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UNITED NATIONS INDUSTRIAL DEVELOPMENT ORGANIZATION

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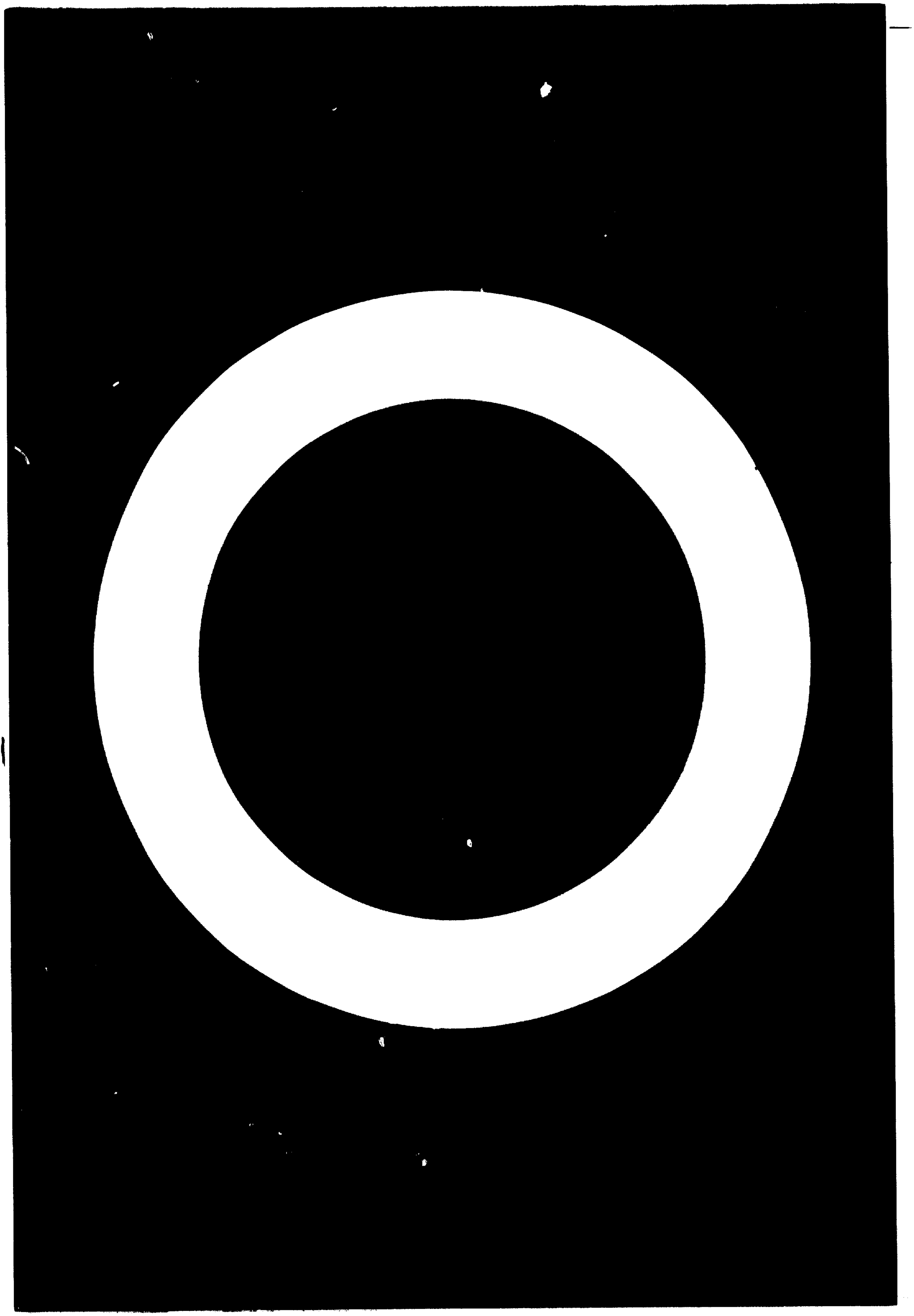
Development and Transfer of Technology Series,

No. 9

PROCESS TECHNOLOGIES FOR NITROGEN FERTILIZERS

UNITED NATIONS

PROCESS TECHNOLOGIES FOR NITROGEN FERTILIZERS



UNITED NATIONS INDUSTRIAL DEVELOPMENT ORGANIZATION
Vienna

Development and Transfer of Technology Series No. 9

PROCESS TECHNOLOGIES
FOR
NITROGEN FERTILIZERS

UNITED NATIONS
New York, 1978

Preface

This volume and its companion in the Development and Transfer of Technology Series, ***Process Technologies for Phosphate Fertilizers***, are the first two documents to emanate from the Industrial and Technological Information Bank (INTIB) of the United Nations Industrial Development Organization (UNIDO), which is a component of the UNIDO programme on the development of technology. INTIB is a pilot operation that began in July 1977 for a period of 18 months. Its work is being concentrated on four industrial sectors: iron and steel, fertilizers, agro-industries, and agricultural machinery and implements. Each of these sectors has priority in other UNIDO endeavours also: sectoral studies, consultations, negotiations and technical assistance projects.

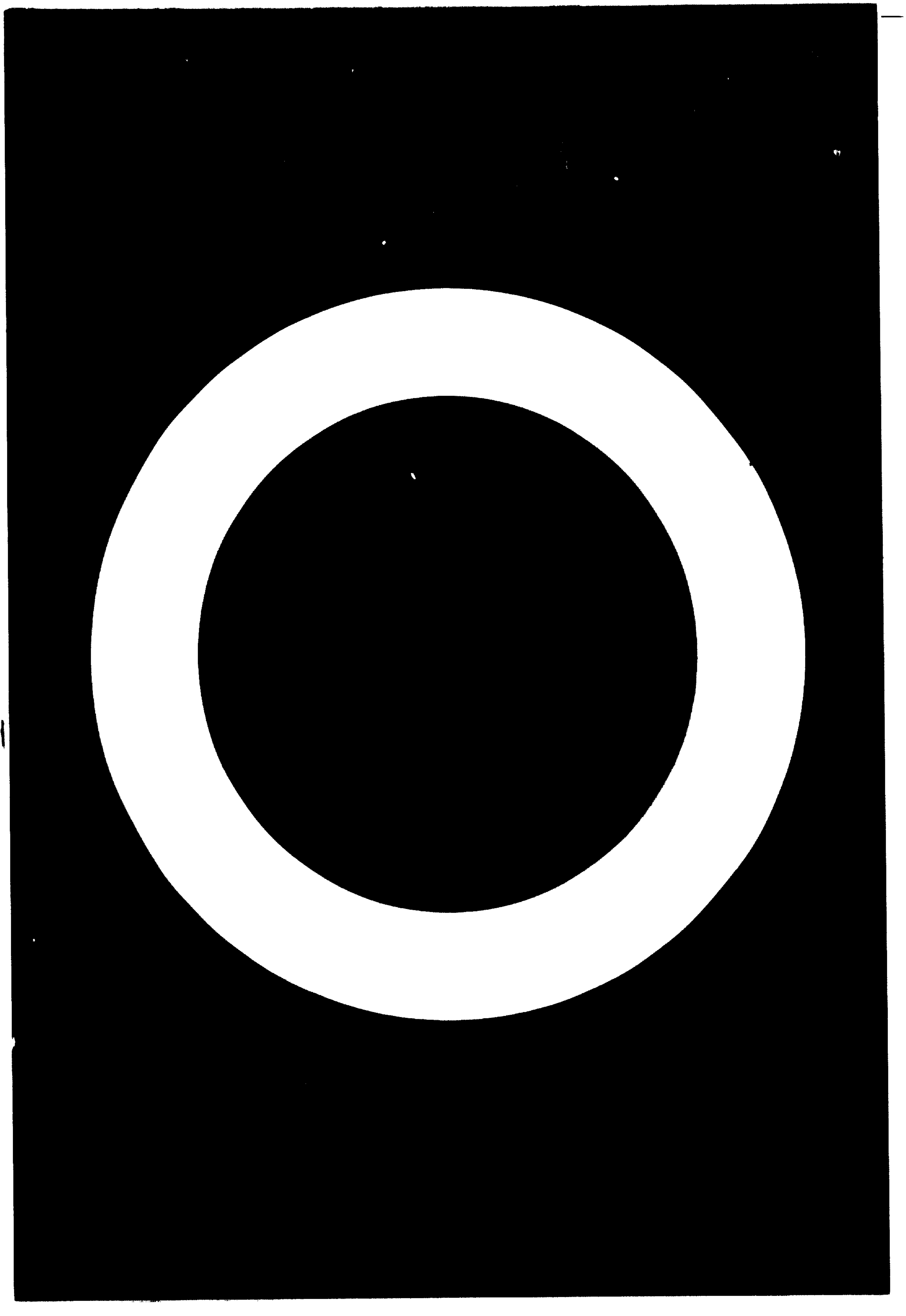
The concept of INTIB has its roots in the Lima Declaration and Plan of Action, adopted at the Second General Conference of UNIDO in 1975, and in various United Nations General Assembly resolutions, all envisaging such a service as an essential instrument for the transfer, development and adaptation of appropriate technologies. To increase the share of developing countries in world industrial output from 7 per cent (in 1975) to 25 per cent by 2000, an objective set by the Lima Conference, decision makers must have adequate information on new investments. Those advising the decision makers—national industrial information centres, technology development institutes and investment banks—also must have this information.

The novel character of INTIB, as compared with the services previously rendered by UNIDO, is that it is addressed to the selection of technology before the technology is acquired. INTIB not only draws upon the services available in the Industrial Information Section, where it is housed, but also relies on the expertise of specialists in the Industrial Operations Division of UNIDO and outside experts to process the information obtained from sources within and outside UNIDO relevant to technology selection. As a result of this effort, UNIDO is able to supply information in anticipation of, as well as in response to, demand. An example is the series of technology profiles and monographs being prepared, to which this volume belongs, concerning matters to consider when selecting a technology from a variety of alternatives.

The "customers" INTIB is designed to serve include ministries of industry, planning and industrial development institutes, multipurpose technological institutions, and agencies concerned with the transfer of technology. The intention is to serve all those who are responsible for selecting technology, whether in an advisory role or decision-making capacity, in each of the four priority industrial sectors selected for the pilot phase.

Further information about INTIB and its related activities can be had on request by writing to the Chief, Industrial Information Section, UNIDO, P.O. Box 707, A-1011 Vienna, Austria.

This description of nitrogen fertilizer production technologies was prepared by V. S. Pillai, acting as a consultant to UNIDO; the views expressed are those of the consultant and do not necessarily reflect the views of the secretariat of UNIDO.



EXPLANATORY NOTES

References to dollars ($) are to United States dollars.

The units employed are those of, or accepted for use with, the International System of Units (SI); in particular:

t	tonne (metric ton: 1 t = 1 000 kg)
t/d	tonne per day
bar	bar (1 bar = 10^5 Pa = 0.987 atm = 1.02 kgf/cm^2)

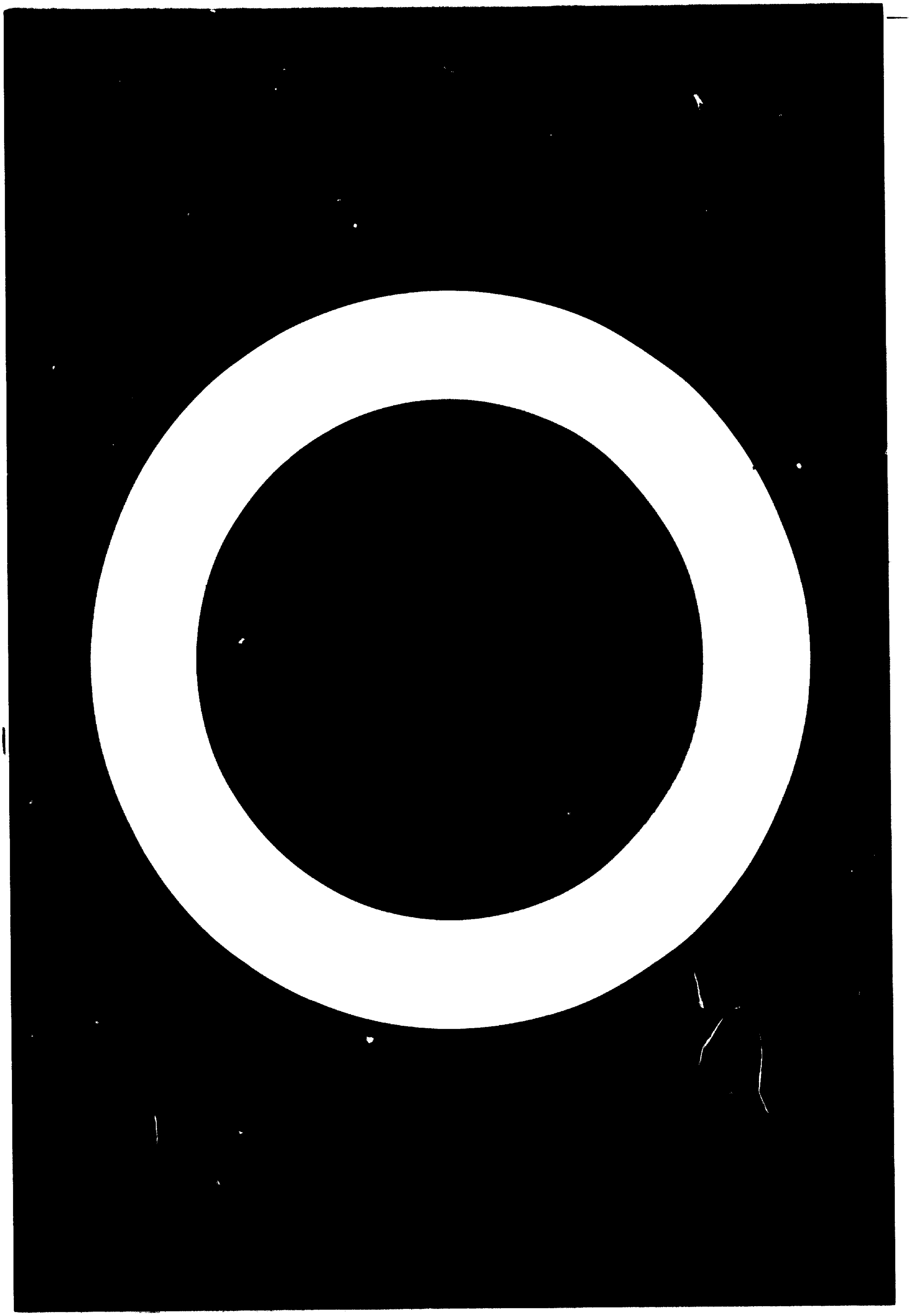
Besides the common abbreviations, symbols and terms, the following have been used:

Economic and technical

f.o.b.	free on board
f.o.r.	free on rail
ppm	parts per million
STP	standard temperature and pressure

Organizations

CPI	Chemical Process Industries
FCI	Fertilizer Corporation of India
ICI	Imperial Chemical Industries
IMI	Israeli Mining Industry
SBA	Société Belge de l'Azote et des Produits Chimiques du Marly
TVA	Tennessee Valley Authority



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NITRIC ACID *(continued)*

Introduction

The purpose of this compendium of the most important processes used for making nitrogen fertilizer materials is to provide a guide to the selection of process technologies for developing countries interested in initiating efforts in this sector. The processes for a given product are grouped together, and in every case the following information is given:

Description of the process operations

Flow chart

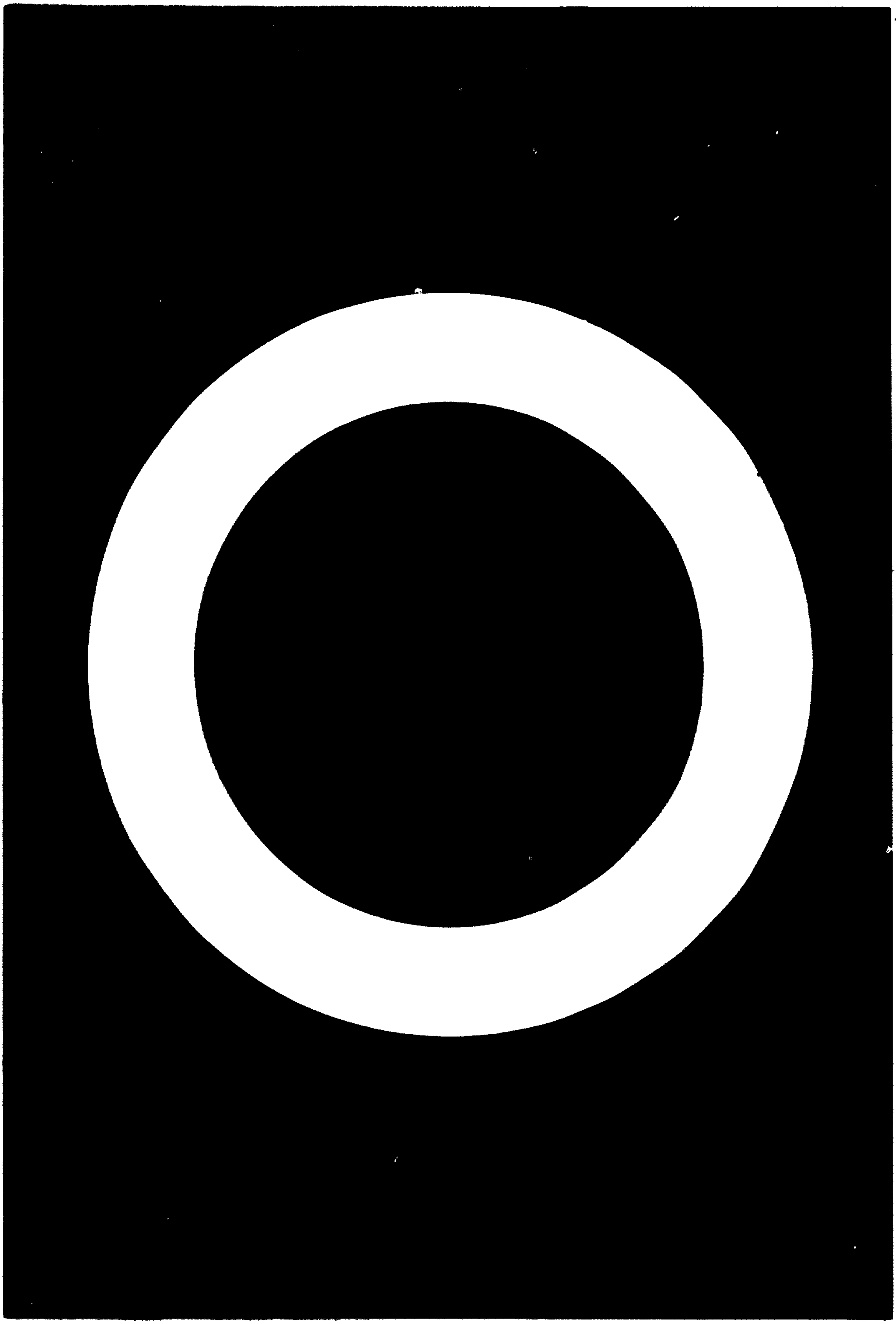
Advantages and disadvantages relative to the other processes in the same section

Owner, in the case of proprietary processes

Engineering licensees, if any

Unless otherwise stated, the know-how fees for proprietary processes are about 5% of the f.o.b. or f.o.r. costs of plant and equipment for processes that lead to ammonia synthesis gas, ammonia or urea (the first three sections) and about 3% for the others. Estimates of the cost (extrapolated to 1977) of erecting typical plants are given, most often in the introduction to each product section. All services are excluded from the estimates.

More details about the processes can be obtained from the firms named in the descriptions, whose addresses are given in the annex, and from the publications listed in the bibliography. One of the publications, *World Guide to Fertilizer Processes and Constructors* (Fifth edition, 1974), was the source of the lists of firms in this volume.



Ammonia synthesis gas

The principal methods used for the manufacture of ammonia synthesis gas ($3H_2 + N_2$) are the steam reforming of light hydrocarbons (naphtha; one process described), the partial oxidation of hydrocarbons with higher molecular weights (oils; two processes) and the gasification of coal (four processes). In special circumstances, an electrolytic method, in which the hydrogen is obtained by electrolysis of water and the nitrogen by distillation of liquid air, is used.

The estimated costs of plant and equipment for producing synthesis gas are included with those for ammonia plants in the next section.

Steam reforming of naphtha

ICI process

The ICI steam reforming process for the manufacture of ammonia synthesis gas consists of the following sequence of operations: feedstock pre-treatment (sulphur removal), primary and secondary reforming, high- and low-temperature shift conversion, CO_2 removal, and methanation.

Naphtha is volatilized, mixed with hydrogen-rich gas and passed through a cobalt molybdate catalyst, where sulphur compounds are converted to hydrogen sulphide, which is separated and burned as a fuel in the boilers. In addition to this hydro-desulphurization, to ensure that gases entering the reformer do not contain more than 0.5 ppm of sulphur, gases are passed through a desulphurizer vessel, containing sandwiched catalyst beds of comox and zinc oxide, which operate at a temperature of 370°-400°C.

The purified feedstock stream is mixed with steam to a steam/carbon mole ratio of 3 and passed through reformer tubes heated from outside and containing nickel catalysts. Reformer tubes are made out of centrifugally cast chrome-nickel (25/20) steel designed for a normal working life of 100 000 h. The reformer operates at a pressure of 27-37 bar and a temperature of 780°-820°C at the reformer outlet.

The partly reformed gas from the primary reformer passes to the secondary reformer, which is a refractory-lined vessel containing nickel catalyst. Air is introduced in the secondary reformer to provide sufficient nitrogen for the synthesis gas. The secondary reformer operates at 980°-1200°C, bringing the methane content of the outlet gases to less than 0.3%.

After heat recovery, the reformed gas from the secondary reformer passes through both high- and low-temperature shift conversion steps, to ensure as much conversion as possible ($CO + H_2O \rightleftarrows CO_2 + H_2$). The proportion of CO at the outlet of the low-temperature shift converter is less than 0.3% by volume.

Removal of CO_2 is an important step in the process, and a variety of proven methods are available. All of them use a solvent, usually a potassium carbonate solution containing activators for maximum absorption and inhibitors for minimum corrosion.

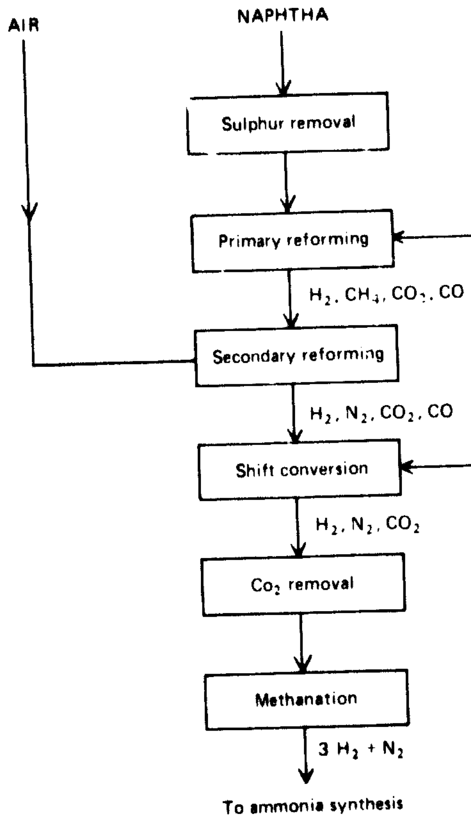
Final purification of the synthesis gas is done by methanation in the presence of a catalyst that converts any CO and CO_2 present in the gas to methane.

Heat is available for recovery from two types of streams: the process gases at loop pressure and the flue gases from the primary reformer. The heat of the process gases is principally used to raise steam at the outlet of the secondary reformer. It is also used to reboil the solvent used in the CO_2 removal system, pre-heat the gas going to the methanator etc. Flue-gas from the primary reformer furnace is used to raise steam, superheat steam and pre-heat process air, combustion air etc. as required.

The gas at the outlet of the methanator contains N_2 and H_2 in the correct stoichiometric ratio, and is sufficiently pure, for the ammonia synthesis.

Advantages

- Almost complete elimination of electrical energy possible by use of recovered heat and steam-driven machinery
- Lower compression cost and smaller plant size because of increased reformer pressure
- A good process when feedstock naphtha is available at an attractive price



Ammonia synthesis gas by steam reforming of naphtha (ICI process)

Disadvantages

- Increased pressure and temperatures require expensive materials of construction
- Catalyst tubes in the reformer cannot be used for pressure above 37 bar. Also, they do not last long if operated outside a rather narrow temperature range
- Because of low conversion efficiency, two reformers are necessary for complete reforming

Process owner

Imperial Chemical Industries Ltd

Engineering licensees

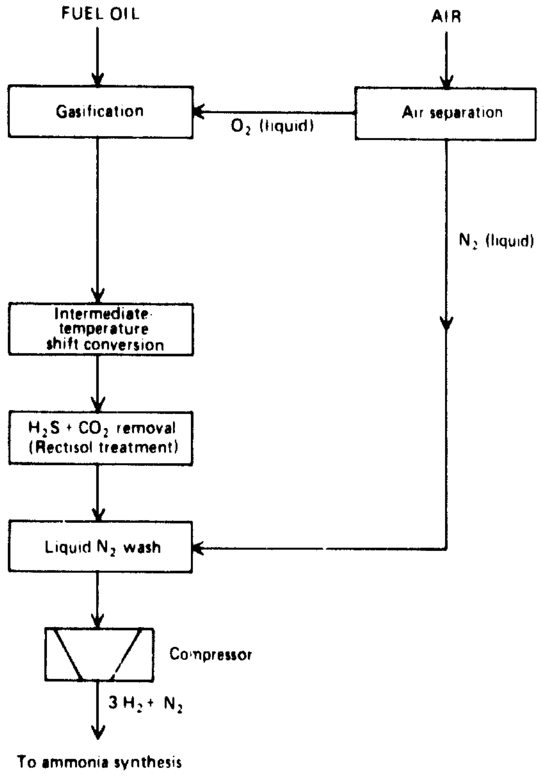
Davy Powergas Ltd
The Fertilizers and Chemicals Travancore Ltd
Foster Wheeler Corporation
Friedrich Uhde GmbH
Humphreys and Glasgow Ltd
The M. W. Kellogg Company
Selas Corporation of America

Partial oxidation of oil

Texaco process

Partial oxidation is a versatile process for production of ammonia synthesis gas using high-sulphur feedstocks with a wide range of properties and composition – from methane to heavy residual oil. The process consists of synthesis-gas generation, carbon extraction and recovery, shift conversion, acid-gas separation and liquid-nitrogen wash.

In the Texaco partial oxidation process, the feedstock heavy oil is partly burned with oxygen in a refractory-lined gasifier, where reaction temperatures are high enough to obviate the use of a catalyst. Fuel consumption is approximately 4.6 t per tonne of final product hydrogen. The gasifier operates at a pressure of about 80 bar. The hot gas in the generator is directly quenched with water so that the process heat is utilized to increase the water-vapour content of the gas enough to make it suitable for the CO shift conversion. Owing to the relatively high temperature in the reactor, the methane content of the product gas comes down to less than 0.6% by volume, even at high pressure.



Ammonia synthesis gas by partial oxidation of fuel oil (Texaco process)

The 1%-3% of the feedstock that is converted to soot in the generator is almost entirely removed from the gas in its water quench chamber, with the final traces being removed in a scrubbing nozzle, in which the gases are mixed with water at high shear velocities.

The water-soot stream that is separated from the gas stream is then mixed with naphtha to transfer the soot to the naphtha phase. The two phases are then separated in a decanter, and the naphtha-carbon slurry is recycled to the gasifier, thereby completely recovering and reusing all the soot formed.

The gas from the carbon-removal section is passed through an intermediate-temperature shift catalyst. This catalyst contains cobalt and molybdenum and requires sulphur in the feed gas for activation. The operating temperature is 60°-80°C lower than that of the commonly used high-temperature iron oxide shift catalyst. The CO content in the exit gas is reduced to 0.9-2.5 vol%. This low level means that the load in the subsequent liquid-nitrogen wash system is reduced.

After shift conversion the gas is passed through a physical absorption acid-gas removal system that is particularly effective on sulphur-containing feedstocks. This treatment, called the Rectisol process, not only reduces the acid gas to a low level but also separates out H_2S. The output CO_2 is pure enough for use in urea production, and the H_2S can be further processed to recover elemental sulphur.

The gases, freed of H_2S and CO_2, are then treated in a liquid-nitrogen wash unit, which, in addition to removing CO and CH_4, adds the nitrogen required for ammonia synthesis. The mixture of N_2 and H_2 from this unit is stoichiometric and sufficiently pure for ammonia synthesis.

Advantages

The high pressure in the gasifier loop reduces the cost of compressing the synthesis gas. It also enables use of a liquid-oxygen pump to boost the oxygen pressure to that required for gasification, eliminating the safety problem of compressing oxygen in high-pressure centrifugal compressors

CO_2 can be pumped in liquid form for use in urea production, again eliminating compression costs

Feedstock containing up to 6% sulphur can be processed, and there is good feedstock flexibility

All the soot formed is reused, eliminating problems of carbon disposal or pollution

- The process is a good choice in countries where the burning of fuel oil in power plants is not permitted because of pollution hazards
- Sulphur can be recovered in elemental form if necessary to eliminate sulphur pollution
- Costly catalysts are not required for gasification

Disadvantages

- More than one gasifier is necessary for ammonia production rates greater than 450 t/d
- The air-separation plant requires a large investment

Process owner

Texaco Development Corporation

Shell process

The sequence of operations followed in the Shell process is generally the same as for any partial oxidation process. However, there are a few distinguishing features:

(a) The gasifier normally operates at a lower pressure, about 60 bar, and uses a waste-heat boiler after gasification for recovering heat by raising steam, instead of quenching the hot gas with water;

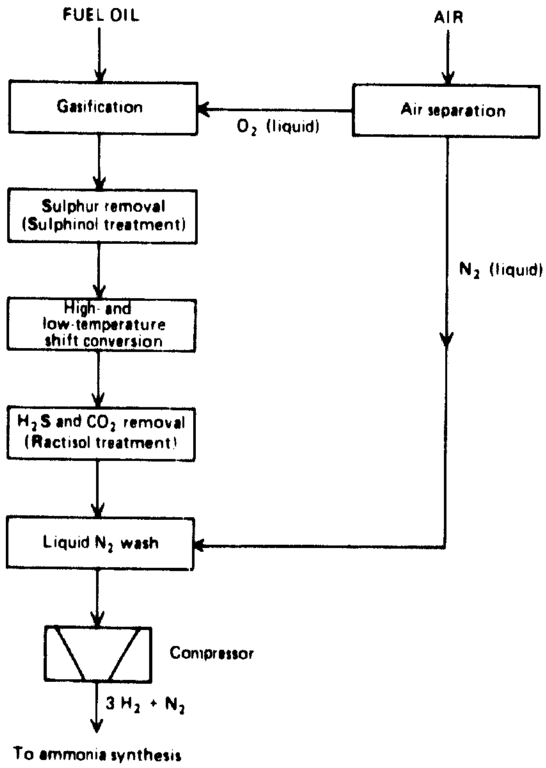
(b) The gases coming from the waste-heat boiler are cooled to the dew point for efficient removal of carbon in a two-stage water wash that brings carbon down to less than 1 ppm. Carbon is recovered from the carbon-water slurry in the form of pellets, which are slurried with fuel oil and used to fire boilers;

(c) After gasification, heat recovery and carbon removal, the gas is first desulphurized by the Sulphinol process, which brings the sulphur level down to 1-2 ppm, making the gas pure enough for the normal high- and low-temperature CO shift conversion steps.

As in the Texaco process, acid-gas removal is by the Rectisol treatment, and a liquid-nitrogen wash for final purification and addition of nitrogen follows. The gas can now be further processed for ammonia synthesis.

Advantages

- The high pressure in the gasifier loop reduces the cost of compressing the synthesis gas
- Choice of feedstock is flexible; feedstock can be processed
- The process is a good choice in countries where the burning of high-sulphur fuel for power is disallowed



Ammonia synthesis gas by partial oxidation of fuel oil (Shell process)

Disadvantages

- A number of gasifier units are necessary for ammonia production rates greater than 450 t/d
- Waste-heat recovery needs a special, non-fouling type of boiler
- The air-separation plant requires a large capital investment
- The oxygen supplied to the gasifier is in the form of gas, and centrifugal compressors are used to handle it. At gasification pressures of 60 bar, there is no problem with compressing oxygen gas in centrifugal compressors; above 70 bar, problems have been reported
- CO_2 cannot be taken out in liquid form since the pressure in the gasification loop is only 60 bar
- In the absence of power recovery from process steam and quenching in the gasifier, it is claimed that there is no particular advantage in gasification pressures higher than 60 bar
- Recovered carbon is not returned to the gasifier but used in boilers as fuel. That might add to pollution problems

Process owner

Shell Development Company

Engineering licensees

The Fertilizer Corporation of India Ltd
Heinrich Koppers GmbH

Gasification of coal

The sequence of operations followed in gasification of coal consists of two main steps: gasification and gas processing and purification. Although the first step is uniquely adapted for coal, the second essentially follows the same sequence as in the partial oxidation of fuel oil units.

Coal gasification, which is achieved by blowing oxygen and steam on to a bed of coal, can be done with the fuel in a fixed bed or suspended in a gas. The Lurgi and Winkler processes are examples of the former type of process, and the Koppers-Totzek process is an example of the latter.

Lurgi process

Run-of-mine coal is crushed and screened, and 64% of the coal particles sized between 5 and 30 mm is gasified in a fixed bed with oxygen and steam at a pressure of 25 bar. The balance (36%) is used as fuel in a boiler, generating steam for driving machinery and for processing. The plant is self-supporting with respect to energy supplies; electricity is purchased for small drivers only as a matter of convenience.

In this process, most of the hydrogen is produced by the reaction of steam with carbon in the gasifier, and only a small portion is produced in the downstream CO shift conversion section. The steam in the gasifier also helps maintain the temperature in the combustion zone.

The crude gas leaving the gasifier is intensively washed in an attached scrubber, its sensible heat being recovered in a waste-heat boiler. Wet scrubbing under pressure with a gas liquor containing hot tar eliminates all problems that particulates may otherwise create.

The gas is then passed through a crude-gas CO shift-conversion stage, which contains a catalyst insensitive to the sulphur compounds and products originating from coal gasification, such as tar and naphtha.

When the gas is cooled, partly in waste-heat boilers and partly in air or water coolers, steam and tars, which are valuable by-products, are condensed and separated.

After the crude-gas shift conversion, the gas passes through the acid-gas removal section, which uses the Rectisol process. The solvent, methanol below 0°C, can remove large volumes of various impurities that are normally present in coal gasification, and the result is a high purity gas suitable for further processing. The Rectisol process also removes CO_2 from the reformed gas coming from the steam reforming process arranged as a side stream.

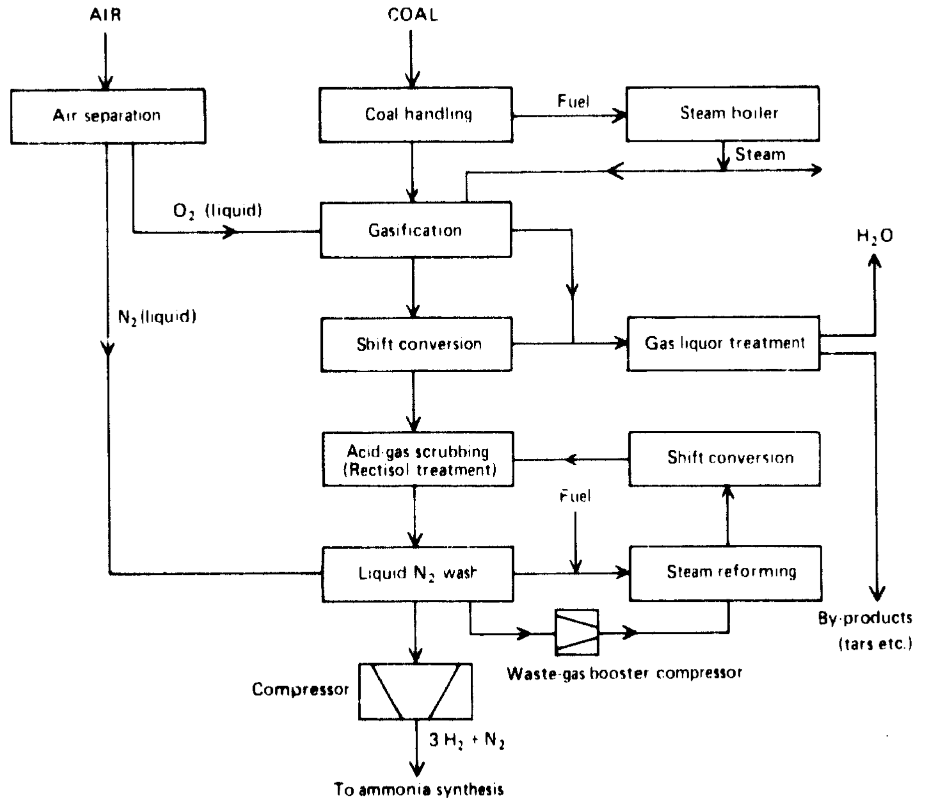
The purified gas passes through a liquid-nitrogen wash for the removal of CH_4 and CO. Additional nitrogen is added here in order to adjust to the stoichiometric ratio required for ammonia synthesis.

The methane fraction separated in the liquid-nitrogen wash consists of roughly 70% CH_4 and 25% CO. This gas is compressed to a pressure of 28 bar and reformed in the side-stream reformer mentioned above. Operating conditions in this steam reformer are not stringent, and also slight fluctuations in the main stream gas composition are easily balanced in the side-stream reformer.

If the by-products are not in demand, they can be reformed completely, and there will be only one product from the main plant.

Advantages

- Plant is self-supporting with respect to energy supply
- Coal containing up to 45% ash with a high fusion point can be used
- High pressure in gasification loops reduces cost of compressing the synthesis gas
- A good choice in places where coal is available but petroleum feedstocks are scarce
- Process consumes only 300 kg O_2 per 1 000 m^3 (STP) of ($CO + H_2$)



Ammonia synthesis gas by gasification of coal (Lurgi process)

Disadvantages

- Capital intensive; cost is approximately 57% greater than that of a steam reforming plant
- Normally, only coal from a known source and of known quality can be used; variations can create difficulties
- Needs very large coal producing and handling facility. The requirement is 2.2 t of coal per tonne of ammonia
- More than one gasifier needed to get high production rates: four may be needed for a rate of 1 000 t/d
- Good on-stream factors may be lacking. Hence, over-design of the plant and provision for spare equipment is essential
- The air-separation plant requires a large capital investment
- Disposal of by-products may be a problem, although they can be reprocessed so that the plant finally has only one product

Process owner

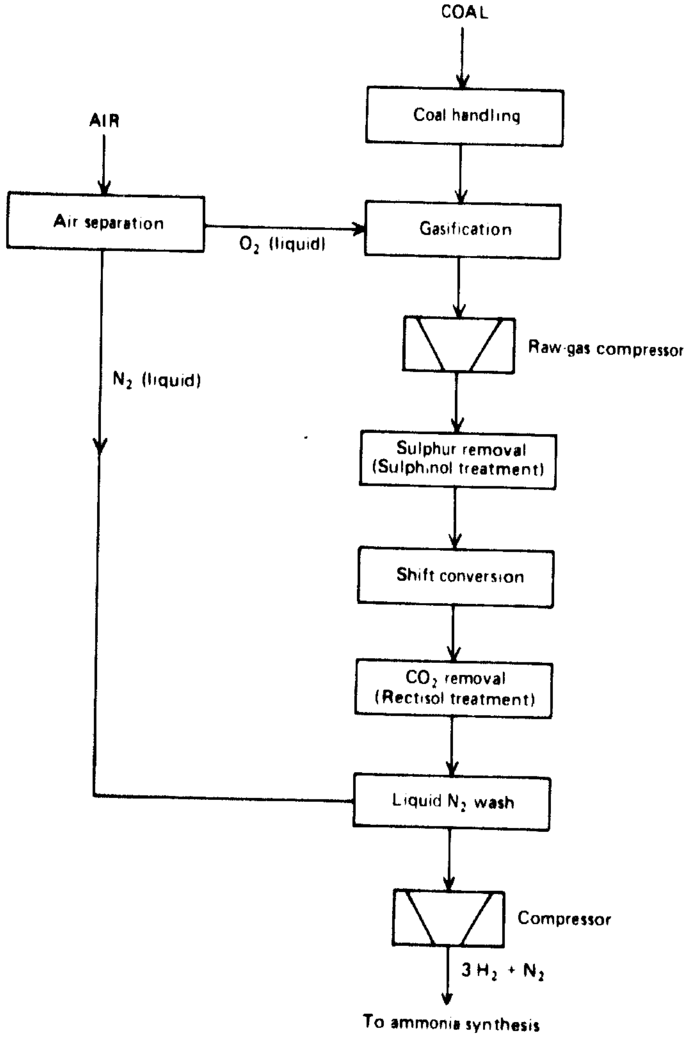
Lurgi Mineralöltechnik GmbH

Koppers-Totzek process

Powdered coal (75% through a Tyler sieve of 200 mesh) is gasified in a stream of oxygen and steam at atmospheric pressure. All types of coal as well as petroleum residues can be handled in the gasifier. The high temperature in the gasifier, 1 500°-2 000°C, converts the coal completely to simple molecular species, such as H_2, CO_2 and CO, with a CH_4 content as low as 0.1%-0.2% and practically no tar.

The raw gas is then cooled by passing it through a waste-heat boiler and cleaned to remove all suspended matter: ash, grit and unburnt fuel, in the case of coal, and carbon soot, in the case of fuel oil. The gas then goes through a gas treatment and purification section.

The reaction mechanism and the quality of gas produced by coal dust gasification are similar to those encountered in partial oxidation of heavy oil (see above). Therefore, the gas treatment and purification sections consist of sulphur removal using Sulphinol, high- and low-temperature CO shift conversion, acid-gas removal by Rectisol, and a final liquid-



Ammonia synthesis gas by gasification of coal (Koppers-Totzek process)

nitrogen wash. The Rectisol process can be used for removal of both sulphur and carbon.

The gas coming out of the liquid-nitrogen wash contain N_2 and H_2 in the correct stoichiometric ratio, and is sufficiently pure, for the ammonia synthesis.

Advantages

- Feedstock flexibility very good, as the process can handle coal as well as residual oils and tars
- Self-sufficient with respect to energy supply
- There is no by-product disposal problem
- Fabrication of the gasifier and its machinery is easy because it operates at atmospheric pressure
- Operation is simple

Disadvantages

- Capital intensive; cost is approximately 83% greater than that of a steam reforming plant
- Energy requirement for fine-crushing of coal works out to approximately 100 kWh per tonne of ammonia produced
- Gas compression cost is higher since gasifier operates at atmospheric pressure
- Needs large coal producing and handling facility
- Several gasifiers required
- Excess designed capacities and a good stock of spares are necessary to ensure high stream factors
- Needs an oxygen plant having high capital investment. Oxygen consumption is 500 kg per 1 000 m^3 (STP) of $(CO + H_2)$

Additional compressor required for compressing raw gas, since gasifier works at atmospheric pressure

Process owner

Heinrich Koppers GmbH

Engineering licensees

The Fertilizer Corporation of India Ltd

Winkler process

The Winkler process uses a fluidized bed to gasify coal. The gasifier operates at a pressure of 3 bar. After gasification, the gas is cooled by passing it through a waste-heat boiler and cleaned to remove all suspended matter (ash, grit, unburnt fuel etc.).

After cleaning, the gas is compressed in a raw-gas compressor and sent through the same sequence of steps as in the Koppers-Totzek process, namely, desulphurization by Rectisol, high- and low-temperature CO shift conversion, acid-gas removal by Rectisol, and the final liquid-nitrogen wash.

The gas coming out of the liquid-nitrogen wash contains N_2 and H_2 in the correct stoichiometric ratio, and is sufficiently pure, for ammonia synthesis.

Advantages

Oxygen consumption is lower than in other coal gasification plants

Because of slightly higher pressure operation than in the Koppers-Totzek process, gas cleaning is possible with wet-cyclone and venturi scrubbers instead of electrostatic precipitators

Operation is simple

No by-product is produced

Disadvantages

Gas compression cost is high as it operates at low pressure and needs a raw-gas compressor

Needs large coal producing and handling facility

Several gasifiers, an adequate stock of spare equipment and additional design capacity are necessary to ensure good stream factors

Needs an oxygen plant that has a high capital investment

Has always to have coal from the same known source; otherwise, there can be difficulties

The process can handle only coal

Process owner

BASF Aktiengesellschaft

Electrolytic method

de Nora process

The sequence of operations is as follows:

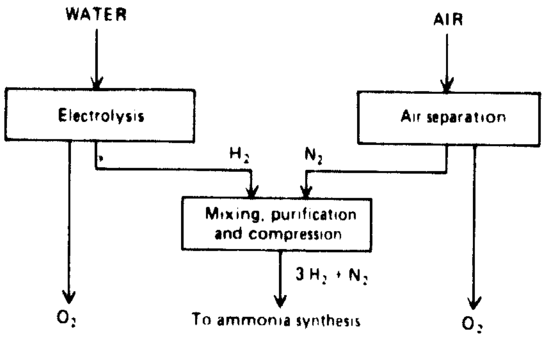
Production of H_2 by electrolysis of water
Production of N_2 by air separation
Mixing
Purification
Compression

The raw material for electrolysis is water to which a small quantity of pure NaOH has been added.

The products of electrolysis ($2H_2 + O_2$) are stored in separate gas holders. The electrolytic cells operate at slightly above atmospheric pressure, and the gases can go direct to the gas holders without being compressed.

In the second step, air is purified, compressed, liquefied and fractionated into N_2 and O_2.

Since the feedstock for synthesis is a stoichiometric mixture of N_2 and H_2 that contains only a few parts per million of O_2 as an impurity, the only



Ammonia synthesis gas by the electrolytic method

purification required is removal of this O_2 by passing the mixed gases through a palladium catalyst. The gas entering the purifier should be dry; otherwise, it has to be slightly heated a few degrees above saturation temperature to prevent any condensation of water in the catalyst bed, in which the O_2 reacts with H_2 to form H_2O.

The N_2 and H_2, in the ratio of 1 to 3, are drawn by the synthesis-gas compressor through the mixing vessel and purifier and compressed to the pressure required for the ammonia synthesis.

Advantages

Oxygen is a useful by-product
Since the gases contain very little impurity, not much inert material builds up in the synthesis loop
Adjunct heavy-water manufacture is possible

Disadvantages

The electrical power requirement is high and hence cost of production is comparatively high
Compression cost is high for ammonia production since the gases have to be compressed from the gas-boiler pressure to a pressure of about 345 bar
An air-separation plant is necessary
There is some risk of explosion in the electrolysis cell

Process owner

Oronzio de Nora (Impianti Elettrochimici SaS)

Owners of a similar process

Consolidated Mining and Smelting Company

Ammonia

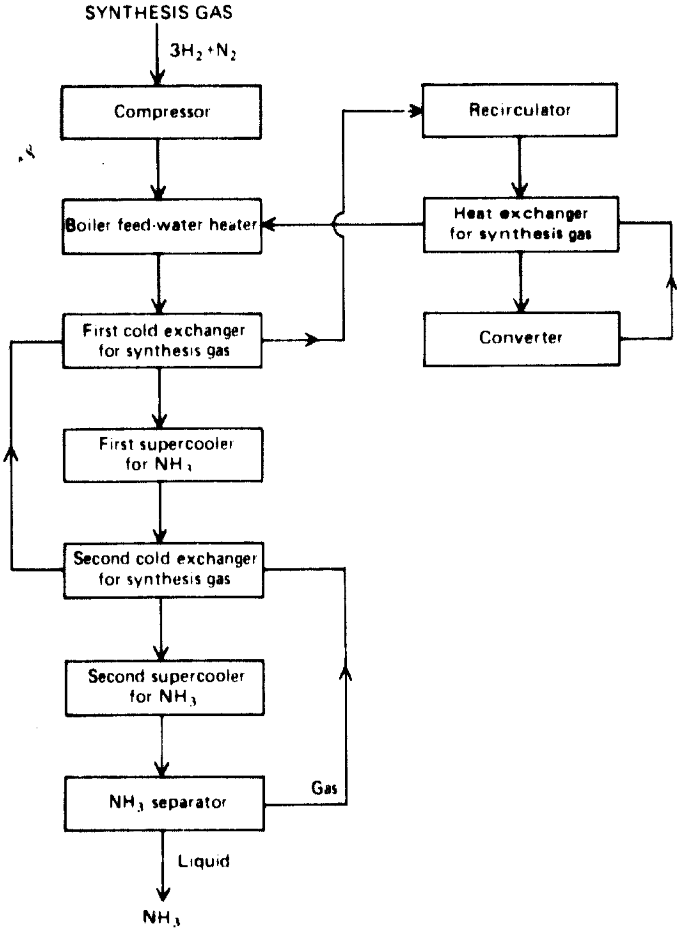
$3H_2 + N_2 \rightarrow 2NH_3$

A major breakthrough in ammonia production technology occurred about 1963. An increase in plant size, the use of centrifugal compressors, the optimization of ammonia-synthesis pressure, an increase in space velocities in the converter and improvements in energy recovery were some of the important changes.

The catalyst in the converter is divided into several beds, with cooling in between achieved by quenching with cold gas or heat exchange with other process streams.

The main differences among the four process designs described here are in the type of converters used; the sequence of steps is the same in all.

The table below gives the estimated cost of erecting a complete ammonia plant (involving both synthesis gas manufacture and ammonia synthesis) as a function of daily



Ammonia synthesis

capacity and feedstock. The electrolytic method is not included, since it is used only in special circumstances. The cost is for a battery limit plant erected in Western Europe and includes the cost of equipment and material f.o.b. a European port, civil engineering, erection, and engineering and licence fees. It is only approximate, having been extrapolated to 1977 from 1970 prices. Excluded are the costs of the following items: boiler feed-water treatment, steam boiler, cooling towers, instrument and plant air supply, transformer station, product storage facilities, mobile equipment, spare parts.

Daily NH_3 capacity (t)	Cost (millions of dollars)				
				Coal[a, b]	
	Natural gas	Naphtha	Oil[a]	Bed process	Powder process
300	*33*	*35*	*48*	*56*	*66*
600	*50*	*52*	*72*	*81*	*94*
1 000	*68*	*71*	*94*	*107*	*125*
1 500	*89*	*92*	*118*	*133*	*155*

[a] *Including cost of oxygen plant.*
[b] *Excluding cost of coal-handling facilities.*

ICI process

Large plants use centrifugal compressors for the synthesis gas, for process air and for refrigeration. One or two stages at the high-pressure end of the synthesis-gas compressor are commonly used for recirculating the gas, with a diaphragm being used to separate the gases in the compression and recirculator casings.

The ICI process, which operates at high pressure (300-350 bar), uses a converter consisting of a vertical pressure-vessel, with a fully closed, flat top and a hemispherical bottom. The catalyst is contained in a single annular basket around a heat exchanger. Quench gas is introduced through distributors at intermediate points down the catalyst bed.

The main gas flow enters the converter at the bottom and goes first through the annular space between the converter shell and the catalyst basket to cool the outer shell, and then enters the heat exchanger at the top. After two passes through the heat exchanger, one in the tube side and one in the shell side, the gas has reached reaction temperature and enters the catalyst bed at the top.

The temperature of the catalyst bed is kept at 450°-500°C by admitting the cold quench gases in the catalyst bed. The hot gases finally leave the catalyst basket to go through the central heat exchanger, where they heat the gases coming into the catalyst bed.

The hot gases leaving the converter pass through a series of heat exchangers to cool the gases and condense the ammonia formed. In the process they heat the fresh gases going to the converter, as well as the other process streams used for heat exchange.

Advantages

Since the catalyst is in one bed, removal and recharging takes minimum time.

Provision is made in the converter shell and basket to empty spent catalyst before opening the top cover, saving time

Basket assembly is easy

Disadvantages

The pressure drop across the converter can be high since the catalyst is in one bed and the flow is downwards; higher pressure drop increases power cost

Converter temperature may not be so uniform as in a multi-bed catalyst

Since loop pressure is 300-350 bar, an expensive three- or four-barrel synthesis-gas compressor is required

Process owner

Imperial Chemical Industries Ltd

Engineering licensees

Davy Powergas Ltd
Foster Wheeler Corporation
Hitachi Ltd
Humphreys and Glasgow Ltd
Kakoki Kaisha
Ralph M. Parsons Company Ltd

Kellogg process

The Kellogg converter consists of a high-pressure vertical shell with a hemispherical bottom and a flat, full-closure top. The catalyst sections are in several beds supported on grids, with the heat exchanger located beneath them. The catalyst-bed sizes vary, with the largest bed at the bottom. Cold quench gas is injected before each bed. The top quench-point permits direct entry of cold gas to the first bed, which also acts as a temperature-control device.

Feed gas enters the converter at the top and flows downwards in the annular space between the catalyst basket and shell, cooling the converter shell. The gas then enters the bottom heat exchanger on the shell side and goes to the top of the first catalyst bed through a central tube in the catalyst basket. In its passage through the heat exchanger, the gas picks up heat from the hot outlet gas leaving the converter. This gas, mixed with the cold quench gas going to the first bed, enters the catalyst at a temperature of 370°-430°C, at which the reaction begins in the top bed.

The gases flow downwards through the catalyst bed, increasing in temperature as the ammonia reaction proceeds, and through the catalyst supporting grids into the spaces between the beds. Here quench gas is introduced to bring down the temperature and ammonia content to the proper levels required for the second bed. Similarly, gases flow through other beds until they finally enter the heat exchanger on the tube side before leaving the converter.

The sequence of operations after the gases leave the converter is more or less similar to that of other processes.

For very large ammonia capacities, Kellogg uses horizontal converters instead of vertical ones, with the object of reducing the pressure drop across the converters.

Kellogg uses two processes for synthesis, one using medium pressures (150-250) bar and the other using a pressure of 300-350 bar. The medium-pressure loops also use a greatly simplified design with only one ammonia separator for the whole loop.

Advantages

The multi-bed quench-converter gives uniform temperature in the beds

For the low-pressure loops, simple two-barrel centrifugal compressors are sufficient for synthesis gas compression and for recirculation

Disadvantages

Catalyst discharge and recharging take more time because of the grid assembly

The low-pressure loop needs larger vessels and pipelines

Process owner

The M. W. Kellogg Company

Topsøe process

The Topsøe converter is a vertical vessel having a hemispherical bottom and a flat, full-closure top. The catalyst is arranged in beds and quench gases are introduced between beds. The heat exchanger is located below the catalyst beds.

Two gas streams enter the catalyst bed at the top, one through the annular space between the catalyst basket and the converter shell, thence through the heat exchanger, the other straight through the catalyst bed, by-passing the heat exchanger.

The gases enter the bed in a radial path, instead of the conventional axial one; the flow path is thus shorter, resulting in a considerable reduction of the pressure drop across the converter. Because of that, the converter can also use a catalyst with smaller particle size, which will increase the yield of ammonia.

The heat exchange inside the converter and the sequence of operations in the synthesis loop are more or less the same as in other processes.

The Topsøe process uses high pressure (300-350 bar) in the synthesis loop.

Advantages

The radial-flow converters, because of their reduced pressure drop, require less power to operate

Large units can be built, owing to compact design

A more finely divided catalyst can be used to get higher conversion per pass

Disadvantages

Because of the pressure, a costly synthesis-gas compressor with three or more barrels is needed

Process owner

Haldor Topsøe A/S

Engineering licensees

Chiyoda Chemical Engineering and Construction Company Ltd

Montedison process

Like the other ammonia processes, the Montedison process uses multiple beds of catalysts and an internal feed-effluent exchanger, but the temperature control in the converter is basically different. The cooling of gases between beds is by an internal, easily removable tube bundle for recovering the heat of reaction by the production of high-pressure by-product steam.

The converter operates at high pressure (300-350 bar).

Other details of the loop are more or less similar to those of other processes.

Disadvantages

For large plants, cooling the gas by means of cooling coils is not regarded with favour by engineers

The converter design is not compact enough for large capacities

The pressure drop across the converter can be high and energy costs will be correspondingly high

Maintenance of the converter can be complicated

Because of the pressure in the synthesis loop, a costly synthesis-gas compressor with three or more barrels is needed

Process owner

Montedison SpA

Engineering licensees

The Fertilizer Corporation of India Ltd

Urea

Ammonia and carbon dioxide constitute the feedstock for all processes for the synthesis of urea (NH_2CONH_2). They react to form an intermediate product, ammonium carbonate (NH_2COONH_4), which then decomposes to form urea and water. The feedstock and recycled intermediate are brought together in a reactor at a temperature of 170°-230°C and a pressure of 120-280 bar. The effluent from the reactor contains urea, water, excess ammonia and substantial quantities of the intermediate, which is simply called carbamate.

In all urea processes, the carbamate must be removed from the urea solution produced in the reactor. The removal operation differs for the different processes in the ways in which the carbamate is decomposed and removed and the off-gases produced in the decomposition are treated. There are three categories of processes: "stripping" (two processes described), total recycle (three) and gas-separation recycle (one).

The finishing operations are more or less the same for all processes depending on the amount of the impurity, biuret ($NH_2CONHCONH_2$), that can be tolerated in the final product.

Only the cost of a total-recycle urea plant is given here (see page 22).

Stripping processes

Stamicarbon process

In the Stamicarbon stripping process, carbamate is decomposed at the reaction pressure by reducing its partial pressure with an atmosphere of carbon dioxide. Recombination of ammonia and carbon dioxide to form carbamate also takes place at this pressure and at high temperature, thereby aiding heat recovery in the form of steam production. The vessels in this section, the reactor, stripper and condenser, are so positioned that the recycled carbamate solution flows into the reactor from the condenser by gravity.

The reactor is a vessel lined with stainless steel and containing a series of trays to assist mixing of reactants. Traces of air are added to the reactor via the feedstock carbon dioxide to inhibit corrosion.

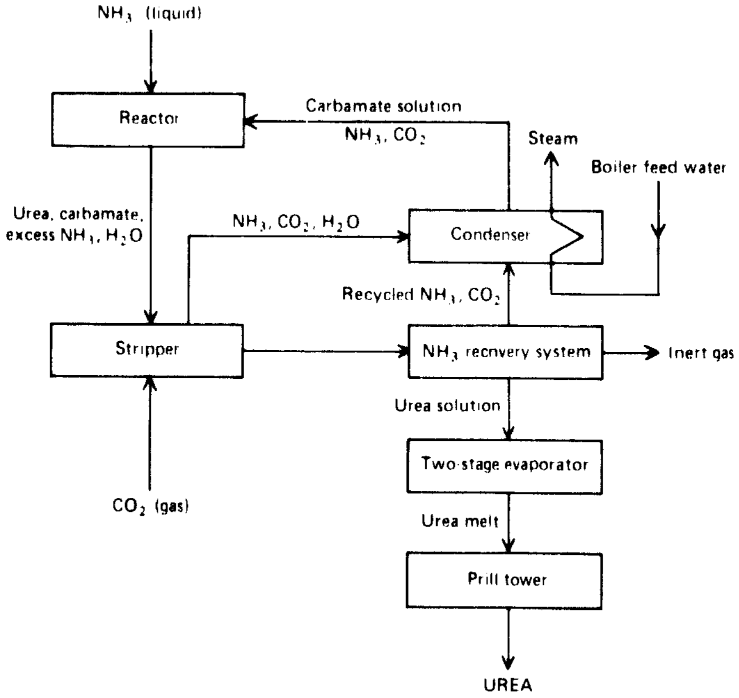
The optimum NH_3/CO_2 mole ratio of 2.8 is maintained in the reactor by feeding NH_3 into it. This gives the minimum equilibrium pressure, allowing savings in equipment and compression costs. The reactor temperature and pressure are kept in the ranges 180°-190°C and 120-150 bar. The conversion, based on the product leaving the reactor, is 50%-60%; based on the product leaving the stripper, it is about 85%.

Stripping takes place at the reaction pressure in a vertical steam-heated tubular exchanger having fixed tube sheets and a special distributor for the CO_2 feed. Uniform liquid distribution is essential. The steam used for heating the solution is at a pressure of about 25 bar.

The stripped ammonia and carbon dioxide recombine to form carbamate in a condenser, operating at the same pressure as the reactor. The heat of reaction and the sensible heat of the solution are used to raise low-pressure steam in the shell of the condenser. The reaction is allowed to proceed to 80% completion by manipulation of the steam pressure, and hence the temperature in the condenser. The optimum NH_3/CO_2 ratio in the condenser feed is 2.4. This value gives the maximum equilibrium temperature, which is most favourable for steam production. Ammonia is added at the condenser inlet to maintain the ratio. The reactant temperature at the condenser outlet is 170°C.

On leaving the stripper, urea solution is let down in pressure to 3-6 bar and heated with steam to release the small amount of ammonia, carbon dioxide and water vapour it still contains. These residuals are condensed in a water-cooled condenser, and the resulting weak carbamate solution is pumped back to the high-pressure condenser. Inert gases are purged from the reactor, and any ammonia or carbon dioxide present in it is absorbed in water and reused.

The urea solution is then pumped to a storage tank, from which it is drawn for further processing. If a biuret concentration of 0.9%-1.2% in the final product is permissible, vacuum evaporation followed by prilling is all the finishing necessary. Urea that must contain less than 0.5% biuret, however, requires



Urea by the Stamicarbon stripping process

an intermediate crystallization stage before melting and prilling.

Because of the corrosive nature of the process fluids, special stainless steels are used in the construction of all process equipment.

Advantages

- The process has an exceedingly simple layout with comparatively little equipment
- A large, expensive and troublesome carbamate pump is not required
- The consumption of utilities is relatively low
- The process operates at comparatively low pressures and temperatures; hence less severe operating conditions
- The process maintains an NH$_3$/CO$_2$ mole ratio that is considerably lower than for the total-recycle process, allowing savings in equipment and compression costs. It also gives the maximum equilibrium temperature for steam production
- Final carbamate separation is completed in only one separator operating at reduced pressures, compared to the three decomposers required for the total-recycle systems
- The CO$_2$ compressor need not be large
- Several critical control valves normally used in total-recycle streams are eliminated
- The process allows for relatively high cooling-water temperatures without appreciably increasing utility consumption

Process owner

Stamicarbon BV

Engineering licensees

C. F. Braun and Company
Chiyoda Chemical Engineering and Construction Company Ltd
Continental Engineering (Ingenieursbureau voor de Processindustrie BV)
Coppée-Rust SA
Didier Engineering GmbH
Foster Wheeler Corporation
Friedrich Uhde GmbH
Humphreys and Glasgow Ltd
The Lummus Company
Sim-Chem Division, Simon-Carves Ltd

Snam Progetti process

In the Snam Progetti stripping process, ammonia and carbon dioxide react at high pressure to yield urea and carbamate. The carbamate content of the reactor effluent is decomposed at the same pressure as the reactor by reducing its partial pressure with a stream of pure ammonia instead of carbon dioxide as in the Stamicarbon process. The reactor operates at a pressure of 130-160 bar and an NH$_3$/CO$_2$ mole ratio of 3.

Liquid ammonia is supplied from a holding tank and pumped to the urea reactor by reciprocating pumps. Part of the ammonia is vaporized for use in the high-pressure stripper. Carbon dioxide is compressed to reaction pressure and fed direct to the reactor.

Reaction products pass to the stripper, where carbamate decomposes and leaves the urea solution. Overhead vapours from the stripper pass direct to the high-pressure carbamate condenser, where ammonia and carbon dioxide are recovered for recycling to the reactor, by gravity alone. The heat evolved in carbamate condensation at elevated temperature is used to raise steam.

The urea purification and recovery train consist of three stages of evaporation at lower pressures accompanied by recovery of residual ammonia and carbon dioxide. Each stage operates at a successively lower pressure, and in the first two stages heat is added. The final urea solution contains 75% urea with virtually no ammonia.

The off-gases released from each stage are condensed in two steps, condensation and absorption of ammonia and carbon dioxide, to produce a concentrated solution, which is returned to the reactor through the high-pressure carbamate condenser.

The overhead from the high-pressure absorber in the recovery section is relatively pure ammonia, which is condensed and returned to the holding tank.

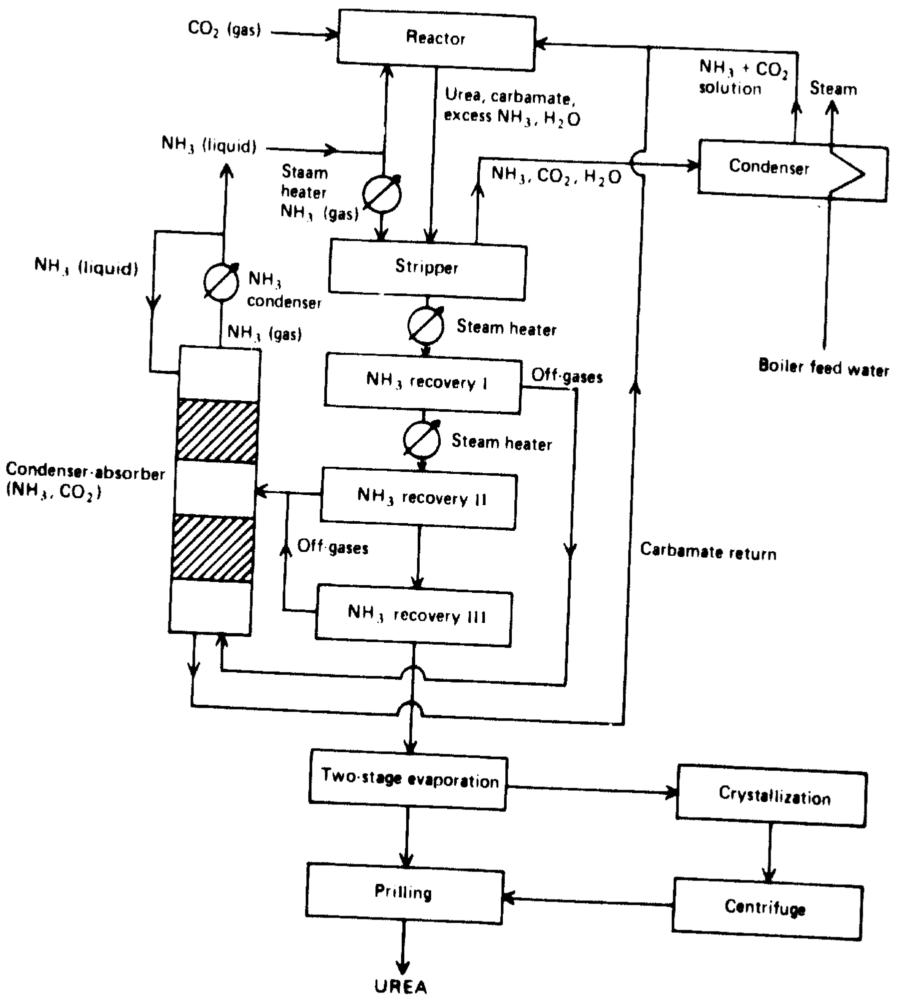
The finishing operation is the same as for other urea processes.

Advantages

The process has all the advantages of a stripping process (see above)
Utilities consumption is relatively low
Most of the critical control valves normally used in conventional plants are eliminated

Disadvantages

The low-pressure recovery ammonia system uses more stages of operation than the Stamicarbon process



Urea by the Snam Progetti stripping process

Process owner

Snam Progetti SpA

Engineering licensees

C. & I./Girdler, Inc.
Fluor Corporation
Woodall-Duckham Ltd

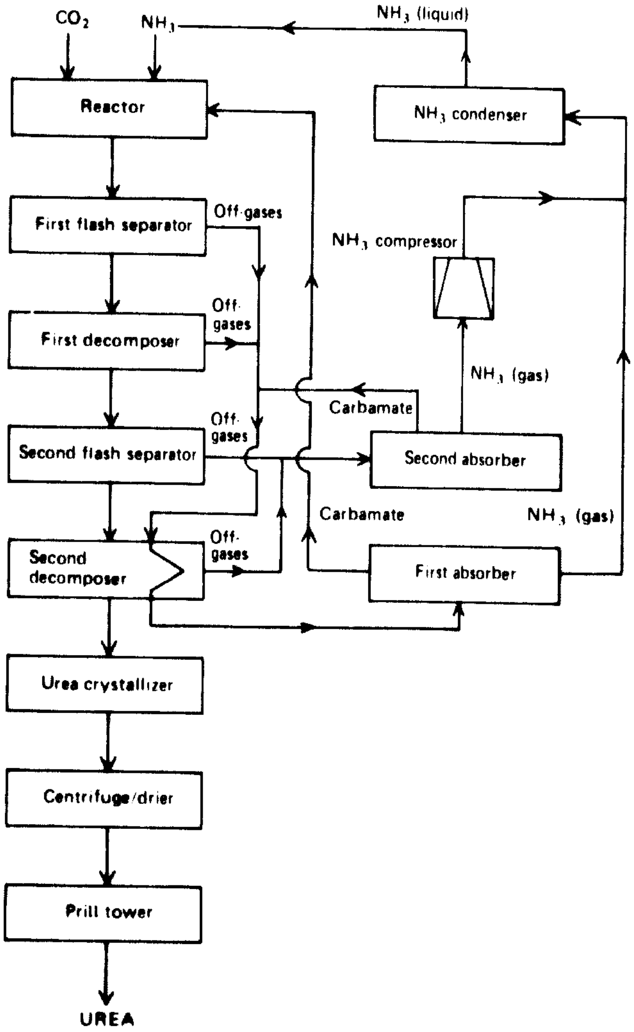
Total-recycle processes

Chemico process

In the Chemico total-recycle process, gaseous carbon dioxide, liquid ammonia and recycled carbamate solution are fed into a reactor at a NH_3/CO_2 mole ratio of 4. The reactor, operating at 190-230 bar and 175°-200°C, converts about 70% of the CO_2 to urea.

Two stages of decomposition and condensation, with two recycle loops and an ammonia recycle, are used. The reactor effluent, containing urea, excess ammonia and unconverted carbamate, is expanded to a pressure of 20-25 bar and fed to the first flash separator and then into the first decomposer, in which most of the carbamate is decomposed, with the aid of steam for heating, into ammonia and carbon dioxide. In the decomposition stages, the aim is to decompose carbamate with the least amount of water vapour; excess water in the recycle adversely affects reactor operation. To achieve that aim, each decomposition step is preceded by a flash separation.

The vapour phases leaving the first flash evaporator and first decomposer are combined and made to flow to the shell side of the second decomposer where they supply heat for decomposition by undergoing partial absorption in the weak carbamate solution from the bottom of the second



Urea by the Chemico total-recycle process

absorber. The combined stream from the shell of the second decomposer then enters the first absorber.

The second flash separator, working at 1-2 bar, removes the flashed gases from the first decomposer effluent solution, and most of the remaining carbon dioxide and ammonia are removed in the second decomposer and its recovery separator. The final urea solution concentration at the end of the second decomposition step is about 76%.

The first absorber is a tall tower operating at about 17 bar and having a lower, packed section and an upper, tray section. The solution and gases from the shell side of the second decomposer enter this tower below the packed section, where ammonia, carbon dioxide and water are partially condensed by a circulating carbamate solution flowing down the packing. The gases leaving the packed section of the absorber contain about 1% CO_2; this is further reduced to about 5 ppm by stripping with an ammonia reflux through the upper tray section. The gas leaving the absorber is thus pure ammonia gas.

The carbamate solution from the first absorber is withdrawn and pumped to the reactor as carbamate recycle.

The off-gases from the second flash separator and second decomposer are absorbed in the second absorber, operating at about 1 bar, by the carbamate solution being recycled in the absorber. The second absorber also has an ammonia reflux at the tray section, and the gas leaving the absorber is NH_3 containing less than 5 ppm CO_2.

Ammonia vapour from the top of the second absorber is compressed, combined with that from the first absorber and condensed by cooling water. The condensate goes to the ammonia storage tank for reuse.

The finishing section is the same as for other urea processes, except that in this process special provision is made to steam-heat a small portion of the crystallizer circulating solution.

Advantages

The heat recovery system is advantageous

Disadvantages

- Conversion in the reactor is only about 70%
- More vessels and equipment are used than in the stripping process
- Utilities consumption is greater than in the stripping process
- The high-pressure carbamate recycle pumps that must be used require a great deal of maintenance
- Additional steam is required in the crystallizer section

Process owner

Chemical Construction Corporation (Chemico)

Mitsui Toatsu process

The Mitsui Toatsu total-recycle process is based on the use of a three-stage decomposer train to recover carbamate. Carbon dioxide gas, recovered carbamate solution and liquid ammonia are reacted in a special titanium-lined reactor operating at 190°-220°C and 230-250 bar. The NH_3/CO_2 mole ratio in the reactor is kept at 4. By operating the reactor at the highest possible temperature and pressure and at the same time minimizing the water content in the carbamate recycle, a conversion rate of up to 72% is achieved. Evaporation of water is minimized in the decomposition stages to ensure the minimum recycle of water back to the reactor.

The solution from the reactor passes through a high-pressure decomposer operating at 18-20 bar, where the bulk of the unreacted carbamate decomposes to leave a urea solution containing the minimum of unseparated ammonia and carbon dioxide.

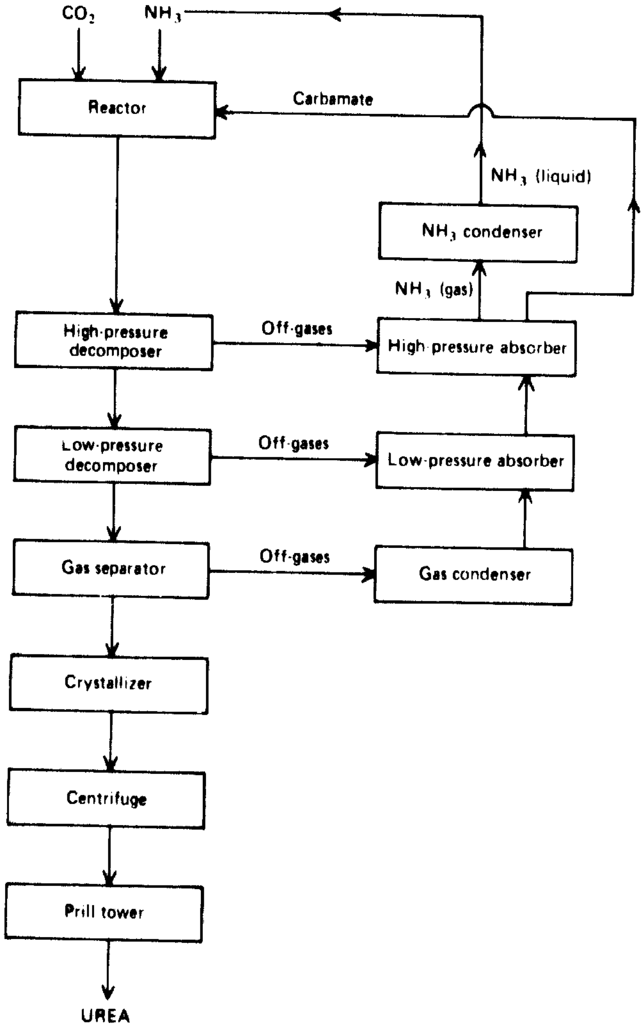
The remaining ammonia and carbon dioxide are removed by treatment in a low-pressure decomposer operating at 1-2 bar, followed by a gas separator operating at near-atmospheric pressure. The solution leaving the gas separator contains about 74% urea.

Overhead gases from the high-pressure decomposer, which consist of excess ammonia together with carbon dioxide and ammonia from the dissolution of unreacted carbamate, are sent to the bottom section of the high-pressure absorber, where they are partially condensed in the circulating absorbent solution coming from the low-pressure absorber. The top, tray section of the high-pressure absorber has a liquid-ammonia reflux. The gas leaving the absorber is pure NH_3; it is condensed using cooling water and recycled to the reactor. The large heat of absorption of CO_2 in the bottom section of the high-pressure absorber is utilized to concentrate the urea solution in subsequent finishing stages.

Overhead gases from the low-pressure decomposer and from the gas separator are condensed in the low-pressure absorber and the gas condenser, respectively. This solution is used as an absorbent solution in the high-pressure absorber.

The reduction in water content in carbamate is ensured by increasing the efficiency of high-pressure decomposition, minimizing the evaporation of water in the decomposition stages and evaporating the remaining water in the crystallizer by utilizing the heat of absorption of carbamate.

A titanium-lined reactor, which can easily withstand the severe pressure and temperature conditions of the process, should be used. Other sections of the plant use stainless steel of varying grades according to the severity of the operating conditions. Passivation air is added to the reactor and the high-pressure decomposer.



Urea synthesis by the Mitsui Toatsu total-recycle process

The finishing process is more or less the same as for other urea processes. Using a crystallizer, this process can produce urea with a biuret content of 0.25%-0.30%.

Advantages

- The process is simple to operate even though it uses more vessels and equipment than the stripping process
- Conversion in the reactor is as high as 72%
- The plant is very flexible and can be operated at turn-down ratios as low as 40% without losing efficiency
- Utilities consumption is low for a total recycle process
- Urea containing a very low biuret content can be obtained

Disadvantages

- Since differential expansion of titanium and steel is considerable, the reactor has to be operated without temperature shocks or large temperature differences between the shell and liner for a long reactor life
- The process uses complicated high-pressure reciprocating carbamate and ammonia pumps, which require much maintenance. (However, trouble-free centrifugal pumps are now available for this service)

Process owner

Mitsui Toatsu Chemicals, Inc.

Engineering licensees

Davy Powergas Ltd
Fluor Corporation

H. K. Ferguson Company, Inc.
J. F. Pritchard and Company
Lurgi Chemie und Hüttentechnik GmbH
The M. W. Kellogg Company
Toyo Engineering Corporation

Cost of typical total-recycle urea plant

The cost given, as a function of daily capacity, is for a battery limit, single-stream plant erected in a Gulf Coast area of the United States of America. Services are excluded. The cost is only approximate, having been extrapolated from 1967 prices.

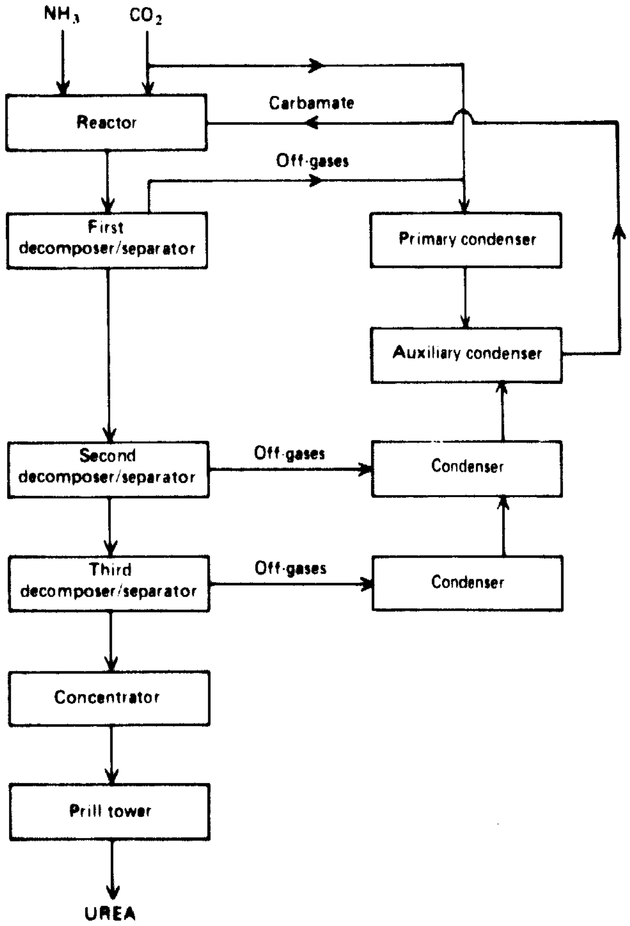
Daily urea capacity (short tons)	*Cost (millions of dollars)*
300	9
600	14
800	16
1 000	17

Montedison process

In the Montedison process, pre-heated ammonia, carbon dioxide and recycled carbamate solution are fed into a reactor operating at about 200 bar and 195°-200°C. The NH_3/CO_2 mole ratio is maintained at 3.5. Conversion in the reactor is about 60%.

The carbamate decomposition takes place in three stages. The reactor effluent is transferred to the first stage decomposer/separator, operating at about 80 bar and 185°-190°C. Here most of the excess ammonia is evaporated and most of the carbamate is decomposed into gaseous ammonia and carbon dioxide at the expense of steam. The gaseous effluent from this stage, together with 20%-30% of feed carbon dioxide enter the primary condenser, which operates at 80 bar and 145°C. Here, excess ammonia reacts with feed carbon dioxide to form carbamate.

Effluents from the primary condenser are transferred to an auxiliary condenser operating at



Urea by the Montedison total-recycle process

80 bar but at a lower temperature (about 115°C). Condensation is completed and inert gases are vented. The carbamate solution formed in this section is recycled to the reactor using high-pressure carbamate pumps.

The urea solution separated in the first decomposer/separator is passed through the second decomposer/separator, operating at 12 bar, then on to the third decomposer/separator, operating at 2-3 bar.

The off-gas from the second decomposer/separator is condensed in a condenser and the aqueous solution thus obtained is recycled to the primary condenser. The off-gas from the third decomposer/separator is condensed in another condenser, from which the aqueous solution is recycled to the medium-pressure condenser that handles the off-gas from the second decomposer/separator.

The 75% urea solution obtained at the outlet of the third decomposer/separator is further concentrated in vacuum evaporators, and the final 99.7% urea melt is sprayed into the prilling tower. The finishing processes are almost the same as those used in other urea processes.

Disadvantages

This is a total recycle process and hence uses more equipment and vessels than a stripping process

Utilities consumption is greater than in stripping processes

The carbamate recycling pumps require much maintenance

Operation is not simple

The first condensation takes place at high pressure

More pressure vessels are used than in other total recycle processes

Conversion in the reactor is only 60%

Process owner

Montedison SpA

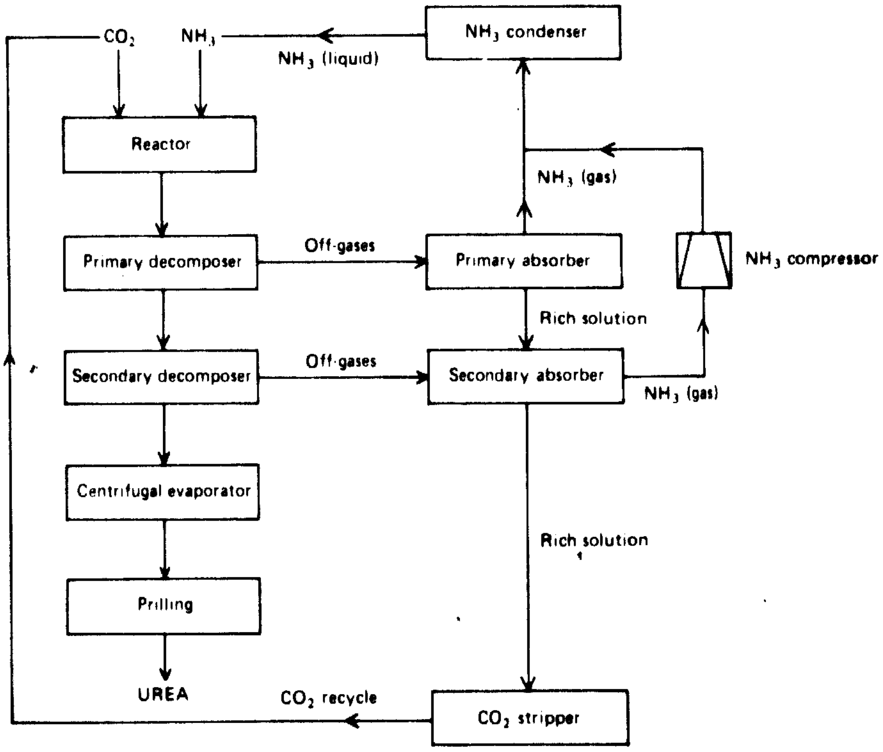
Engineering licensees

The Fertilizer Corporation of India Ltd

Gas-separation recycle process

CPI/Allied Chemical process

Unlike the stripping and total-recycle processes, the CPI/Allied Chemical process recycles unconverted ammonia and carbon dioxide as separate pure components by the use of solvent-extraction techniques to separate CO_2 from the gases leaving the



Urea by the CPI/Allied Chemical gas-separation recycle process

decomposer. Recycled carbamate solution is thus completely eliminated in this process.

Another distinguishing feature of this process is the use of a zirconium-lined reactor, which because of its resistance to corrosion, allows the synthesis reactions to take place at higher temperatures, up to around 230°C, thus increasing conversion efficiency.

Ammonia and carbon dioxide are fed to the reactor, in the mole ratio 4-4.5 and the reactor operates at a pressure of about 300 bar and at temperatures in the range 195°-230°C. Under these conditions, carbon dioxide conversion in the reactor is as high as 85%.

The reactor effluent (excess ammonia, urea and unreacted carbamate) goes to the primary decomposer where ammonia, carbon dioxide, and water are flashed off and stripped out. Approximately 90% of the unconverted carbon dioxide is decomposed in the primary decomposer, and the urea solution containing small quantities of the remaining dissolved carbamate is then passed to the secondary decomposer for final decomposition.

Gaseous products from the decomposition stages are passed through two absorption towers in which monoethanolamine is used for the selective absorption of carbon dioxide and moisture, leaving pure ammonia for recycling. Carbon dioxide is regenerated for recycling by heating the rich solution in a stripping column.

The urea solution coming from the secondary decomposer is further concentrated in a centrifugal evaporator and prilled. The finishing process is more or less the same as for the other urea processes.

Advantages

The corrosion problems associated with carbamate recycling are eliminated

No troublesome equipment for pumping carbamate is required

The CO_2 conversion to urea per pass in the reactor is as high as 85%

Higher conversion per pass is also achieved by eliminating water from the recycling stream; water adversely affects conversion in the reactor

Disadvantages

The carbamate decompositions take place at low pressure and hence the heat balances are not favourable

There is no heat recovery in the main process stream, as in the other processes

Reactor operates at higher pressure and temperature and requires a special lining

Cooling water and steam consumption are higher because of the additional CO_2 absorption and regeneration system

Process owner

Allied Chemical Corporation

Ammonium sulphate

Numerous methods are used for the manufacture of ammonium sulphate ($(NH_4)_2SO_4$), depending on the availability of raw materials and local conditions. The following three are the principal ones:

Direct neutralization (reaction of ammonia with sulphuric acid)

Gypsum (reaction of ammonium carbonate with natural or by-product gypsum)

Coke-oven gas (scrubbing of this gas in steel plants with sulphuric acid)

For each method, there are many proprietary processes, but there is not much difference between them. Only a general description of each method is given below.

The estimated cost of erecting a battery limit, single-stream direct-neutralization plant with a capacity of 300 short tons per day in the Gulf Coast area of the United States of America is $4 million.

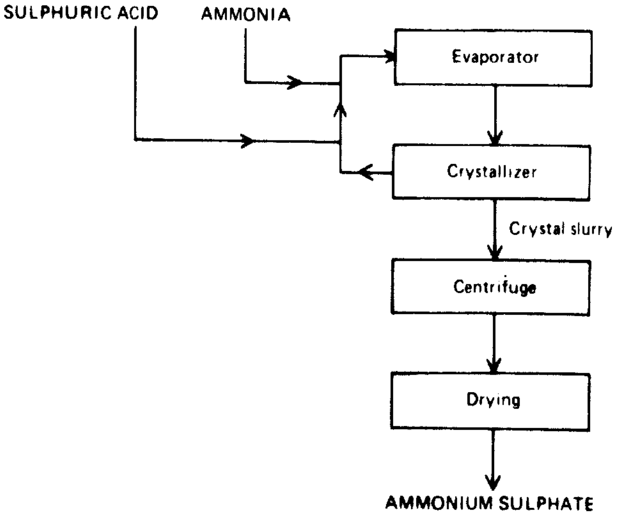
Direct-neutralization method

In the direct-neutralization method, ammonium sulphate is produced by direct reaction of anhydrous ammonia and concentrated sulphuric acid in saturator crystallizers operating in vacuum or under atmospheric pressure.

Ammonia gas and sulphuric acid are introduced in the circulation line of an evaporator-crystallizer known as a "Krystal" or "Oslo" unit and the heat of the exothermic reaction is utilized to superheat the solution, which is subsequently flashed in the vaporizer in a vacuum of 730-775 mbar (55-58 mm Hg). The flashed vapours are condensed, and the vacuum maintained, by a barometric condenser.

The pH of the crystallizer solution is maintained at 3.0-3.5. Excessive acidity promotes overgrowth of crystals in addition to giving rise to corrosion, and insufficient acidity can cause ammonia loss.

After the initial precipitation of crystals, the solution in the crystallizer body is kept at a metastable state of supersaturation so that the solution will release its supersaturation to a bed of



Ammonium sulphate by direct neutralization

growing crystals in the crystal container of the body of the crystallizer. The crystallizer temperature is maintained at 63°-66°C to get the best yield.

Crystal slurry from the crystallizer, containing approximately 30%-40% solids, is pumped to centrifuges or filters to separate the crystals. The crystals are dried in air-swept driers to a moisture content of less than 1%. The mother liquor is returned to the crystallizer through a mother-liquor tank.

Small amounts of phosphoric acid and arsenic trioxide are added to the sulphate solution to act as a corrosion inhibitor and a crystal-size modifier.

Since ammonium sulphate liquor is corrosive, all parts that come in contact with it are made of either stainless steel or rubber-lined carbon steel.

Advantages

The process is simpler than the gypsum process, and investment costs are lower

The process is a good choice if sulphur is available at a low price

Exothermic heat is utilized for the evaporation of the solution; hence no additional steam is required

Various process owners and their engineering licensees

Process owner	*Engineering licensees*
BASF Aktiengesellschaft	-
The Fertilizer Corporation of India Ltd	–
Chemical Construction Corporation (Chemieo)	Hitachi Zosen
Mitsui Toatsu Chemicals, Inc.	Toyo Engineering Corporation
Montedison SpA	-
Showa Denko KK	–
Fisons Ltd	Davy Powergas Ltd Foster Wheeler Corporation Lurgi Chemie und Hüttenteehnik GmbH
Kaltenbach et Cie SA	Davy Powergas Ltd ENSA, Cruesot-Loire Entreprises SYBETRA SA (Syndieat Belge d'Entreprises à l'Etranger) Toyo Engineering Corporation Woodall-Duckham Ltd
Stamiearbon BV	Chiyoda Chemical Engineering and Construction Company Ltd Coppée-Rust SA Sim-Chem Division, Simon Carves Ltd

Gypsum process

The gypsum process is also known as the Mersiburg process. It is based on combining ammonia and carbon dioxide to form ammonium carbonate, and then reacting it with gypsum ($CaSO_4 \cdot 2H_2O$) to yield ammonium sulphate solution and calcium carbonate ($CaCO_3$) solids.

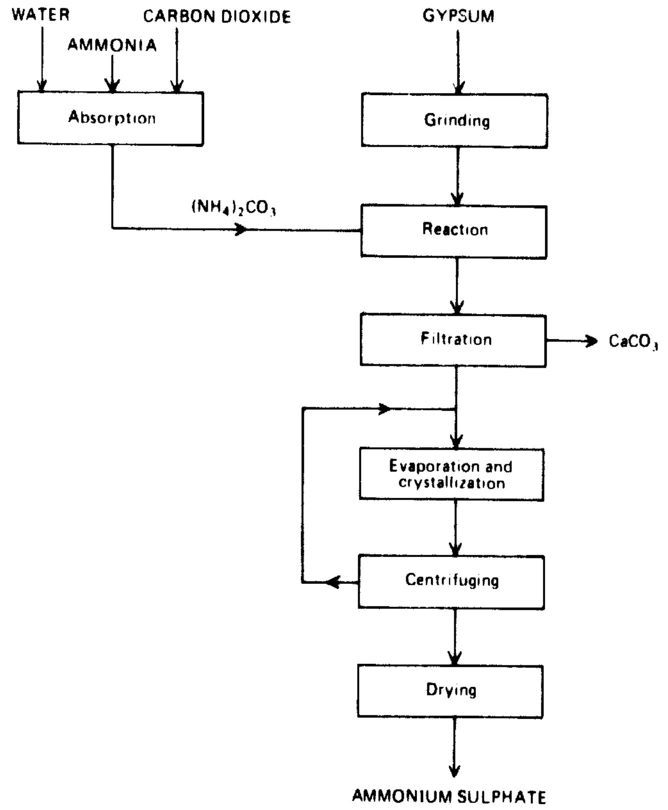
In the preparation of ammonium carbonate ($(NH_4)_2CO_3$), ammonium hydroxide (NH_4OH) is made first and made to react with carbon dioxide. In both steps the heat of reaction has to be removed in water-cooled or ammonia-cooled exchangers. Ammonia and CO_2 absorption can be done either in packed towers or jet absorbers. The preferred strength of the ammonium carbonate solution is about 170 g/l; of the ammonia and carbon dioxide solutions, it is 225 g/l. Ammonium bicarbonate (NH_4HCO_3) formation is prevented by maintaining the NH_3/CO_2 ratio in the liquor at 0.75-0.85

In the Mersiburg process, gypsum is fine-crushed (90% 'through a Tyler sieve of 120 mesh). The reaction is carried out in agitated wooden or steel tanks. A total retention time of 4-6 h is necessary for the reaction to be complete.

The reaction slurry is filtrated in a continuous travelling-belt filter or a rotating-type filter. The filtrate is pumped through pressure-type leaf-filters to the ammonium sulphate clear-solution tank to remove the final traces of calcium carbonate turbidity in the liquor.

The operations of solution concentration, crystallization, centrifuging, drying etc. are the same as in a direct-neutralization process, except that steam has to be added for heating the liquor in the circulating solution of the crystallizer, in a built-in heat exchanger. A multiple-effect evaporator-crystallizer is installed in this process for steam economy.

In the process using by-product gypsum from a phosphoric acid plant, the gypsum has to be slurried in water to wash off impurities, and the resulting slurry has to be filtered in rotary filters to get a good quality gypsum with minimum moisture content. Reaction, filtration, evaporation and crystallization are done in the same way as in the process using natural gypsum.



Ammonium sulphate by the gypsum process

Advantages

The method is a good one to use if by-product gypsum which would otherwise create a disposal problem is readily available, or cheaper to use than sulphur

Disadvantages

The steam required for concentrating the solution is not produced in the process, as it is in a direct-neutralization process

Investment costs are higher than for a direct-neutralization process

The operations are not as simple as those of a direct-neutralization process

Various process owners and their engineering licensees

Natural gypsum processes

Process owner	*Engineering licensees*
Chemie Linz AG	Davy Powergas Ltd
The Fertilizer Corporation of India Ltd	
Chemical Construction Corporation (Chemico)	Hitachi Zosen
Snam Progetti SpA	Bamag Verfahrenstechnik GmbH C. & I./Girdler, Inc. Fluor Corporation Woodall-Duckham Ltd
Stamicarbon BV	C. F. Braun and Company Chiyoda Chemical Engineering and Construction Company Ltd Coppée-Rust SA Didier Engineering GmbH Foster Wheeler Corporation Friedrich Uhde GmbH Humphreys and Glasgow Ltd Krebs et Cie SA The M. W. Kellogg Company Sim-Chem Division, Simon-Carves Ltd Stone and Webster Engineering Ltd

By-product gypsum processes

Process owner	*Engineering licensees*
BASF Aktiengesellschaft	–
The Fertilizers and Chemicals Travancore Ltd	–

Coke-oven gas

By-product ammonia is available for recovery from high-temperature solid-fuel carbonization units, such as the coking plants in the iron and steel industry. The entire gas stream, which contains about 1% NH_3, is first cooled to remove as much tar as possible and then passed through a saturator of the bubbler type or a scrubber of the spray type, where it is washed with sulphuric acid.

The ammonium sulphate solution formed is then concentrated and crystallized in crystallizers. The other operations are the same as in the direct-neutralization and gypsum methods.

Advantages

The process is actually a necessary operation in all coke-oven plants that yield ammonium sulphate as a by-product

Process owners and engineering licensees

Since this involves only simple operations there are no special process owners and special know-how and therefore no know-how fees. Designs for this process should be available from any of the process owners or engineering licensees given for the direct-neutralization and gypsum processes.

Ammonium chloride

Ammonium chloride (NH_4Cl) is rarely used as a fertilizer, though it contains 26% N, because of its chlorine content, poor keeping qualities and corrosive nature. However, in certain countries, it is freely used for certain crops, with good results. The production of ammonium chloride is also a useful way to use any surplus chlorine from caustic-soda plants. The best known processes for ammonium chloride manufacture are:

Direct neutralization

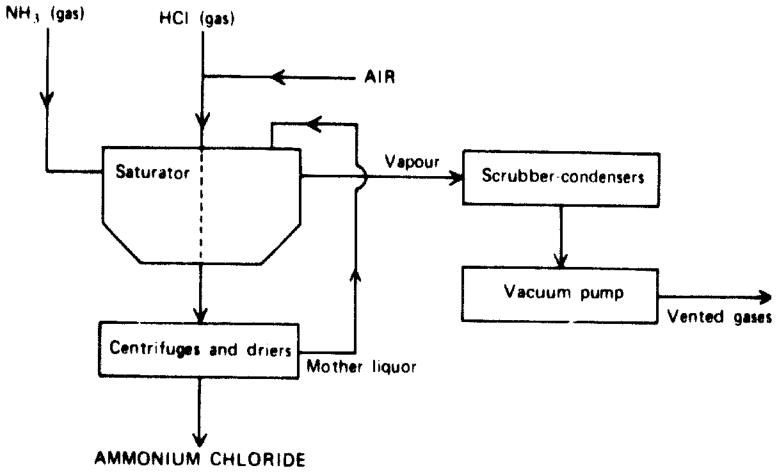
Soda-ash cycling process (also known as the dual-salt process)

The estimated cost of erecting a battery limits, direct-neutralization plant with a capacity of 300 short tons per day in the Gulf Coast area of the United States of America is $4.5 million. Cost data were not readily available for the soda-ash cycling process at the time this guide was being prepared.

Ugine Kuhlmann direct-neutralization process

Anhydrous ammonia vapour and hydrogen chloride (HCl) gas are made to react in a rubber-lined saturator with a conical bottom lined with special acid-resistant bricks and operating at the reduced pressure of 330-400 mbar (25-30 cm Hg) and at a temperature of 75°-80°C. The crystals formed are transferred from the bottom of the saturator, in the form of 80% slurry, to batch-type centrifuges where the solids are separated, washed, dried and discharged. If further drying is required, it is accomplished in a flash-drying system. The mother liquor is pumped back to the saturator through a storage vessel.

The concentrated HCl gas coming from the caustic soda plant is diluted to 20% with air before it enters the saturator through a vertical sparger tube dipping in the solution in the saturator. Ammonia gas is sparged through tangential nozzles on the side of the saturator, at the conical bottom. The air introduced with HCl gas provides sufficient agitation in the saturator. The pH of the saturator solution is maintained at 7 or slightly higher to prevent corrosion of the stainless steel used in the plant. A higher pH would in any case cause a loss of ammonia.



Ammonium chloride by the Ugine Kuhlmann direct-neutralization process

The vapour from the saturator goes through two water-washed, packed, scrubber-condensers, before it is exhausted by a water-ring vacuum pump.

Traces of free chlorine in HCl gas can combine with ammonia, especially in an acidic medium, and form nitrogen trichloride, which is highly explosive. To prevent such a condition and to isolate the HCl gas in emergencies, continuous monitoring of the HCl gas is done by bubbling a sample of it through a potassium iodide and starch solution. A blue colour in the solution indicates free chlorine.

Since ammonium chloride has a tendency to cake hard in storage, it is usually stored in moisture-proof bags. The ammonium chloride made by this process will pass industrial as well as pharmacopoeia standards if proper precautions are followed.

Advantages

The product made by this process is quite pure

The process is a good way to use up surplus chlorine from caustic-soda plants

The process is a very simple one

Disadvantages

Wetted parts in crystallizer have to be lined with rubber acid-proof brick; stainless steel cannot be used

The HCl has to be free of Cl_2 to prevent formation of explosive compounds with NH_3

Process owner

Ugine Kuhlmann SA

Engineering licensees

Krebs et Cie SA

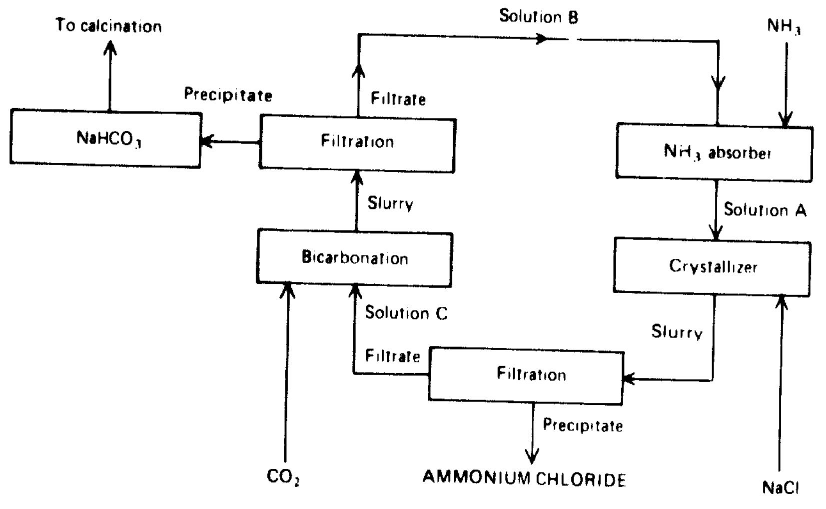
Asahi Glass soda-ash cycling process

The Asahi Glass process for making ammonium chloride is a modification of the Solvay process for the manufacture of soda ash. In the Solvay process an ammoniated solution of about 30% sodium chloride (NaCl) is treated with carbon dioxide in large absorption towers to form ammonium carbonate. Additional carbonation produces ammonium bicarbonate. The addition of sodium chloride yields sodium bicarbonate ($NaHCO_3$) and ammonium chloride. The sodium bicarbonate is separated by centrifuging and calcined to produce sodium carbonate (Na_2CO_3) and carbon dioxide, which is recycled. The mother liquor, after separation of sodium bicarbonate, is reacted with lime liquor to recover ammonia for reuse in the process. Ammonia is not a raw material in the process; however, small amounts must be added to make up losses.

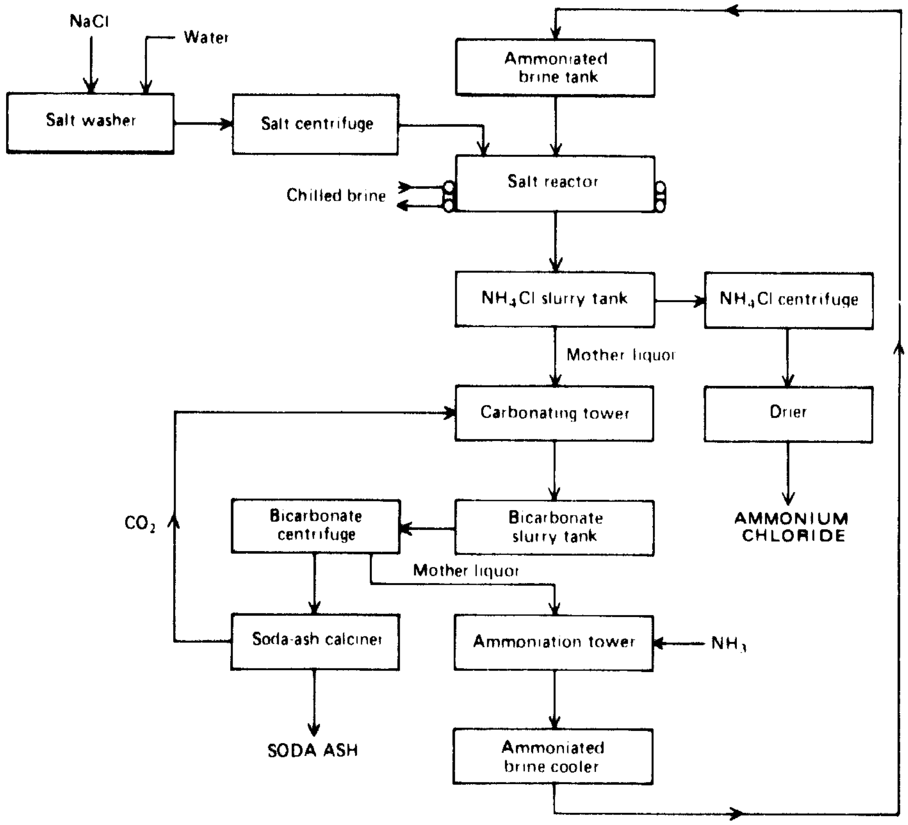
In the Asahi Glass process, ammonia is dissolved in the ammonium bicarbonate solution (solution **B**) left after the separation of the sodium bicarbonate from the slurry coming from the bicarbonating towers, which are quite similar to those used in the conventional Solvay process (see simplified flow chart).

The total amount of ammonia necessary for the whole process is added at this stage; that is the most important feature of the process, since it prevents co-deposition of sodium bicarbonate in the subsequent ammonium chloride precipitation stage.

The ammoniated solution (solution **A**) obtained by the addition of ammonia to solution **B** is cooled to 0°-25°C, and common salt is added in solid form. The salt dissolves, and the ammonium chloride that precipitates is filtered out and dried. The mother liquor obtained after filtration (solution **C**) is warmed



Ammonium chloride by the Asahi Glass soda-ash cycling process (simplified flow chart)



Ammonium chloride by the Asahi Glass soda-ash cycling process (flow chart)

by heat exchange with solution A and sent to the carbonating towers, where CO_2 is added.

Filtration or centrifuging separates the sodium bicarbonate, which is calcined to sodium carbonate. The CO_2 liberated is reused.

Unlike the Solvay process, this process requires equipment to wash the solid salt and for ammonium chloride production, crystallizers, filters, driers, cooling equipment etc. In addition, ammonia must be supplied, perhaps from the same source that supplies the CO_2 for the bicarbonation.

Because the mother liquor is circulated, it is necessary to give special attention to the water balance throughout the system. A close control is made on the wash water coming into the system from the ammonium chloride and sodium bicarbonate wash etc.

Since ammonium chloride is corrosive, the material of construction for the process equipment should be rubber-lined steel, special plastics or stainless steel.

Advantages

Less sodium chloride is needed than in the normal Solvay process

Produces two products at the same time: a fertilizer and an industrial chemical

There are fewer corrosion problems than in the neutralization process, since HCl gas is not handled

Disadvantages

Requires an ammonia plant as a source for ammonia and CO_2

Process owner

Asahi Glass Company Ltd

Nitric acid

The most important method for the manufacture of nitric acid (HNO_3) is the catalytic oxidation of ammonia. Pre-heated air is mixed with superheated ammonia to produce a 12%-14% ammonia concentration. This mixture is burnt to nitrogen monoxide (NO) over a catalyst, consisting of several layers of fine-mesh platinum-rhodium gauze. The NO reacts with atmospheric oxygen to form nitrogen dioxide (NO_2). The addition of further atmospheric oxygen and water finally converts NO_2 to nitric acid (HNO_3).

Pressures of 1-11 bar and temperatures of 800°-900°C are maintained in the process. The precise values depend on the type of process.

Pressure adversely affects the degree of oxidation of ammonia, but increases the rate of absorption of nitrogen oxides (NO_x) in water and in dilute nitric acid. This rate increases proportionally with the cube of the pressure.

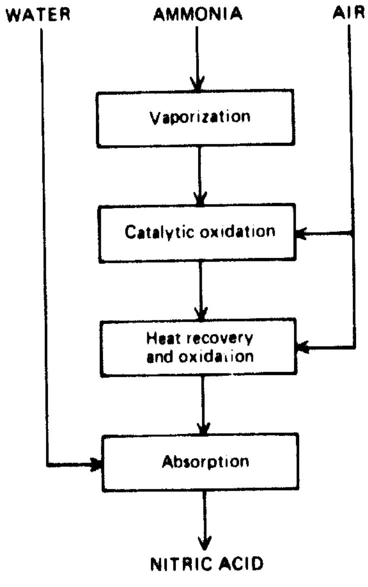
Nitric acid processes fall into two general classes:

(a) *Mono-pressure processes, in which ammonia oxidation and absorption occur at equal pressures;*

(b) *Mixed-pressure processes, in which ammonia oxidation and absorption occur at different pressures.*

In the following table, the cost given is for a battery limits plant located in the Gulf Coast area of the United States of America. The cost includes supply, erection, storage of 750 t (800 short tons), and is an approximation based on 1967 prices. All services are excluded from the cost. The acid is produced in a strength of 50%-60% HNO_3.

Daily capacity		Estimated cost
(t)	(short tons)	(millions of dollars)
275	*300*	*6.9*
550	*600*	*9.2*
730	*800*	*10.3*



Nitric acid synthesis

Uhde process

There are three variants of the Uhde process, one employing atmospheric combustion, a second equal-pressure combustion and absorption, and a third combustion and absorption at different elevated pressures.

1. *Atmospheric combustion (a mixed-pressure process)*

Pre-heated air mixed with superheated ammonia is delivered to the burner, where the gases are passed over platinum-rhodium alloy catalyst gauzes to convert the ammonia to a mixture of NO and NO_2. To achieve greater heat recovery the burners are designed to carry out the partial oxidation of NO to NO_2. The heat of reaction is used to generate superheated steam and to heat the tail gas from the absorption unit. The steam and tail gas are utilized in turbines to drive air or NO_x compressors, depending on the process.

After heat recovery, the gas is cooled, and compressed to 3-5 bar in an NO_x compressor. It is then passed through an absorption tower in which the gas absorbs water, and nitric acid is formed. Such absorption towers are designed as sieve-tray columns with internal cooling coils.

The gases leaving the absorption tower are heated by hot combustion products and are used to drive the NO_x compressor in combination with superheated steam produced in the burner.

Steam is produced by utilizing the exothermic heat of the reaction in the burner in forced-circulation water coils fitted into the carbon-steel burner vessel below the catalyst gauzes. This makes the design compact and saves space.

2. *Equal-pressure combustion and absorption (a mono-pressure process)*

In this process both combustion and absorption are carried out under the same pressure (4-10 bar). Since air, rather than NO_x, is being compressed, there is no risk of corrosion; this risk arises in mixed-pressure operation, where the compression of NO_x is a critical operation. The air compressor is driven by the tail gas expansion turbine and generated-steam turbine.

This process gives an NO_x concentration of about 600 ppm in the tail gas. This concentration can be further reduced to 200 ppm by caustic scrubbing.

Apart from these features, the equal-pressure combustion and absorption process follows the same sequence of operation as is used in the atmospheric combustion process.

3. *Combustion and absorption at different and elevated pressures (a mixed-pressure process)*

In this process combustion is carried out at a pressure of 3-5 bar and absorption at 11 bar. An NO_x compressor is needed to boost the pressure after the combustion stage. Both the air and NO_x compressors are driven by a tail-gas expansion turbine and a generated-steam turbine combined into a single turbo-set on one shaft.

Because of the high pressure used for the absorption stage, the NO_x content in the tail gases can be brought down to as low as 200 ppm.

Other than these differences, the details of operational route and sequences are more or less the same in this as in the other two variants.

Comparison of the three variants

The following table compares data on the three variants. The values for energy and catalyst consumption and for steam production are calculated per tonne of 100% acid.

Item	*1*	*2*	*3*
Operating pressure (bar)			
Combustion	1	5	3
Absorption	5	5	10
Nitrogen yield (%)	> 97	96	96.5
Maximum concentration of acid (%)	70	70	70
Electrical energy consumption (kWh)	9	9	10
Steam produced for outside use (t at 40 bar and 400°C)	0.31	0.35	0.2
Net platinum loss (mg)	15	80	40
Conversion efficiency	High	Lower	Lower
Capital investment	High	Low	Lowest
Compressors required			
Air	1	1	1
NO_x	1		1
NO_x in tail gas (ppm)	> 600	600	200

Process owner

Friedrich Uhde GmbH

Grande Paroisse process

The Grande Paroisse process is a mixed-pressure process that consists of combustion at medium pressure (3-4 bar) and absorption at high pressure (7-8 bar).

The products of combustion leave the burner and are progressively cooled by heat exchange in a steam superheater, waste-heat boiler and condenser before they are compressed to 7-8 bar in an NO_x compressor.

Normally, the NO_x content in the tail gas is around 500 ppm after absorption in this process. This can be reduced to 200 ppm by adding another absorption tower.

Basically, the process route and sequence of operation are the same as in the Uhde process except in the design of individual items of equipment, particularly the burners and absorption towers.

Advantages

The investment cost is lower in this process than in an atmospheric-pressure combustion process

NO_x content in tail gas is about 500 ppm for a normal plant

Disadvantages

Due to medium-pressure combustion, ammonia conversion is lower and catalyst consumption higher than in atmospheric-pressure operation. Catalyst consumption is about 90 mg per tonne of 100% nitric acid

Because of mixed elevated-pressure operation, an NO_x compressor is necessary

Process owner

Société Chimique de la Grande Paroisse

Pintsch-Bamag process

This process uses both the mono-pressure and mixed-pressure processes operating at low, medium or high pressure (1-3 bar, 3-5 bar, and 7-11 bar respectively). The process route and sequence of operation followed are the same as in the processes described previously. The main differences are in the design of the burners and absorption units.

The Pintsch-Bamag process uses two absorption towers equipped with perforated plates. Most of the nitrogen oxide entering the first absorption tower is oxidized to the dioxide in the lower part of the tower and then absorbed in the downflow of weak acid produced by the introduction of chemically pure water in the second tower. On reaching the final absorption plate at the bottom of the first absorption tower, the nitric acid is at full strength and is drawn off. Heat liberated during absorption is removed by water flowing through cooling coils on the plates.

Some data on the variants are shown in the following table. Values are per tonne of 100% acid.

Item	*Medium pressure*	*High pressure*
Overall nitrogen yield (%)	96	96
Electrical energy consumption (kWh)	12	10
Platinum loss (mg)	130	300
Excess steam (t)	0.7	0.5
NO_x in tail gas (ppm)	800	500

The NO_x content of the tail gas increases to 1 200 ppm in the low-pressure variant.

Advantages

All the usual advantages of low-, medium- and high-pressure processes

Disadvantages

The process uses two absorption towers

The NO_x in the tail gas is high for all pressures (see table)

All the usual disadvantages of low-, medium- and high-pressure processes

For the mixed-pressure process an NO_x compressor is required

Process owner

Bamag Verfahrenstechnik GmbH

Engineering licensees

Davy Powergas Ltd

Stamicarbon process

This process consists of a mono-pressure process either at a medium pressure of 4-7 bar or at a high pressure of 7.5-10 bar. The process route and sequence of operation are more or less the same as the previously described processes, with certain differences in equipment.

Absorption is carried out in a plate column with internal coolers, rather than in packed columns (as previously practised by Stamicarbon).

Some data on the two variants are in the following table (per tonne of 100% acid). To bring NO_x levels to 200 ppm or below, an additional catalytic process has to be used.

Item	*Medium pressure*	*High pressure*
NO_x in tail gas (ppm)	1 000	800
Concentration of acid produced (%)	55	65
Catalyst consumption before recovery (mg)	95	170
Electrical energy power consumption (kWh)	8	8
Excess steam (t)	0.550	0.20

Advantages

The process does not need an NO_x compressor

Only one absorber is needed

Disadvantages

The high-pressure variant has a lower ammonia conversion efficiency and consumes more catalyst than the medium-pressure variant

Investment costs are lower for the high-pressure variant than for the medium-pressure variant

Process owner

Stamicarbon BV

Engineering licensees

Arthur McKee and Company
C. F. Braun and Company
Chiyoda Chemical Engineering and Construction Company Ltd
Coppée-Rust SA
Didier Engineering GmbH
Foster Wheeler Corporation
Friedrich Uhde GmbH
Humphreys and Glasgow Ltd
Krebs et Cie SA
The M. W. Kellogg Company
Sim-Chem Division, Simon-Carves Ltd
Stone and Webster Engineering Corporation

Weatherly process

This is a mono-pressure process operating at approximately 9 bar in both combustion and absorption.

Air, pre-heated to approximately 260°C, is mixed with gaseous ammonia and passed through catalyst gauze in the combustion unit, which operates at 900°C. Heat recovery from this hot gas includes the heating of tail gas, pre-heating of air, production of by-product steam to drive turbines, steam for external use etc.

The heat exchangers, along with the ammonia converter and platinum gauze, are butted against each other, forming a compact unit that permits high heat recoveries and saving in space. This arrangement also partially oxidizes nitrogen monoxide to dioxide before the process stream condenses.

Partially cooled process gas from the heat exchanger passes into a special cooler condenser of shell-and-tube design. There, some weak acid is formed as soon as the water vapour from the ammonia oxidation condenses and absorbs a portion of the nitrogen dioxide. This weak acid is separated and introduced into the middle tray of the absorption tower while the gas fraction enters at the bottom. In the tall absorption tower nitrogen dioxide reacts with water to form nitric acid. Nitric acid of a concentration of about 58% is made in the tower.

The tail gas goes through a catalyst burner that uses natural gas or ammonia-plant waste gases as fuel. This combustion reduces the residual oxides of nitrogen so that the final tail gas is a colourless stream consisting mostly of nitrogen, oxygen and carbon dioxide. The purified waste stream passes through an expansion turbine, which provides part of the drive for the main compressor before eventual release to the atmosphere through a stack.

The overall nitrogen efficiency is 95%.

Advantages

Since this is a mono-pressure operation, an NO_x compressor is not required

Tail gas passes through a catalytic process for reduction of NO_x gases. The tail gas is therefore colourless and free from pollution hazards

Steam is available for external use

Disadvantages

This is an elevated pressure and mono-pressure operation. Though investment cost and operation cost are low, ammonia conversion efficiency is lower and catalyst consumption is higher than in atmospheric combustion process

Process owner

The D. M. Weatherly Company

Chemico process

The Chemico process is a mono-pressure process operating at 8 bar. The process route and operating sequences followed are more or less the same as in the other processes discussed except for minor changes in the method of heat recovery, and in the type of equipment used.

A separate air pre-heater is not used in the process, but air at 230°C is admitted to the mixer by utilizing the compression heat in the compressor by carefully adjusting the compressor intercooler.

As in the other processes, heat is recovered in a variety of ways; the way chosen depends on individual plant conditions.

Advantages

As in all other elevated mono-pressure operations, the investment costs and operating costs are low

This process does not use an NO_x compressor

Disadvantages

Catalyst consumption is high and ammonia conversion efficiency is low (93%)

Process owner

Chemical Construction Corporation (Chemico)

SBA process

The SBA process is a mixed-pressure process that consists of combustion at 3 bar and absorption at 7-9 bar.

Filtered air compressed to 3 bar is mixed with ammonia gas and fed into the burner. The burner consists of several platinum-rhodium gauzes and it operates at about 850°C.

The heat of reaction is recovered in the form of superheated steam. The products of combustion are cooled further by raising steam and pre-heating boiler feed-water. The water formed in the reaction is condensed and the nitrogen oxides are further compressed to 7-9 bar in the second stage of the centrifugal air compressor. The gas then passes through a series of heat exchangers and finally enters the absorption column.

The absorption column is of the perforated-plate type and is equipped with a system of highly efficient internal cooling coils. Process water is fed into the top of the absorber and raw acid is removed from the base. The gas pressure is then reduced to 4 bar and the gas is passed to an oxidation and de-nitration column before being reheated to 400°C in a heat-recovery system. A small quantity of hydrocarbon is injected into it. The mixture is passed over a catalyst, which causes the combustion of hydrocarbons at the expense of residual oxygen and converts most of the nitrogen dioxide back to nitric oxide. The gas is then passed at 600°C to power a recovery turbine, which drives the air and nitrous oxide compressor as well as a steam turbine.

About two thirds of the steam produced in the ammonia oxidation reaction, that is, nearly 750 kg per tonne of 100% nitric acid produced, is available for external use.

The normal concentration of the acid produced is 60%-62%, but acid of a concentration of up to 70% can be made by using a new SBA technique and ammonia refrigeration.

Advantages

- This is a mixed-pressure process at elevated pressure, and the investment cost is thus less than in the atmospheric combustion process
- The process and operation are simple
- The off-gases from absorption are almost colourless

Disadvantages

- Acid with concentration of only 60%-62% is normally produced
- The ammonia conversion efficiency is lower and catalyst conversion higher than in the atmospheric combustion process
- An NO_x compressor is required

Process owner

Société Belge de l'Azote et des Produits Chimiques du Marly (SBA)

Ugine Kuhlmann process

The Ugine Kuhlmann process is a mixed-pressure process, with combustion at atmospheric pressure and absorption at 5.4 bar.

The catalytic reaction is carried out at atmospheric pressure to give maximum conversion of ammonia and minimum loss of platinum gauze. The overall nitrogen efficiency is 97%. The burner operates at a temperature of 810°-820°C. Homogeneous gas distribution and mixing is achieved by a special mixing arrangement made in the burner.

The heat-recovery boiler is of the natural-circulation type. Steam is available for export after plant use.

The absorption tower is of the plate type and acid of a concentration of 69% is produced in this process.

Advantages

- Due to the use of atmospheric combustion, the overall conversion efficiency of nitrogen is high at 97%
- The use of holding plates in the absorber eliminates the release of NO_x on start up

Disadvantages

- The investment cost is high but is compensated to some extent by low catalyst consumption and the high absorption efficiency of the process
- An NO_x compressor is required

Process owner

Ugine Kuhlmann SA

Engineering licensees

Bignier Schmid Laurent SA

Fauser-Montedison process

The Fauser-Montedison process is a mono-pressure process operating at 5-6 bar. The process sequence is the same as in any other nitric acid process, namely, air compression, catalytic oxidation of ammonia, NO_x cooling and absorption.

Air is compressed to 5-6 bar by a centrifugal or axial compressor, usually coupled to a gas turbine, which expands the previously heated tail gas, and a condensing steam turbine, which utilizes a part of the steam generated in the plant. The air is mixed with ammonia and fed into the burner. The burner is of such a size as to ensure uniform distribution of the air-ammonia mixture over the catalyst. An adequate gas-stream velocity avoids any backflow of reacted gas to the catalyst and thus ensures the long life of the catalyst gauze.

The heat of reaction in the reactor (burner) is recovered for generating superheated steam and for heating the tail gas prior to its expansion in a turbine. The steam produced is at a pressure of 20 bar and temperature of 350°-400°C. The tail gas is heated to 400°C.

The water-condensation reaction, in which 30%-35% nitric acid is produced, takes place in a standard vertical water-tube bundle exchanger, made out of type 304 stainless steel.

The absorption of NO_x by water to produce nitric acid takes place in two tray columns. A cooling system is provided in the first part of the column for continuous heat removal from the gaseous and liquid streams. The gaseous stream entering the absorption column is mixed with a measured air flow. The acid concentration reached in the process is 58%-65%. The overall nitrogen yield is about 95%-96%. The NO_x content in the tail gas is about 0.20% by volume at 30°C.

Advantages

Since this is a mono-pressure process, a NO_x compressor is not needed

Disadvantages

Two absorption towers are used

The NO_x in the tail gas is high, approximately 0.2% by volume at 30°C

Process owner

Montedison SpA

C. & I./Girdler process

The C. & I./Girdler process is an elevated-pressure/mono-pressure process, and is an adaptation of the Dupont high-pressure process.

Air and ammonia are mixed in a specially designed mixer with gas-distribution nozzles that ensure an even distribution over the catalyst surface; from the mixer, the gas is passed on to the converter. The resultant mixture of nitrogen oxides, water vapour, oxygen and nitrogen leaves the converter and passes through a series of heat exchangers, which recover the heat in the gases and essentially complete the oxidation of the ammonia to nitrogen dioxide. These exchangers include a reheater (which reheats the tail gas for heat recovery in expanders that drive the air compressor), a superheater, a waste-heat exchanger (which generates steam), and a cooler/condenser (where water is used to condense the hot gases and cool them to the correct temperature for admission into the absorption column).

Uncondensed gases enter the absorption tower and flow upward through the column trays counter-current to the water used as an absorption medium. The tail gases from the absorber pass through the reheater and then on to a catalytic fume-abatement unit where fuel gas, burning on a catalyst, is used to decolorize the gas. The colourless gas is expanded in the turbine driving the air compressor.

The NO_x content in the tail gas is less than 0.2% by volume.

Advantages

This is a mono-pressure process and so there is no NO_x compressor

The investment cost is lower than for the atmospheric combustion process

Disadvantages

All the disadvantages of a high-pressure process apply

Process owner

C. & I./Girdler, Inc.

Ammonium nitrate

Several proprietary processes for ammonium nitrate (NH_4NO_3) manufacture are available; these involve various combinations of different neutralization, evaporation, drying and finishing methods. Solid ammonium nitrate is produced in the form of prills, crystals and granules, either alone or in combination with other fertilizer materials.

In the following table, the cost is given for a battery limits, single-stream plant located in the Gulf Coast area of the United States of America. The cost does not include a nitric acid plant. The cost is an approximation based on 1967 prices.

Daily capacity		Cost
(t)	(short tons)	(millions of dollars)
275	*300*	*5.3*
550	*600*	*8.5*
730	*800*	*10.3*
910	*1 000*	*12.2*

Kaltenbach process

The Kaltenbach process uses a pressure neutralizer to produce prilled ammonium nitrate containing 34.5% nitrogen.

Metered quantities of vaporized anhydrous ammonia and 55% nitric acid are fed into a neutralizer operating at 4.4 bar and 175°C. Ammonium nitrate solution at a concentration of about 80% is produced in the neutralizer. The exothermic heat of reaction in the neutralizer produces steam, which is used for evaporation in subsequent steps. About one tonne of steam can be produced for each tonne of ammonia neutralized if 64% acid is used. The steam consumption per tonne of 100% ammonium nitrate produced is about 0.155 t.

The ammonium nitrate solution then flows to the primary evaporator, where the solution is further concentrated to 95%, using a falling-film evaporator employing steam as the heating medium.

The solution from the primary evaporator is then mixed with recycled fines (i.e., powder from the final stage of the process) in a heated vessel and pumped to a second falling-film evaporator located on the top of the prill tower, where it is further concentrated to 99.8%.

Ammonium nitrate solution at this concentration is sprayed into the prill tower. The droplets solidify, harden and cool during their fall in this tower in a counter-current of air. The prills are further cooled with air that has been used for ammonia evaporation, and screened before being stored. Dust from the screens is mixed with ammonium nitrate solution from the primary evaporator and recycled.

Advantages

Most of the steam needed to concentrate the ammonium nitrate solution is generated by the heat produced in the neutralizer

The electrical energy consumption per unit of 100% ammonium nitrate produced is fairly low, about 15.5 kWh/t

Disadvantages

Operating a neutralizer at elevated pressure is not as simple as at atmospheric pressure

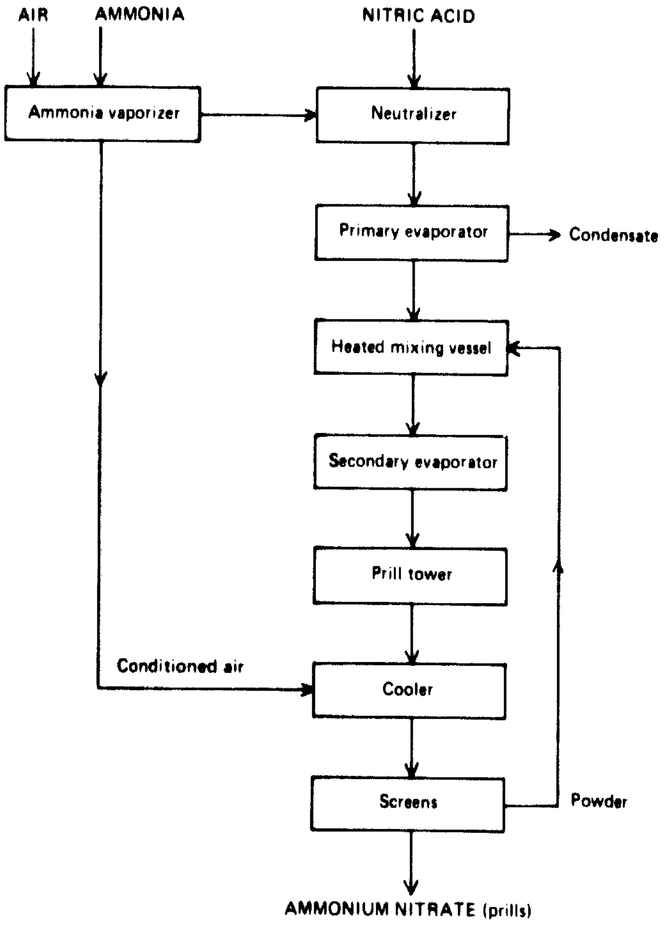
The investment cost required will be higher than that for an atmospheric-pressure type neutralizer system

Process owner

Kaltenbach et Cie SA

Engineering licensees

Davy Powergas Ltd
ENSA, Cruesot-Loire Entreprises
SYBETRA SA (Syndicat Belge d'Entreprises à l'Etranger)
Toyo Engineering Corporation
Woodall-Duckham Ltd



Ammonium nitrate by the Kaltenbach process

Stamicarbon process

The Stamicarbon process produces prilled ammonium nitrate and uses a pressure neutralizer. Ammonia and 53% nitric acid are fed into a neutralizer operating at a pressure of 4 bar and a temperature of about 180°C. The solution leaves the neutralizer at a concentration of 79% and passes through two steps of evaporation before it is taken to the top of the prill tower for prilling. The first step in the evaporator (which uses by-product steam for heating) brings the concentration of the nitrate solution up to 94%, and the second step to 99.7%, a melt, which is pumped to the top of the prill tower for prilling. Other finishing steps are the same as in the other ammonium nitrate processes.

Disadvantages

By-product steam is used for the first evaporation step only

Since neutralization is done under pressure, this process is not as simple to operate as an atmospheric-pressure process

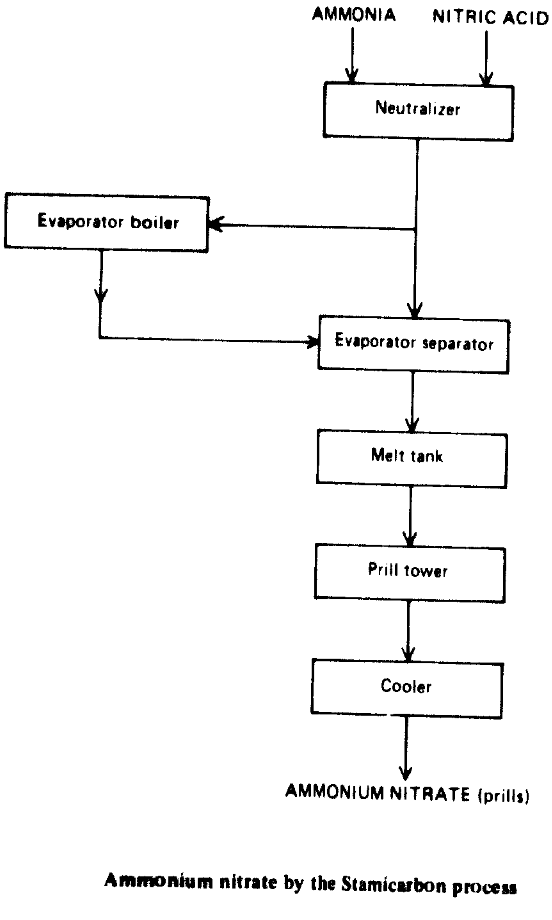
The investment cost is higher than that for an atmospheric-pressure process

Process owner

Stamicarbon BV

Engineering licensees

Arthur McKee and Company
C. F. Braun and Company
Chiyoda Chemical Engineering and Construction Company Ltd
Coppée-Rust SA
Didier Engineering GmbH
Foster Wheeler Corporation
Friedrich Uhde GmbH
Humphreys and Glasgow Ltd
Krebs et Cie SA
The M. W. Kellogg Company
Sim-Chem Division, Simon-Carves Ltd
Stone and Webster Engineering Corporation



Ammonium nitrate by the Stamicarbon process

SBA process

The SBA process uses a pressure neutralizer to produce granular ammonium nitrate containing 33.5% nitrogen.

Ammonia and pre-heated 50% nitric acid are reacted in a neutralizer at a pressure of approximately 5 bar. The resultant ammonium nitrate solution passes through two steps of evaporation and reaches a final nitrate concentration of 98% without using any external heat. This process efficiently utilizes exothermic heat for both primary and secondary evaporation of the ammonium nitrate solution, as well as for pre-heating the nitric acid. The heating for the secondary evaporation is provided by passing the pre-concentrated solution through a coil inserted in the neutralizer.

The concentrated ammonium nitrate solution passes through a normal granulation unit and the granular product is stored.

Electrical energy consumption per unit of 100% ammonium nitrate produced is about 30 kWh/t.

Advantages

This process not only efficiently utilizes all exothermic heat for two-step evaporation, but also produces an extra 0.205 t of low-pressure steam per tonne of 100% ammonium nitrate produced

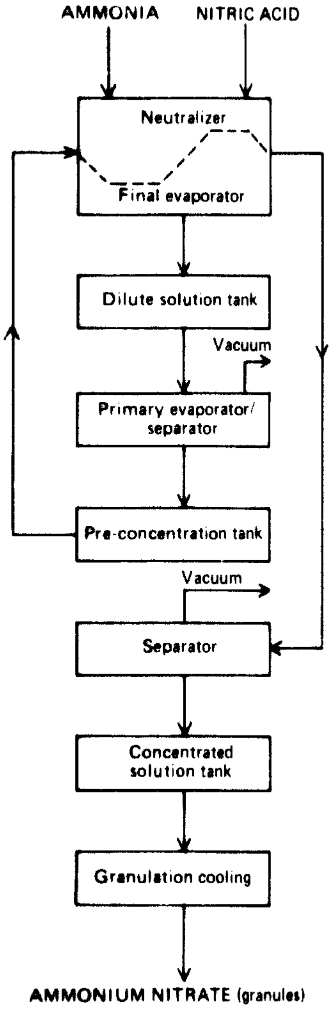
Disadvantages

This is a pressure-operated system and therefore the investment cost will be higher and operation less simple than that for an atmospheric-pressure system

Electrical energy consumption is fairly high

Process owner

Société Belge de l'Azote et des Produits Chimiques du Marly (SBA)



Ammonium nitrate by the SBA process

ICI (Nitram) process

The ICI process uses two neutralizers operating under atmospheric conditions to produce prilled ammonium nitrate containing 34.5% nitrogen.

Gaseous ammonia and 57% nitric acid in which recycled fines are dissolved pass into the main neutralizer. This neutralizer operates at the boiling point of ammonium nitrate solution and at atmospheric pressure. Neutralization is maintained at pH 3-4 to reduce ammonia losses. The ammonium nitrate liquor thus formed overflows into the second neutralizer, where further ammonia is added to raise the pH of the solution to the neutral point (7).

The ammonium nitrate solution, which is at a concentration of 87% at the outlet of the second neutralizer, now enters a falling-film evaporator where the concentration is raised to 99.5%. This concentrated solution is sprayed from the top of a prill tower against a counter-current flow of air. Prills are cooled in a fluidized-bed cooler at the bottom of the prill tower to a temperature of 40°C. The prills are then classified by means of a screen: the product-quality prills are stored, and the fines and oversize prills are dissolved in the 57% nitric acid that goes to the first neutralizer.

Advantages

Even though there are two neutralizers in this process, they are simple in design and easy to operate since they work at atmospheric pressure

The equipment is easy to manufacture and the investment cost is low

Electrical energy consumption is low (17 kWh/t)

Disadvantages

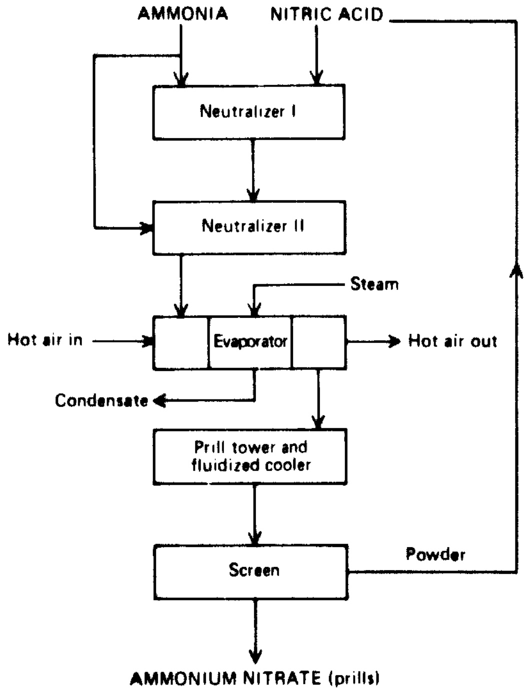
Since waste heat is not used, steam consumption per tonne of 100% ammonium nitrate produced is high (0.5 t)

Process owner

Imperial Chemical Industries Ltd

Engineering licensees

CJB (Projects) Ltd
Friedrich Uhde GmbH



Ammonium nitrate by the ICI (Nitram) process

C. & I./Girdler process

The C. & I./Girdler process uses a neutralizer to produce prilled ammonium nitrate containing 33.5% nitrogen.

Ammonia vaporized by waste steam from the neutralizer and nitric acid in which powdered nitrate is dissolved are fed into the neutralizer. The heat of reaction is sufficient to concentrate the ammonium nitrate solution in the neutralizer to 83%.

The solution from the neutralizer is taken to a weak-liquor storage tank and then pumped to the prill tower through a falling-film evaporator located on top of the prill tower. The concentration of ammonium nitrate reaches 99% and the melt flows through spray nozzles downwards in the prill tower against a counter-current of air.

The prills at the bottom of the prill tower go through a rotary cooler and coating drum before they are stored. Fines from the rotary drums are collected in wet cyclones and the solution produced in these is sent to the neutralizer. The cooled prills are screened and the oversize and undersize prills are recycled to the neutralizer.

Advantages

This is a non-pressure operation. Therefore the investment cost is lower than that for a pressure system and operation is simpler

Equipment is easy to manufacture

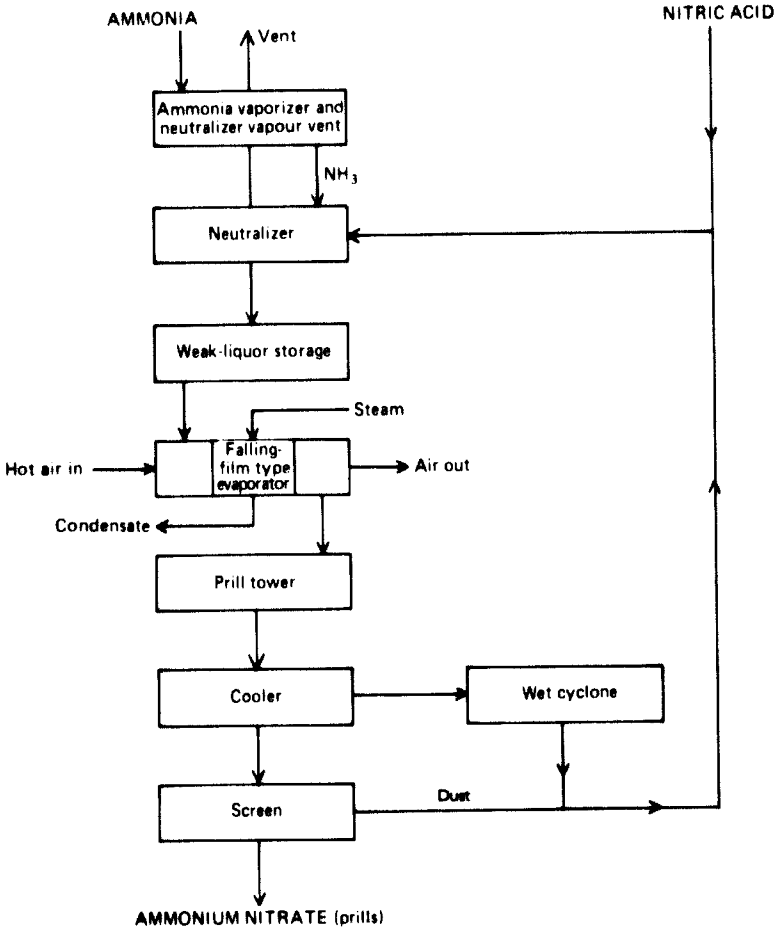
Disadvantages

Steam is not fully recovered and hence steam consumption is high

Power consumption is also higher than in process using pressure-type units

Process owner

C. & I./Girdler, Inc.



Ammonium nitrate by the C. & I./Girdler process

Montedison process

The Montedison process produces granular ammonium nitrate containing 34.5% nitrogen and uses a neutralizer at atmospheric pressure.

Pre-heated nitric acid and vaporized ammonia are reacted together in a neutralizer at a temperature below 145°C. Neutralizer vapour is used to pre-heat the nitric acid. The neutralizer solution is further concentrated to between 93% and 97% in a concentrator. The concentrated solution is then passed through a screw mixer, into which fine powder also enters, before it goes to the granulating drum. Ammonium nitrate granules are screened and the fines are recycled to the screw mixer.

Advantages

This is a non-pressure operation. Hence operation is simple and investment cost is lower than in pressure operation

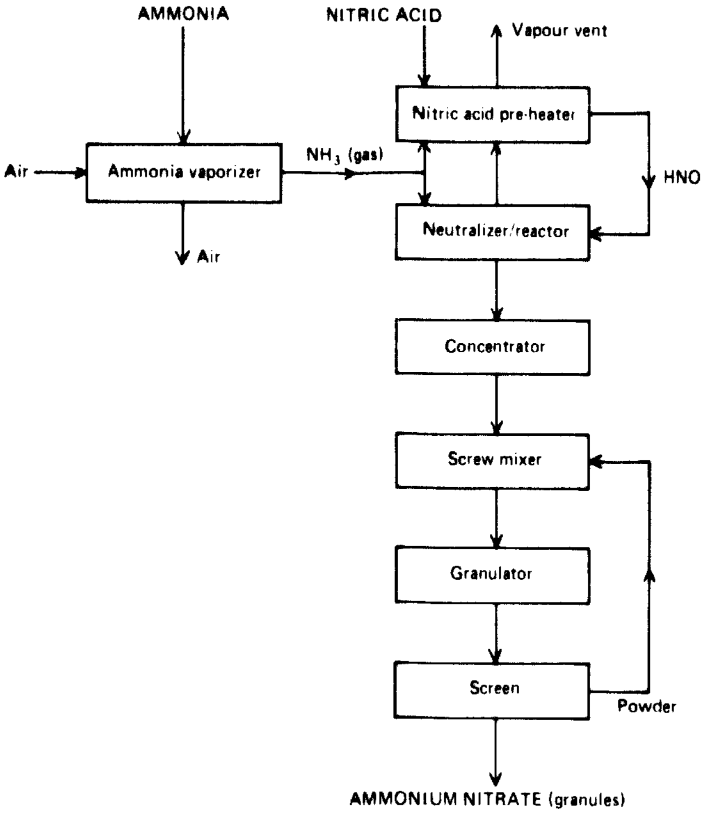
Equipment is easy to manufacture

Disadvantages

Steam consumption is higher in this process than in a pressure operation

Process owner

Montedison SpA



Ammonium nitrate by the Montedison process

Uhde process

The Uhde process produces ammonium nitrate containing 33.5% nitrogen in the form of granules and uses two neutralizers operating at atmospheric pressure.

Ammonia gas and nitric acid are fed to the first neutralizer where a weak ammonium nitrate solution is formed. The heat of neutralization is used to concentrate the solution in a falling-film evaporator. The ammonium nitrate solution, concentrated to approximately 95%, goes to the second neutralizer where ammonia is also added to adjust the pH of the solution. The solution is further concentrated in a second evaporator, before entering the granulating unit.

The granulator receives the ammonium nitrate liquor along with recycled material. The hot granules are dried in a rotary drum. The dried material is screened and classified. The fines from the drier cyclones and dust from the screens and crushed oversize granules are recycled to the granulator.

Advantages

Investment is low and operation is simple since this is a non-pressure operation

It is easy to manufacture the equipment required

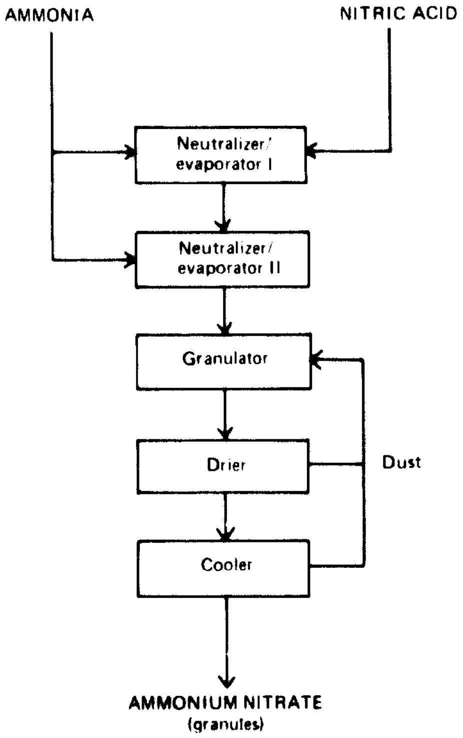
This process can also handle ammonia-bearing gases, such as ammonium carbamate from a urea plant

Disadvantages

This process consumes more steam than a pressure operation

Process owner

Friedrich Uhde GmbH



Ammonium nitrate by the Uhde process

Fisons process

The Fisons process is the same as the other ammonium nitrate processes except for the method of prilling: a fluidized bed of fine dust is used to solidify the ammonium nitrate droplets, rather than the typical counter-current of air. This results in large particles suitable for bulk blending. The melts are called "nitro-top".

Ammonium nitrate melt (99.7%) is sprayed from the top of the 7-m tower into a bed of dust about 2 m deep. As the dust is used up in the fluidizing process, more dust is supplied through a pneumatic conveying system. Two air streams are blown at the bed. The combined effect of the two air streams is to fluidize the dust bed and raise a cloud some 3-5 m deep above the surface of the bed. In the half-second or so that it takes the ammonium nitrate droplets to fall through this cloud, a coating of dust particles forms around them which also partly solidifies to form a hard shell.

The ammonium nitrate particles next enter the dense phase of the fluidized dust system, in which they are rapidly cooled to about 50°C and solidification is completed.

As the bulk of the heat is removed at this point, the bed is provided with water-cooled coils or plates. Since most of the heat is removed in the bed rather than by the air, the volume of air, and thus the cross-sectional area of the tower, need not be as great as in the conventional air prilling process.

Most of the loose dust adhering to the prills is removed and blown back into the bed as the prills pass against a counter-current of air down a tube into a small vessel immediately beneath the base of the prilling tower. The prills then pass through a final deduster, which is a small fluidized bed through which clean air is passed. Finally the product is screened and stored.

Air and dust from the top of the prill tower go through a cyclone dust-separator and a bag filter, resulting in a clean stack without any pollution hazards.

Advantages

The stack gas emerging from the prill tower is clean air, since it has passed through a bag filter

The prill-tower height and diameter are very small compared with those of conventional counter-current air-drying prill towers

All the cooling of prills takes place in the bed at the bottom of the prill tower rather than in the air, as in conventional prill towers

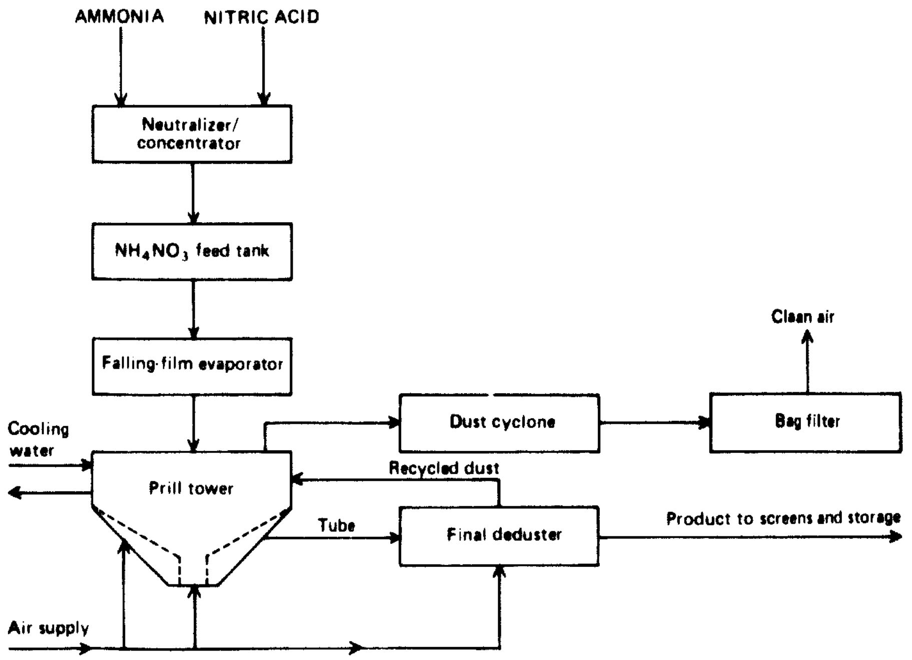
Prills are good for bulk blending

Process owner

Fisons Ltd, Fertilizer Division

Engineering licensees

Davy Powergas Ltd
Foster Wheeler Corporation
Lurgi Chemie und Hüttentechnik GmbH



Ammonium nitrate by the Fisons process

Stengel process

In the Stengel process, ammonium nitrate can be produced in molten form, as well as in granules. Nitric acid (60%) is either heated to about 170°C or combined with ammonia vapour superheated to about 150°C in a packed, stainless-steel reactor operating at approximately 240°C and 3.3 bar. The resulting molten ammonium nitrate, steam and traces of ammonia are separated in a cyclone; air, pre-heated to about 200°C, is blown through the molten salt, to reduce the moisture content from about 2% to about 0.2%. Air leaving the separator is reheated, stripped of residual ammonium nitrate in a condenser, and recycled through the melt.

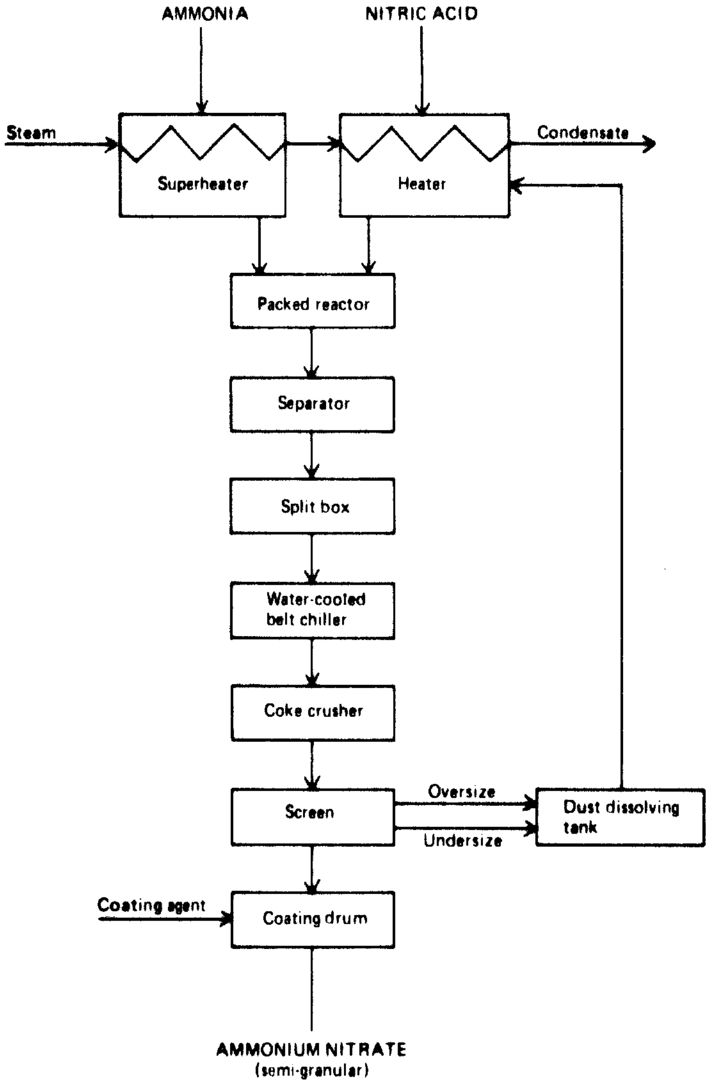
The molten salt flows through a weir box to a water-cooled stainless-steel belt; the chilled nitrate is fractured, coarse-ground, screened, coated and bagged as a 33.5% nitrogen, semigranular product. Fines are recycled.

Disadvantages

Steam needs to be supplied from other sources

Process owner

C. & I./Girdler, Inc.



Ammonium nitrate by the Stengel process

Ammonium sulphate nitrate

$((NH_4)_2SO_4 \cdot NH_4NO_3)$

The double salt ammonium sulphate nitrate is a straight fertilizer containing both ammoniacal and nitrate nitrogen in the ratio 3:1. It is produced in either granular or crystalline form in a simple way and has certain practical advantages over the single salts that constitute it: a higher percentage of N than the sulphate (but lower than the nitrate) and better keeping qualities than the nitrate or mechanical mixtures of the nitrate and sulphate. The addition of ferrous salts further improves the keeping qualities, the granules of the final product requiring no protective coating.

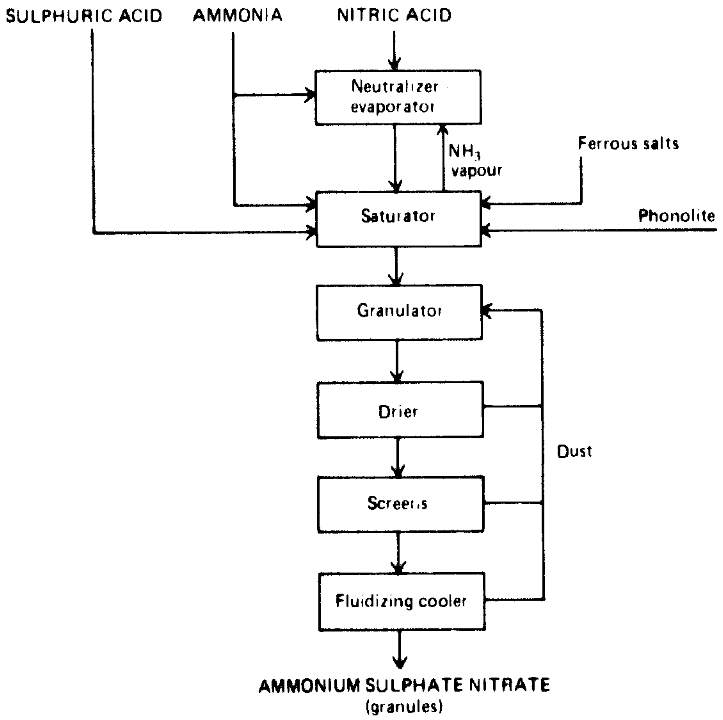
There are several processes for making the double salt, with very small differences between them. Only two are described here; other processes are merely listed by their owners' names.

The cost of a battery limits plant in the Gulf Coast area of the United States of America with a capacity of 275 t/d (300 short tons per day) is about $5.5 million. This figure, an extrapolation from 1967 prices, does not include the cost of plants to make the starting materials ammonia and nitric acid.

Uhde-Hibernia process

The Uhde-Hiberna process yields granular ammonium sulphate nitrate containing 26%-28% nitrogen.

Aqueous nitric acid is neutralized with gaseous ammonia in a neutralizer-evaporator system to form ammonium nitrate solution. The exothermic heat of reaction is utilized to concentrate the solution. The



Ammonium sulphate nitrate by the Uhde-Hibernia process

ammonium nitrate solution then flows to a saturator, into which sulphuric acid and ammonia are fed. Simultaneously, ferrous salts and special silicates (e.g. phonolite) are added to the saturator to reduce subsequent caking and to improve the storage properties of the product. The ammonium sulphate produced forms a double salt with ammonium nitrate.

The heat of reaction liberated in the formation of ammonium sulphate leads to the vaporization of water so that the ammonium sulphate nitrate solution is brought to the required final concentration of about 3% water.

To keep ammonia losses to the minimum, the ammonia-bearing vapours leaving the saturator are sent back to the neutralizer, where the ammonia is recovered through reaction with nitric acid.

The melt from the saturator and the recycled materials are processed in a granulator, after which the granules are heated in a drier using hot combustion gases. The dried granules are screened and classified. The temperature of the product-size granules is brought down to the level desired with cooled air in a fluidized-bed cooler.

The exhaust air from the drier and the fluidized cooler are sent through a dust cyclone for dust removal. The fines, crushed oversize granules, and dust from the cyclones are sent back to the granulator as recycled material.

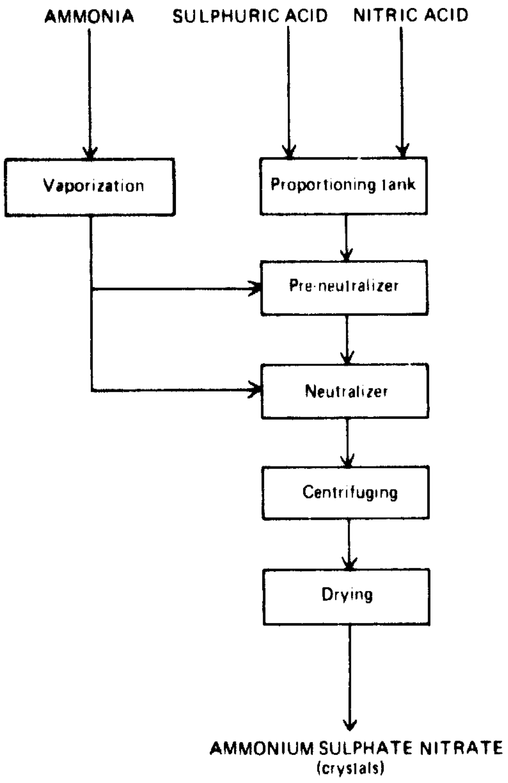
The granules, which are normally between 2 mm and 4 mm in size, are extremely hard and possess good storage properties. They do not need any coating.

Process owner

Friedrich Uhde GmbH

FCI process

The FCI process makes ammonium sulphate nitrate containing a minimum of 26% nitrogen in crystalline form. Equimolar proportions of nitric acid and sulphuric acid are first ammoniated in a pre-neutralizer and then concentrated and neutralized with additional ammonia. The crystals formed in the neutralizer are separated in a centrifuge and dried to a moisture content of less than 1%.



Ammonium sulphate nitrate by the FCI process

Process owner

The Fertilizer Corporation of India Ltd

Other processes

Various other process owners and engineering licensees available for manufacturing ammonium sulphate nitrate are listed below.

Process owner	*Engineering licensees*
BASF Aktiengesellschaft	
Didier Engineering GmbH	
Fisons Ltd. Fertilizer Division	Davy Powergas Ltd Foster Wheeler Corporation Lurgi Chemie und Hüttentechnik GmbH
Kaltenbach et Cie SA	Davy Powergas Ltd ENSA Creusot-Loire Entreprises SYBETRA SA (Syndicat Belge d'Entreprises à l'Etranger) Toyo Engineering Corporation Woodall-Duckham Ltd
Société Belge de l'Azote et des Produits Chimiques du Marly (SBA)	

Calcium ammonium nitrate

Calcium ammonium nitrate (CAN), or nitro-chalk, a mixture of limestone ($CaCO_3$) *or lime* (CaO) *and ammonium nitrate, is one of the straight nitrogenous fertilizers, with a nitrogen content that can be varied from 20% to 30% by adding the proper amount of the calcium-containing component. The product is not so hazardous as ammonium nitrate and stores well because of the coating applied to the particles during manufacture.*

CAN fertilizers are made by simple processes in the form of prills or granules. The main process consists of the following steps:

Making ammonium nitrate melt by any standard process

Mixing it with ground limestone or lime meal

Granulating or prilling the mixture as required

Though there are various processes, differences among them are not significant.

A prilling process and a granulating process owned by the Friedrich Uhde Company are described below. The other process owners and their engineering licensees are listed separately.

In the following table, the cost is given for a battery limits plant located in the Gulf Coast area of the United States of America. The cost does not include a nitric acid plant. The cost is extrapolated from 1967 prices.

Daily output (25% N; prills)		Cost
(t)	(short tons)	(millions of dollars)
275	*300*	*5.7*
550	*600*	*9.3*
730	*800*	*11.5*
910	*1 000*	*13.7*

Uhde prilling process

In a reactor-evaporator, ammonia gas and nitric acid are reacted to form ammonium nitrate solution. This solution passes through the reactor by forced circulation; in the evaporator, part of the water introduced with the nitric acid is vaporized by the exothermic heat of reaction. The water vapour produced in the vaporizer is subsequently condensed and the vacuum is maintained in the evaporator at the level required. The vacuum evaporator helps to maintain the temperature within the safety limits required even if concentrated nitric acid is used.

The concentration of the nitric acid used determines the ammonium nitrate concentration; the latter should reach about 95%. Ammonia gas is added to the solution going out of the reactor-evaporator to maintain the pH value of the solution higher than that of the evaporator. The solution is further concentrated to 99.5% in a falling-film evaporator.

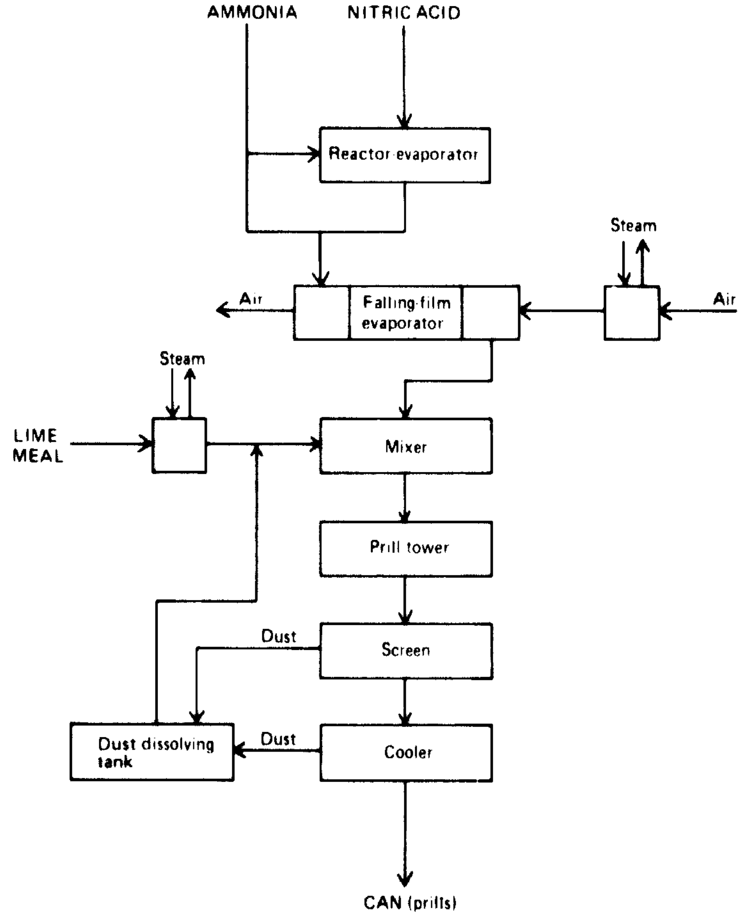
The highly concentrated solution coming out of the evaporators is thoroughly mixed with heated lime meal and dissolved recycled powder from the dust removal system in an agitated mixing vessel and sprayed into the prill tower by means of a rotating spray-basket. The prills solidify during their fall against a counter-current stream of air. The prills withdrawn from the bottom of the tower are classified, cooled and sent to a coating drum for coating, in order to prevent caking and improve storage qualities.

Advantages

This is a simple process, which nevertheless produces good and strong prills

Process owner

Friedrich Uhde GmbH



Calcium ammonium nitrate by the Uhde prilling process

Uhde granulating process

Gaseous ammonia and aqueous nitric acid are reacted together in a reactor-evaporator, using forced circulation. Part of the water introduced through the nitric acid is vaporized in the vacuum evaporator. Due to the exothermic heat of reaction, the ammonium nitrate solution reaches a concentration of about 95% (the precise value depends on the concentration of the nitric acid used).

Ammonia is added to the solution coming out of the reactor-evaporator; the strength of the ammonium nitrate solution is further increased to the final value desired in a second neutralizer, which uses steam for heating. The addition of ammonia helps to maintain the pH at the value desired.

Metered quantities of concentrated ammonium nitrate solution from the second neutralizer are fed into the granulator, where they are mixed with powdered lime (the amount is determined by the nitrogen content required in the final product) and recycled materials (consisting of crushed oversize material from the screens and dust from the screens and coolers). The metering facilities provided make it possible to maintain the nitrogen content of the final product within extremely small tolerances.

Granules from the granulator outlet first pass through a drier, which uses hot combustion gases for drying, then through classifying screens and finally through a fluidized cooler, which uses cold air. Oversize granules from the drier are crushed and, together with powder from the screens and drier, form the recycled material for granulation.

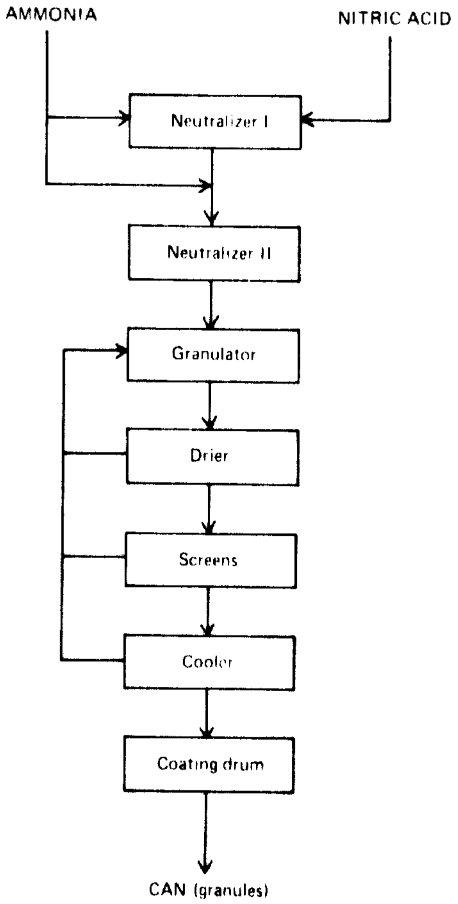
The cooled product is coated to prevent caking and improve storage qualities.

Advantages

- The product contains a low calcium nitrate content owing to the short residence time and low temperature in the granulator
- The process is very simple and the investment cost is low

Process owner

Friedrich Uhde GmbH



Calcium ammonium nitrate by the Uhde granulating process

Other processes

Process owner	*Engineering licensees*
BASF Aktiengesellschaft	—
Fisons Ltd, Fertilizer Division	Davy Powergas Ltd Foster Wheeler Corporation Lurgi Chemie und Hüttentechnik GmbH
Imperial Chemical Industries Ltd	
Kaltenbach et Cie SA	
Norsk Hydro AS	Davy Powergas Ltd Humphreys and Glasgow Ltd Lurgi Chemie und Hüttentechnik GmbH Toyo Engineering Corporation
Stamicarbon BV	C. F. Braun and Company Chiyoda Chemical Engineering and Construction Company Ltd Coppée-Rust SA Didier Engineering GmbH Foster Wheeler Corporation Friedrich Uhde GmbH Humphreys and Glasgow Ltd Krebs et Cie SA The M. W. Kellogg Company Sim-Chem Division, Simon-Carves Ltd Stone and Webster Engineering Corporation

Sodium nitrate

Before the availability of cheap synthetic ammonia and its derivatives, sodium nitrate ($NaNO_3$) was used as a fertilizer for the surface dressing of soils. It was also used as a raw material in nitric acid manufacture.

The most widely used method of manufacturing sodium nitrate is to extract it from natural deposits, most of which occur in Chile. A typical, high-content Chilean deposit contains about 18% $NaNO_3$, 30% other soluble salts and 50% insoluble matter. Extraction is the only method available for large-scale manufacture of sodium nitrate and can only be applied at places where ore is available in large quantities. The well-known Guggenheim extraction process is the one described here.

Methods of synthesizing sodium nitrate exist but are rarely used. In some nitric acid plants, sodium nitrate is made by scrubbing the tail gases with caustic-soda solution. A process using ammonia and sodium carbonate as starting materials is described here.

In view of the remarks above, the usual details about process ownership and costs are omitted.

Guggenheim process

A process for the manufacture of sodium nitrate from natural deposits was developed by the Guggenheim brothers in 1920. It is a low-temperature leaching process based on two important principles: *(a)* if leaching is conducted at sufficiently low temperatures (say 40°C), only sodium nitrate is extracted, with most of the impurities, such as sodium sulphate and sodium chloride, being left behind as slimes; and *(b)* if the leaching solution initially contains certain protective salts, such as $CaSO_4$, $MgSO_4$ and K_2SO_4, the sparingly soluble double salt in the ore, $NaNO_3 \cdot Na_2SO_4$, is decomposed, and therefore more sodium nitrate can be extracted.

This process permits even ore containing less than 10% nitrate to be profitably worked.

The run-of-mine ore, which is in large pieces, is crushed to sizes in the range 1-2 cm and leached in a series of vats, each having a capacity of about 10 000 t of crushed ore. The leaching solution is made up by combining mother liquor from the crystallizing plant with strong wash liquor from the washing cycle. The solution has a nitrate concentration of 350 g/l. In order to maintain a temperature of about 40°C throughout the cycle, the underflow from each vat is heated before it is pumped to the next vat (the heat of solution is negative).

Fines from the crushers are pulped and filtered. The filtrate is combined with the solution from the leach tanks. When the solution comes out of the last vat, it has built up its nitrate content to about 450 g/l after a contact time of about 40 h. It is then sent to the crystallizing plant, where it is cooled to a temperature of less than 10°C, at which the sodium nitrate crystals form. The coolant for the above solution is a combination of a solution from the cold mother liquor from the centrifuge as well as liquid ammonia. Shell-and-tube heat exchangers are used for the cooling. The crystal slurry from the cooler is pumped to batch-type bucket centrifuges where the crystals are separated, rinsed and dried. The discharged crystals are pure white and contain about 3% moisture. The size of crystals is about 48 mesh.

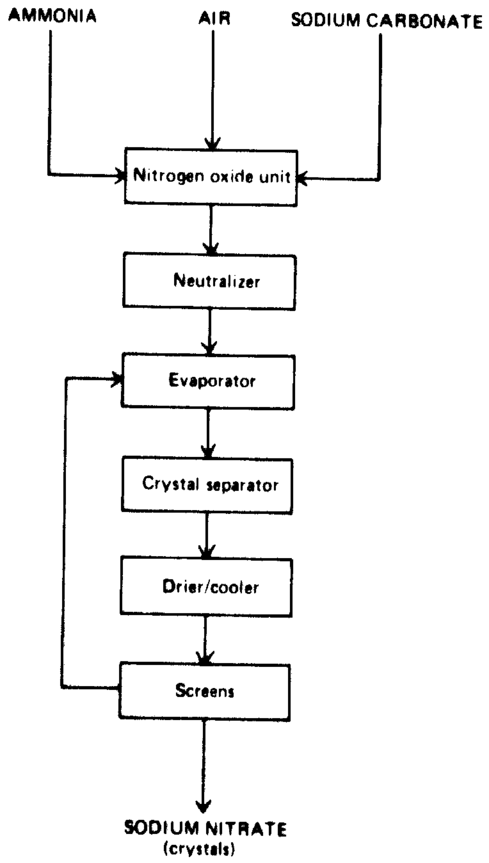
When a prilled product is required, the centrifuged salt is melted at about 325°C in oil-fired reverberatory furnaces and sprayed into large prill towers. The prills are classified, and oversize and undersize prills are recycled to the melter. The product-size prills (8-10 mesh) are cooled to a temperature below 36°C and sent to storage silos. The final product has about 98.5% sodium nitrate and 0.2%-0.3% moisture.

Nitrogen-oxide process

Synthetic sodium nitrate is manufactured by the nitrogen-oxide process, in which oxidized ammonia vapours are reacted with an alkali solution, such as sodium carbonate, to yield sodium nitrate, nitrogen oxide, carbon dioxide and water, as shown in the following reaction:

$$6NH_3 + Na_2CO_3 + 9O_2 \rightarrow 2NaNO_3 + 9H_2O + 4NO + CO_2$$

Unconverted NO is recycled for further processing. The weak sodium nitrate solution is evaporated, crystallized, centrifuged, dried and screened. Fines are recycled along with weak solution and reprocessed.



Synthesis of sodium nitrate by the nitrogen-oxide process

Potassium nitrate

Potassium nitrate (KNO_3) can be used as a component in solid or solution-type fertilizers, although its cost is relatively high. Moreover, it is a hazardous chemical because of its strong oxidizing properties.

There are two or three methods of manufacturing potassium nitrate by chemical means. The well-known solvent-extraction process of the Israeli Mining Industry (IMI) is described below. It is a simple process that produces hydrochloric acid as a by-product, which in turn can be used in the manufacture of phosphoric acid.

The IMI process is based on the use of an organic solvent (commercial grade pentanol) for promoting the reaction between solid potassium chloride (KCl) and 60%-65% nitric acid without the use of heat. The hydrochloric acid formed enters the solvent, and a simple solid-liquid separation yields solid potassium nitrate. The solvent is washed in a suitable liquid-liquid contactor and recycled. The dilute hydrochloric acid is concentrated and used for other purposes, such as the manufacture of phosphoric acid (also a process by IMI).

Process owner

IMI Institute for Research and Development

Engineering licensees

Davy Powergas Ltd
Exportlife Engineering Company Ltd

Nitrogen solutions

Nitrogen solutions are aqueous solutions of ammonia (NH_3), ammonium nitrate (NH_4NO_3) or urea (NH_2CONH_2), separately or in combination. They include aqua ammonia but not anhydrous ammonia or fertilizer solutions containing phosphorus and potash.

Nitrogen solutions are classified according to which of the three components they contain, as follows:

Ammonia only (aqua ammonia)

Ammonia + ammonium nitrate

Ammonia + urea

Ammonia + ammonium nitrate + urea

Ammonium nitrate alone or with urea

In commerce, nitrogen solutions are identified by a symbol giving the component concentrations to the nearest percentage unit, e.g., the solution designation 26-50-12 means that it contains 26% NH_3, 50% NH_4NO_3 and 12% NH_2CONH_2.

None of the manufacturing processes for these solutions described below is proprietary.

Aqua ammonia

Aqua ammonia is a good source of nitrogen for direct application. There is a variety of methods for making it. The basic operation involves proportioning the flows of water and ammonia, cooling the freshly formed liquor to remove the heat of reaction, and measuring the concentration of ammonia. The solution can be simply prepared in the field by injecting anhydrous ammonia into the irrigation water.

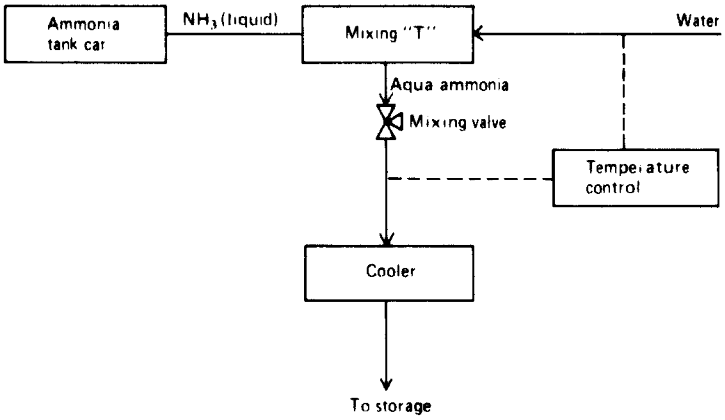
Liquid ammonia flows from a tank car under its own pressure and is line-mixed with a controlled flow of soft water. The proportioning of the flows of water and anhydrous ammonia can be regulated by the heat of absorption. The ammonia flow is not controlled and may vary during the course of unloading as the tank-car pressure decreases. The streams of water and anhydrous ammonia are brought together in a "T" and the solution flows through a globe valve, which completes the mixing. The pressure drop across the globe valve is manually adjusted to between 0.7 and 1.4 bar. A temperature recorder-controller measures the temperature of the mixture and automatically maintains this temperature at a predetermined value by adjusting the flow of water. This predetermined value is selected on the basis of the temperature of the incoming water, the initial pressure in the tank car and the desired concentration of the aqua ammonia. Since aqua ammonia is commonly used at a concentration of 20%, values of the control temperature are shown below for the production of this concentration.

REQUIRED CONTROL TEMPERATURE AFTER MIXING VALVE (°C)

Inlet water temperature (°C) \ *Initial tank-car pressure (bar)*	*4.1*	*5.5*	*6.9*	*8.2*	*9.6*
10	43	45	46	47	48
13	46	47	48	49	50
15	48	49	50	52	53
18	50	52	53	54	55
21	52	54	55	56	57
24	54	56	57	58	59

Owing to the variations in the temperature of the ammonia leaving the tank car during unloading there will be minor variations in the concentration of aqua ammonia produced. (The amount of this variation will be less than ± 1%.)

An installation using 3-in. (7.62-cm) piping for liquid ammonia and 4-in. (10.16-cm) for water and aqua ammonia should be able to unload a 38-m^3 tank car in about six hours.



Manufacture of aqua ammonia

Other methods of proportioning the flows of water and ammonia are based on the concentration of a recirculating stream of aqua ammonia as indicated by a hydrometer. Removal of the heat of absorption is a major consideration. Cooling is accomplished by various methods, including refrigeration, tube-and-shell heat exchangers, or tube-and-spray tower evaporative coolers. The cooling system usually comprises the main part of aqua-ammonia converters.

Advantages

Storage tanks can be made of carbon steel

Disadvantages

Tanks for the 20% solution must withstand a pressure of 7 bar

Cost of typical capacity plant

The 1977 prices of a stationary unit capable of converting anhydrous liquid ammonia in a 38-m^3 tank car into 20% aqua ammonia in 3-16 h, ranges from $13,280 to $26,500. A portable unit of the same capacity, suitable for mounting on trailers, will cost from $17,000 to $37,460. These prices are approximate, and have been derived from a rough extrapolation and adjustment of 1967 prices.

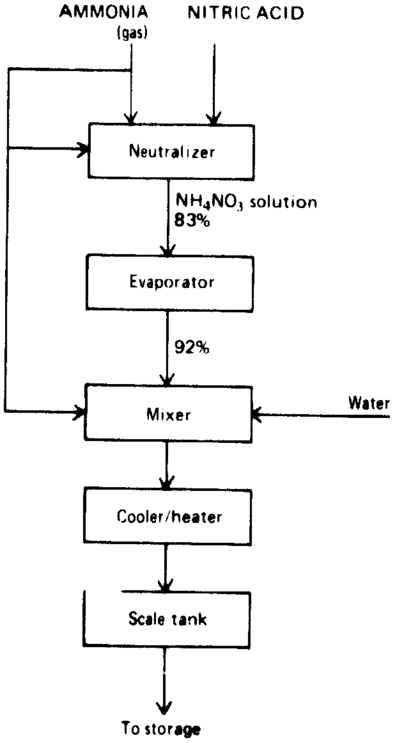
Ammonia + ammonium nitrate

Solutions containing ammonia and ammonium nitrate are produced by injecting ammonia into ammonium nitrate solutions. Although such solutions are usually produced in an ammonia plant, they can also be made from ammonia obtained elsewhere. In the latter case, a nitric acid plant is required to convert a portion of the ammonia into nitric acid. The nitric acid is then neutralized with ammonia to prepare a solution of ammonium nitrate; ammonia is added to the ammonium nitrate solution to prepare the final product. Such an arrangement is economical in locations where the delivered cost of anhydrous ammonia is less than the cost of producing ammonia.

Nitric acid is first neutralized with ammonia in a neutralizer. Ammonium nitrate solution at a concentration of about 83% is produced, which is then further concentrated to 92% in an evaporator. The solution flows from the evaporator to a mixer, where ammonia gas and water are added as necessary. The solution is then cooled, weighed and sent to a storage tank as the final product.

The composition and properties of some commercial ammonia + ammonium nitrate solutions are shown below.

Solution designation	*Composition (%)*				*Salting-out temperature (°C)*	*Gauge pressure at 40°C (bar)*	*Temperature at which gauge pressure is zero (°C)*
	N	NH_3	NH_4NO_3	H_2O			
17-67-0	37.0	16.6	66.8	16.6	9	0.07	38
22-65-0	41	22.2	65.0	12.6	6	0.69	26
26-56-0	41	26.3	55.5	18.2	32	1.17	20
19-74-0	41.4	19.0	74.0	7.6	18	0.55	26
24-70-0	44	23.8	69.8	6.4	-3	1.23	19
28-60-0	44	28	60.0	12.0	38	1.72	14
25-69-0	44.8	25.0	69.0	6.0	14	1.17	16
26-68-0	45.1	26.0	68.0	6.0	-21	1.65	16
30-64-0	47.1	30.0	64.0	6.0	36	2.06	8
34-60-0	49.0	34.0	60.0	6.0	46	3.43	4



Manufacture of ammonia + ammonium nitrate solution

Advantages

The process can be used for mixed-fertilizer manufacture

Disadvantages

The salting-out temperature is critical in manufacture and storage
The solution is corrosive to carbon steel

Cost of typical capacity plant

In 1977, for a plant capacity of 225 t of 34-60-0 solution per eight-hour day, the cost will, be approximately $3.55 million. This includes, among other items, a nitric acid plant with a capacity of 135 t/d and a neutralizer with a capacity of 165 t/d. The ammonia used is not locally produced. The cost is an extrapolation of the 1967 figure.

Ammonia + urea

Usually, ammonia + urea solutions are used for manufacturing mixed fertilizers rather than for direct application. The solutions can be made only in urea plants, by adjusting the composition of the process liquor. They contain small quantities of carbamate but less water than solutions of equal grades without carbamate. Liberated carbon dioxide helps to maintain a safe and inert atmosphere in the mixer in which the solution is made.

The compositions and properties of some commercial ammonia + urea solutions are shown in the table below.

Cost of typical capacity plant

The process is simple and can be carried out in a urea plant; the cost is therefore quite low and no attempt to estimate it has been made.

Solution designation	*Composition (%)*				*Salting-out temperature (°C)*	*Gauge pressure at 40 °C (bar)*	*Temperature at which gauge pressure is zero (°C)*
	N	NH_3	NH_2CONH_2	H_2O			
20-0-41	35	19.6	40.6	39.8	14	0.62	27
37-0-33	45.5	36.8	32.5	30.7	−9	3.91	−2
31-0-44	46.0	31.1	43.8	25.1	5	3.50	−1
37-0-33	46.0	37.3	32.9	29.8	−17	4.12	−6

Ammonia + ammonium nitrate + urea

Nitrogen solutions containing all three components are rarely used for direct application; they are used mainly in the manufacture of mixed fertilizers. They are made in the same way as ammonia + ammonium nitrate solutions, the urea being added either as a solid or as a carbamate-free solution.

The compositions and properties of some commercial ammonia + ammonium nitrate + urea solutions are shown in the table below.

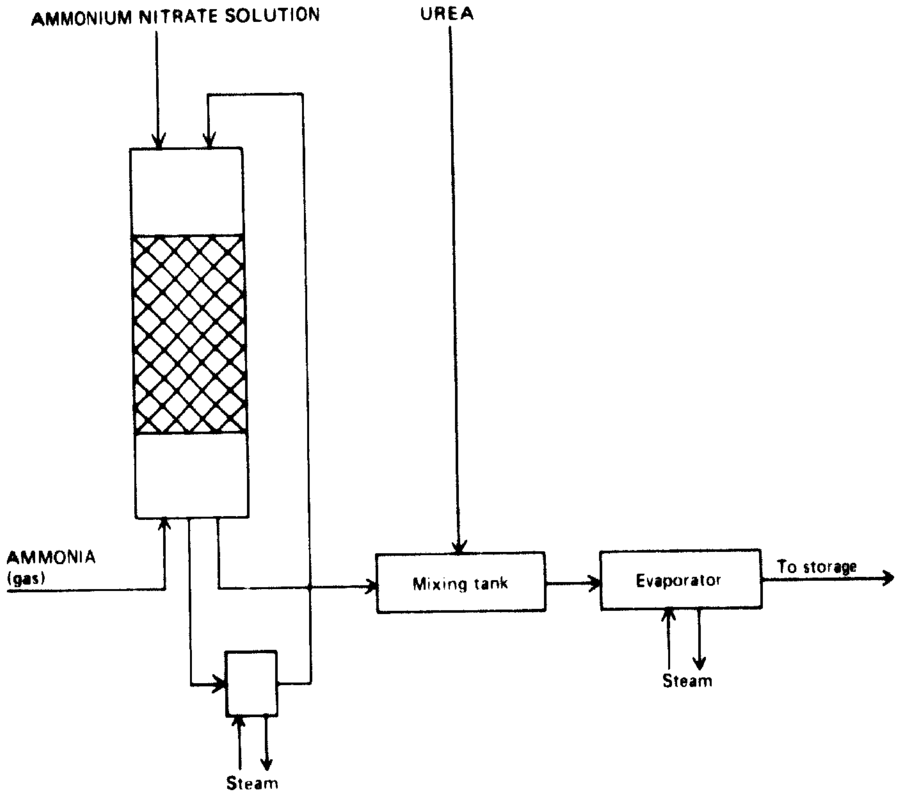
Advantages

The addition of a relatively small proportion of urea to an ammonia + ammonium nitrate solution modifies and improves the crystal habit of certain compounds present in mixed fertilizers made from the solution, thus reducing the tendency towards caking

Disadvantages

The solutions are corrosive to carbon steel

Solution designation	*Composition (%)*					*Salting-out temperature (°C)*	*Gauge pressure at 40°C (bar)*	*Temperature at which gauge pressure is zero (°C)*
	N	NH_3	NH_4NO_3	NH_2CONH_2	H_2O			
19-58-11	41.0	19.0	58.0	11.0	12.0	14	0.69	27
28-40-15	44	28.0	40.0	15.0	17.0	17	1.85	11
25-56-10	44.4	24.5	56.0	10.0	9.5	26	1.51	17
25-55-10	44.4	25.0	55.0	10.0	10.0	29	1.51	13
26-50-12	44.4	26.0	50.0	12.0	12.0	22	1.65	12
33-45-13	49.0	33.0	45.0	13.0	8.8	25	3.43	2



Manufacture of ammonia + ammonium nitrate + urea solutions

Cost of typical capacity plant

Since the process is simple and can be incorporated in an ammonium nitrate plant, no attempt to estimate costs has been made.

Non-ammoniacal solutions of ammonium nitrate and urea

Unpressurized nitrogen solutions containing ammonium nitrate alone or with urea are often used for surface application with no loss of ammonia. Such solutions can be made economically in an ammonium nitrate plant.

The compositions and properties of some commercial solutions are tabulated in the table below.

Advantages

A pressurized storage vessel is not needed

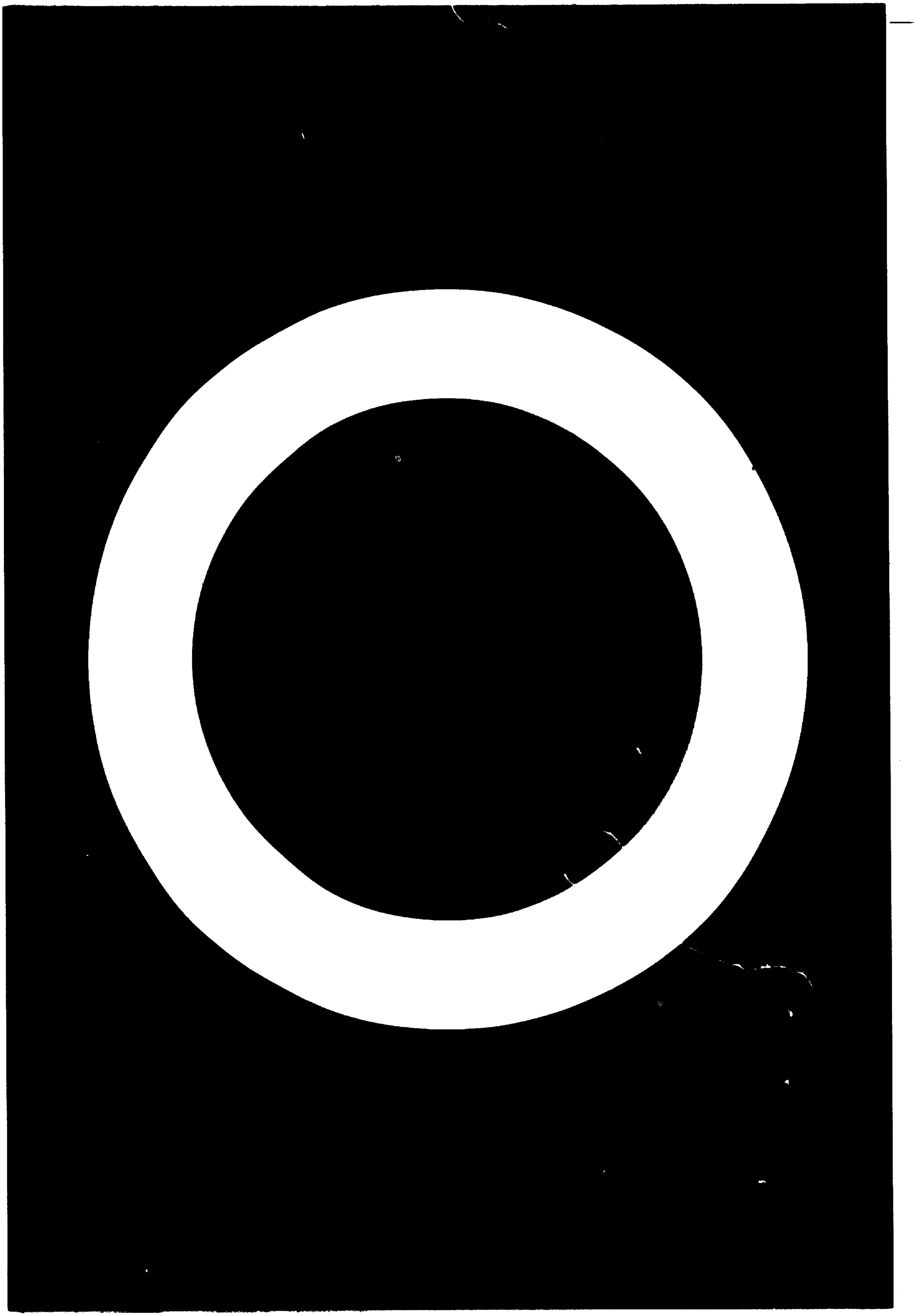
Disadvantages

The solution is corrosive to carbon steel

Cost of typical capacity plant

Since the process is simple and can be incorporated in an ammonium nitrate plant, no attempt to estimate costs has been made.

Solution designation	*Composition (%)*				*Salting-out temperature (°C)*
	N	NH_4NO_3	NH_2CONH_2	H_2O	
0-46-0	16	45.7		54.3	12
0-50-0	17.5	50.0		50.0	-6
0-54-0	19.6	54.3		45.7	1
0-57-0	20.0	57.3		42.7	6
0-40-30	28.0	39.5	30.5	30.6	-17
0-42-33	30.0	42.2	32.7	25.1	-9
0-44-35	32.0	44.3	35.4	20.3	0



Annex

LIST OF FIRMS

Allied Chemical Corporation
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Arthur McKee and Company
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Consolidated Mining and Smelting Company
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Canada

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(Ingenieursbureau voor de Procesindustrie NV)
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Shell Development Company
Division of Shell Oil Company
Patents and Licensing Division
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Showa Denko KK
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Simon-Carves Ltd
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Snam Progetti SpA
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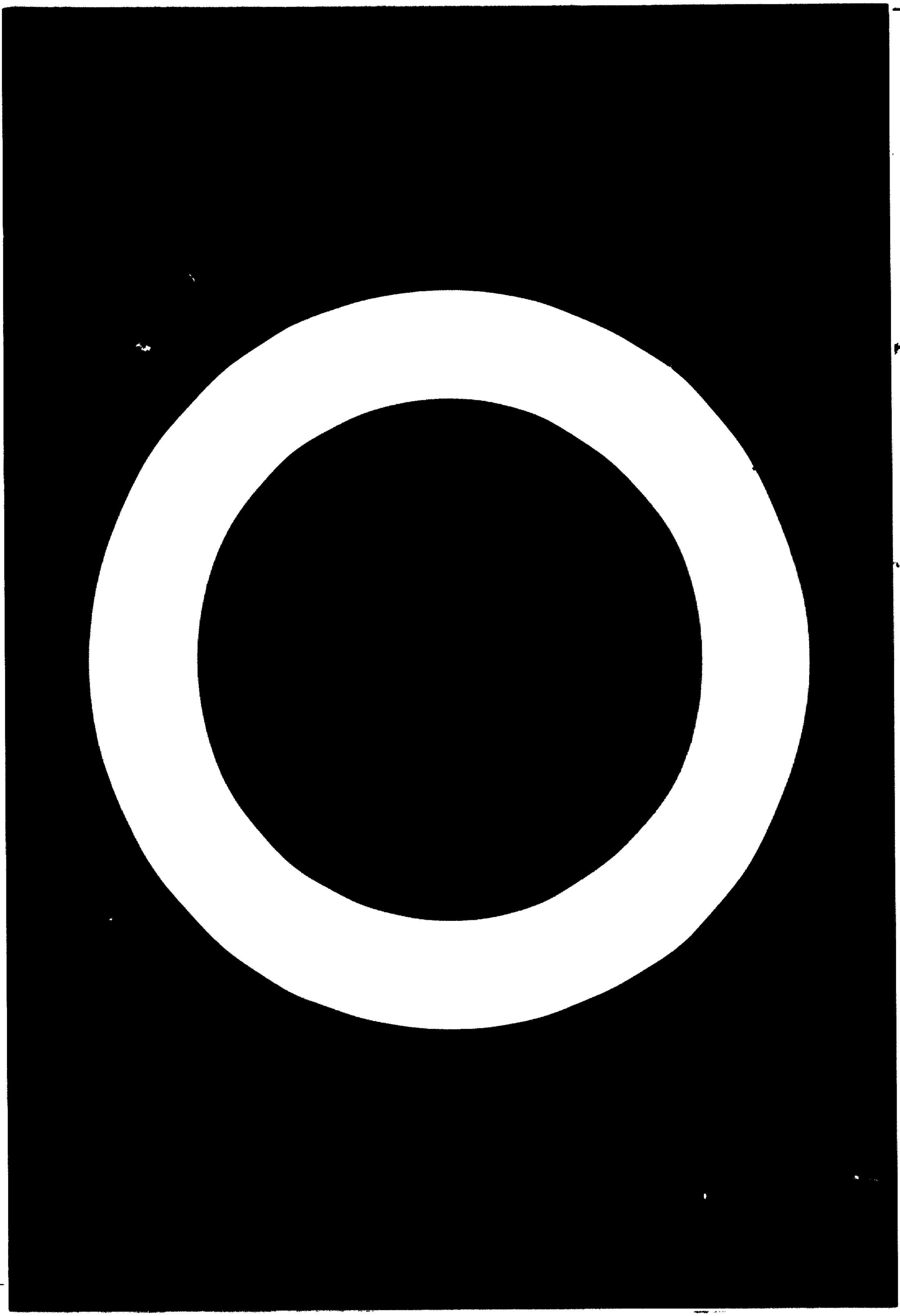

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