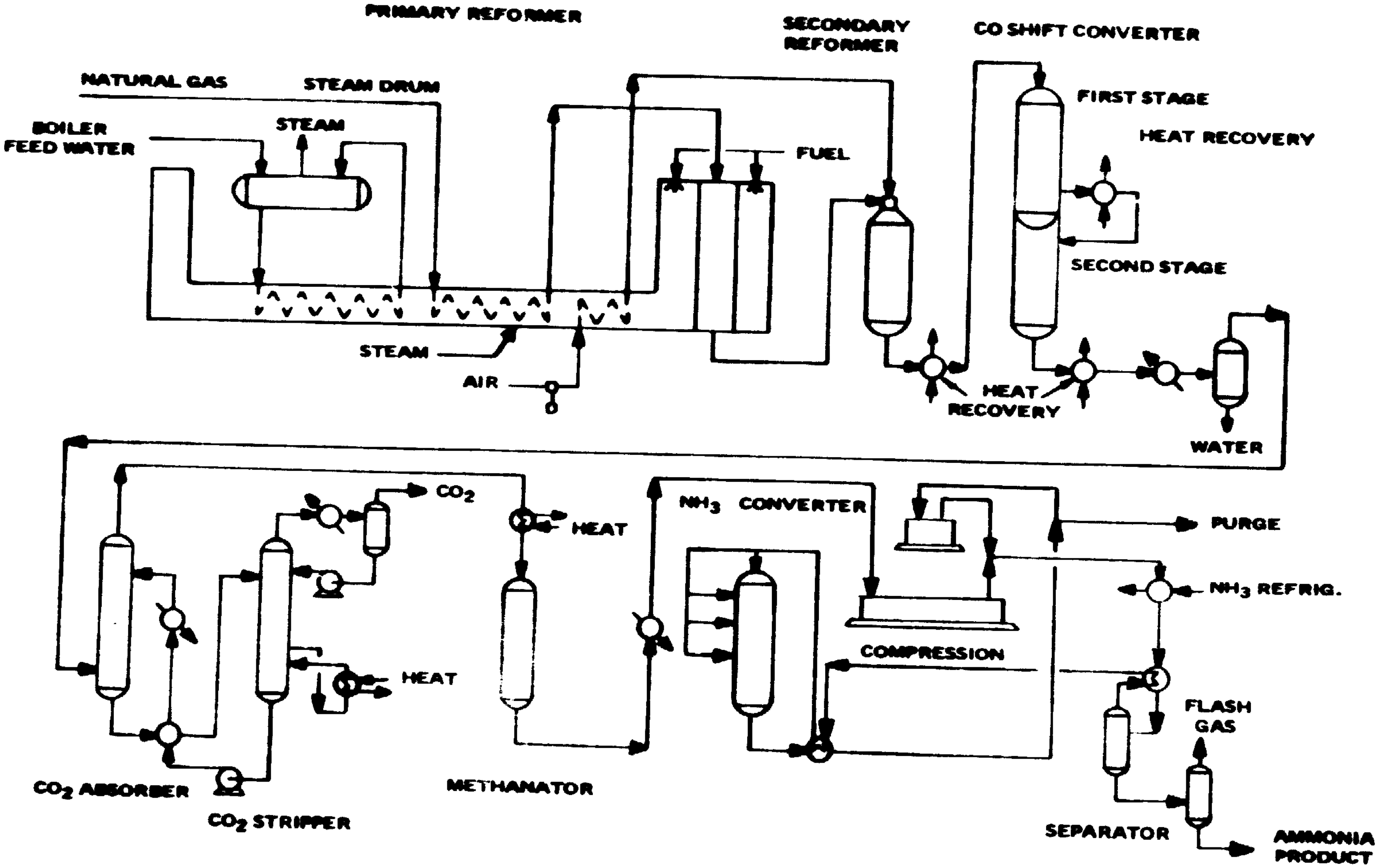


FIGURE III TYPICAL FLOWSHEET FOR NITRIC ACID PRODUCTION

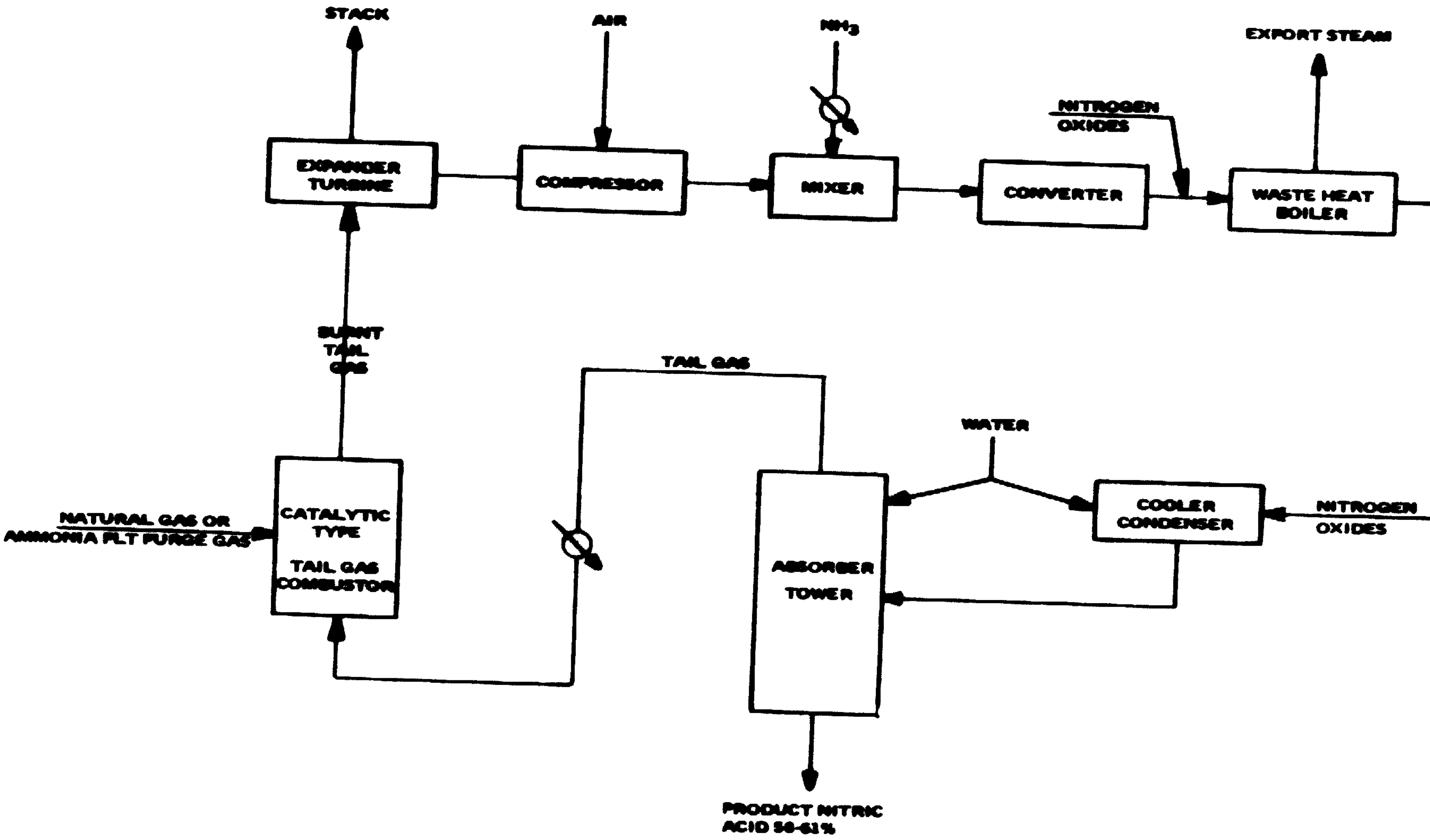


FIGURE IV TYPICAL FLOWSHEET FOR AMMONIUM NITRATE PRODUCTION
SOURCE: US EPA REPORT 12020 FPD 09/71

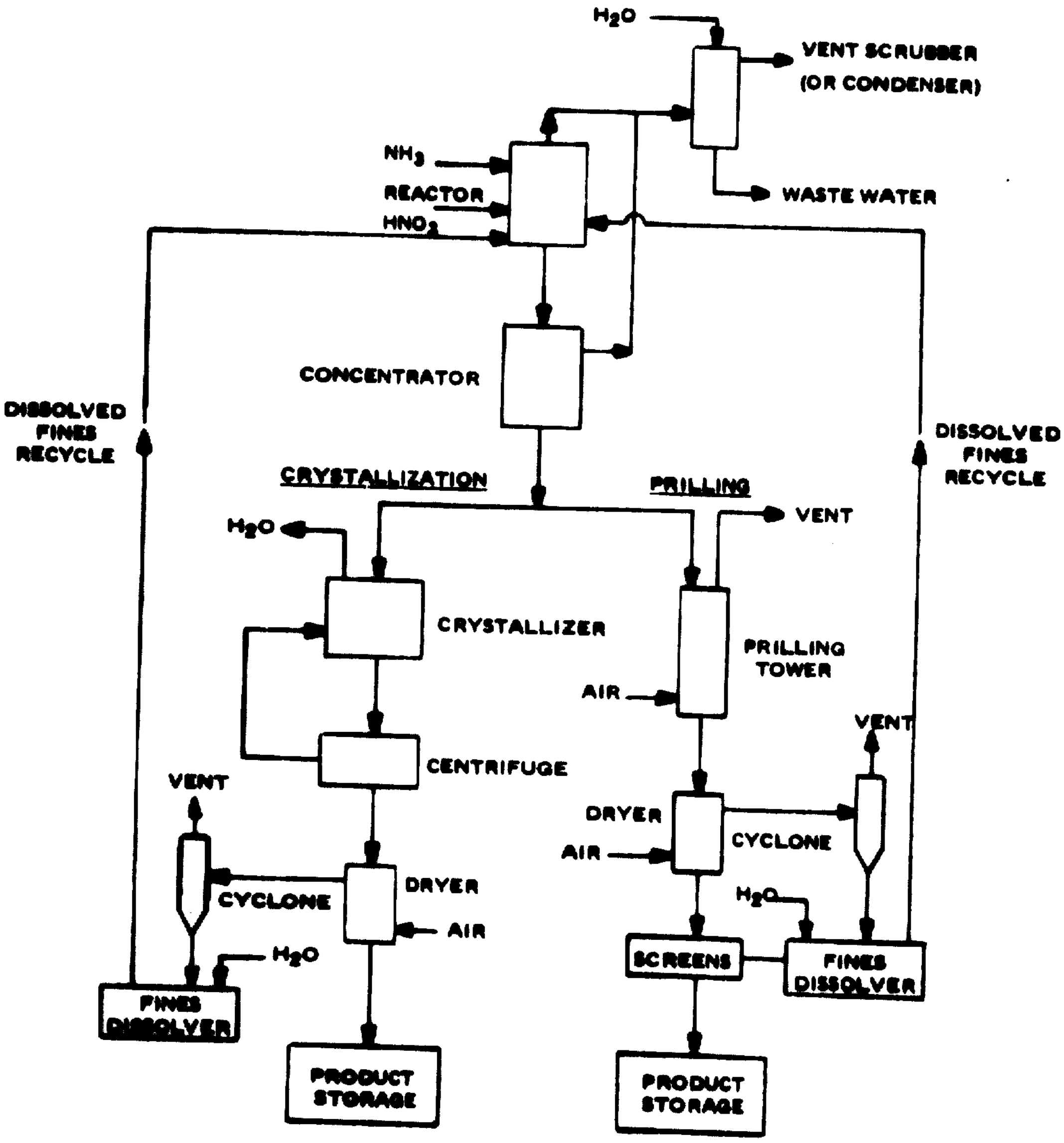


FIGURE V TYPICAL FLOWSHEET FOR UREA PRODUCTION – TOTAL RECYCLE AND PRILLING TOWER
SOURCE: US EPA REPORT 12020 FPD 09/71

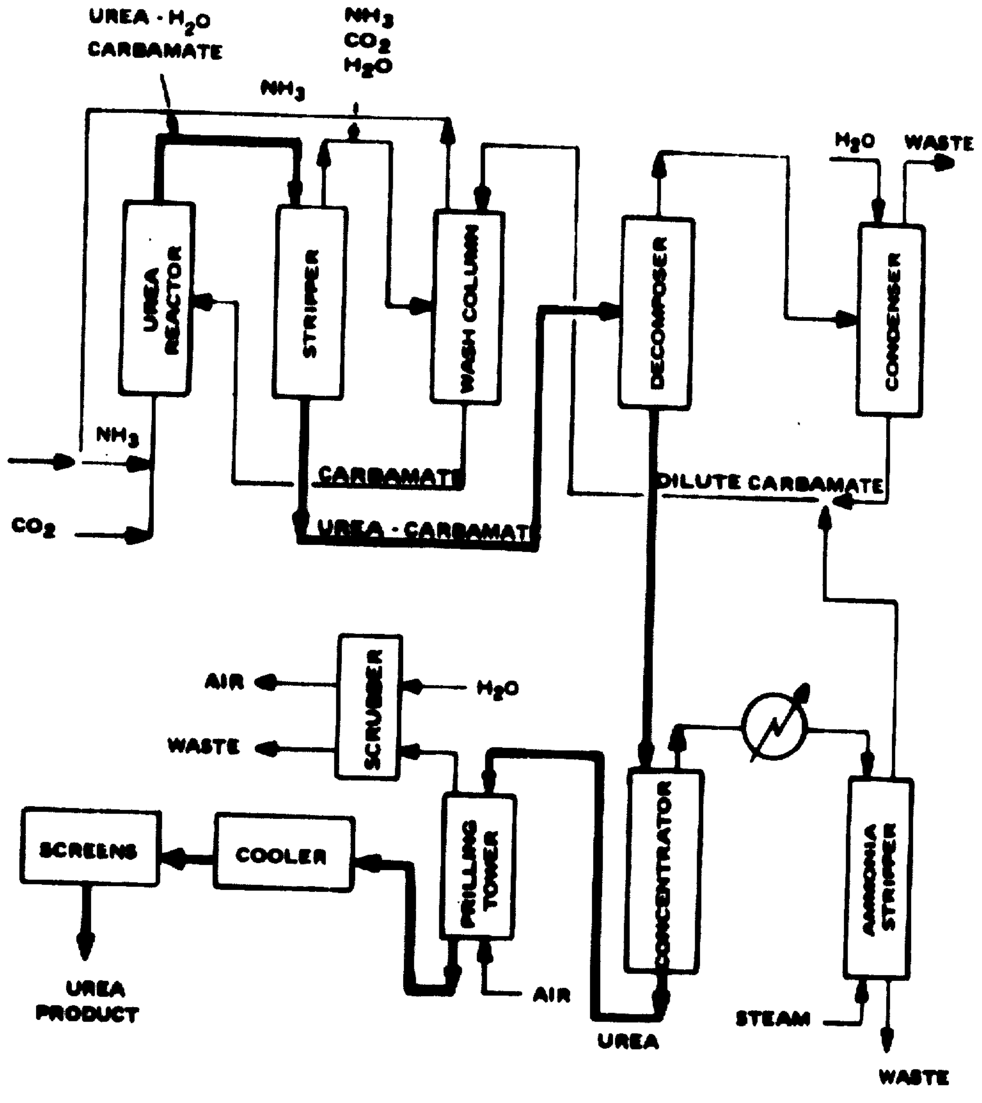


FIGURE VI FLOWSHEET FOR AMMONIA PLANT PROCESS CONDENSATE RECOVERY

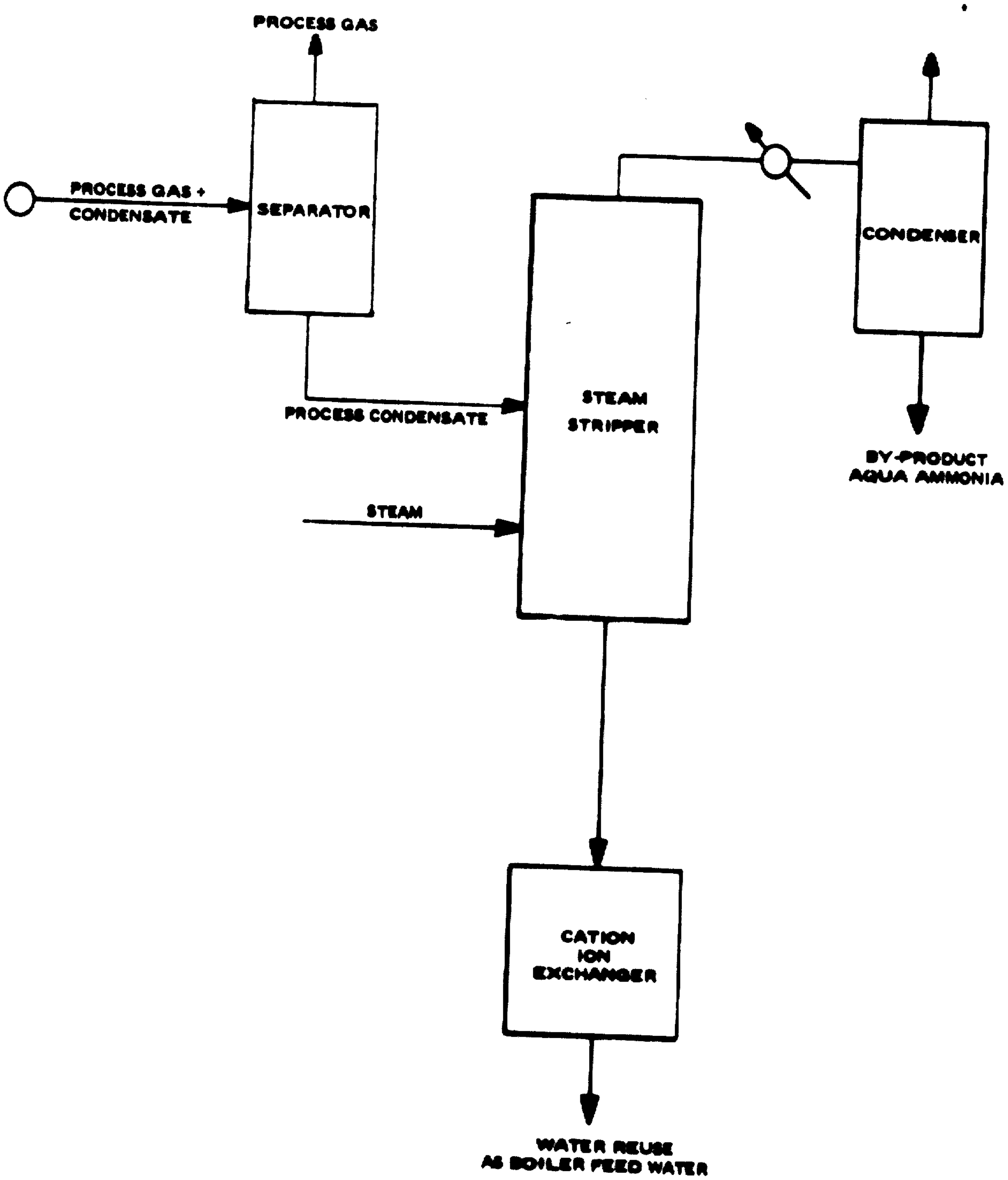


FIGURE VII FLOWSHEET FOR END-OF-THE-PIPE EFFLUENT TREATMENT FOR COMPLETE WATER REUSE AT TYPICAL NITROGEN FERTILIZER MANUFACTURING COMPLEX

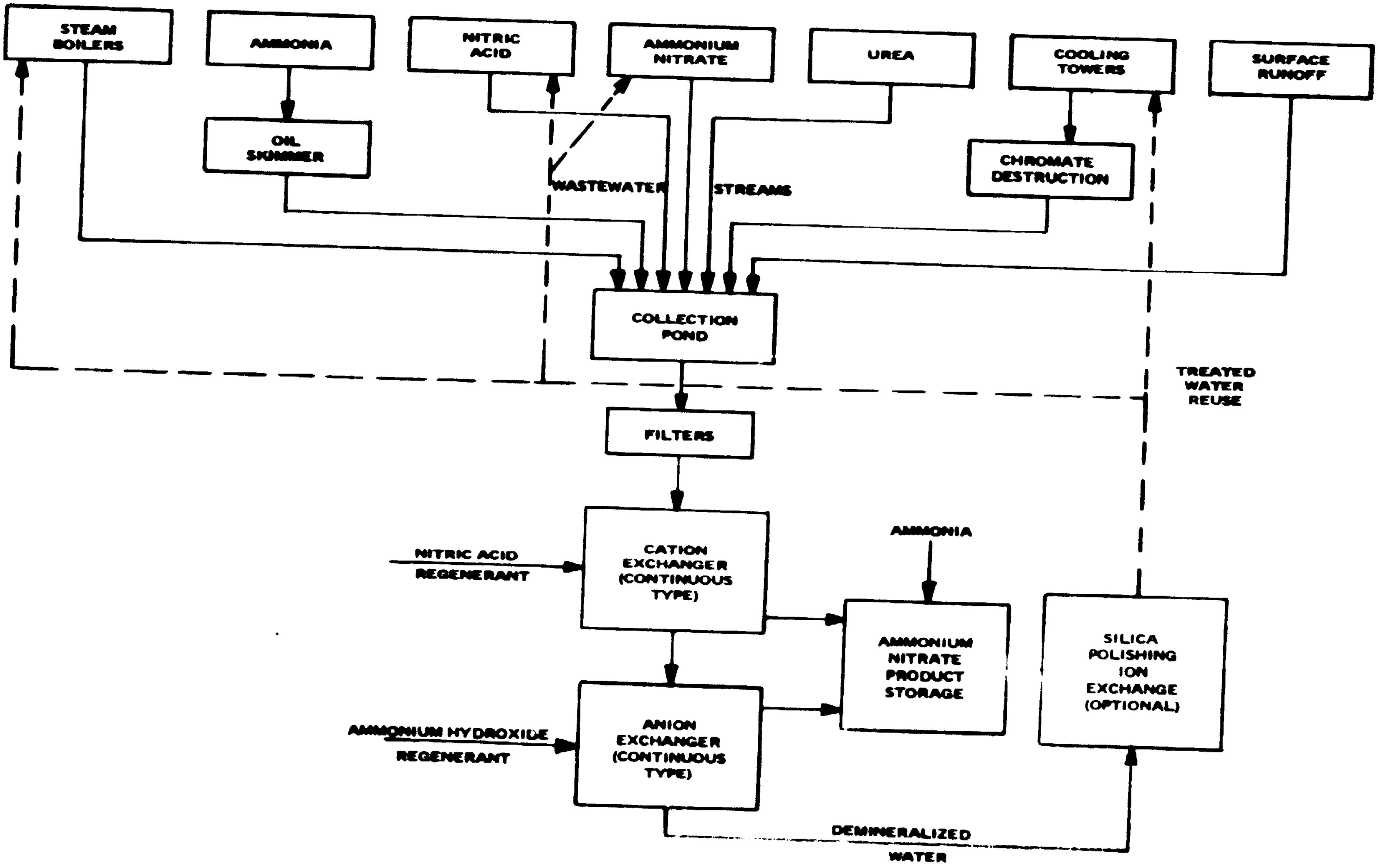


Table 1. Characteristic Wastewater Composition
(parts per million)

Component	ppm	as $CaCO_3$
NH_3	340	1000
Mg	4.8	20
Ca	60	150
Na	0	0
NO_3	1240	1000
Cl	53	75
SO_4	72	75
SiO_2	15	---
Urea	27	---

Table 2. Influent and Effluent Water Quality
(parts per million)

Component	Influent (ppm)	Effluent (ppm)
NH_3	340	2-3
Mg	4.8	0
Ca	60	0
Na	0	0
NO_3	1240	7-11
Cl	53	0
SO_4	72	0
SiO_2	15	15
pH	5.0-9.0	5.9-6.4

Ammonium Nitrate removal is 99.4 percent.

Table 3. Composition of Recovered Product
(Percentage)

Component	Percent
NH_4NO_3	17.830
Ca	0.260
Mg	0.020
NH_3	4.070
NO_3	14.880
Cl	0.220
SO_4	0.312
Total Solids	19.762
Water	80.238

Table 4. Recovered Product Material Balance
(From 0.9 million US Gal. wastewater per Table 1)
(pounds per day)

Component	Recovered Product		
	From Cation	From Anion	Blended
$Ca(NO_3)_2$	1,848	---	1,848
$Mg(NO_3)_2$	222	---	222
NH_4Cl	---	600	600
$(NH_4)_2SO_4$	---	699	699
NH_4NO_3	12,021	12,021	31,211
Water	82,255	56,780	139,035
HNO_3	5,585	---	---
NH_3	1,290*	294	---

Total Product Ammonium Nitrate Solution 173,614

*NH_3 added to neutralize excess HNO_3

Table 5. Catalytic Combustion Reactions

Hydrogen-rich Gas Fuel	
$H_2 + NO_2 \rightarrow NO + H_2O$	Decolorization
$H_2 + \frac{1}{2}O_2 \rightarrow H_2O$	Oxygen Combustion
$H_2 + NO \rightarrow \frac{1}{2}N_2 + H_2O$	NO_x Abatement

Natural Gas Fuel	
$CH_4 + 4NO_2 \rightarrow 4NO + CO_2 + 2H_2O$	Decolorization
$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$	Oxygen Combustion
$CH_4 + 4NO \rightarrow CO_2 + 2H_2O + 2N_2$	NO_x Abatement

TABLE 6
NO_x ABATEMENT METHODS FOR PRESSURE NITRIC ACID PLANTS
ADVANTAGES AND DISADVANTAGES

ADVANTAGES	*DISADVANTAGES*
Catalytic Reduction (Combustion)	
Meets NO_x abatement criteria Provides good power recovery Proven capability and reliability Most widely used Moderate capital investment Moderately compatible with existing plants	Destroys rather than recovers NO_x - no increase in plant capacity Operational difficulties - especially from catalyst poisoning High operating cost potential High energy costs
Extended Absorption	
Meets NO_x abatement criteria Recovers NO_x increasing plant capacity Proven capability and reliability Increasing industry acceptance Low operating cost Simple operation Easily compatible with most plants Low energy costs	Some decrease in power recovery Relatively high capital investment required
Absorption - Alkaline Scrubbing (Na_2CO_3 or $NaOH$)	
Moderate industry acceptance Low to moderate capital investment required Moderate operating cost Easy operation Moderate compatibility Low energy requirements	Borderline compliance with NO_x abatement criteria No power recovery capability No capability to increase plant production Limited proof of NO_x abatement capability Problem of disposal of by-product salt
Acid Scrubbing (Continuous Catalytic Absorption)	
Recovers NO_x increasing plant capacity Moderate capital investment required Moderate operating cost Moderately easy operation Moderate compatibility Moderate energy requirements	NO_x abatement capability unknown and unproven No power recovery capability

	ADVANTAGES	*DISADVANTAGES*
Silica Gel Adsorption	Recovers NO_X with potential for increasing plant capacity Moderate capital investment required Moderate operating cost Moderately easy operation Moderate compatibility	NO_X abatement capability unknown and unproven No power recovery capability
Molecular Sieve Adsorption	Meets NO_X abatement criteria Recovers NO_X increasing plant capacity Increasing industry acceptance Moderate capital investment required Moderate compatibility	No power recovery capability Capability and reliability yet to be proven Moderate to high operating cost High energy requirements - high heat requirements for desorption
Incineration (Flaring)	Potential power recovery Moderate capital investment required Simple operation Easily compatible with most plants	NO_X abatement capability unknown and yet to be proven Excessively high operating costs Destroys NO_X - no increase in plant capacity High energy requirements
Tall Stack with Venturi Device	Low capital investment, operating cost and energy requirements Simple operation Easily compatible	No positive treatment of NO_X No power recovery capability No capability for increase in plant capacity Little industry acceptance
Refrigeration	Can meet NO_X abatement criteria Good possibility of increased plant yield thru NO_X recovery Moderate capital investment required Easy operation Easily compatible	No power recovery capability Capability and reliability yet to be proven Probable high operating cost High energy requirements

TABLE 7

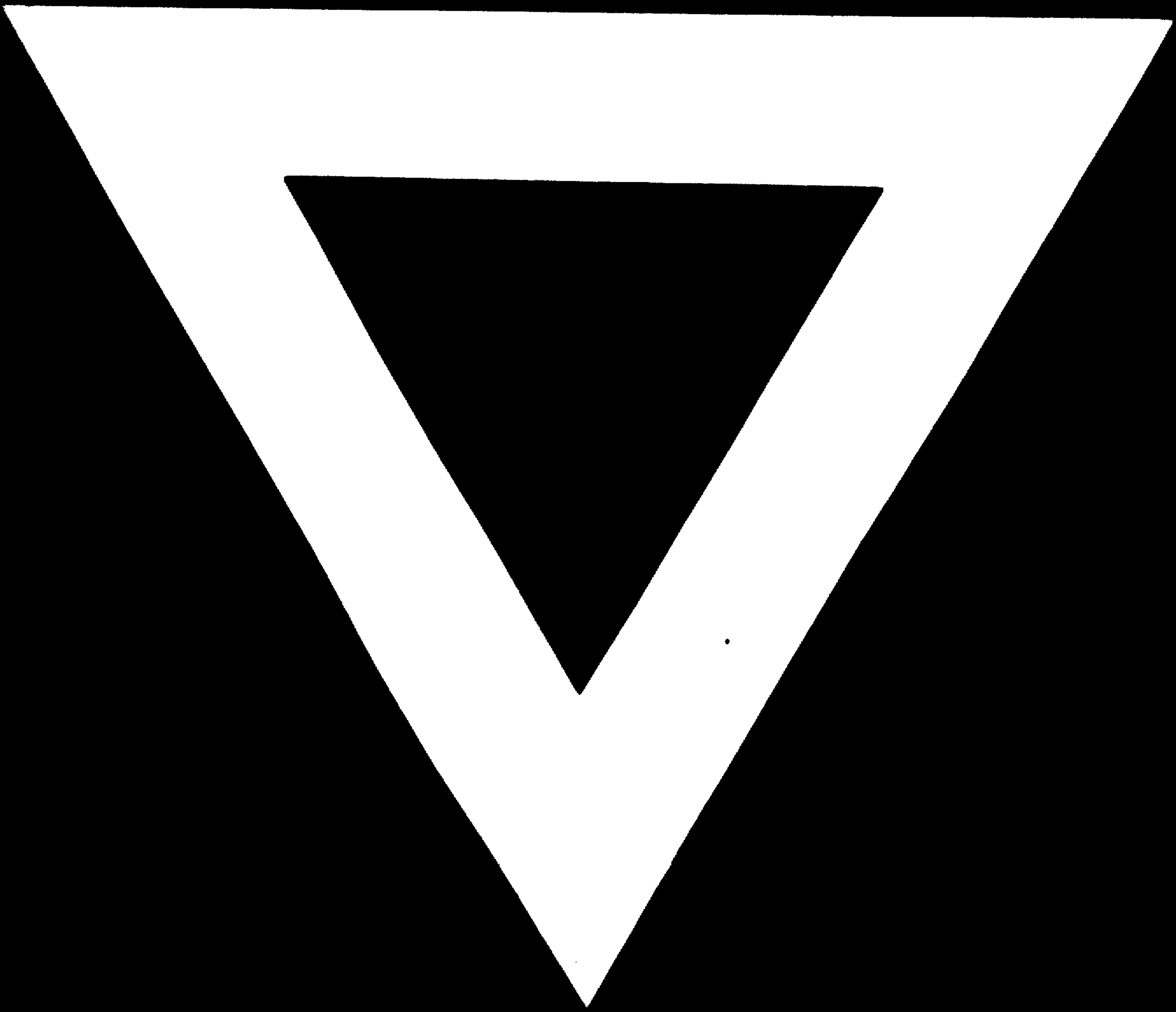
NO_x ABATEMENT METHODS FOR PRESSURE NITRIC ACID PLANTS

COMPARISON OF PRINCIPAL FEATURES

DEGREES

H - HIGH
M - MODERATE
L - LOW
O - ZERO
? - QUESTIONABLE

ABATEMENT METHODS	FEATURES											Remarks and Special Problems
	Compliance with NO_x Abatement Criteria	Power Recovery Capability	Plant Production Increase Capability	Proven NO_x Abatement Capability	Industry Acceptance	Capital Investment Requirement	Operating Cost	Energy Requirements	Ease of Operation	Compatibility with Existing Plants	NO_x Destruction (D) or Recovery (R)	
Catalytic Reduction (Combustion)	H	H	O	H	H	M	M-H	H	L-M	M-H	D	Catalyst Poisoning
Extended Absorption	H	O-	H	H	M	M-H	L	L	H	H	R	
Absorption - Alkaline Scrubbing (Na_2CO_3 or NaOH)	L	O	O	L	M	L-M	M	L	H	M	–	Disposal of By-Product
Absorption - Acid Scrubbing (Continuous Catalytic Absorption)	?	O	H	O	O	M	M	M	M	M	R	
Silica Gel Adsorption	?	O	?	O	O	M	M	?	M	M	R	Basis for Wisconsin Thermal Fixation Mfg. Process
Molecular Sieve Adsorption	H	O	H	M	M	M	M-H	H	?	M	R	High Heat Requirement for Desorption
Incineration (Flaring)	?	?	O	L	L	M	H	H	H	H	D	Excessively High Operating Costs
Tall Stack (usually with Venturi Device for Max Dilution)	O	O	O	O	L	L	L	L	H	H	–	No Positive Treatment
Refrigeration	H	O	M	?	?	M	M-H	H	H	H	R	



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