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Environmental Guidelines for the Fertilizer Industry

October 1992

Prepared by Norsk Hydro AB

for UNIDO

in the project "UNIDO/World Bank Industrial Pollution Guidelines"

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Pollution Control Guideline - Fertilizer Production Section

1.0 INTRODUCTION

This guideline is concerned with environmental issues resulting from the production of chemical fertilizers. It does not cover organic fertilizers and environmental issues concerned with the use of fertilizers are only briefly mentioned.

Fertilizers are plant nutrients and their production in a form available to the crop requires activities ranging from mining operations, through chemical plant processing to final material handling operations.

The main plant nutrients for growth are nitrogen (N), phosphorous (P) and potassium (K). Generally the elements occur in nature in a form not directly available to the crops; some processing is required.

The basic raw materials are found throughout the world and there is a considerable world trade in raw materials, chemical intermediates and finished products.

Fertilizer nitrogen originates from ammonia produced from atmospheric nitrogen and hydrogen. The hydrogen is produced from steam mainly by the use of natural gas. The process results in the release of carbon dioxide which can be combined with ammonia to produce urea, a major fertilizer product.

Ammonia can also be catalytically burned in air to nitrogen oxides which are absorbed in water to give nitric acid. This acid can be reacted with ammonia to give ammonium nitrate, another major fertilizer product.

The raw material for phosphate fertilizers is phosphate rock. The majority of the rock is reacted with sulphuric acid to produce phosphoric acid and gypsum as waste product. This acid can then be reacted with ammonia to give ammonium phosphates.

Some rock is reacted with sulphuric acid or phosphoric acid to give superphosphates or reacted with nitric acid to nitrophosphates and calcium nitrate. In all cases the insoluble phosphate rock is converted to a soluble form available for plants.

Sulphuric acid is mostly made from elemental sulphur.

Potassium occurs naturally in deposits of potash (potassium chloride) in the earth. It can be applied directly to the land but is usually combined with other phosphorous and/or nitrogen based fertilizers to give compound fertilizers containing all or some NPK nutrients.

This guideline covers the above processes, a summary of them is given in Figure 1.

A major environmental problem facing the fertilizer industry is the safe disposal of the phosphogypsum produced from the production of phosphoric acid by the wet process. The phosphogypsum contains heavy metals and other substances which may be harmful to the environment if released to the sea or not properly contained when disposed of on land. The nitro phosphate route of production avoids this problem as calcium nitrate, a useful by product, is produced in place of phosphogypsum.

The processes involved in the production of fertilizers give off emissions containing pollutants that may contribute to global environmental problems (e.g. green house effects) and local environmental problems (e.g. acid rain, water acidification, eutrophication, chemical mist)

If fertilizer production facilities are to achieve the lowest environmental impact, both locally and globally, it is important that high standards of operation and maintenance are achieved, or measures taken to reduce polluting emissions will be less effective than designed.

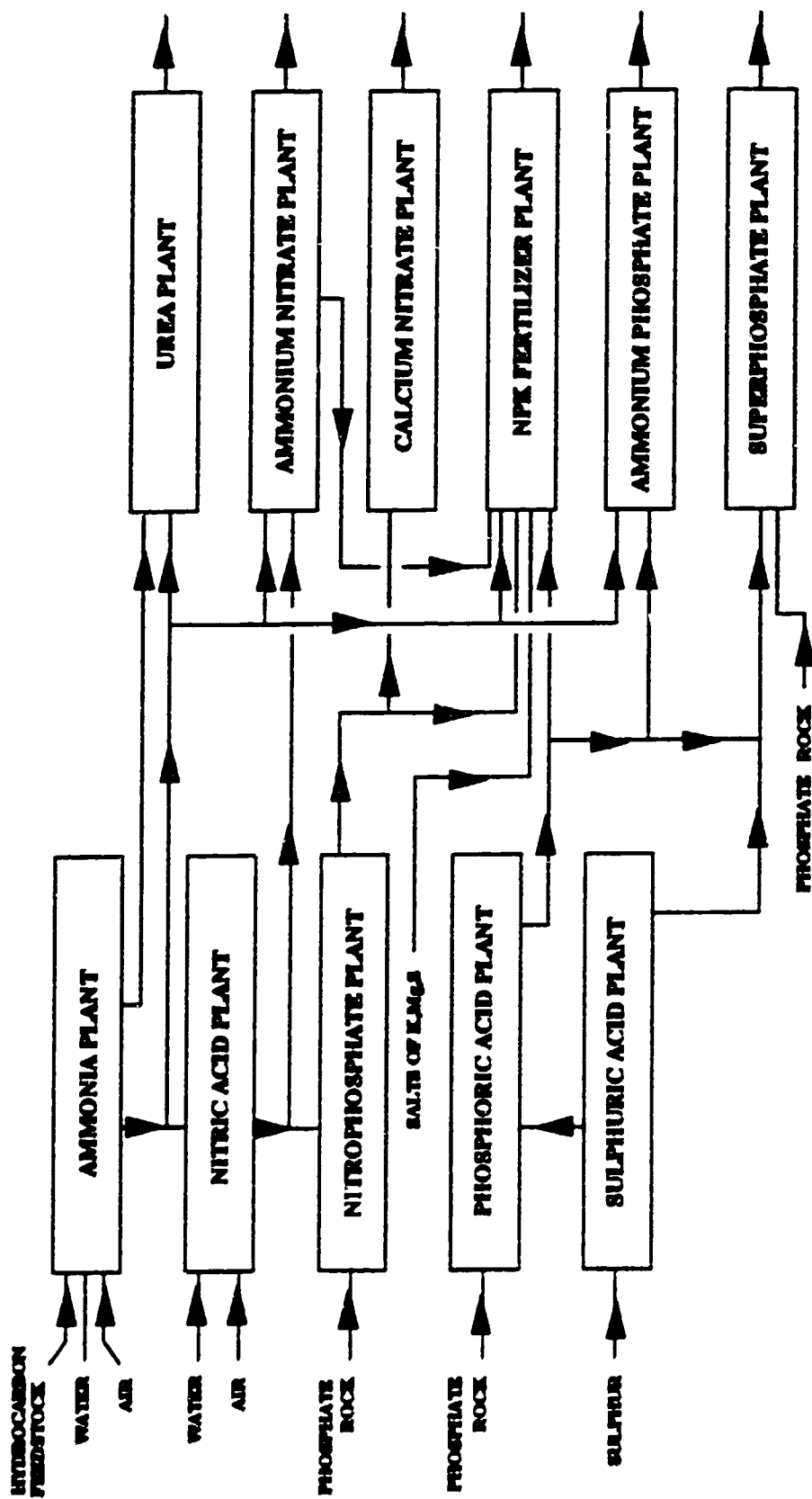
It is also necessary to monitor the emissions to air and discharges to water from the production plants. This will enable the operators of the plant to take corrective action if the effluents deviate from design conditions.

The costs of pollution control measures in the fertilizer industry is difficult to generalise. It depends on a number of factors, such as:

- the emission target or standard to be obtained
- type of process, other process on site, production volumes, type of raw materials being used, etc.
- whether the plant is new so that the design could be optimized with respect to pollution abatement, or whether the plant is an existing one requiring "add on" pollution abatement equipment.

Generally, it is more economical to incorporate the pollution abatement at the process design stage rather than "adding on" equipment at a later stage.

Hence, any costs included in this document are indicative. An environmental impact assessment should be made as part of the feasibility study for any fertilizer production project.



FERTILIZER PRODUCTION ROUTES

FIGURE 1

2.0 SULPHURIC ACID PRODUCTION

2.1 MANUFACTURING PROCESS

2.1.1. Process Description

Sulphuric acid for use in fertilizer production is usually produced from elemental sulphur by the contact process. The sulphur is burned in air to give sulphur dioxide (SO₂), which is catalytically converted to sulphur trioxide (SO₃) by reaction with excess oxygen and the sulphur trioxide is absorbed in concentrated sulphuric acid. The reactions are as follows:-



There are two basic contact processes, single absorption and double absorption.

In the single absorption plants the SO₃ is absorbed at the end of the process. For double absorption SO₃ is absorbed at two stages in the process, this allows a much higher sulphur usage efficiency to be obtained.

Sulphuric acid is also produced from SO₂ released from the roasting of sulphide ores.

2.1.2. Process Flow Diagram

Simplified process flow diagrams for single and double absorption plants are given in figures 2 and 3.

2.1.3. Economic Factors in Process Selection

Sulphuric acid production from elemental sulphur produces a large energy surplus in the form of high pressure steam. This steam can be used to generate electricity or be utilised to run plant equipment.

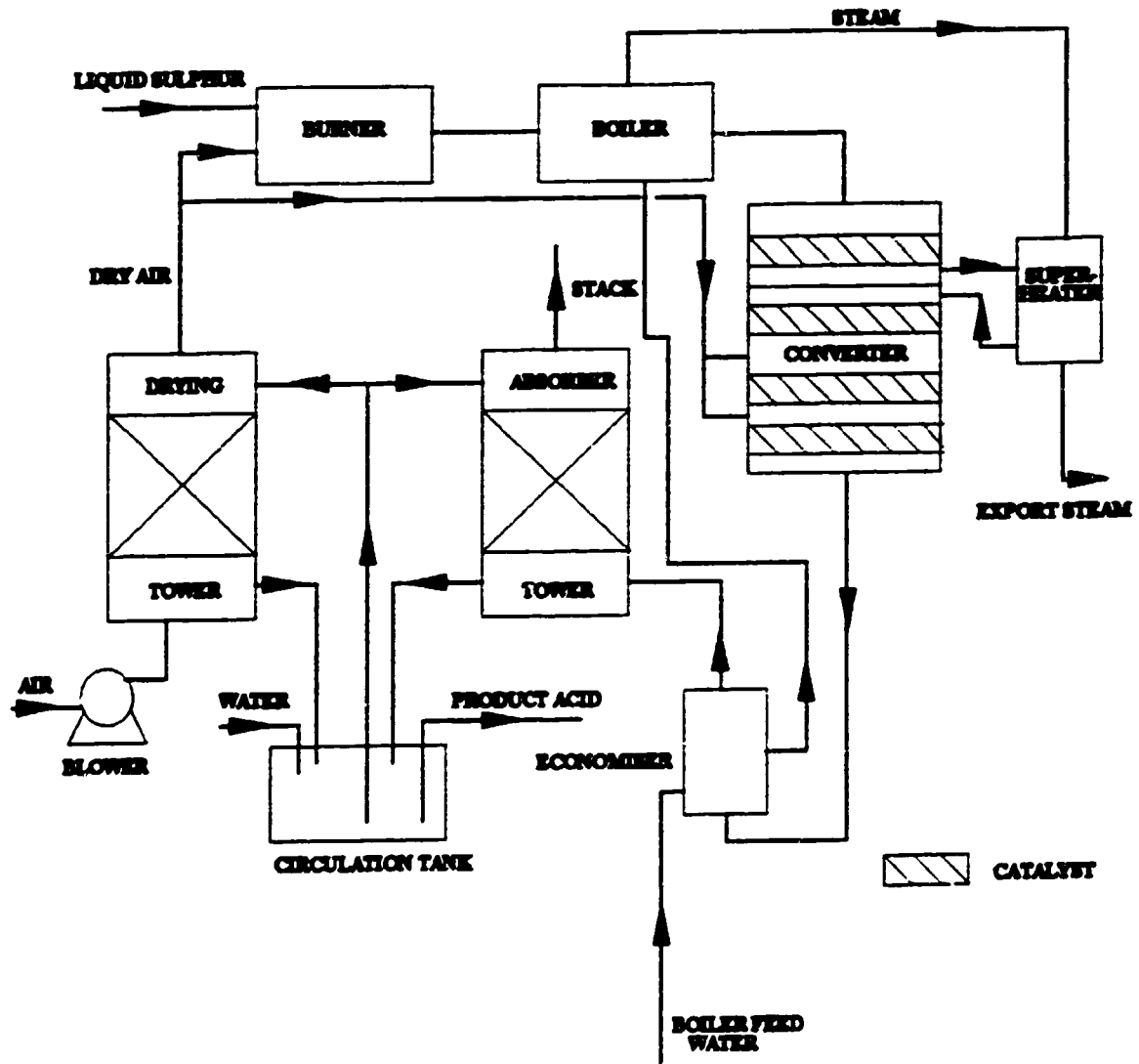
Sulphuric acid plants are generally built in conjunction with wet process phosphoric acid plants, where the steam can be effectively used to concentrate the phosphoric acid.

The economics of the process are greatly affected if the steam produced cannot be efficiently utilised.

2.1.4 Environmental Factors in Process Selection

So far as environmental emissions are concerned the double absorption process is preferred as it produces sulphur dioxide emissions one quarter of those of the single absorption process.

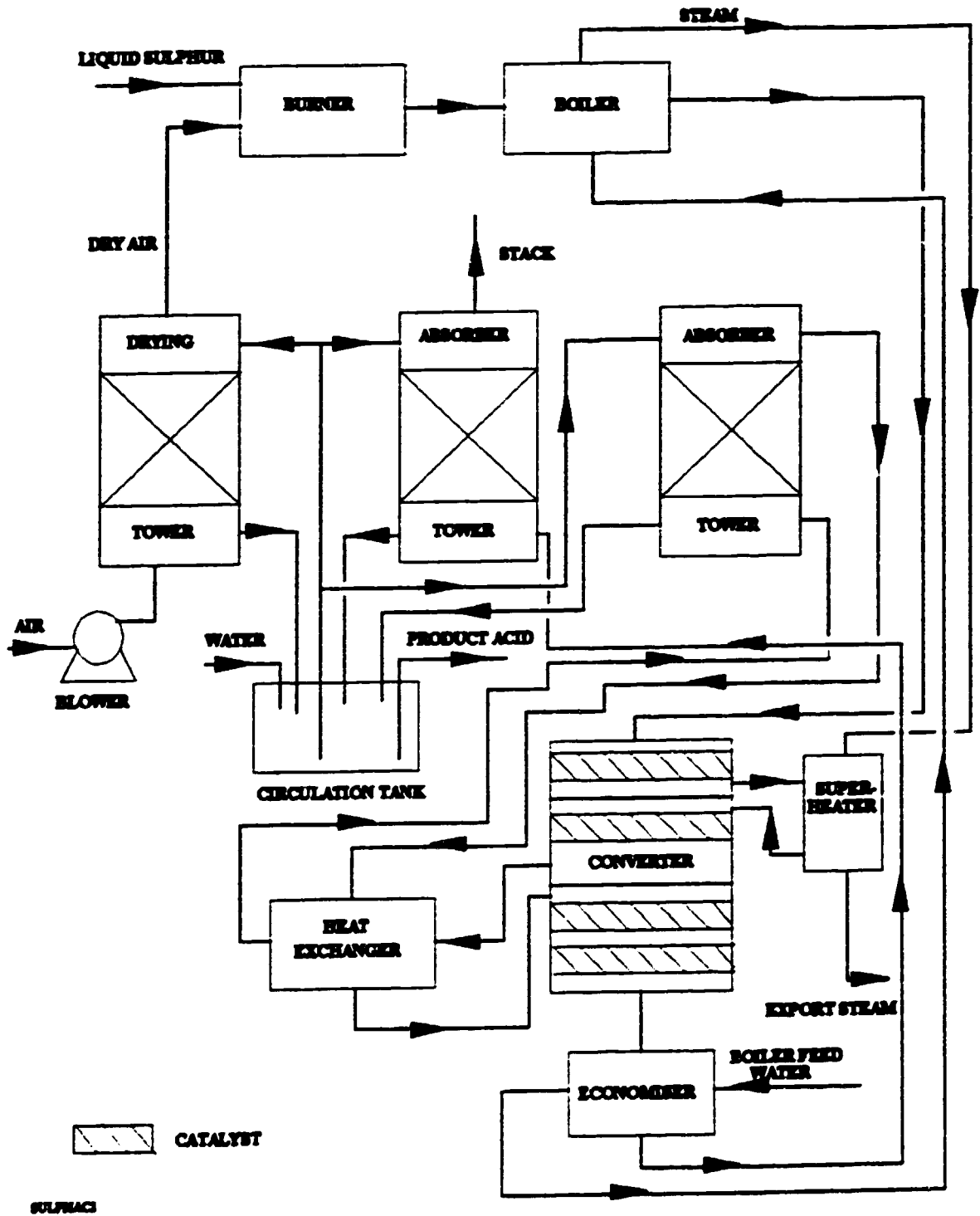
Where sulphuric acid is imported for fertilizer production, that produced from elemental sulphur, as opposed to roaster acid, is preferred as the latter may be contaminated by heavy metals.



SINGLE ABSORPTION SULPHURIC ACID PLANT

FIGURE 2

SULFACI



DOUBLE ABSORPTION SULPHURIC ACID PLANT

FIGURE 3

2.1.5. Primary Raw Materials

Elemental sulphur is the preferred basic raw material.

The sulphur supply is increasingly coming from sulphur recovery from oil and gas processes. It may also be produced from mining operations.

Sulphur is traded world wide in liquid and solid form.

2.1.6. Water, Raw Material and Energy Usage

The production of 1 tonne of 100% sulphuric acid require 0.33 tonne of sulphur and produces 1.8 tonne of high pressure steam.

Process water is required to control the acid strength after SO₂ absorption and demineralised water is required for boiler feed.

Water may also be required for acid cooling duties, the amount required varies widely with the type of heat exchanger used. On some plants air cooling is used.

2.2 WASTE SOURCES AND CHARACTERISTICS.

2.2.1. Atmospheric Emissions

The process has two emissions to atmosphere, sulphur dioxide and acid mist both being released with the waste gas from the final absorber tower.

2.2.2. Solid Wastes

Solid wastes containing vanadium result from the handling of catalyst from the converter. It is produced when the catalyst is renewed or screened to remove accumulated dust.

2.2.3 Liquid Wastes

Apart from boiler blow downs and water treatment plant regeneration this process does not produce liquid effluent.

2.3 WASTE MINIMISATION OPPORTUNITIES

Sulphur of low ash content will produce less catalyst screening and hence less solid waste. Pre-filtration of the sulphur may be necessary and the installation of a hot gas filter before the converter will reduce catalyst screening.

Bright sulphur is preferred to dark sulphur as the latter contains organic materials which result in the production of acid mist in the process which is difficult to remove from the stack gas.

2.4 CONTAMINANTS OF CONCERN

The elemental sulphur process for the production of sulphuric acid does not produce any contamination of the acid.

2.5 ENVIRONMENTAL IMPACTS

Sulphur dioxide and acid mist released to the atmosphere contribute to local and regional acidification of the atmosphere giving rise to acid rain.

There is little impact on local ground waters provided any leaks are collected and returned to the process.

2.6 OCCUPATIONAL HEALTH AND SAFETY ISSUES

SO_x and sulphuric acid mist are highly irritating to the respiratory tract. The acid itself is extremely corrosive to all tissues. Goggles and full protective clothing should be worn when handling the acid. Eye wash bottles and showers should be provided at strategic places throughout the plant.

2.7 HAZARDOUS MATERIALS HANDLING, MANAGEMENT AND DISPOSAL.

Sulphuric acid is normally stored in mild steel tanks at 96% strength. The tanks should be bunded to control any inadvertent release.

The catalyst used in the process contains toxic vanadium salts. Precautions should be taken to avoid breathing the dust during handling and any catalyst or dust should be disposed of safely to a suitable land fill.

2.8 EFFLUENT GUIDELINES

The emissions guidelines for sulphuric acid plants in various countries for SO₂, SO₃ and acid mist are given in table 1 in the appendix.

For plant control and monitoring purposes the SO₂ in the stack gas should be continuously monitored, displayed and recorded to enable the conversion to be controlled. Acid mist and SO₃ slip from the final absorber demister should be measured weekly to optimise absorption efficiencies and detect any problems.

2.9 TARGET/PREFERRED GUIDELINES

Targets related to 99.5% sulphur recovery in the process are to be preferred as these can be achieved by double contact plants with mist elimination after absorption without further abatement. This will give a release of 1.6 kg SO₂/tonne 100% H₂SO₄.

2.10 TREATMENT TECHNOLOGY OVERVIEW

The best available technology for sulphuric acid production is the double absorption process with high efficiency mist eliminators after the final absorption.

The effect of acid emissions on the local environment can be mitigated by the height of the discharge stack.

2.11 ALTERNATIVE TREATMENT TECHNOLOGY AND DISPOSAL OPTION

It is possible to convert single absorption plants to double absorption or add an alkaline tail gas scrubbing section after the absorber.

2.12 CAPITAL AND O & M COSTS

For a 1000 tpd single absorption plant the cost to convert to double absorption would be approximately 5m US\$ whereas to add alkaline scrubbing to the plant would cost in the order of 3-4m US\$. The former option however, can result in energy recovery whereas the latter produces by products that require safe disposal. A 1000 tpd double absorption plant would cost new approximately 26m US\$.

2.13 CONCLUSIONS

Double contact plants with high efficiency mist eliminators and no further abatement are recommended.

3.0 PHOSPHORIC ACID

3.1 MANUFACTURING PROCESS

3.1.1 Process Description

Phosphoric acid for fertilizer production is produced by the wet process from the reaction of sulphuric acid with finely ground phosphate rock concentrate. The reaction is given below.



Calcium sulphate is of low solubility and is removed by vacuum filtration. It can be precipitated as the dihydrate (gypsum) or the hemi hydrate dependent on the reaction conditions. This gives rise to two basic processes, the dihydrate (DH) or hemihydrate process(HH). The DH process produces acid of 30% strength as P_2O_5 , and the HH of 40-50% strength. In the production of fertilizers, phosphoric acid in the range 47-50% strength is required, hence in the DH process concentration of the acid is required. Both HH and DH have a phosphorous recovery efficiency of 94-96%.

There is also a HDH process where the hemihydrate produced in the HH process is further reacted to produce gypsum. The gypsum can be more easily filtered than the HH raising the phosphate recovery efficiency to 97-99%.

Rock concentrate is produced from naturally occurring phosphate ore by the removal of sand, clay, limestone and other materials by the process of beneficiation. The beneficiation process may range from a crude dry screening process to a very sophisticated process involving, washing, wet screening, magnetic separator, centrifugation, filtration, calcination, settling/decantation and drying.

3.1.2 Process Flow Diagram

Simplified process flow diagrams for the DH and HDH process are given in figures 4 and 5.

3.1.3 Economic Factors in Process Selection

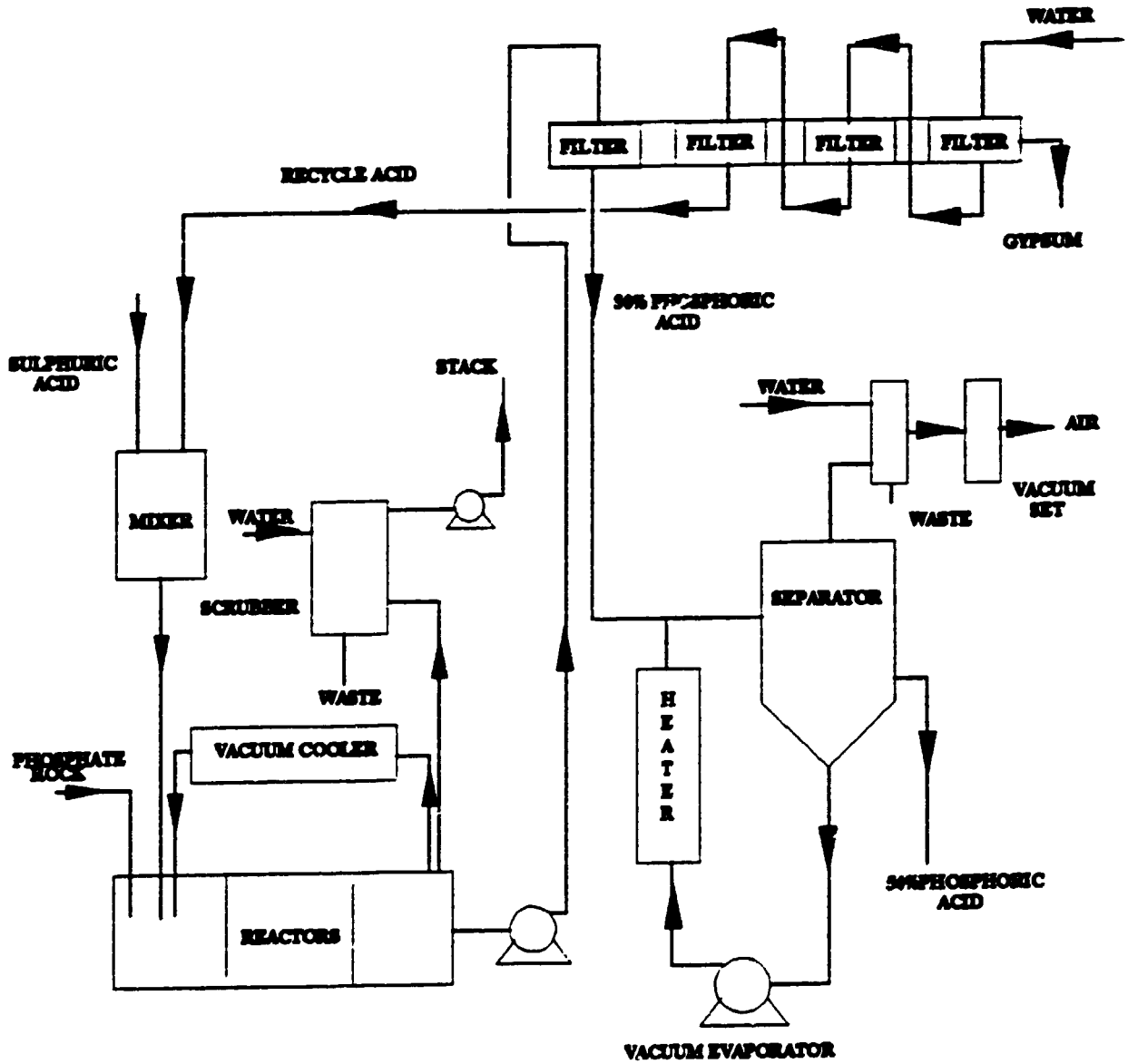
DH phosphoric acid plants are usually built in conjunction with sulphuric acid plants to take advantage of the steam production from the sulphuric acid plant to concentrate the product phosphoric acid.

If energy is not available to concentrate the acid then the HH or HDH process may prove more economical as a more concentrated acid is produced.

The HDH process is also more efficient in phosphate recovery.

3.1.4 Environmental Factors in Process Selection

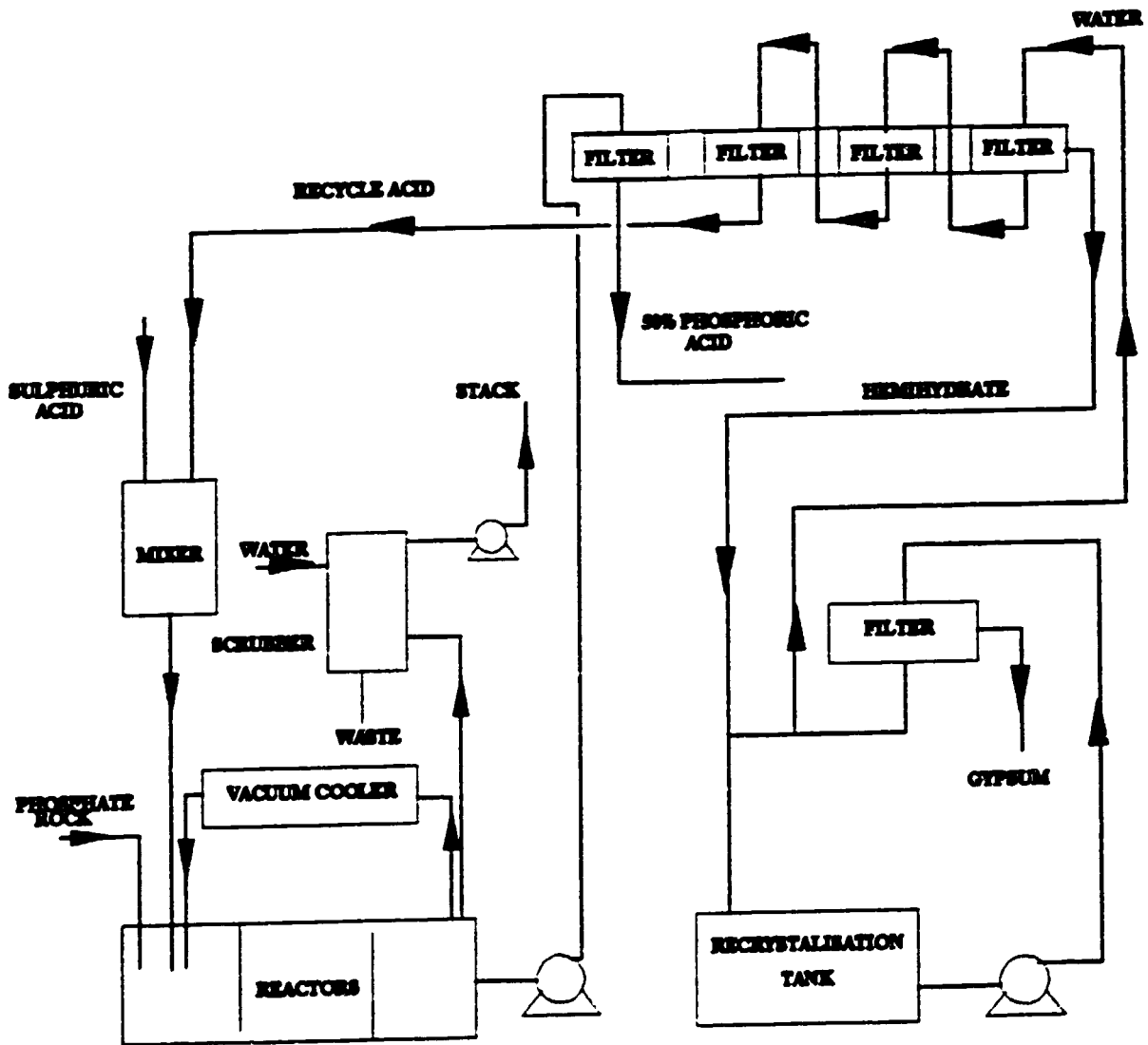
In the HDH process there will be less phosphate in the phosphogypsum due to the higher conversion efficiency.



PHOSPH

PHOSPHORIC ACID -DH PROCESS

FIGURE 4



PHOSPHORIC

PHOSPHORIC ACID HDH PROCESS

FIGURE 5

3.1.5 Primary Raw Materials

The basic raw materials for phosphoric acid production are phosphate rock concentrate and sulphuric acid.

Deposits of phosphate ore containing 15-30% P_2O_5 are found throughout the world with major deposits in North America, Morocco, China and the former USSR. Phosphate ore is mainly recovered by surface mining techniques followed by a concentration process, beneficiation, to produce a concentrate suitable for acid production.

3.1.6 Water, Raw Material and Energy Usage.

Fresh water is required for the process. It is generally introduced on the final filtration stage. The filtrate is returned to the process via primary filtration stages.

The make up water required for this process is about 7-10 tonne per tonne P_2O_5 produced and includes rain water.

The phosphogypsum can be slurried up with water and pumped to lagoons. The water collected after settling is returned to the process. For some plants the slurry is pumped into the sea or estuary requiring additional water.

There are benefits when the DH process is carried out with co-production of sulphuric acid. The high pressure steam from the acid production can be used to produce electricity and the low pressure pass out steam used for phosphoric acid vacuum concentration. This reduces the amount of fossil fuel that would otherwise be required to produce steam and electricity.

The waste from the beneficiation process is mixed with water and transported to settling lagoons. The water is recirculated but a net consumption of 7 tonne of water per tonne of concentrate is required for the beneficiation process.

3.2 WASTE SOURCES AND CHARACTERISATION.

3.2.1 Atmospheric Emissions

The process produces fluorine emissions in the form of silicon tetrafluoride or hydrogen fluoride. The amounts vary with the source of the rock and process conditions.

3.2.2 Solid Wastes

When phosphate ore is mined, up to 5 tonne of solid waste per tonne of rock concentrate can be produced.

Approximately 5 tonne of phosphogypsum is made per tonne of phosphoric acid produced (as P_2O_5). This waste contains part of the trace elements in the rock, including cadmium and some radio active elements. The concentration depends on the type of process and rock composition. Other solid wastes are produced during plant cleaning from scale deposits and deposits of gypsum in storage tanks.

3.2.3 Liquid Wastes

In most cases the water used to transport phosphogypsum to storage is recirculated back to the process. The maintenance of a water balance in the plant is of great importance in plant operation. The details of which will depend of plant location and type of process.

The phosphogypsum stacks will require treatment of the run off water for several years after the acid plant has ceased production.

In other cases slurried gypsum is pumped into the sea or river.

3.2.4 Fugitive Emissions

Dust can be released to the atmosphere from mining and handling operations of phosphate ore and concentrate.

3.3 WASTE MINIMISATION OPPORTUNITIES

The amount of waste can be minimised to an extent by the careful choice of rock source and process, to achieve a high efficiency of phosphate recovery.

The recycling of water from the process will also reduce the amount put into water courses as will a high level of maintenance of the water balance of the plant.

The phosphogypsum can be processed and used to make construction materials or converted to sulphuric acid and other useful products. Unfortunately the processes are not presently economic.

The fluorine in the waste gases produced in the process can be scrubbed out with water to produce hexafluorosilicic acid. This can be sold to a limited market, otherwise the wash waters are returned to the process and discharged with the phosphogypsum.

The release of waste water from the transportation of wastes from the beneficiation process can be minimised by the careful containment of the storage site.

3.4 CONTAMINANTS OF CONCERN

All phosphate ore contains traces of radioactive elements and a number of metals which are being studied in relation to the health of people and the environment (see appendix table 2). During processing these are partitioned between (1) beneficiation process wastes, (2) the waste from the further processing into intermediate and finished fertilizer products, and (3) some end up in the final product.

The cadmium level in product fertilizers is increasingly causing concern. This may influence the choice of phosphate rock used in the process. Phosphate rock from volcanic sources contains very little cadmium whereas sedimentary sources contain widely varying amounts of cadmium.

3.5 ENVIRONMENTAL IMPACT

Phosphate mining and beneficiation operations require large areas of land and depending upon a number of site-specific factors, may affect the environment to varying degrees in one or more of the following ways:

- Topography changes including the loss of aesthetic value, soil fertility, and soil moisture-holding capacity.
- Loss of natural plant and wildlife habitat.
- Loss of recreational, historical, and archaeological values.
- Disturbance of shallow aquifers.
- Contamination of surface and groundwater resources caused by the intrusion of contaminated water from mine sites and phosphate clay and sand tailings disposal sites.
- Temporary depletion of groundwater resources due to extraction of water used for processing.
- Erosion caused by wind and water.
- Concentration and/or escape of radionuclides that may be harmful to human health.
- Atmospheric contamination due to exhaust fumes and noise from mining/reclamation equipment.

For phosphogypsum disposal on land, the disposal site should preferably be lined to prevent leakage of contaminated wastewater to the groundwater, with monitoring wells at strategic positions around the site. Any excess flow of contaminated water should be neutralized by liming before being released.

Upon closure of a gypsum stack, the stack should be covered by a liner to prevent additional runoff of contaminated water caused by rainfall.

Where phosphogypsum is discharged to the sea or estuary the environmental impact will depend to a great extent on the actual location of the plant. For example the environmental effect on land locked waters may be greater than disposal at sea.

3.6 OCCUPATIONAL HEALTH AND SAFETY ISSUES

The radioactive components of the rock are concentrated to a degree in various parts of the plant during processing, particularly during vacuum filtration. A high level of hygiene should be observed when maintenance is carried out in these parts of the plant to avoid ingestion of the scale.

Dust masks should be worn where there is a high level of rock dust.

Sulphuric and phosphoric acids are corrosive to tissue therefore protective clothing and goggles should be worn when handling the acids.

Eye wash bottles and showers should be provided at strategic places throughout the plant.

3.7 HAZARDOUS MATERIALS HANDLING, MANAGEMENT AND DISPOSAL

Phosphoric acid is highly corrosive to mild steel. Much of the plant is fabricated using stainless steel or rubber lined mild steel pipes and vessels.

Storage tanks should be banded.

3.8 EFFLUENT GUIDELINES

The effluent guidelines are given in tables 5 and 6 in the appendix, which is a compilation of emission and discharge levels for the phosphate industry.

They may reflect local conditions, e.g. the vulnerability of the receptor waters. Such factors should also be taken into account when a process is evaluated.

Fluorine emissions to atmosphere should be measured daily.

For phosphogypsum storage on land, typical monitoring parameters and frequencies for the discharge of wastewater are (from Florida, USA):

- flow	- continuous
- pH	- continuous
- P	- 2/week
- N	- weekly
- sulphate	- monthly
- gross alpha particle activity	- monthly
- unionized ammonia	- daily
- fluorides	- daily
- specific conductance	- daily
- dissolved oxygen	- daily
- groundwater quality	- quarterly

For phosphogypsum disposal to sea, cadmium is typically monitored on a weekly basis.

3.9 TARGET/PREFERRED GUIDELINES

The target guidelines for phosphoric acid production will depend on the process, the rock source, the site and type of receptor water for effluent. The water balance of the plant will also play a major role in the determination of what targets for effluent discharges can be set.

As regards fluorine emissions to air from phosphoric acid plant, the recommended target should be 10 g F per tonne P_2O_5 .

The preferred guidelines would be those in table 6 of the appendix relating to US values.

For phosphogypsum disposal to the sea, the North Sea Declaration of 1990 calls for a 70% reduction of cadmium to the North Sea by 1995 on a 1985 baseline, and a further reduction has been targeted to 90% by the year 2000 based on 1985. The target set for plants around the North Sea is 0.5 g cadmium per tonne of gypsum disposed to the sea, and this can serve as the preferred target also elsewhere.

3.10 TREATMENT TECHNOLOGY OVERVIEW

Gaseous contaminants are removed by scrubbing the waste gases with water. Treatment to reduce acidity and remove fluorides from water seepage from phosphogypsum stacks after the plant has been shut down will be required during stack closure.

There are at present no commercial processes for the removal of cadmium from phosphoric acid, but extensive research is presently being carried out in view of the stricter regulations/requirements on cadmium emissions.

3.11 ALTERNATIVE TREATMENT TECHNOLOGY AND DISPOSAL OPTIONS

For the production of phosphoric acid itself there are no low cost innovative options available.

3.12 CAPITAL AND O & M COSTS

The battery limit cost of a new 1000 tpd (P_2O_5) HDH phosphoric acid plant is of the order of 75m US\$.

To convert a similar sized DH process acid plant to HDH process would cost approximately 34m US\$.

Reported costs for reclamation on mined-out land as practised in Florida, USA, range from about US \$ 5000/ha to US \$25000/ha depending upon the site, desired end use, and the method used to manage the surface water. This represents a cost of reclamation per tonne of P_2O_5 in the range of about US \$1-\$5.

The cost of liming recirculated process water to pH 3.5 in typical US phosphoric acid plant is US \$ 70 per tonne P_2O_5 .

The cost of building a new gypsum stack with a single bottom liner, with a 20-year life for a production 3 million tonnes of gypsum per year, is about US \$ 20 million.

The cost of closing a gypsum stack is site dependent, but a recent closure in US cost US \$ 5.5 million. Another has been estimated to cost US \$ 18 million.

3.13 CONCLUSIONS

The manufacture of phosphoric acid results in the production of large amounts of phosphogypsum. If the phosphogypsum is stored on land considerable costs are involved in the efficient management of the stock pile if environmental problems are to be avoided. Management of the phosphogypsum deposits may also be required for many years after the phosphoric acid plant has ceased production, with additional treatment of run off of waters.

Where phosphogypsum is discharged to water, the vulnerability of the receptor waters should be checked for the life of the plant.

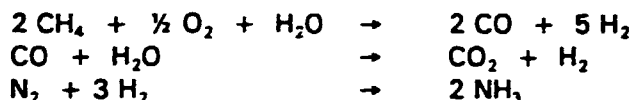
4.0 AMMONIA PRODUCTION

4.1 MANUFACTURING PROCESS

4.1.1 Processing Description

Ammonia is produced by the iron catalyzed synthesis of elemental hydrogen and nitrogen at high pressure and elevated temperature. The hydrogen source is hydrocarbons and water while nitrogen comes from air.

The majority of plants (Ca 90%) use steam reforming of natural gas or other light hydrocarbons (LPG), followed by carbon monoxide shift sections to produce a stoichiometric mixture of hydrogen and nitrogen which are combined to ammonia. Simplified reactions are as follows:



Carbon in the feedstock is rejected as carbon dioxide and can be used either to produce urea or other byproducts or vented to the atmosphere.

A few plants use heavy fuel oil or coal as feedstock and are based on partial oxidation or gasification technology and shift reactions to produce the mixture of hydrogen and nitrogen.

In steam reforming plants the front end pressure is normally between 25-35 bars while the synthesis loop is at 80-270 bars, depending on age of plant and local optimization. Modern ammonia production plants are characterized by extensive heat integration and energy recovery to obtain good efficiency.

4.1.2 Process Flow Diagrams

Figure 6 gives simplified block flow diagrams for ammonia production by steam reforming and partial oxidation.

4.1.3 Economic Factors in Process Selection

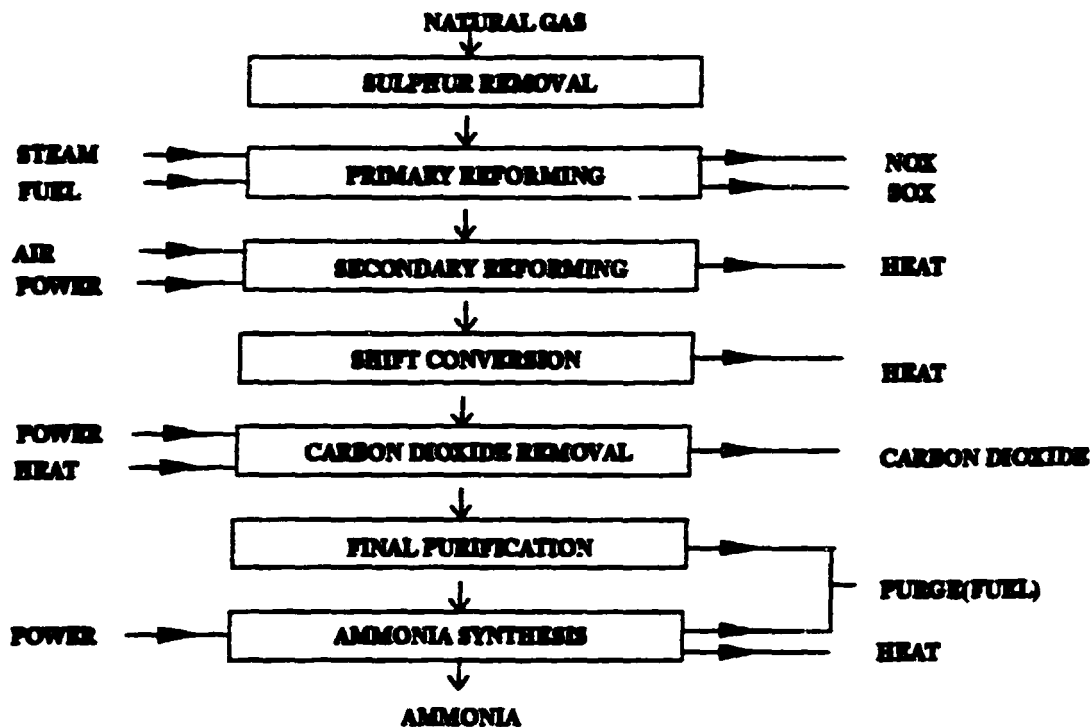
Energy costs (hydrocarbon based) are the most important factor in process design and selection. Ammonia plants can be designed to be energy balanced, but typically a small steam export and electric power import is the case.

To obtain good economy of scale plants should have capacities in the range 1500-1800 tpd.

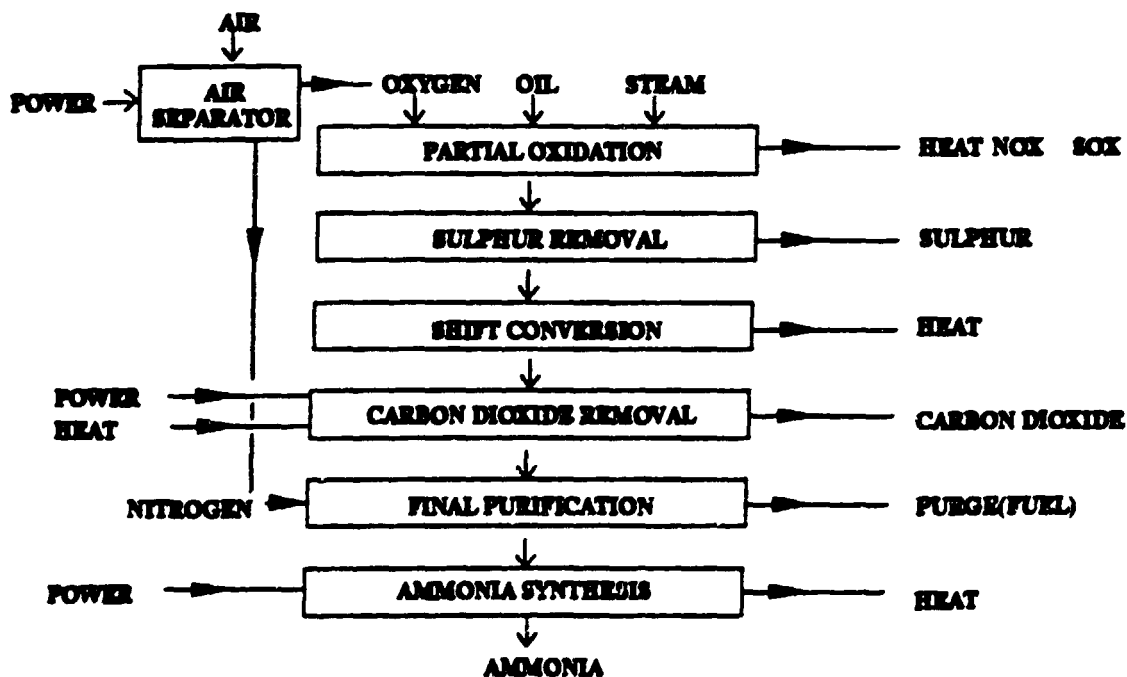
Capital costs are typically higher for partial oxidation plants compared to steam reforming plants.

4.1.4 Environmental Factors in Process Selection

Modern steam reforming plants can be designed with very low emissions to the surroundings. Small quantities of NO_x and SO_x are emitted from the reforming section depending on fuel used and burner design.



AMMONIA FROM NATURAL GAS



AMMONIA FROM HEAVY OIL

FIGURE 6

Carbon dioxide (greenhouse gas) is vented to the atmosphere and is directly related to the energy efficiency of the plant.

Generally, ammonia plants based on partial oxidation of heavy fuel oil give higher emissions unless special precautions are taken.

4.1.5 Primary Raw Materials

Ammonia plants use hydrocarbons (natural gas mainly), water and air as basic raw materials.

4.1.6 Water, Raw Material and Energy Use

Ammonia plants need water as a process raw material and in some cases it is also used for cooling duties. Demineralized water is used for process and steam drum feed. Cooling towers are used in some locations. An extensive utility system is normally associated with ammonia plants for energy recovery and conversion into mechanical energy or electric power by use of turbines.

Typical energy use, including raw materials, for modern ammonia plant is 30-35 GJ/tonne ammonia.

4.2 WASTE SOURCES AND CHARACTERIZATION

4.2.1 Atmospheric Emissions

The main emission to the atmosphere is carbon dioxide and small quantities of nitrogen and sulphur oxides. Typically a modern steam reforming plant emits 2.2 tonnes of carbon dioxide per tonne of ammonia, while the NO_x (as NO₂) is less than 1.0 kg per tonne of ammonia. The sulphur emission is low, typically less than 0.2 kg (as SO₂) per tonne of ammonia.

4.2.2 Waste Water

Modern plants recycle process condensate and hence give no waste except from boiler blowdown, boiler water treatment and cooling water with low environmental effects.

4.2.3 Solid Wastes

The steam reforming process contains 8-9 different catalytic steps and the catalysts are replaced after every 2-6 years in service. Partial oxidation plants use typically 2-3 different catalysts.

Most of the catalyst can be recycled to catalyst manufacturers or other metal handling firms for reclamation of valuable metals. The other catalysts can be used by other companies for various purposes.

Resins are used in the boiler water treatment plant and these have to be replaced periodically. They can be taken back to the supplier.

4.2.4 Hazardous Wastes

Spent catalyst may contain oxides of hexavalent chromium, zinc, iron and nickel. They are returned to the manufacturer or other metal recovery companies.

4.2.5 Fugitive Emissions

Minor amounts of light hydrocarbons, ammonia, hydrogen, carbon oxides may be released due to leaks from flanges, stuffing boxes, during maintenance operations etc.

Catalyst handling and chemicals used in water treatment may also cause minor releases.

4.3 WASTE MINIMIZATION OPPORTUNITIES

Atmospheric emissions (mainly carbon dioxide and nitrogen oxides) can be minimized by lowering plant energy use, but margins are small. Spent catalysts should be recycled for metal reclamation or disposed of for other purposes.

4.4 CONTAMINANTS OF CONCERN

No contaminants of concern are present in the product ammonia.

4.5 ENVIRONMENTAL IMPACTS

Carbon dioxide is a green house gas and oxides of nitrogen and sulphur contribute to acid rain. The emissions are however, low compared to other sources.

4.6 OCCUPATIONAL HEALTH AND SAFETY ISSUES

Ammonia is toxic and is stored at -33 C in sealed tanks with proper safety installations. Leaks of gas mixtures containing hydrogen from plant may cause fire or explosions if ignited. Proper safety installations are required.

Eye wash bottles and showers should be provided at strategic points on the plant. Operators should be provided with a high level of training and instructions to obtain required safety standards. Proper management guidelines and procedures are also important.

4.7 HAZARDOUS MATERIALS HANDLING, MANAGEMENT AND DISPOSAL

Ammonia is stored, transported and handled in sealed tanks with proper materials and instruction guidelines.

Catalyst disposal and handling should likewise be handled properly.

4.8 **EFFLUENT GUIDELINES**

4.8.1 **Emissions**

Effluent emissions from ammonia plant in Europe are not in general specified. However, due to their high thermal input standards applied to combustion processes are taken into account in certain countries. Examples of such standards are given in table 3 in the appendix.

The reformer stages should be monitored for NO_x and SO_x on a monthly basis.

4.9 **TARGET/PREFERRED GUIDELINES**

Modern, gas heated reformer plants, can achieve very low energy consumption and hence low carbon dioxide emissions and virtually no NO_x emissions.

4.10 **TREATMENT TECHNOLOGY OVERVIEW**

New ammonia plants can achieve satisfactory emissions without abatement of fuel gases from reformer section, which is the main source of emissions.

4.11 **ALTERNATIVE TREATMENT TECHNOLOGY**

No low cost, simple processes are available for ammonia production today.

4.12 **CAPITAL AND O & M COSTS**

No add on abatement processes are necessary on modern ammonia plants.

4.13 **CONCLUSIONS**

New gas heated reforming technology based on natural gas is recommended for ammonia production. This technology secure low energy use and minimal emissions to the environment.

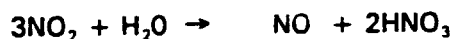
5.0 NITRIC ACID PRODUCTION

5.1 MANUFACTURING PROCESS

5.1.1. Process Description

Nitric acid is produced for fertilizer manufacture in the range 50-65% strength. Ammonia (NH₃) is vaporised, mixed with air and burned over a platinum/rhodium gauze catalyst to produce nitric oxide (NO). The nitric oxide is oxidised to nitrogen dioxide (NO₂) and the nitrogen dioxide is absorbed in water to produce nitric acid.

The reactions are as follows:-



The efficiency of the ammonia oxidation stage is favoured by low pressures and the heat produced by the reaction is utilised to pre-heat waste gas and produce high pressure super heated steam.

The oxidation of nitric oxide and the absorption in water is maximised by high pressures and low temperatures.

These considerations give rise to two basic types of nitric acid plant, single-pressure plants and dual-pressure plants.

In the former the oxidation and absorption steps take place at essentially the same pressure, whereas in dual pressure plants, absorption takes place at a higher pressure than the oxidation stage, hence a nitric oxide compressor is required.

Plants can be classified as low pressure (< 1.7 Bar) medium pressure (1.7 -6.5 Bar) or high pressure (> 8 Bar) for the combustion stage and the absorption stage. New plants are constructed for pressures above 4 Bar.

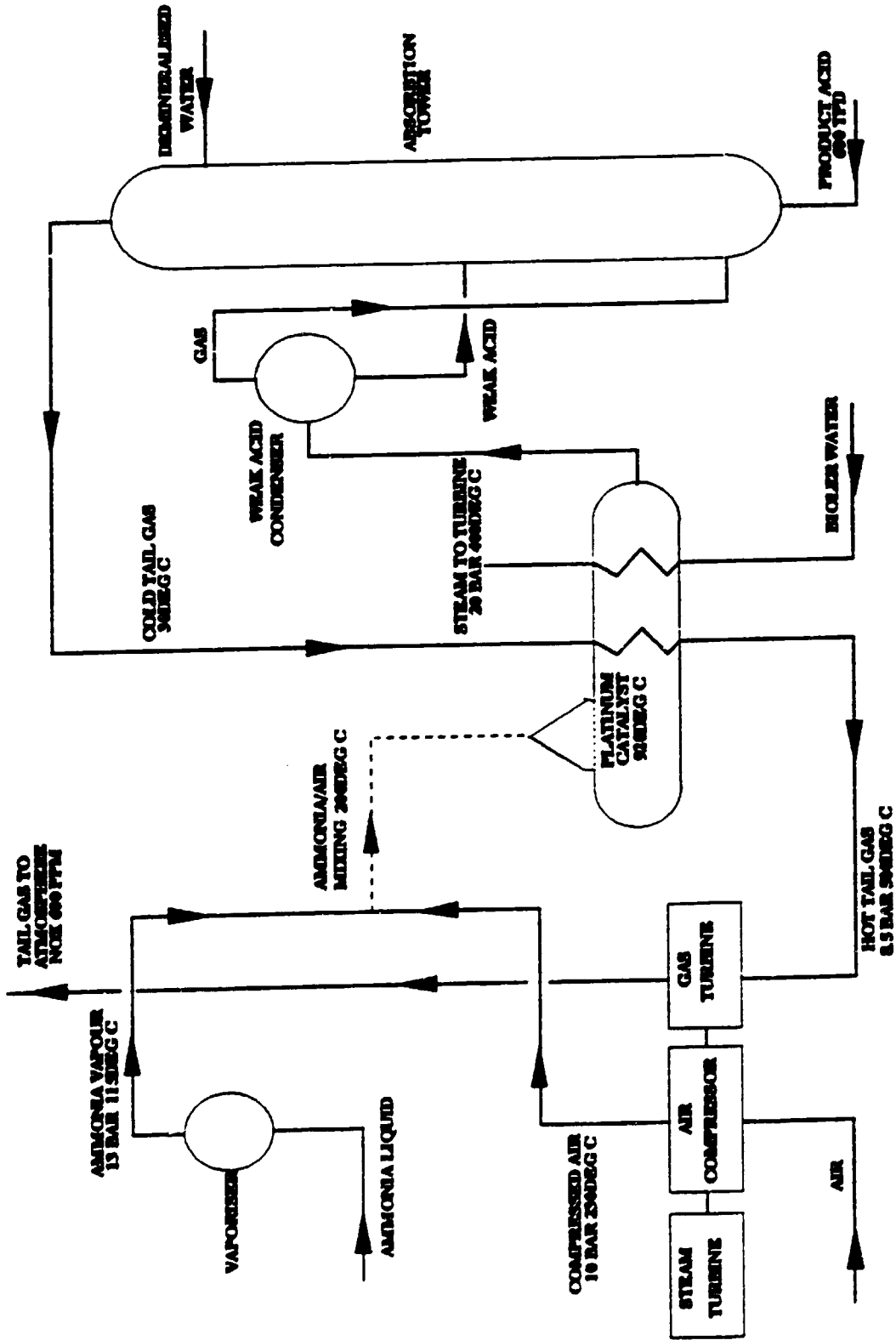
5.1.2 Process Flow Diagrams

Simplified process flow diagrams for single and dual pressure plants are given in figures 7 and 8.

5.1.3 Economic Factors in Process Selection

The production of nitric acid produces a surplus of energy in the form of high pressure steam. For the overall economics of the process it is essential to be able to utilise this energy for electricity generation or for other user processes.

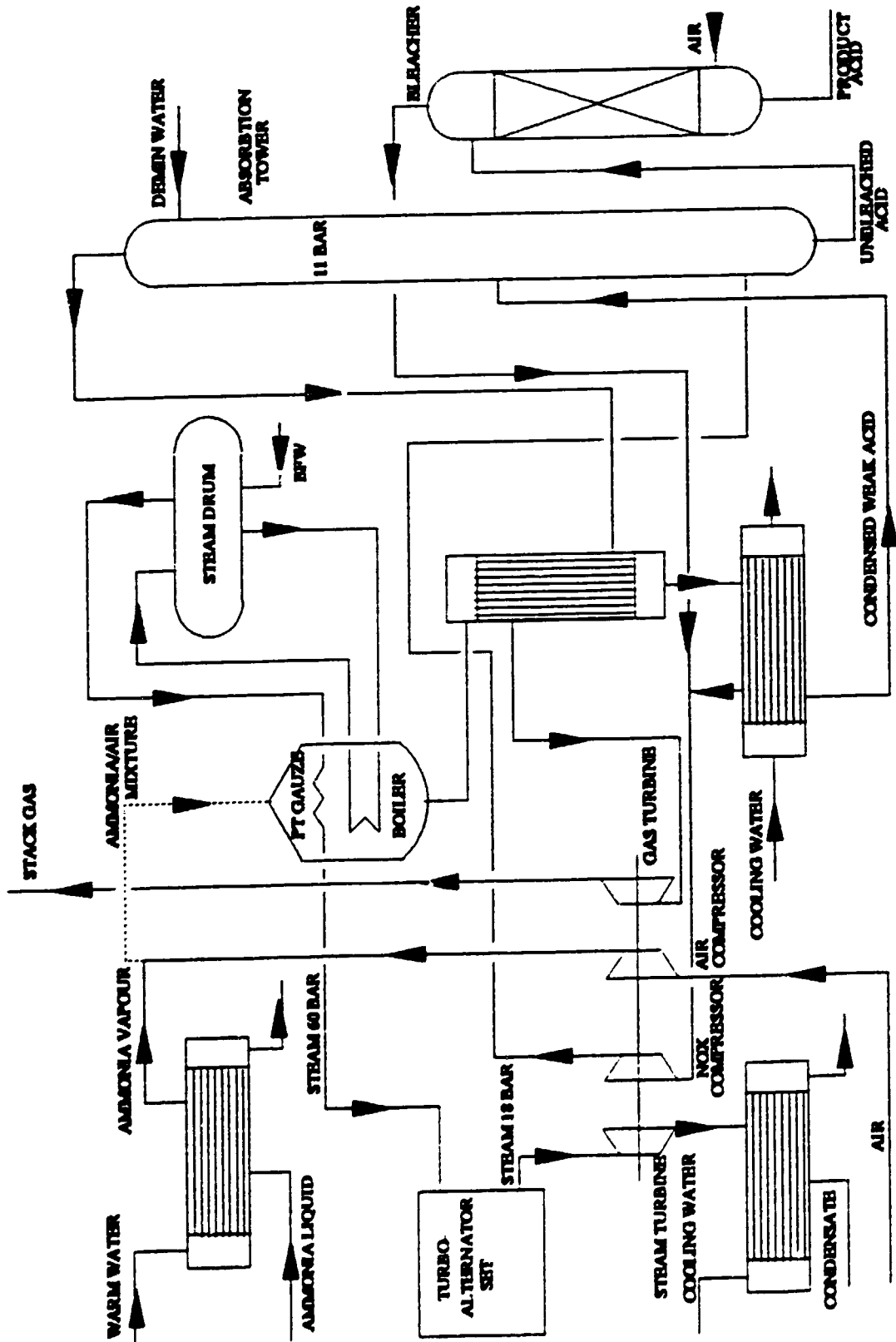
The capital cost of the plant will vary with design pressure and type which in turn will be dependent on emission standards and on the overall process chemical efficiency required.



HIGH PRESSURE/SINGLE PRESSURE NITRIC ACID PLANT

FIGURE 7

UNIDO



HIGH PRESSURE/DUAL PRESSURE NITRIC ACID PLANT

FIGURE 8

UNIDO

5.1.4 Environmental Factors in Process Selection

The main environmental factor that will influence the process selection will be the NO_x emission levels permitted for the specific location of the plant. This could vary dependent on the effect of other plants already in the area and on air quality standards. The proximity of centres of population, sites of special scientific interest and other environmentally sensitive areas could also influence the design of the plant.

5.1.5 Primary Raw Materials

The Nitric acid plants use anhydrous ammonia, air and water as the basic raw materials. Air pollution can cause a decrease in ammonia oxidation efficiency due to the poisoning of the catalyst.

5.1.6 Water, Raw Material and Energy Usage

The process uses water for cooling and as a process raw material. Saline or poor quality water can be used for steam turbine condensation purposes but for other cooling duties a high quality water is required, especially as regards process make up water chloride levels.

Recycled process condensate or demineralised water is normally used for the absorption tower feed and for other cooling duties good quality water can be used but if this is not available, a closed circuit of good quality water will be required being cooled itself by heat exchange with poor quality water.

Ancillary water treatment plant is also required for boiler feed water make up. Dependent on the presence of other steam raising plants on the site it may be necessary to have a boiler installed for start up of the nitric acid plant or an electric motor may be installed to drive the compressor.

Cooling towers may also be required for removing the heat from cooling and condensing water streams.

5.2 WASTE SOURCES AND CHARACTERISATION

5.2.1 Atmospheric Emissions

The main emission to atmosphere from the process are oxides of nitrogen (NO_x) and nitrous oxide (N₂O).

Emissions of NO_x are in the concentration range of 75 - 2000 ppmv (parts per million volume) dependent on type of process. The level of NO_x emitted depends primarily on the absorption tower pressure and design, and temperature of the tower cooling water.

5.2.2. Waste Waters

Waste water from the process can originate from blowdown of cooling tower water to control dissolved solids, from boiler blowdown and water treatment plants. In all cases the water will contain dissolved salts which have a low environmental effect.

5.2.3. Solid Wastes

The platinum/rhodium catalyst requires replacing after a certain campaign length depending on the combustion pressure and due to its high cost is returned to the manufacturer for refurbishing.

Deposits of catalyst can be recovered from various parts of the plant. These are also returned to the catalyst manufacturer for recovery of Platinum and Rhodium.

5.2.4 Hazardous Wastes

The process does not produce hazardous solid wastes.

5.2.5 Fugitive Emissions

Small amounts of ammonia are released from vaporiser blow downs and from maintenance operations. Similarly there can be small amounts of nitric acid released during maintenance.

NOx fumes are released from nitric acid storage.

5.3. WASTE MINIMISATION OPPORTUNITIES

The emissions to atmosphere can be reduced by plant design. Make up and cooling water temperature will affect the absorption stage and hence emissions of NOx.

Catalyst wastes are recycled.

5.4 CONTAMINANTS OF CONCERN

There are no contaminants of particular concern in this process.

5.5 ENVIRONMENTAL IMPACTS

The main impact on the environment is from NOx and N₂O emissions to atmosphere. NOx contributes to acid rain whereas nitrous oxide is a green house gas, and may contribute to ozone depletion.

Of the total N converted in the nitric acid plants, 0.09 - 0.6% is lost as NOx and 0.4 - 1.5% is lost as N₂O to the atmosphere.

5.6 OCCUPATIONAL HEALTH AND SAFETY ISSUES

NOx fumes are highly toxic with an 8hr TLV of 3ppm and 10 minutes limit of 5ppm. The breathing of NOx fumes should be avoided and breathing apparatus should be worn if necessary.

Nitric acid is extremely corrosive to all tissue. When handling the acid a fully protective suit, goggles, face shield, PVC gloves and boots should be worn.

Eye wash bottles and showers should be provided at strategic places throughout the plant.

Operators should be provided with a high level of instruction, training and supervision to enable them to operate the plant at the maximum efficiency.

5.7 HAZARDOUS MATERIALS HANDLING, MANAGEMENT AND DISPOSAL.

Nitric acid should be stored in bunded stainless steel tanks. The plant areas should have impermeable flooring with all surfaces draining to a neutralisation pit, to deal with small acid discharges from maintenance operations.

Small amounts of nitrate salts produced from the neutralization pit would normally be discharged with cooling water blowdown to waste.

5.8 EFFLUENT GUIDELINES.

The emission guidelines for nitric acid plants in various countries are given in table 4 of the appendix.

Continuous analysis of NO_x levels in the stack gas should be provided.

5.9 TARGET/PREFERRED GUIDELINES

Modern high pressure plants without abatement action on exhaust gas can achieve NO_x levels in the tail gas below 200 ppmv. With medium pressure plants 500-800ppmv can be achieved. Smaller low pressure plant may emit up to 2000ppmv, when unabated.

The standard of 200ppmv for new plant is recommended as a realistic target.

5.10 TREATMENT TECHNOLOGY OVERVIEW

New high pressure nitric acid plants can achieve satisfactory emission levels of NO_x and N₂O without abatement of the tail gas.

For other plants various abatement methods are available for the reduction of NO_x emissions:-

- Alkaline absorption
- Non-selective Catalytic Reduction (NSCR)
- Selective Catalytic Reduction (SCR).

No abatement system is available for existing plants for N₂O emissions.

5.10.1 Alkaline Absorbtion

Alkaline absorption involves treating the waste gas with sodium hydroxide. This can reduce emissions to 200ppmv but produces nitrite/nitrate solutions which require safe disposal or further utilisation.

5.10.2 NSCR

Hydrogen or hydrocarbon fuel is burned in the tail gas over a platinum/rhodium/palladium catalyst, to remove NOx gases and excess oxygen. Dependant on the amount of fuel used the nitrogen dioxide can be reduced to nitric oxide (decolourisation) or to nitrogen. In the latter case to obtain 200ppmv NOx an excess (10-25%) of fuel is required over the original NOx concentration.

One disadvantage of this process is that the waste gas contains carbon monoxide as well as hydrocarbons.

5.10.3 SCR

Ammonia is used as the reducing agent over a catalyst to convert the NOx gases to nitrogen. The process can reduce NOx emission to 100ppm. For plants of low capacity with medium pressure absorption it can offer economic advantages over the high pressure process.

5.11. ALTERNATIVE TREATMENT TECHNOLOGY AND DISPOSAL OPTIONS

The production of nitric acid is a high technology process and no low cost, simpler processes are available.

5.12 CAPITAL AND O & M COSTS

A new 1000 tpd dual pressure nitric acid plant will cost approximately 45m US\$ to battery limits.

To reduce emission levels on a similar sized existing plant from 500 ppm to 200 ppm by SCR the capital costs would be in the region of 600,000 US\$ with an increase in operating costs of 83,000 US\$ per annum and increased maintenance cost of 15,000 US\$.

To achieve the same results by the installation of a new absorber tower would cost in capital terms 1.5m US\$ with an increase of 15,000 US\$ per annum on maintenance costs. The operating cost would, however, fall by 24,000 US\$ as the increase in acid recovery would out weigh any energy losses.

5.13 CONCLUSIONS

For maximum process efficiency and minimisation of emission of NOx large dual high pressure plants without abatement on the exit gas are recommended.

Where small production plants are required, the medium pressure process with SCR may be economically compared to the high pressure plant with similar NOx emissions

6.0 FERTILIZER PRODUCTION

6.1 MANUFACTURING PROCESS

6.1.1. Process Description

Figure 1 summarises the production routes and raw materials for the manufacture of the major fertilizer products. They usually result in a granular or prilled product with a mean size range of 2 - 5 mm in diameter.

In the prilling process a melt of materials low in water content (<0.5%) is introduced into a tower as droplets. The droplets solidify as they fall down the tower against a counter current of air. The solid prills are then cooled, screened and coated, as required, to produce the final product.

In the granulation process material containing the desired size range is produced by means of a rotating drum or pan, fluid bed or other process. The moisture content of the slurry or melt entering the granulation unit is between 3 and 15%. The slurry/melt is sprayed on recycled particles (crushed oversize or fines from screening) which act as a cooling medium for solidifying the slurry/melt. A drying stage is required before cooling, screening and coating.

The production details are given below.

- Superphosphate

There are two main superphosphate fertilizers, single superphosphate (SSP) and triple superphosphate (TSP). Both are produced from ground phosphate rock by the action of sulphuric acid in the case of SSP and phosphoric acid in the case of TSP. Usually the superphosphate powder is stored in a pile for several days to allow the chemical reactions to complete. They are then either processed in a conventional granulation plant or used as one of the raw materials in the production of compound fertilizers.

- Ammonium Phosphates - Monammonium Phosphate (MAP) or Diammonium Phosphate (DAP).

Ammonium Phosphates are produced by the reaction of ammonia with phosphoric acid to give MAP or DAP. They can be produced as finished product fertilizers and applied directly to the land or used in blending to produce compound fertilizers.

The reaction may be carried out in a recycle slurry process or in a pipe reactor and then processed in a granulation plant.

Powdered material may also be produced which can be used as one of the raw materials in a granulation plant producing compound fertilizers.

- **Nitrophosphates**

The Nitrophosphates process involves the digestion of phosphate rock with nitric acid. The resulting solution is cooled causing calcium nitrate to crystallise out which is removed by filtration. The filtrate containing phosphoric acid with some nitric acid and free Ca ions is then neutralised with ammonia. More ammonium nitrate (or nitric acid + ammonia) is added dependent on the required N/P₂O₅ ratio. The neutralised solution may be evaporated to reduce the water content before granulation. A range of additives (i.e. potash, sulphates, magnesium, etc.) can be introduced to the slurry/melt before granulation.

In the nitrophosphate prilling process, the slurry is further treated in vacuum evaporator before introducing additives to the melt and prilling.

The calcium nitrate filtered earlier in the process can be further treated with ammonia to produce a calcium nitrate fertilizer, treated to produce pure calcium nitrate or reacted with ammonia and carbon dioxide to give ammonium nitrate and calcium carbonate.

- **Ammonium Nitrate (AN), Calcium Ammonium Nitrate (CAN), Ammonium Sulphate Nitrate (ASN).**

AN is made by the reaction of 60% nitric acid and anhydrous ammonia. The heat of reaction is utilised to drive off water and produces a solution of up to 95-96% ammonium nitrate. This solution can be fed to a granulator or further concentrated to greater than 99% and solidified by a prilling process.

Another fertilizer product, CAN, is also produced by adding dolomite (calcium/magnesium carbonate) to the melt prior to prilling or granulation.

ASN is produced by granulating ammonium sulphate and AN.

- **Urea**

Urea is produced by reacting liquid ammonia with carbon dioxide under conditions of high pressure (140 Bar) and temperature (175°C). The carbon dioxide is usually supplied from an ammonia plant. The reaction produces ammonium carbamate which partially decomposes to give urea.

The mixture of urea, carbamate, water, ammonia and carbon dioxide is then concentrated at lower pressures to give urea solution and carbamate solution. The latter solution is returned to the reaction stage whereas the urea solution is concentrated to 99.8% purity under vacuum.

Most product urea is produced by prilling the melt but granulation processes are also used.

- **Ammonium Sulphate**

Ammonium sulphate can be made by the reaction of ammonia with sulphuric acid. The reaction produces a large amount of heat of neutralisation which is used to concentrate the liquor by removing steam under vacuum.

Ammonia sulphate crystals are removed by a centrifuge or filtration.

However, most ammonium sulphate is produced as a by product of other chemical processes.

The material can be used directly as a fertiliser but is usually incorporated into compound fertilizers.

- **Potash (Potassium Chloride)**

Mineral deposits of potassium chloride are found throughout the World. They are usually found in the presence of sodium and magnesium salts. Refining of the deposits obtained from mining is necessary to produce potash for the fertilizer industry. Flotation techniques are most widely practised to give a free flowing crystalline product.

Potash is normally incorporated in compound fertilizer before application as a fertilizer.

- **Compound Fertilizers**

Compound fertilizers can be produced by several methods.

They may be produced by simply physically blending together other fertilizer products, such as AN, MAP, DAP granular potash etc., to give the desired analysis. Compound fertilizer may also be produced by the granulation process, using solid raw material such as, SSP, TSP, Potash MAP, the agglomeration process being assisted by the addition of steam and/or water. Some granulation processes use liquid feeds of AN in conjunction with the solid materials to produce the compound fertilizer.

Compound fertilizers may also be produced by the prilling process where additives are added to low moisture melts to give the required analysis before prilling to produce the final product.

6.1.2. Process Flow Diagram

Basic flow diagrams for a granulation process and for a prilling process are given in figures 9 and 10.

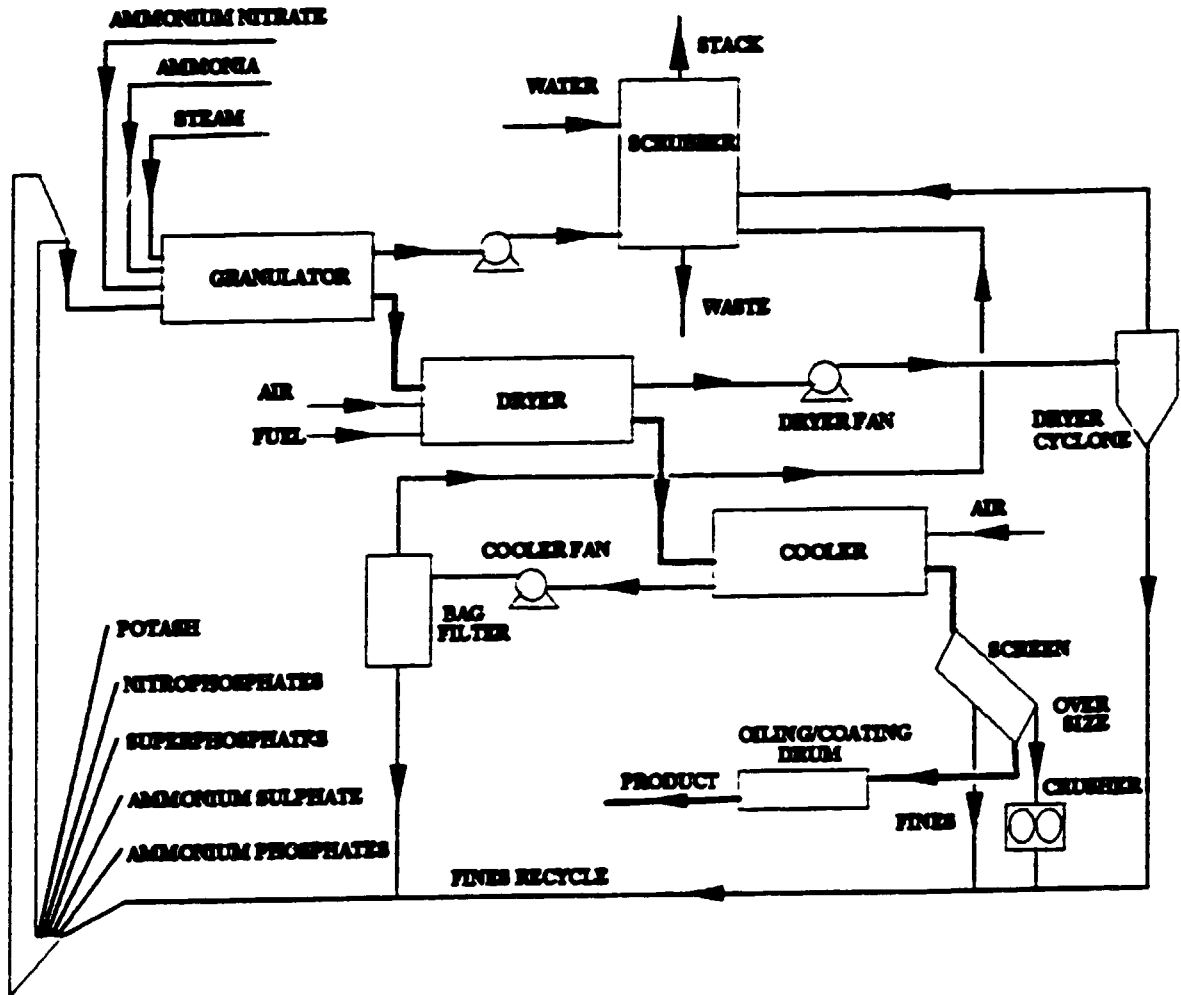
6.1.3 Economic Factors in Process Selection

There are many factors that will contribute to the most economic combination of plants for a particular application.

The types of crop to be grown (or growing) in the area to be served by the plants and the soil nutrient level will be important in determining the formulation of fertilizer required.

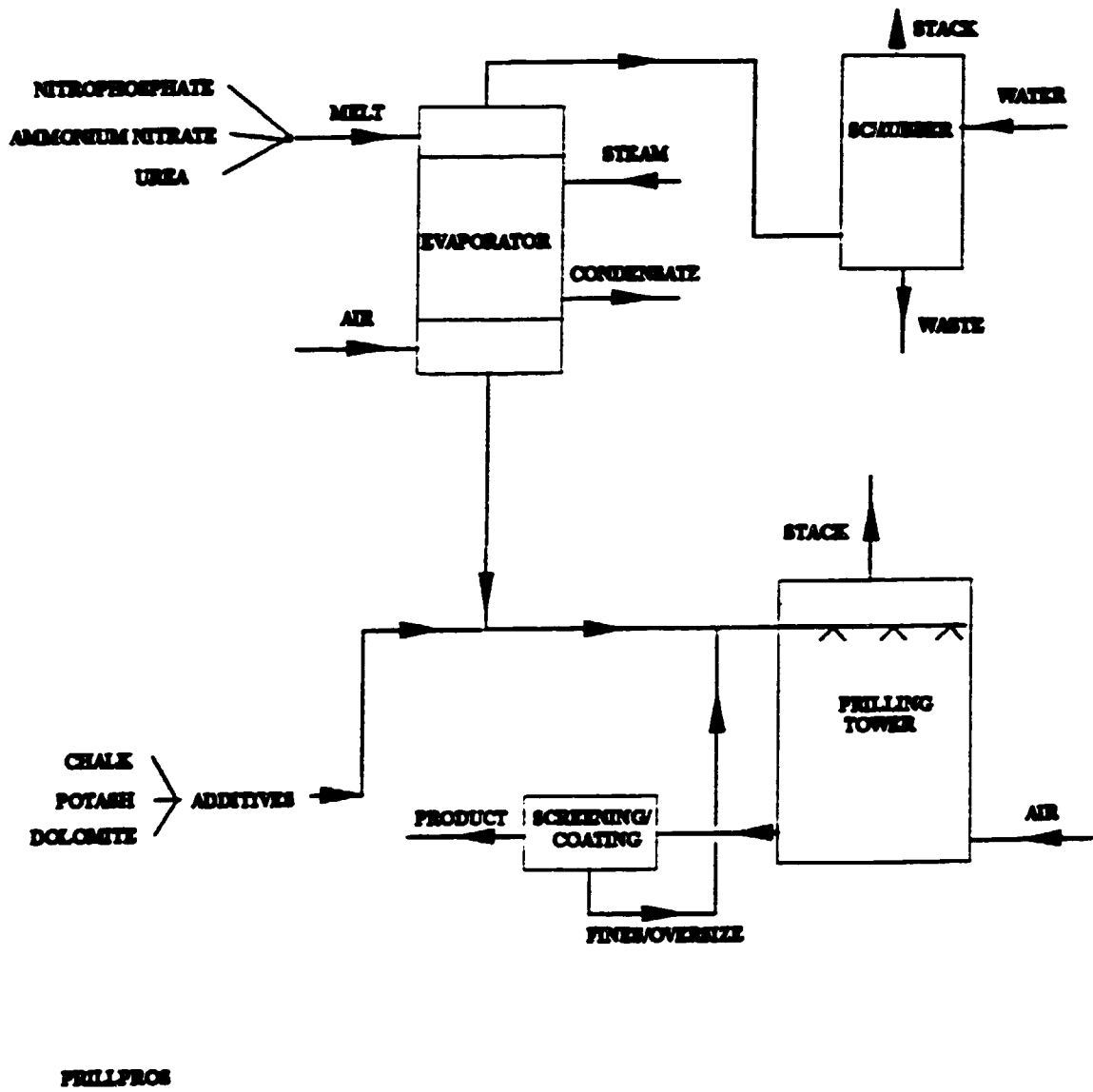
The choice of the site and type of plant will be dependant on the proximity and price of raw materials, intermediates or indeed finished product.

The availability of land and water supply will also affect the economics of the processes chosen.



GRANULATION PROCESS

FIGURE 9



PRILLING PROCESS

FIGURE 10

6.1.4 Environmental Factors in Process Selection

The processes described above all give, to a greater or lesser extent emission to air water and land.

The choice of the siting of the fertilizer production process may influence the type of process used, or visa versa.

The proximity of centres of population, areas of special scientific interest, crops, type of water environment, availability of land etc will all influence the amount of emissions that may be discharged by the process. They should not impact on the local environment to any great extent.

6.1.5 Water, Raw Materials and Energy Usage

Many of the fertilizer production processes use water to scrub off gases to reduce atmospheric emissions of various pollutants. Granulation plants burn natural gas or fossil fuels in the drying process.

The detailed requirements of a particular fertilizer complex will depend on the types of plants on the site.

6.2 WASTE SOURCES AND CHARACTERISATION

6.2.1 Atmospheric Emissions

The main pollutants emitted to atmosphere from fertilizer production units are ammonia, fluoride, nitrogen oxides, carbon dioxide, hydrogen chloride, dust and fume. On most units the abatement plant is part of the process, i.e. liquors and dust from scrubbers, cyclones and filters are fed back into the process.

- **Superphosphate**

The production of TSP and SSP produce fluorine compounds. Most of them are retained in the product during the production of TSP but 25% are released to atmosphere in SSP production.

There will also be fluoride emissions from the maturing heaps of material.

- **Ammonium Phosphates**

The production of ammonium phosphates results in the release of quantities of steam containing ammonia from the wet side and ammonia and dust from the dry side of the plant.

- **Nitrophosphates**

During the process of acidulation or digestion of the phosphate rock oxides of nitrogen and fluorine compounds are given off. From the evaporation stage of the process ammonia is emitted.

The prilling or granulation process will give emission of dusts.

- **AN/CAN/ASN**

The main emission to atmosphere for these processes are associated with the production of AN. The neutralisation of nitric acid with ammonia releases amounts of steam which will contain some AN and ammonia.

Dust is also released to atmosphere from the prilling tower or dry granulation side.

- **Urea**

The gaseous effluent from the prilling towers contain dust and some ammonia.

- **Ammonium Sulphate**

Ammonia is given off in the steam produced by the neutralisation of sulphuric acid with ammonia.

- **Potash**

The mining and handling of potash ores and the final product will give dust emission to the atmosphere.

6.2.2 **Liquid Effluents**

Liquid effluents from fertilizer production processes are low. Water is used to scrub the waste gases to remove pollutants. In many cases the scrubbing liquors are recirculated and the concentrated liquid returned to the process.

In plants where the scrubbing liquids cannot be used, once through scrubbing systems with treatment of the effluent are used.

A liquid balance across the processes is essential if liquid effluent is to be avoided.

6.2.3 **Solid Wastes**

Solid wastes are not generally produced in fertilizer production processes as all waste material can be recycled back to the process.

6.3 **WASTE MINIMISATION OPPORTUNITIES**

Wastes can be minimised by a high level of maintenance and operation to avoid spillages. Any spillage whether solid or liquid should be returned to the process.

NO_x emissions from the nitrophosphate process can be controlled by the addition of urea to the digestion stage.

6.4 CONTAMINANTS OF CONCERN

There are no contaminants of major concern in fertilizer production apart from the cadmium contained in certain phosphate fertilizers.

6.5 ENVIRONMENTAL IMPACT

Fertilizer production processes that are suitably abated do not release materials in harmful quantities to atmosphere.

However, high levels of fluorine emissions cause damage to vegetation and cause harm to live stock which may consume the vegetation. High levels of ammonia can cause local damage to vegetation and contributes ultimately to acid depositions in the soil.

Dust may also be released to the atmosphere from certain processes which is of nuisance value.

If plant nutrients are released to the aquatic environment from scrubber systems or run off water it is possible that eutrophication of water sources may take place. The type of receptor water would be important as to whether the eutrophication would take place.

The emission of ammonia or acidic fumes may give rise to mists in the locality of the plants.

6.6 OCCUPATIONAL HEALTH AND SAFETY ISSUES

During the production process the major hazards are from the acids and ammonia used in the process, as described previously. Fertilizer products are of low hazard, the main hazards being dust levels in the plant especially from some coating materials that may contain crystallised silica.

6.7 HAZARDOUS MATERIALS HANDLING, MANAGEMENT AND DISPOSAL

Fertilizer products are generally of low hazard. Ammonium nitrate and high ammonium nitrate fertilizers are considered to be oxidising agents and require special transport and storage requirements to keep them apart from flammable materials. If involved in a fire, fertilizers give off toxic fumes.

6.8 EFFLUENT GUIDELINES

Effluent guidelines for fertilizer production in various countries are given in tables 4 and 5 in the appendix.

6.9 TARGET/PREFERRED GUIDELINES

The level of fluoride and ammonia emissions and dusts to atmosphere should be controlled to avoid problems in the vicinity of the plant.

High efficiency mist elimination with acidic scrubbing can reduce ammonia emissions to less than 35 mg/m³ and ammonium nitrate emission to less than 15 mg/m³.

6.10 TREATMENT TECHNOLOGY OVERVIEW

Fluoride emissions from certain processes are controlled by scrubbing the effluent gases with water. Ammonia can also be removed in the same way, but prior scrubbing with phosphoric acid may be necessary where the ammonia load is high.

The scrubber liquors can be recirculated to give a concentration of effluents and the liquor bled back into the process to contain emissions.

If the type of process does not allow the bleeding back of liquors then treatment may be required before the scrubber water is returned to the aquatic environment. The amount of treatment will depend on the vulnerability of the receptor water, type and level of pollutants.

The treatment of waste waters with lime and polyelectrolyte can precipitate phosphate prior to discharge of the waters.

Dust generated in the processes can be passed through cyclones to return the larger particles to the process. For finer particles a bag filter or hydro cyclone may be required.

To remove AN fume and ammonia acid irrigated low velocity filter candles (brink mist eliminators) may be necessary on certain plants.

It is important to obtain a liquid balance across the processes to avoid liquid effluents. All spillage and run off water should be collected and recycled to the process.

The precise combination of abatement plant and treatment required will be dependent on the types of process plant available and the water environment into which any wastes may be discharged.

Fertilizer production processes do not yield solid wastes that cannot be returned to the process.

6.11 ALTERNATIVE TREATMENT TECHNOLOGIES AND DISPOSAL OPTIONS

There are no innovative low cost technologies for plant abatement. Simple scrubbing systems are relatively cheap but bag filters and low velocity filter candles become much more expensive.

6.12 CAPITAL AND O & M COSTS

For a fertilizer plant the cost of pollution control equipment can be 10-20% of the total cost of a new plant. The operational and maintenance costs relating to environmental control, can be 10-20% of the total production costs. In new plants, however, the process design would integrate environmental control with the need for high efficiency and productivity, and hence it is difficult to single out the costs of environmental control.

The cost of adding on equipment to an existing plant must be considered case by case since it is related to the size and type of plant, type of equipment to be installed, and the pollution control requirements to be met.

UNIDO/World Bank

As an example the installation of low velocity filter candles on a 1200 tpd ammonium nitrate vaporiser entails a capital cost of approximately 750,000 US\$ with candle replacement cost of 90,000 US\$ every 3 years.

It is also estimated that the addition of a venturi tray plate scrubbing unit on a 1000 tpd urea granulation plant would have capital costs of 1.2 m US\$ with operating and maintenance costs of 155,00 US\$ and 12,000 US\$ per annum respectively.

On a similar size CAN plant the costs would be 2m US\$ capital, 167,000 US\$ per annual operating costs and 54,000 US\$ per annum maintenance costs.

6.13 CONCLUSIONS

The technology to abate emissions for fertilizer production plants is widely used and reduces the environmental impact of such plants to an acceptable level in most situations.

7.0 FERTILIZER USE

This paper is primarily concerned with environmental issues concerned with fertilizer production. The use of fertilizers however, can contribute to certain environmental problems. The main issues are listed below:

- Nitrate contamination of drinking water supplies
- Eutrophication of inland and coastal water
- Deposition of cadmium on land from certain phosphate fertilizers

The leaching and run off of nutrients to water can be substantially reduced by good agricultural practice.

As part of good agricultural practice farmers should develop fertilizer application plans which should take into account, the correct type of fertilizer, optimum amounts to be applied, optimum time to apply the fertilizer, high standards of care during storage and use, and other considerations.

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TABLE 1			
SULPHURIC ACID PLANTS EMISSION GUIDELINES			
Country	SO₂	SO₃	Acid Mist
Denmark	5 kg/t H ₂ SO ₄ (1)	0.5 kg/t H ₂ SO ₄ (1)	
Germany	97.5-99.5 sulphur conversion rate (4)	60-120 mg/m ³ (4)	
Greece	10 kg/t H ₂ SO ₄ (5600 mg/Nm ³) (2)	0.8 kg/t H ₂ SO ₄ (2) (6)	615 mg/Nm ³
Spain	1425 mg/m ³ (2) 2850 mg/m ³ (1) 1425 mg/m ³ (3)	500 mg/m ³ (2) 300 mg/m ³ (1) 150 mg/m ³ (3)	
France	6 kg/t H ₂ SO ₄ (7)	0.5 kg/t H ₂ SO ₄ (7)	
UK	Sulphur as SO ₂ + SO ₃ not to exceed 0.5% sulphur burned		
India	5 kg/t H ₂ SO ₄		50 mg/m ³
Thailand	500 ppm	35 mg/m ³	35 mg/m ³
Turkey		0.5 kg/t H ₂ SO ₄	
Jordan	2 kg/t H ₂ SO ₄	75 g/t H ₂ SO ₄	75 g/t H ₂ SO ₄
Mexico	3-28 kg/t H ₂ SO ₄		
USA	2 kg/t H ₂ SO ₄		75 g/t H ₂ SO ₄
(1)	New plants		
(2)	Existing plants		
(3)	Plants built after 1980		
(4)	Depending on SO ₂ content in raw gas and its variability		
(5)	No limitation		
(6)	H ₂ SO ₄ mist		
(7)	These figures are not official or national emission limits; they are used as guide values by licensing authorities during registration procedures		

TABLE 2
APPROXIMATE RADIOACTIVITY OF SELECTED PHOSPHATE MATERIALS AND
BACKGROUND SOIL

MATERIAL	RADIOACTIVE ELEMENT	
	U-238 (pCi/g)	RA-228 (pCi/g)
<u>Phosphate Concentrate*</u>		
Sedimentary origin	40	38
Igneous origin	2	1-2
<u>Phosphogypsum*</u>		
Central Florida	3	31
Background Soil	0.3	0.5

a. Source: Economic Commission for Europe and FAD/IAF/ESCAP
 b. Source: British. Proceedings of the Third International Symposium on Phosphogypsum

SUMMARY OF POTENTIALLY HAZARDOUS ELEMENTS
IN SELECTED PHOSPHATE CONCENTRATIONS

PHOSPHATE CONCENTRATE	ELEMENT *						
	As (ppm)	Cd (ppm)	Cr (ppm)	Hg (ppb)	Pb (ppm)	Se (ppm)	V (ppm)
<u>Sedimentary Origin</u>							
Israel (Arad)	4-7 (5.5)	12-17 (14)	- (130)	- (480)	- (2)	- (3)	- (203)
Jordan (El Hassa)	5-12 (8)	3-12 (5)	50-127 (92)	- (-)	- (2)	- (3)	60-81 (70)
Morocco (Khouniga)	10-25 (13)	3-27 (15)	188-212 (200)	- (1000)	2-29 (10)	- (4)	- (108)
Morocco (Youssefouh)	- (10)	4-19 (15)	- (-)	- (-)	21-22 (21-7)	- (-)	- (-)
Senegal (Taiba)	4-28 (17)	60-115 (87)	- (140)	- (-)	2-10 (8)	- (5)	237-810 (524)
Togo	8-14 (10)	48-57 (58)	- (101)	- (600)	8-9 (8.3)	- (5)	- (60)
Tunisia	5-4 (4.5)	30-56 (40)	- (144)	- (-)	- (4)	- (9)	- (27)
United States (Central Florida)	4-25 (11)	3-20 (9)	37-100 (60)	25-200 (171)	9-56 (17)	2.5-3 (2.8)	70-160 (108)
United States (North Florida)	- (7)	3-10 (5)	62-58 (65)	- (-)	10-13 (12)	- (-)	98-108 (102)
United States (North Carolina)	7-13 (11)	20-51 (38)	129-197 (158)	85-400 (261)	3-20 (8)	- (5)	19-32 (26)
United States (Western Deposits)	14-40 (24)	40-150 (92)	330-1000 (537)	- (500)	5-16 (12)	4-13 (9)	300-1737 (769)
<u>Igneous Origin</u>							
Republic of South Africa (Phalaborwa)	5-27 (13)	1-1.6 (1.3)	- (1)	- (-)	- (11)	- (4)	- (8)
Former Soviet Union (Kola)	- (10)	0.3-2 (1.2)	- (-)	- (33)	- (-)	- (-)	- (-)

a. Values in parentheses () indicate average concentration of element based on indicated range. A dash (-) indicates lack of sufficient data.

TABLE 3			
EMISSION LIMIT VALUES APPLIED IN THE NETHERLANDS FOR NEW AND EXISTING COMBUSTION PLANTS			
	SO _x (mg/m ³)	NO _x (mg/m ³)	Dust (mg/m ³)
New, 300 MW or more			
- Coal	400 ¹	800/400 ²	50 ³
- Gas	35)	—
● Refinery gas	—)	—
● Natural gas	—)	—
● Oxygen	35) 350/200 ²)
● Blast-furnace gas	200)) 20
● Coke-oven gas	800))
New, below 300 MW			
- Coal	700	800/500 ²	50 ⁴
- Oil	1700	450/300 ^{2,5}	—
- Gas	same as limits for "New, 300 MW or more"		
Existing, 300 MW or more			
- Coal	400 ^{1,6}	1000 ⁶	—
- Oil	400 ^{1,7}	700 ^{6,8}	—
- Gas	same as "New" ¹¹	500 ¹⁰	same as "New" ¹¹
Existing, below 300 MW			
- Coal in electric power station max. sulphur cont.	0.8%	—	—
- Oil	1700 ¹²	700 ^{6,8}	—
- Gas	same as "New" ¹¹	500 ¹⁰	same as "New" ¹¹
¹ Desulphurization at least 85% ² First figure if licence granted before 1-8-1988, second figure if granted after 1-8-1988 ³ Combustion emission of process furnaces: state of the art; correction when N-content of oil is above 0.3% ⁴ Combustion emission of process furnaces with respect to basic environmental protection: correction when N-content of oil is above 0.3% ⁵ Bandwidth to 20 mg/m ³ ⁶ With effect from 1-12-1988 for plants operating after 1994 or 1999; up to that time max. sulphur content 0.8% ⁷ With effect from 1-12-1988 for plants operating after 1994; otherwise 1700 mg/m ³ ⁸ As at 1-1-1988 still in use for 10,000 hrs. the same for pulverized coal 1,100 mg/m ³ ; bandwidth to 800 mg/m ³ ⁹ As at 1-1-1988 if still in use for 10,000; bandwidth to 450 mg/m ³ ¹⁰ Same, bandwidth to 350 mg/m ³ ¹¹ As at 1-1-1988 ¹² As at 1-8-1987			

TABLE 3 (CONT'D)

**EMISSION LIMIT VALUES FOR COMBUSTION INSTALLATIONS INCLUDING
CHEMICAL REACTORS IN THE FEDERAL REPUBLIC OF GERMANY**

Dust	Solid fuel installations > 50 MW Existing lignite Coal Liquid fuel installations < 50 MW	50 mg/Nm ³ 80 mg/Nm ³ 125 mg/Nm ³ 50 mg/Nm ³
SO ₂	<p>a. <u>Solid Fuel Installations:</u> New: > 50 < 100 MW Except fluidised > 100 < 300 MW Except fluidised > 300 MW Existing: > 50 < 100 MW</p> <p>b. <u>Liquid Fuel Installations:</u> New: > 50 MW > 100 MW > 300 MW Existing: As for solid fuels</p> <p>c. <u>Gasous Fuel Installations:</u> > 100 MW</p>	<p>2000 mg/Nm³ 400 mg/Nm³ 2000 mg/Nm³ 400 mg/Nm³ 400 mg/Nm³ 2500 mg/Nm³ until 1983, then same limits as for new plants</p> <p>1700 mg/Nm³ 1700 mg/Nm³ 400 mg/Nm³</p> <p>35 mg/Nm³</p>
NO _x	<p>a. <u>Solid Fuel Installations > 50 MW:</u> New: Except pulverised coal/wet ash (> 50 MW > 300 MW Existing: Except pulverised coal Wet ash Dry ash (> 50 MW Pulverised coal/wet ash (> 300 MW</p> <p>b. <u>Liquid Fuel Installations > 50 MW:</u> New: (> 50 MW > 300 MW Existing: (> 50 MW > 300 MW</p> <p>c. <u>Gasous Fuel Installations > 100 MW:</u> New: (> 100 MW > 300 MW Existing: (> 100 MW > 300 MW</p>	<p>800 mg/Nm³ 1800 mg/Nm³ 400 mg/Nm³ 200 mg/Nm³ ¹ 1000 mg/Nm³</p> <p>2000 mg/Nm³ 1300 mg/Nm³ 650 mg/Nm³ ¹ 1300 mg/Nm³ 200 mg/Nm³ ^{1,2}</p> <p>450 mg/Nm³ 300 mg/Nm³ 150 mg/Nm³ ¹ 700 mg/Nm³ 450 mg/Nm³ 150 mg/Nm³ ¹</p> <p>350 mg/Nm³ 200 mg/Nm³ 100 mg/Nm³ ¹ 500 mg/Nm³ 350 mg/Nm³ 100 mg/Nm³ ^{1,2}</p>
<p>¹ Figures in brackets required by the Environmental Minister of the Federal States of Germany for unlimited lifetime</p> <p>²</p>		

TABLE 4				
NITRIC ACID PRODUCTION - EMISSION GUIDELINES				
COUNTRY Date of Publication	NEW PLANTS			
	Limit Value	Averaging Time	Date of Implementation	Excursions
Germany 2/1986	450 mg/m ³ dry NO _x expr. in NO ₂ (219 ppmv)	24 h	3/1986	Double 2% time
France 7/1974	4.5 kg HNO ₃ /t HNO ₃ , 100%		7/1974	400 h/y 48 h can. sec 6 kg/t
Netherlands 500 t/d 8/1987	220 ppmv (NO _x)	1 h	8/1987	No limit shutdown & startup
UK 5/1987	200 ppmv		5/1987	Limit not to be exceeded at any time for normal operation
Ireland				
Denmark	Limit values will be set for each plant (General regulations is in preparation. 200-225 ppm NO _x is expected)			
Spain 2/1975	3 kg NO _x /t HNO ₃ , 100% 1.5 kg/t	2 h	...1975 ...1980	
Portugal	400 mg/m ³ (NO ₂) (2% O ₂)			
India				
Turkey				
Thailand				
USA				
Greece	5 kg NO _x /t HNO ₃ , 100%			

COUNTRY Date of Publication	EXISTING PLANTS			
	Limit Value	Averaging Time	Date of Implementation	Excursions
Germany 2/1986	450 mg/m ³ dry NO _x expr. in NO ₂ (219 ppmv)	24 h	Low - med pressure 3/1936	
France 7/1974	4.5 kg HNO ₃ /t HNO ₃ , 100%			Flexible approach case by case
Netherlands 500 t/d 8/1987	600 ppmv	1 h	1992	
UK 5/1987	1000 ppmv		1992	Limit not to be exceeded at any time for normal operation
Ireland	200 ppmv (NO _x)		1976	
Denmark	Limit values are set for each plant			
Spain 2/1975	20 kg NO _x /t HNO ₃ , 100%	2 h		
Portugal				
India	5 kg/t HNO ₃			
Turkey	800 mg/m ³			
Thailand	2000 mg/m ³			
USA	1.5 kg/t NO _x HNO ₃			
Greece				

COMPONENT	AUSTRIA (b)	BELGIUM	GERMANY (FR)
Particulate (dust)	75 mg/m ³		55-75 mg/m ³
NH ₃	20 mg/m ³		50-300 mg/m ³ (h)
HF	5 mg/m ³		5 mg/m ³
HCL	30 mg/m ³		30 mg/m ³
F		(300-600 mg/L) (f)	1 kg/t P ₂ O ₅ (i)
NH ₄ ⁺ -N (d)		(150 mg/L)	2 kg/t-n (h)
NO ₂ -N (d)		(225 mg/L)	2 kg/t N (i)
NOx (e)			500 mg/m ³ (not NA)
Cd		(2-0.3 mg/L) (g)	100 mg/t P ₂ O ₅ (i)
P		(50-300 mg/L) (f)	0.5 kg/t P ₂ O ₅
Chemical Oxygen Demand		(300-450 mg/L) (f)	
Total Suspended Solids		(200-600 mg/L)	
pH		(5-9.5)	
Temperature			

COMPONENT	GREECE	INDIA	IRAN (c)
Particulate (dust)	150 mg/m ³	150 mg/m ³	
NH ₃			
HF			
HCL			
F	100 mg/m ³ (6 mg/L)	25 mg/m ³ (10 mg/L) (n)	(2.0-2.5 mg/L)
NH ₄ ⁺ -N (d)		(50 mg/L)	(0.5-2.5 mg/L) (k)
NO ₂ -N (d)		(10-20 mg/L) (o)	(1.0-50 mg/L) (k)
NOx (e)			
Cd			(0.01-1.0 mg/L)
P	(10 mg/L)	(5 mg/L)	(1.0 mg/L)
Chemical Oxygen Demand			
Total Suspended Solids	(40 mg/L)	(100 mg/L)	(30 mg/L)
pH	(6-9)	(6.5-8.0)	6.5-8.5/5-9 (well)
Temperature	(35 °C)		

COMPONENT	KOREA	EGYPT	INDIA
Particulate (duet)		150 mg/m ²	150 mg/m ²
NH ₃		(100 ppm)	
HF			
HCL			
F	10 mg/m ²	(0.5 mg/L)	29 mg/m ² (1.5-10 mg/L)
NH ₄ ⁺ -N (d)		(34 ppm)	
NO _x -N (d)		(116 ppm)	
NO _x (e)			
Cd			
P			(5 mg/L)
Chemical Oxygen Demand			
Total Suspended Solids			(100 mg/L)
pH			7-9
Temperature			

COMPONENT	TAIWAN	THAILAND
Particulate (duet)	50 mg/m ²	500 mg/m ²
NH ₃	50 mg/m ²	25 mg/m ²
HF		10 mg/m ²
HCL		200 mg/m ²
F	10 mg/m ² (15 mg/L)	0.14 kg/t
NH ₄ ⁺ -N (d)		
NO _x -N (d)	30 mg/L	
NO _x (e)		1000 mg/m ² (f)
Cd		(100 ppb)
P		
Chemical Oxygen Demand	(100 mg/L)	
Total Suspended Solids	(30 mg/L)	
pH	6-9	
Temperature	35 °C	

TABLE 5 (CONT'D)			
FERTILIZER PRODUCTION - EMISSION GUIDELINES (a)			
COMPONENT	ITALY	JORDAN (m)	SAUDI ARABIA
Particulate			
NH ₃	(15 mg/L)	(2.5 mg/L)	
HF			
HCL			
F	(6 mg/L)		
NH ₄ ⁺ -N (d)			(5 mg/L)
NO ₃ ⁻ -N (d)	(20 mg/L)		
NOx (e)			
Cd		(0.01 mg/L)	
P	(10mg/L)		(0.5 mg/L)
Chemical Oxygen Demand		(100 mg/L)	
Total Suspended Solids		(30 mg/L)	(15 mg/L)
pH	(6.5-9)	(6.8-7.2)	(6-9)
Temperature	(5°C above ambient outfall temperature)	(30°C)	(35°C)

COMPONENT	TURKEY	ZIMBABWE	MEXICO
Particulate	200 mg/m ³		
NH ₃			
HF			
HCL			
F	10 mg/m ³ (15 mg/L)	(1 mg/L)	(20 mg/L)
NH ₄ ⁺ -N (d)	(50 mg/L)	(10 mg/L) (j)	(50-150 mg/L) (p)
NO ₃ ⁻ -N (d)	(50 mg/L)		
NOx (e)	800 mg/m ³		
Cd	(0.5 mg/L)	(0.01 mg/L)	
P	(35 mg/L)	(1 mg/L)	(40 mg/L)
Chemical Oxygen Demand	(200 mg/L)		
Total Suspended Solids	(100 mg/L)	(25 mg/L)	(30 mg/L)
pH	(6-9)	(6-9)	(6-9)
Temperature			

TABLE 5 (CONT'D)

- a. Derived from IFA Environmental Legislation Survey (1989) and other reported data. Values in parenthesis () indicate liquid effluents, all others indicate gaseous effluents. Values not shown do not necessarily indicate lack of legislated limit. Gaseous values assumed to be expressed in normal cubic meters (M³).
- b. Values for Austria pertain to new installations.
- c. For Iran, lower values refer to wastewater discharged into wells and high values refer to surface discharge.
- d. Allowable limit calculated as N existing in indicated form
- e. NO_x calculated and indicated as concentration of NO₂.
- f. Higher value pertains to brackish water applications.
- g. Lower value pertains to brackish water applications.
- h. NH₃ regulated at discretion of local authorities; values indicate the range of limits.
- i. Proposed limit using best available technology.
- j. Total N equivalent regardless of form.
- k. Concentration indicated as NH₄ and NO₃.
- l. Combustion Source
- m. Jordan currently has no regulations pertaining to emissions to atmosphere.
- n. Fluoride value may be as low as 1.5 mg/L depending upon recipient stream of outfall.
- o. High value (20 mg/L) is applicable to phosphate fertilizer production units.
- p. High value (150 mg/L) is applicable to urea plants only; values refer to total N equivalent regardless of form.

TABLE 6				
SELECTED FEDERAL ENVIRONMENTAL REGULATIONS TO THE FERTILIZER SECTOR IN THE UNITED STATES				
Substance	Source of Effluent - Production Unit/Operation			
	Sulphuric Acid	Nitric Acid	Wet Process Phosphoric Acid	Superphosphoric Acid Concentration
(Limit (a))				
Ammonia (NH ₃)	(Ammonia is not covered by federal regulations; may be regulated by state and local authorities)			
Ammonia (expressed as N)		0.45-4.5 g/t HNO ₃ (b,c,d) (in wastewater)		
Acid Mist	0.075 kg/t H ₂ SO ₄ (b)			
Fluorides (expressed as F)			10 g/t P ₂ O ₅	5 g/t P ₂ O ₅
Nitrogen Oxides (expressed as NO _x)		1.5 kg/t HNO ₃ (b)		
Nitrate (expressed as N)		23-170 g/t HNO ₃ (b,c,d) (in wastewater)		
Sulphur Dioxide (SO ₂)	2 kg/t H ₂ SO ₄ (b)			
Stack Opacity	Less than 10%	Less than 10%		
Total Suspended Solids				
pH				

Substance	Source of Effluent - Production Unit/Operation		
	Diammonium Phosphate	Triple Superphosphate	Granular Triple Superphosphate Storage Facility
(Limit (a))			
Ammonia (NH ₃)	(Ammonia is not covered by federal regulations; may be regulated by state and local authorities)		
Ammonia (expressed as N)			
Acid Mist			
Fluorides (expressed as F)	30 g/t P ₂ O ₅	100 g/t P ₂ O ₅	0.25 g/h-t P ₂ O ₅ (a)
Nitrogen Oxides (expressed as NO _x)			
Nitrate (expressed as N)			
Sulphur Dioxide (SO ₂)			
Stack Opacity			
Total Suspended Solids			
pH			

TABLE 6 (CONT'D)				
SELECTED FEDERAL ENVIRONMENTAL REGULATIONS TO THE FERTILIZER SECTOR IN THE UNITED STATES				
Substance	Source of Effluent - Production Unit/Operation			
	Phosphate Rock Calciner	Phosphate Rock Grinder	Phosphate Rock Dryer	Process Waste Water
(Limit (a))				
Ammonia (NH ₃)				
Ammonia (expressed as N)				
Acid Mist				
Fluorides (expressed as F)				25-75 mg/L (c)
Nitrogen Oxides (expressed as NO _x)				
Nitrate (expressed as N)				
Particulate (dust)	120 g/t rock (f) 55 g/t rock	6 g/t rock	30 g/kg rock	
Phosphorus (expressed as P)				35-105 mg/L (c)
Sulphur Dioxide (SO ₂)				
Stack Opacity	Less than 10%	0%	Less than 10%	
Total Suspended Solids				50-150 mg/L (c)
pH				6.0-9.5

- a. Indicated limits for phosphate operations refer to phosphate rock of P₂O₅ equivalent fed to process. Except for wastewater, all values refer to discharges to the atmosphere. Additional state and local regulations may also apply.
- b. Based on acid produced: 100% H₂SO₄ or HNO₃. Atmospheric discharge values refer to a maximum 2-h average.
- c. Lower value is average of daily values for 30 consecutive days; higher value is maximum for any one day. Total suspended solids is waived if water is treated to remove phosphorus and fluorine.
- d. Standard for new facility based on gaseous ammonia raw material.
- e. Based on tonnes P₂O₅ equivalent in storage facility.
- f. Refers to calculation of unbeneficiated rock or blends of beneficiated and unbeneficiated rock. Lower value (55 g/t) pertains to calculation of beneficiated rock.

Source: United States Code of Federal Regulations July 1, 1989 and July 1, 1990.