EUROPEAN COMMISSION
DIRECTORATE-GENERAL JRC
JOINT RESEARCH CENTRE
Institute for Prospective Technological Studies (Seville)
Technologies for Sustainable Development
European IPPC Bureau

Integrated Pollution Prevention and Control

Draft Reference Document on Best Available Techniques in the Large Volume Inorganic Chemicals, Ammonia, Acids and Fertilisers Industries

Draft March 2004

Edificio EXPO, C/Inca Garcilaso, s/n, E-41092 Seville, Spain
Telephone: direct line (+34-95) 4488-258, switchboard 4488-318. Fax: 4488-426.
Internet: http://eippcb.jrc.es; Email: eippcb@jrc.es

This document is one of a series of foreseen documents as below (at the time of writing, not all documents have been drafted):

Full title	BREF code
Reference Document on Best Available Techniques for Intensive Rearing of Poultry and Pigs	ILF
Reference Document on the General Principles of Monitoring	MON
Reference Document on Best Available Techniques for the Tanning of Hides and Skins	TAN
Reference Document on Best Available Techniques in the Glass Manufacturing Industry	GLS
Reference Document on Best Available Techniques in the Pulp and Paper Industry	PP
Reference Document on Best Available Techniques on the Production of Iron and Steel	I&S
Reference Document on Best Available Techniques in the Cement and Lime Manufacturing Industries	CL
Reference Document on the Application of Best Available Techniques to Industrial Cooling Systems	CV
Reference Document on Best Available Techniques in the Chlor – Alkali Manufacturing Industry	CAK
Reference Document on Best Available Techniques in the Ferrous Metals Processing Industry	FMP
Reference Document on Best Available Techniques in the Non Ferrous Metals Industries	NFM
Reference Document on Best Available Techniques for the Textiles Industry	TXT
Reference Document on Best Available Techniques for Mineral Oil and Gas Refineries	REF
Reference Document on Best Available Techniques in the Large Volume Organic Chemical Industry	LVOC
Reference Document on Best Available Techniques in the Waste Water and Waste Gas Treatment/Management Systems in the Chemical Sector	CWW
Reference Document on Best Available Techniques in the Food, Drink and Milk Industry	FM
Reference Document on Best Available Techniques in the Smitheries and Foundries Industry	SF
Reference Document on Best Available Techniques on Emissions from Storage	ESB
Reference Document on Best Available Techniques on Economics and Cross-Media Effects	ECM
Reference Document on Best Available Techniques for Large Combustion Plants	LCP
Reference Document on Best Available Techniques in the Slaughterhouses and Animals By-products Industries	SA
Reference Document on Best Available Techniques for Management of Tailings and Waste-Rock in Mining Activities	MTWR
Reference Document on Best Available Techniques for the Surface Treatment of Metals	STM
Reference Document on Best Available Techniques for the Waste Treatments Industries	WT
Reference Document on Best Available Techniques for the Manufacture of Large Volume Inorganic Chemicals (Ammonia, Acids and Fertilisers)	LVIC-AAF
Reference Document on Best Available Techniques for Waste Incineration	WI
Reference Document on Best Available Techniques for Manufacture of Polymers	POL
Reference Document on Energy Efficiency Techniques	ENE
Reference Document on Best Available Techniques for the Manufacture of Organic Fine Chemicals	OFC
Reference Document on Best Available Techniques for the Manufacture of Specialty Inorganic Chemicals	SIC
Reference Document on Best Available Techniques for Surface Treatment Using Solvents	STS
Reference Document on Best Available Techniques for the Manufacture of Large Volume Inorganic Chemicals (Solids and Others)	LVIC-S
Reference Document on Best Available Techniques in Ceramic Manufacturing Industry	CER

EXECUTIVE SUMMARY

This part will be completed when the document is in its final form.

PREFACE

1. Status of this document

Unless otherwise stated, references to "the Directive" in this document means the Council Directive 96/61/EC on integrated pollution prevention and control. As the Directive applies without prejudice to Community provisions on health and safety at the workplace, so does this document.

This document is a working draft of the European IPPC Bureau. It is not an official publication of the European Communities and does not necessarily reflect the position of the European Commission.

2. Relevant legal obligations of the IPPC Directive and the definition of BAT

In order to help the reader understand the legal context in which this document has been drafted, some of the most relevant provisions of the IPPC Directive, including the definition of the term "best available techniques", are described in this preface. This description is inevitably incomplete and is given for information only. It has no legal value and does not in any way alter or prejudice the actual provisions of the Directive.

The purpose of the Directive is to achieve integrated prevention and control of pollution arising from the activities listed in its Annex I, leading to a high level of protection of the environment as a whole. The legal basis of the Directive relates to environmental protection. Its implementation should also take account of other Community objectives such as the competitiveness of the Community's industry thereby contributing to sustainable development.

More specifically, it provides for a permitting system for certain categories of industrial installations requiring both operators and regulators to take an integrated, overall look at the polluting and consuming potential of the installation. The overall aim of such an integrated approach must be to improve the management and control of industrial processes so as to ensure a high level of protection for the environment as a whole. Central to this approach is the general principle given in Article 3 that operators should take all appropriate preventative measures against pollution, in particular through the application of best available techniques enabling them to improve their environmental performance.

The term "best available techniques" is defined in Article 2(11) of the Directive as "the most effective and advanced stage in the development of activities and their methods of operation which indicate the practical suitability of particular techniques for providing in principle the basis for emission limit values designed to prevent and, where that is not practicable, generally to reduce emissions and the impact on the environment as a whole." Article 2(11) goes on to clarify further this definition as follows:

"techniques" includes both the technology used and the way in which the installation is designed, built, maintained, operated and decommissioned;

"available" techniques are those developed on a scale which allows implementation in the relevant industrial sector, under economically and technically viable conditions, taking into consideration the costs and advantages, whether or not the techniques are used or produced inside the Member State in question, as long as they are reasonably accessible to the operator;

"best" means most effective in achieving a high general level of protection of the environment as a whole.

Furthermore, Annex IV of the Directive contains a list of "considerations to be taken into account generally or in specific cases when determining best available techniques... bearing in mind the likely costs and benefits of a measure and the principles of precaution and prevention".

These considerations include the information published by the Commission pursuant to Article 16(2).

Competent authorities responsible for issuing permits are required to take account of the general principles set out in Article 3 when determining the conditions of the permit. These conditions must include emission limit values, supplemented or replaced where appropriate by equivalent parameters or technical measures. According to Article 9(4) of the Directive, these emission limit values, equivalent parameters and technical measures must, without prejudice to compliance with environmental quality standards, be based on the best available techniques, without prescribing the use of any technique or specific technology, but taking into account the technical characteristics of the installation concerned, its geographical location and the local environmental conditions. In all circumstances, the conditions of the permit must include provisions on the minimisation of long-distance or transboundary pollution and must ensure a high level of protection for the environment as a whole.

Member States have the obligation, according to Article 11 of the Directive, to ensure that competent authorities follow or are informed of developments in best available techniques.

3. Objective of this Document

Article 16(2) of the Directive requires the Commission to organise "an exchange of information between Member States and the industries concerned on best available techniques, associated monitoring and developments in them", and to publish the results of the exchange.

The purpose of the information exchange is given in recital 25 of the Directive, which states that "the development and exchange of information at Community level about best available techniques will help to redress the technological imbalances in the Community, will promote the worldwide dissemination of limit values and techniques used in the Community and will help the Member States in the efficient implementation of this Directive."

The Commission (Environment DG) established an information exchange forum (IEF) to assist the work under Article 16(2) and a number of technical working groups have been established under the umbrella of the IEF. Both IEF and the technical working groups include representation from Member States and industry as required in Article 16(2).

The aim of this series of documents is to reflect accurately the exchange of information which has taken place as required by Article 16(2) and to provide reference information for the permitting authority to take into account when determining permit conditions. By providing relevant information concerning best available techniques, these documents should act as valuable tools to drive environmental performance.

4. Information Sources

This document represents a summary of information collected from a number of sources, including in particular the expertise of the groups established to assist the Commission in its work, and verified by the Commission services. All contributions are gratefully acknowledged.

5. How to understand and use this document

The information provided in this document is intended to be used as an input to the determination of BAT in specific cases. When determining BAT and setting BAT-based permit conditions, account should always be taken of the overall goal to achieve a high level of protection for the environment as a whole.

The rest of this section describes the type of information that is provided in each section of the document.

Chapter 1 provides general information on the industrial sector concerned and on the industrial processes used within the sector along with data and information concerning current emission and consumption levels reflecting the situation in existing installations at the time of writing.

Chapter 2 describes in more detail the emission reduction and other techniques that are considered to be most relevant for determining BAT and BAT-based permit conditions. This information includes the consumption and emission levels considered achievable by using the technique, some idea of the costs and the cross-media issues associated with the technique, and the extent to which the technique is applicable to the range of installations requiring IPPC permits, for example new, existing, large or small installations. Techniques that are generally seen as obsolete are not included.

Chapter 3 presents the techniques and the emission and consumption levels that are considered to be compatible with BAT in a general sense. The purpose is thus to provide general indications regarding the emission and consumption levels that can be considered as an appropriate reference point to assist in the determination of BAT-based permit conditions or for the establishment of general binding rules under Article 9(8). It should be stressed, however, that this document does not propose emission limit values. The determination of appropriate permit conditions will involve taking account of local, site-specific factors such as the technical characteristics of the installation concerned, its geographical location and the local environmental conditions. For existing installations, the economic and technical viability of upgrading them also needs to be taken into account. Even the single objective of ensuring a high level of protection for the environment as a whole will often involve making trade-off judgements between different types of environmental impact, with these judgements often being influenced by local considerations.

Although an attempt is made to address some of these issues, it is not possible for them to be considered fully in this document. The techniques and levels presented in Chapter 3 will therefore not necessarily be appropriate for all installations. On the other hand, the obligation to ensure a high level of environmental protection including the minimisation of long-distance or transboundary pollution implies that permit conditions cannot be set on the basis of purely local considerations. It is therefore of the utmost importance that the information contained in this document is fully taken into account by permitting authorities.

Since the best available techniques change over time, this document will be reviewed and updated as appropriate. All comments and suggestions should be made to the European IPPC Bureau at the Institute for Prospective Technological Studies at the following address:

Edificio Expo, c/Inca Garcilaso, s/n, E-41092 Seville, Spain
Telephone: +34 95 4488 284
Fax: +34 95 4488 426
e-mail: eippcb@jrc.es
Internet: http://eippcb.jrc.es

Best Available Techniques Reference Document in the Large Volume Inorganic Chemicals, Ammonia, Acids and Fertilisers Industries

List of figures

List of tables

SCOPE

The chemical industry is a complex industrial sector with a substantial number and diversity of products. Currently some 70000 chemical compounds are manufactured worldwide. Each compound will be different in that each has its own distinct chemical nature and properties, production route(s) and end-use. It has been estimated that there are between 1 and 2 million inorganic compounds within inorganic chemistry.

This BREF covers LVIC-AAF Ammonia, Acids and Fertilisers where large volumes of the specified inorganic compounds are produced.

Generally, the ammonia and acid processes covered here are considered to have the following features; the products from the processes are not consumer products in their own right, but are basic chemicals that are then used, in large quantities, as raw materials in the production of other chemicals. NPK, AN/CAN superphosphates or urea fertilisers however are produced primarily for a particular user although the production of these other chemicals are also made in dedicated continuously operating plants.

The BREF covers the following processes:

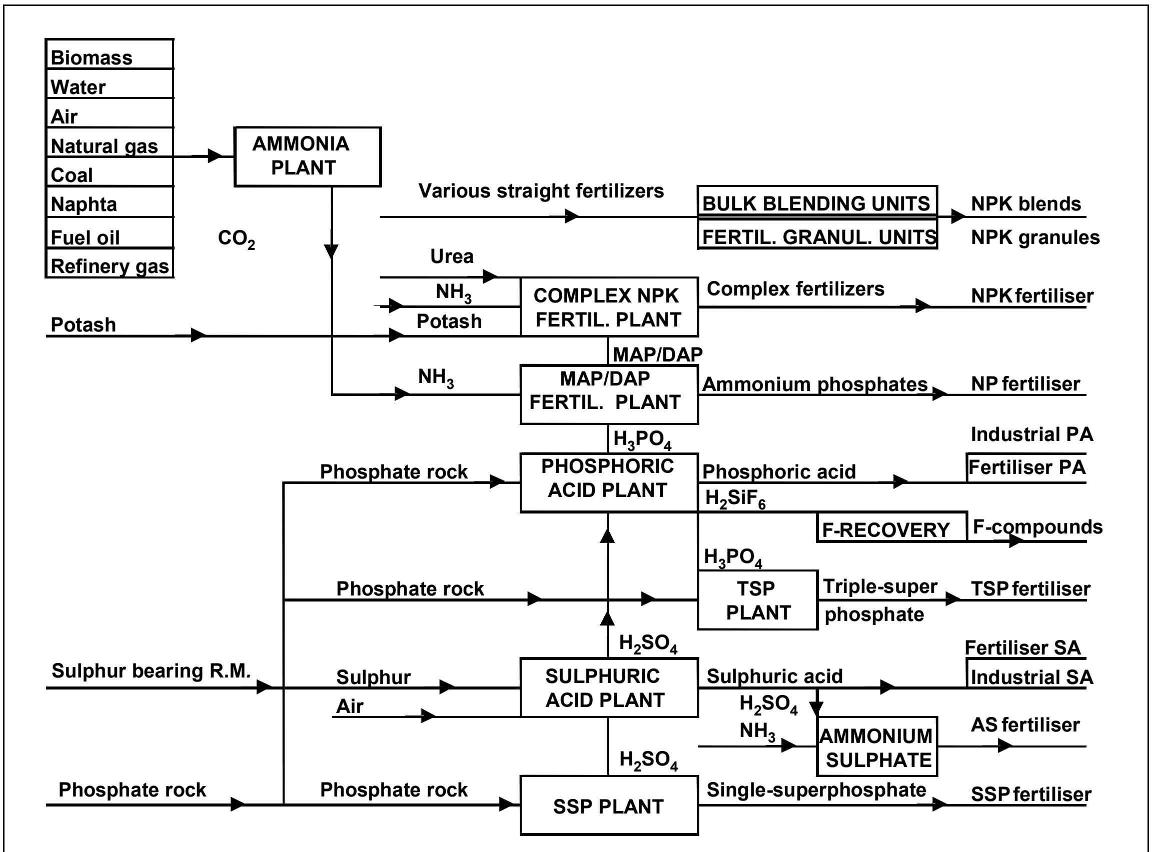
- ammonia
- nitric acid
- sulphuric acid
- phosphoric acid
- hydrofluoric acid
- NPK fertilisers -nitrophosphate and mixed acid route
- Urea, ureas/urea ammonium nitrate
- ammonium nitrate/calcium ammonium nitrate
- superphosphates.

The above processes are chemically interlinked and sometimes may be co-located on the same site as part of an integrated complex of chemical plants. These connections will be developed throughout the BREF. The inclusion of the above mentioned processes was considered by EIPPCB to be a logical package to focus on in this particular BREF because of the inter dependence of the processes. The industrial links between each process provides a focus for the BREF structure.

.

1 GENERAL INFORMATION

The block diagram below is included to show the connections between the separate processes that make up an ammonia acids and fertiliser production complex. The diagram provides a reference point when reading the various sections in the BREF.



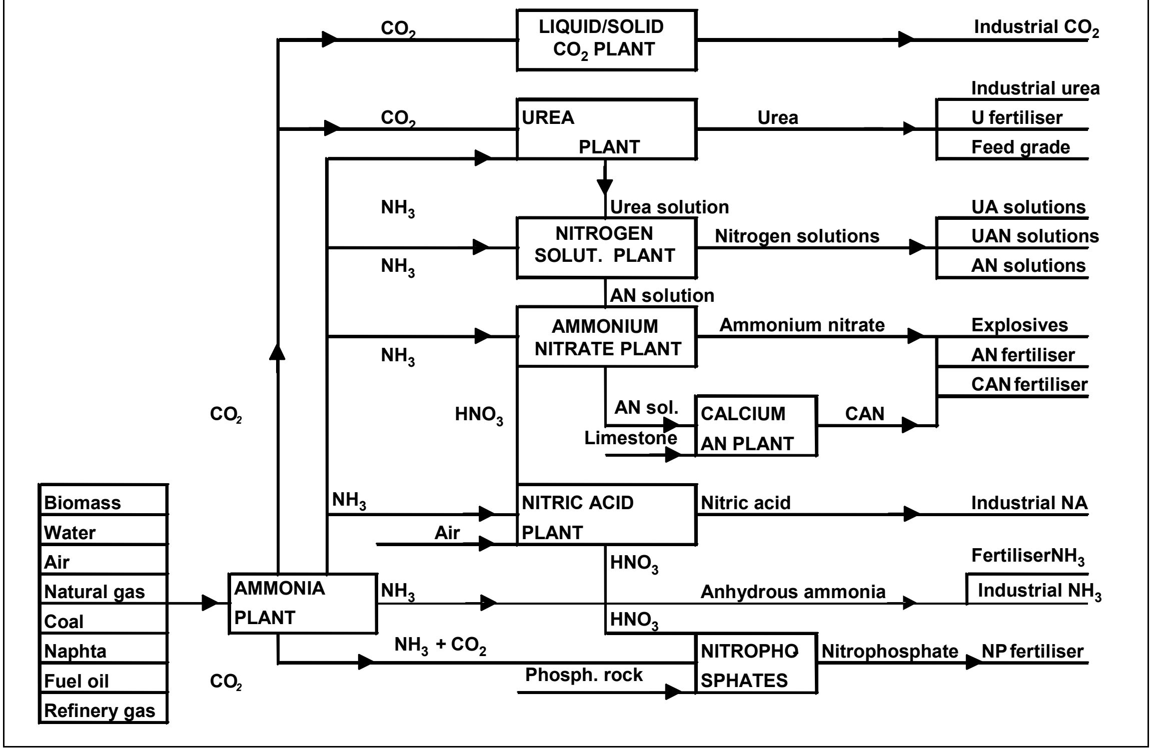


Figure 1.1: Block diagram showing interactions of production plants

The above flow diagram links the range of interactions that exist between the different chemicals production units. In particular the diagram shows the interactions that exist in the production of:

- ammonia
- nitric acid
- sulphuric acid
- phosphoric acid
- hydrofluoric acid
- NPK fertilisers -nitrophosphate and mixed acid route
- Urea, ureas/urea ammonium nitrate
- ammonium nitrate/calcium ammonium nitrate
- superphosphates.

The diagram shows that for this set of chemicals ammonia production is the process central to the manufacture of all the other various production units, particularly for the straight N fertilisers such as ammonium nitrate and urea.

Ammonia is used to produce nitric acid and is one of the base chemicals for the production of a range of combined NPK fertilisers.

The blending of a number of straight fertilisers is included in the diagram as this is often carried out complementary to the various routes for the production of a complete range of fertilisers. Blending alone is not covered in the description of Annex 1 to 96/61/EC.

The hydrocarbon feedstock used for ammonia production as shown on the diagram includes all the potential feed stocks.

The principle feed stocks of natural gas and naptha will be considered in detail but reference will be made to other sources capable of providing the necessary hydrogen for the synthesis of ammonia.

The sulphur bearing raw materials will be covered when consideration is given to the raw materials used for the production of sulphuric acid.

Sulphur burning is the main activity carried out in order to provide the necessary SO_2 for sulphuric acid production but other sources of SO_2 from pyrite roasting, acid recovery, and abatement plants also occur and need to be included as alternatives for sulphuric acid production.

Phosphoric acid produced from the digestion of phosphate rock with sulphuric acid is used to produce a range of compound fertilisers. The various route to produce phosphoric acid will be considered, together with the actual future of phosphoric acid in Europe.

The hydrofluoric acid process has been included as an associated process. Here fluorspar is reacted with sulphuric acid in a rotary kiln to produce the acid. The linkage to the other fertiliser processes is tenuous and indeed it is invariably produced at a separate site. Howevere it was agreed by the TWG that this process should be covered in this BREF.

1.1 Ammonia

The commercialisation of synthetic ammonia production began in 1913. Its particular merit was that for the first time it made viable the fixation of nitrogen from air to ammonia based fertilisers. Accordingly, ammonia production capacity during the past nine decades has been increasing in direct proportion to the growth in world population and today, the ammonia industry is the world’s second largest basic chemical producer, after the sulphuric acid industry.

About 80 % of the ammonia is currently used as the nitrogen source in fertilisers, with the other 20 % being used in several industrial applications, such as the manufacture of plastics, fibres, explosives, hydrazine, amines, amides, nitriles and other organic nitrogen compounds which serve as intermediates in dyes and pharmaceuticals manufacturing. Among the important inorganic products manufactured from ammonia are nitric acid, urea and sodium cyanide. Ammonia is also used for environmental protection measures, e.g. in the removal of NO_x from flue-gases. Liquid ammonia is an important solvent and is also used as a refrigerant. Due to safety reasons the latter application is mainly limited to large-scale industrial refrigeration systems with suitable safety precautions in place (used for the high efficiency it offers).

In 1998, most of the production capacity was located in the following regions:

- America (**15 %** of world capacity)
- China (**22 %**)
- the former USSR, of which 80 % is Russia and the Ukraine, (**17 %)**
- the Near East (**6 %**)
- Indonesia and Japan (**4 %**)
- Mexico and the Caribbean (**3.5 %**).
- West Europe (**9 %),** with this share falling from a level of **13 %** in 1988
- in 1974 the developing countries accounted for **27 %** of ammonia capacity. By 1998 their share had increased to **51 %**.

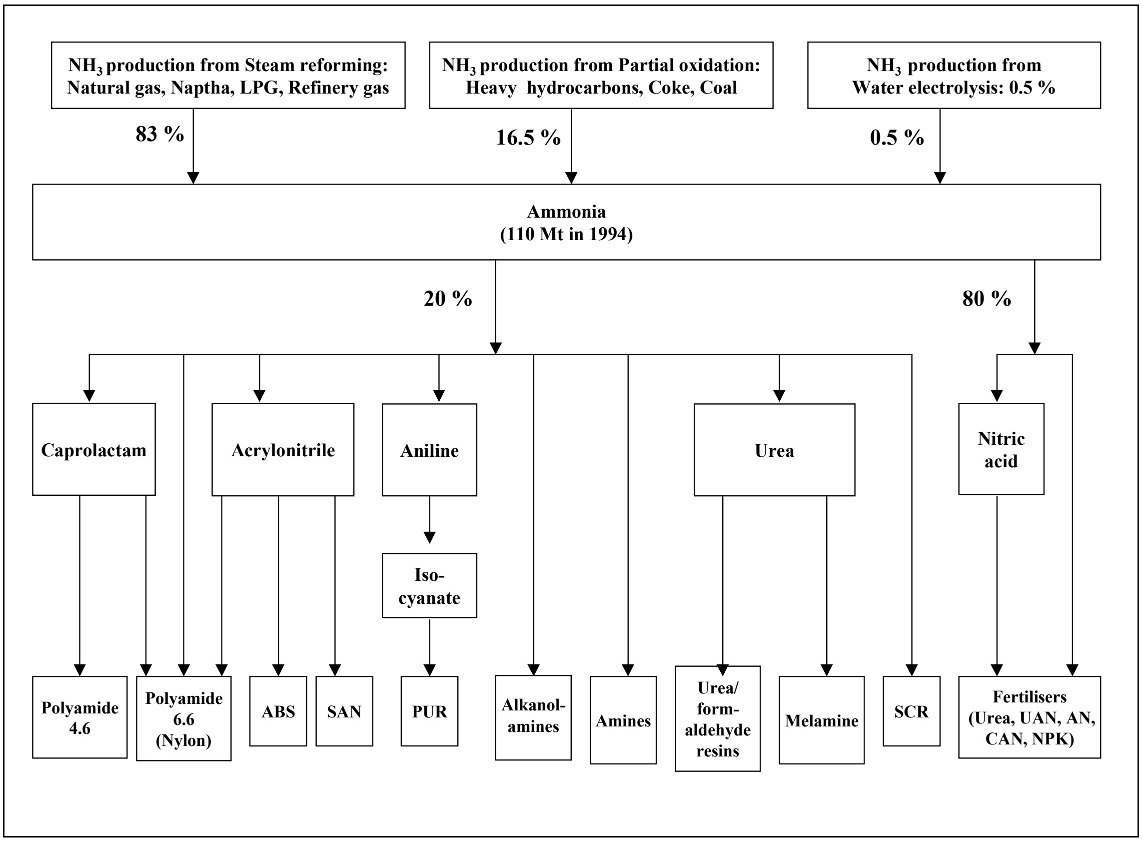


Figure 1.2: Worldwide production and most important uses of ammonia

Notes:
ABS-acrylonitrile-butadiene-styrene resin
SAN-styrene-acrylonitrile-resin
PUR-polyurethane
SCR-selective catalytic reduction

Development of ammonia production capacity: Table 1.1 and Table 1.2 show ammonia production in 1994 for some European Union Member States and for the major regions of the world. Table 1.1 gives a top-ten list of worldwide major ammonia producing countries.

Country	Production in 1994 (Mt N)
1. China	19.788
2. US	13.390
3. India	7.331
4. Russia	7.265
5. Canada	3.489
6. Indonesia	3.010
7. Ukraine	3.006
8. Netherlands	2.479
9. Germany	2.130
10. Mexico	2.027

Table 1.1: Production figures for the ten major ammonia producing countries in the world

The ammonia industry has developed in several phases over the past decades, largely reflecting the expansion of the nitrogen fertiliser industry. Between 1960 and 1980, the world ammonia industry experienced a significant growth, in response to an increase in the rate of nitrogen fertiliser consumption of nearly 10 % per year. The capacity expansion was stimulated mainly by a shift to natural gas as a cheap feedstock (previously coal and heavy hydrocarbons were the main feedstock) and by the construction of highly integrated automated single-train plants. The peak growth rate occurred between 1975 and 1980, when 120 plants, with a total capacity of 28 Mt, were constructed.

The European Union's ammonia industry produces approximately 11 Mt ammonia per year (1994), from around 50 plants. Data on the location of these plants, their capacity, and age and on the type of feedstock used are given in Table 1.2. A modern ammonia plant has a typical capacity of 1000 – 2000 t/d, although new plants are now commonly designed up to 2200 t/d. The plants may be built as stand-alone or integrated with other plants at a site, for instance integration typically takes place with urea production and recently there are emerging trends of combined ammonia with methanol production. Hydrogen and/or carbon monoxide production can also be integrated with ammonia plants. This integration with other plants on-site may take the form of an energy export (e.g. power or steam). An ammonia plant, for instance, can be designed to cater for a larger energy export.

Location	Company	Capacity (t/d)	First commi-ssioned	Status	Feedstock
Austria					
Linz	Agrolinz	850	1974	SNCR at primary reformer, 500t/d Rev. 1987-1990	NG
	Melamin GmbH	500	1966		NG
Belgium					
Antwerp	BASF	1800	1991		
Tertre	Kemira SA-NV	1050	1968	Rev. in June 1996	
France					
Grandpuits	Grande Paroisse	1150	1970		NG
Rouen G. Quevily	Grande Paroisse	1150	1969	Rev.	NG
Gonfreville	Hydro Agri	1000	1969		NG
Pardies	Hydro Agri	450	1961		NG/Hydrogen
Ottmarsheim	Pec Rhin-BASF	650	1967 - 68	Rev. 1996	NG

Location	Company	Capacity (t/d)	First Commi-ssioned	Status	Feedstock
Germany					
Ludwigshafen	BASF	1200/1360	1971/1982		NG
Köln	EC Erdoelchemie GmbH	900	1969 - 70	Rev.	NG
Brunsbuttel	Hydro Agri	2000	1978	Rev. 1989	Vacuum residues
Schwedt an der Oder	PCK Schwedt	450	1968		NG
Wiettenberg	SKW Stickstoffwerke				
Piesteritz	Piesteritz	2 x 1650	1974 - 75	Rev.	NG
Gelsenkirchen-Buer	Veba Oel (Scholven)	1250	1973		Vacuum residues
Greece					
Thessaloniki	EKO Chemicals A.E.	400	1966/1976		Naphtha
Nea Karvali	Phosphoric Fert Industry	400	1986		NG
Italy					
Ferrara	Enichem Agricoltura	1500	1977		NG
Manfredonia	Enichem Agricoltura	1050	1972		NG
Nera Montoro	Enichem Agricoltura	400	1970		NG
S. Giuseppe di Cairo	Enichem Agricoltura	500	1967	Rev.	NG
Terni	Temi/Enichem	150	1969		NG
Priolo	Agrimons/Enichem	900			NG
Netherlands					
Geleen	DSM Agro BV	1360/1360	1971/1984		NG
Sluiskil	Hydro Agri	C: 900	1971	Rev.	NG
		D: 1500	1984		NG
		E: 1750	1987		NG
Portugal					
Barreiro	Quimigal Adubos S.A.	900	1984	Planned revamp	Visbreaker residues, Vacuum residues
Spain					
Sabinanigo	Energía e Industrias Aragonesas	40	1925	Rev. 1980/95	H_2 and N_2 (from other plant)
Huelva	Fertiberia S.L.	1130	1976	Rev. 1986/89	NG
Puertollano	Fertiberia S.L.	600	1970	Rev. 1988/92	NG
United Kingdom					
Billingham, Cleveland	TERRA Nitrogen	1150 name plate capacity current ~1500	1977		NG
Severnside	TERRA Nitrogen	2 x 400	1988		NG
Ince, Cheshire	Kemira Ince Ltd	1050	1970	Rev.	NG
Hull	Kemira Ltd.	275	1989		H_2-rich feedstock (from other plant)
Notes: NG - Natural gas Rev - Revamped					

Table 1.2: Details of ammonia plants operating in the European Union [13, EC, 1997]

1.1.1 Applied Processes and Techniques

Ammonia is synthesised from nitrogen and hydrogen by the following reaction:

$$N_2 + 3H_2 \leftrightarrow 2NH_3$$

The best available source of nitrogen is from atmospheric air. The hydrogen required can be produced from various feedstocks but currently it is derived mostly from steam reforming fossil fuels. Depending of the type of fossil fuel, two different methods are applied: steam reforming or partial oxidation to produce hydrogen for ammonia production.

Presently about 80 % of the ammonia production capacity worldwide is provided by the well-developed steam process. High-level process integration, innovative equipment design and improved catalysts are the main characteristics of ammonia plants today.

Feedstock	Process	% of world capacity
Natural Gas	Steam reforming	77
Naphtha, LPG, Refinery Gas	Steam reforming	6
Heavy hydrocarbon fractions	Partial oxidation	3
Coke, coal	Partial oxidation	13.5
Hydrogen	Water electrolysis	0.5

Table 1.3: Breakdown of the use of feedstocks and applied process routes for ammonia production as a percentage of the world capacity in 1990 [13, EC, 1997]

There has been limited development work of the partial oxidation process in integrated plant concepts. At present a typical plant is a blend of techniques offered by different licensors assembled by the selected contractor. The achieved energy consumptions reported in Table 1.4 suggest that, compared to the steam reforming process there is a potential for energy savings and improvements in the energy efficiency/performance of partial oxidation processes.

Feedstock	Process	Net primary energy[1] consumption GJ/t NH_3 (LHV)	Relative Investment
Natural gas	Steam reforming	28	1
Heavy hydrocarbons	Partial oxidation	38	1.5
Coal	Partial oxidation	48	2 - 3
[1] Best achieved data			

Table 1.4: Relative investment cost and totals energy demand for ammonia production from various feedstocks
[13, EC, 1997]

1.1.1.1 Steam reforming

The descriptions which follow are for a typical plant. Although naturally the actual plant configuration will vary from plant to plant and in real-life operating parameters such as temperatures, pressures, compositions will also vary considerably from the quoted values.

The steam reforming process can process light hydrocarbons feedstocks ranging from natural gas to naphtha. More than 90 % of the Western European ammonia production is based on natural gas.

Steam reforming is generally performed in two steps. The first step is called primary reforming and takes place in catalyst filled tubes, where the natural gas is only partially converted to hydrogen. The heat is supplied indirectly by burning natural gas. The conversion of the remaining unreacted hydrocarbon takes place in a second step using a catalyst filled vessel; this is called secondary reforming. In this step the heat is supplied by the partial combustion of the feed gas with the process air, which also provides the nitrogen needed for the downstream ammonia synthesis.

1.1.1.2 Conventional steam reforming

Feedstock desulphurisation

The catalyst used in the steam reforming process is highly sensitive to any sulphur compounds, therefore these compounds need to be reduced to a minimums concentration of less than 0.15 mg S/Nm^3. To achieve this, the feed gas is preheated up to 350 – 400 °C. Thereafter the sulphur compounds are hydrogenated to H_2S, typically using a cobalt molybdenum catalyst, and then finally adsorbed on pelletised zinc oxide:

$$R\text{-}SH + H_2 \rightarrow H_2S + RH$$
$$H_2S + ZnO \rightarrow ZnS + H_2O$$

Where R= alkyl group

The hydrogen required for the reaction is usually recycled from the synthesis section of the plant.

Primary reforming

The hydrocarbon conversion rate in the primary reformer in the conventional steam reforming plant is about 60 %. The overall reaction is highly endothermic. Gas from the desulphuriser is mixed with steam and the mixture is heated to 500 – 600 °C in the convection section before entering the primary reformer the primary reformer consists of a large number of catalyst filled tubes. In some new or revamped plants, the preheated steam/gas mixture is passed through an adiabatic prereformer and then reheated in the convection section. The applied steam to carbon molar ratio (S/C ratio) is typically around 3.0; although the actual optimum ratio depends on several factors, such as the feedstock quality, purge gas recovery, primary reformer capacity, shift operation, and the plant steam balance. In new plants the optimum S/C ratio may be lower than 3.0. The heat for the primary reforming process is supplied by burning natural gas or other gaseous fuel, in the burners of a radiant box containing the catalyst filled tubes.

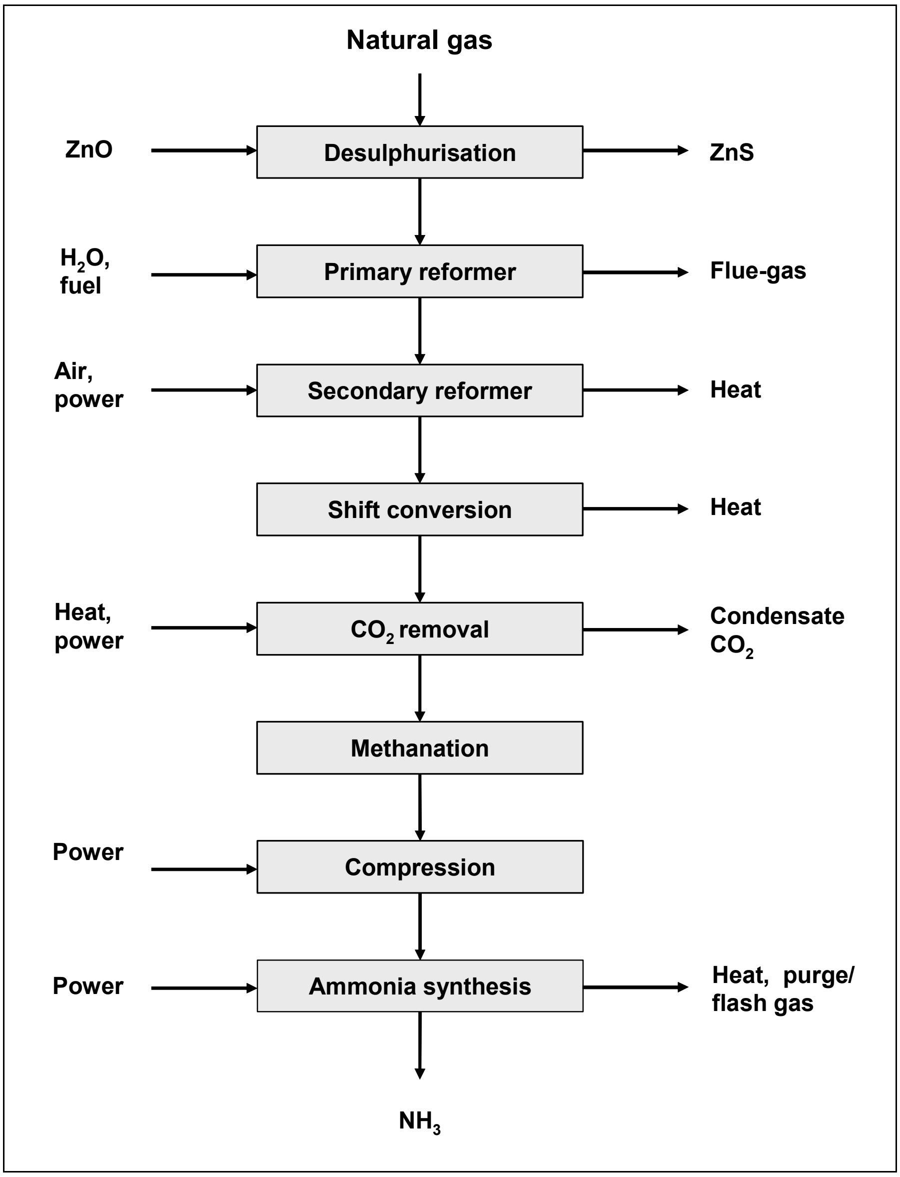


Figure 1.3: Ammonia production by steam reforming
[13, EC, 1997]

About half of the heat is utilised for the reforming reaction, the rest remaining in the flue-gas to maintain it at a temperature higher than 900 °C.

$$CH_4 + H_2O \leftrightarrow CO + 3H_2 \qquad \Delta H_0 = 206 \text{ kJ/mol}$$

Secondary reforming

The main objective of secondary reforming is to add the nitrogen required for the synthesis and to complete the conversion of the hydrocarbon feed. For this purpose, the reaction heat and the required temperature are achieved by an internal combustion of part of the reaction gas before it is passed over the nickel-containing catalysts. The process air is compressed and heated in the primary reformer convection section to around 600 °C, with the result that the methane is converted down to a residual content of around 0.2 – 0.3 %. The reaction proceeds adiabatically, resulting in a gas outlet temperature of about 1000 °C. Heat is removed in a waste heat steam boiler or in a boiler/superheater, cooling the gas to 350 – 380 °C.

Shift conversion

The process gas from the secondary reformer contains 12 – 15 % CO (dry gas base). Most of this CO will be converted in the shift section to CO_2 and H_2, according to the reaction:

$$CO + H_2O \leftrightarrow CO_2 + H_2 \quad \Delta H_0 = -41\ \text{kJ/mol}$$

This reaction is carried out in two steps with intermediate heat removal. Initially the process gas is passed through a bed of iron oxide/chromium oxide catalyst at around 400 °C and then over a copper oxide/zinc oxide catalyst at about 200 – 220 °C. The final residual CO content of the gas is 0.2 - 0.4 %. New developments can enable an isothermal shift one-step conversion to take place, applying an internal cooling of the process gas with cooling tubes running through the catalyst layers.

Process condensates

The gas exiting the low-temperature shift reactor is cooled and after most of the excess steam is condensed and removed it passes into the CO_2 removal system. This is needed to prevent dilution of the CO_2 removal solvent and to maintain the correct equilibrium balance. Condensates normally containing 1500 – 2000 ppm of ammonia and 800 – 1200 ppm of methanol can be recycled to the process in various ways. The heat released during cooling and condensation can be used for several purposes, e.g. to regenerate the CO_2 scrubbing solution, to drive an absorption refrigeration unit, or to preheat the boiler feed-water.

CO_2 removal

This process step removes the CO_2 from the reaction gas, this corresponding to nearly all the carbon introduced as feed gas into the overall process. The residual CO_2 content is usually in the range of 100 - 1000 ppmv, however, depending on the solvent and design of the CO_2 removal, concentrations down to 50 ppmv are achievable. The CO_2 is removed in a chemical or physical absorption process. The solvents used in chemical absorption processes are mainly aqueous amine solutions, e.g. mono ethanolamine (MEA) activated methyl diethanolamine (aMDEA) or hot potassium carbonate solutions. Two typically used physical absorption solvents are glycol dimethylethers (Selexol) and propylene carbonate. The MEA process requires a high regeneration energy.

Another emerging process is Pressure Swing Adsorption (PSA). This process has the potential to combine in one step both the classical CO_2 removal and the methanation (next process step). This is valid for all cases where the CO_2 purity is unimportant. However, if pure CO_2 is needed as a product, then a classical solvent scrubbing of the low-pressure off-gas of the PSA can be used to recover CO_2.

Process name	Solvent/reagent + additives	CO_2 in treated gas (ppm)
Physical absorption systems		
Purisol (NMP)	N-methyl-2-pyrrolidone	Less than 50
Rectisol	Methanol	Less than 10
Fluorsolv	Propylene carbonate	Function of pressure
Selexol	Polyethylene glycol dimethyl ether	Function of pressure
Chemical reagents		
MEA	Water/monoethanolamine (20 %)	Less than 50
Promoted MEA	Water/MEA (25 - 30 %) + amine guard	Less than 50
Benfield	Water/K_2CO_3 (25 - 30 %) + DEA, etc.	500 - 1000
Vetrocoke	Water/K_2CO_3+As_2O_3 + glycine	500 - 1000
Catacarb	Water/K_2CO_3 (25 - 30 %) + additives	500 - 1000
Lurgi	Water/K_2CO_3 (25 - 30 %) + additives	500 - 1000
Carsol	Water/K_2CO_3 + additives	500 - 1000
Flexsorb HP	Water/K_2CO_3 amine promoted	500 - 1000
Alkazid	Water/K_2-methylaminopropionate	To suit
DGA	Water/diglycolamine (60 %)	Less than 100
MDEA	Water/methyl diethanolamine (40 %)+ additives	100 - 500
Hybrid systems		
Sulfinol	Sulphones/DIPA	Less than 100
TEA-MEA	Triethanolamine/monoethanolamine water/sulpholane/MDEA	Less than 50

Table 1.5: Major carbon dioxide removal processes
[12, EIPPCB, 2000]

Methanation

The small amounts of CO and CO_2, remaining in the synthesis gas, can poison the ammonia synthesis catalyst and must be removed usually by conversion to CH_4 by hydrogenation in the methanator:

$$CO + 3H_2 \rightarrow CH_4 + H_2O$$
$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$$

These reactions take place at a temperature of around 300 °C in a reactor filled with a nickel based catalyst. The residual concentration of these carbon oxides is usually less than 10 ppmv. Methane is not involved in the synthesis reaction, but the water formed must be removed before entering the converter. This is achieved by cooling, followed by condensation downstream of the methanator and finally by condensation/absorption in the product ammonia either in the loop or in a make-up gas drying unit.

Synthesis gas compression

Modern ammonia plants use centrifugal compressors to pressurise the synthesis gas to the required level for ammonia synthesis. Molecular sieves are used after the first compressor stage to remove the last traces of H_2O, CO and CO_2 from the synthesis gas. These compressors are usually driven by steam turbines, utilising steam produced from the excess process heat. A small quantity of condensates is removed from the synthesis gas during compression. These condensates still contain ammonia. Lubricating oils from mechanical equipment, which are typically removed in oil/water separators, can contaminate them.

Ammonia synthesis

The synthesis of ammonia takes place on an iron catalyst at pressures usually in the range 100 - 250 bar and at temperatures of between 350 and 550 °C:

$$N_2 + 3H_2 \leftrightarrow 2NH_3 \qquad \Delta H_0 = -46 \text{ kJ/mol}$$

Only 20 - 30 % of the synthesis gas is converted per pass to ammonia, due to unfavourable equilibrium conditions. The unreacted gas is recycled after removing the ammonia formed. Fresh synthesis gas is supplemented in the loop.

As the exothermic synthesis reaction proceeds there is a reduction in volume and so a higher pressure and lower temperature favours the reaction. The temperature of the catalyst needs to be controlled, as the heat of reaction at the necessary equilibrium and reaction rate produces a rise in temperature. Subdividing the catalyst into several layers is one technique which can achieve this temperature control. In this technique, between the layers, the gases are cooled either directly by adding cooled synthesis gas or indirectly by generating steam. Various converter designs can be utilised for this purpose.

For ammonia condensation from the loop, cooling with just water or air is insufficient to achieve low ammonia concentration at the inlet. For this reason vaporising ammonia is used to chill the gas. The ammonia vapours are liquefied by means of a refrigeration compressor. The various synthesis configurations may differ with respect to the point where the make-up gas is added or where liquefied ammonia and purge gas is withdrawn.

New developments refer to the use of more active catalysts such as cobalt-promoted iron and ruthenium. These catalysts allow a lower synthesis pressure and allow a lower energy consumption to be achieved.

Conventional reforming with methanation as the final purification step produces a synthesis gas containing unreacted gases and inerts (methane and argon) In order to prevent the accumulation of these inerts a continuous purge gas stream has to be applied. Purge gas basically contains ammonia, nitrogen, hydrogen and inerts. The size of this purge stream controls the level of inerts in the loop, keeping these to about 10 - 15 %. The purge gas is scrubbed with water to remove ammonia, before then being used as fuel or before being sent for hydrogen recovery.

Steam and energy system

The high amount of surplus heat available from the flue-gas of the primary reformer, secondary reformer, shift conversion and the ammonia synthesis requires the design of an efficient overall steam system in which high-pressure steam, usually in excess of 100 bar, is generated. Generally all the high-pressure steam will be fed to steam turbines driving the synthesis gas compressor. At an intermediate pressure level a part of the steam is extracted from this turbine to supply the process steam for the reforming reaction and to drive other compressors, pumps and fans. The rest of the steam in the main turbine is condensed. Modern ammonia plants do not import energy to drive mechanical equipment, but in fact most cases export energy to other consumers either as steam or as electricity. A way to improve the plant efficiency is to use a gas turbine to drive the air compressor and to use the hot exhaust gases as preheated combustion air for the reformer. In this case the energy loss encountered by steam condensation in the usually employed steam turbine is avoided.

The same approach is also applied for the refrigeration compressor, which is needed for condensation of the ammonia product, and for the compressor used for pressurising process air in the secondary reforming step. A special advantage of these machines is that they can be driven directly by steam turbines, using steam generated in the plant mainly from waste heat. This allows an efficient integration into the energy system of the whole plant. In addition, the high degree of reliability and the lower investment and maintenance costs compared to reciprocating compressors improve the plant economics.

1.1.1.3 Steam reforming with excess air secondary reforming

Some processes are designed for reduced primary reforming by transferring some of the duty to the secondary reformer because of the marginal low efficiency of the primary reformer.

Decreased firing in the primary reformer

In this configuration the transfer of some of the primary reformer function to the secondary reformer reduces the level of primary reforming that is carried out. The consequence of this is less firing and a correspondingly lower NO_X formation. The heat supply in the primary reformer is reduced and the process outlet temperature is lowered to about 700 °C, the firing efficiency is increased, and the size and cost of the primary reformer are reduced. The milder operation conditions prolong the life of catalyst tubes and the outlet header. The extent of reforming is reduced according to the lower heat supply and lower temperature. There is a slight decrease, in steam to carbon ratio, compared to the conventional concept but this is acceptable.

Increased process air supply to the secondary reformer

A decreased heat supply in the primary reformer means that increased internal firing is necessary to achieve approximately the same degree of total reforming. A somewhat higher methane slip, and this results in a lower secondary reformer outlet temperature which is acceptable and preferable in this type of process, as any methane will be removed in the final purification step.

The process air requirement is up to 50 % higher than in the conventional process. This requires an increased compression capacity and energy consumption. The process air compressor can be driven by a gas turbine, with the exhaust gas from the turbine being used as combustion air in the primary reformer. Some excess steam is available for export when a gas turbine is used.

Shift conversion, CO_2 removal and methanation

These steps are not significantly different to the conventional process. Figure 1.3.

Cryogenic final purification

In the Purifier process, excess nitrogen, residual methane and part of the argon are removed from the synthesis gas by condensation at a temperature of around -180 °C. The separated methane and nitrogen mixture is used as fuel in the primary reformer. The purified synthesis gas is then almost free of impurities, except for a small amount of argon. Compared to the conventional process, the high degree of purity avoids a sizeable purge gas stream in the ammonia synthesis loop. The flash gas which originates from depressurising the condensed ammonia, does entrain a the small amount of argon still in the loop. The cooling energy is provided by expansion of the main gas stream in a turbo expander and by the expansion of the methane containing waste gas fraction.

Ammonia synthesis

The removal of essentially all the impurities from the make-up synthesis gas is a significant improvement, compared to the conventional purification by methanation only. Together the higher conversion per pass and reduced purge flow result in a more efficient process.

1.1.1.4 Heat-exchange autothermal reforming

From a thermodynamic point of view it is wasteful to use the high level heat of the secondary reformer outlet gas and the primary reformer flue-gas, both at temperatures of around 1000 °C, just to raise steam. Recent developments aim to recycle this heat to the process itself, by using the heat content of the secondary reformer gas in a newly developed primary reformer (gas heated reformer, heat-exchange reformer), thus eliminating the need for a fired furnace. Surplus air or oxygen-enriched air is required in the secondary reformer to meet the heat balance in this autothermal design.

Emissions to the atmosphere are reduced significantly by eliminating the flue-gas from the primary reformer. NO_X emissions may be reduced by 50 % or more, depending on the extent of auxiliary combustion in the plant compared to conventional steam reforming.

So far only three installations of small capacity (about 500 t/d each) have been built and operated. Capacities of about 1000 t/d seem to be feasible for single stream units [2, EFMA, 2000], but future developments will probably increase the capacity limit.

1.1.1.5 Partial oxidation

The partial oxidation process is used for the gasification of heavy feedstocks such as residual oils and coal. The process is very flexible and can handle the full range of hydrocarbon feedstock, from natural gas up to the heaviest asphalt including waste materials such as plastics.

Air separation plant

This produces the oxygen required for the partial oxidation step. This unit also supplies pure nitrogen for the stoichiometric demand in the ammonia synthesis reaction and for the liquid nitrogen wash applied for the final purification of the synthesis gas.

Gasification of heavy hydrocarbons

The gasifier consists of an empty pressure vessel lined with heat resistant alumina bricks. Hydrocarbons, oxygen and steam are introduced through nozzles and react non-catalytically to yield carbon monoxide and hydrogen at elevated pressures up to 80 bar:

$$2CH_n + O_2 \rightarrow 2CO + nH_2$$

Apart from CO and H_2, the reaction gas (raw gas) contains about 4 – 5 % CO_2, 0.5 % CH_4 and 1.5 – 2 % soot based on the amount of feedstock material. The CO/H_2 ratio depends on the feedstock composition and the quantity of steam added to atomise the feedstock and to moderate the reaction, which raises the temperature in the gasifier up to 1400 °C.

The hot raw gas containing soot is cooled either by water quench or in a waste heat boiler. The carbon is subsequently removed by water scrubbing in a packed tower. Different methods can be applied for recovering and recycling the soot. In one process it is extracted with naphtha. After separation from the water, the soot -naphtha suspension is mixed with the hydrocarbon feedstock and the naphtha is topped off in a distillation column. The topped naphtha is recycled to the extraction section. The resulting carbon/heavy hydrocarbon mixture is recycled to the partial oxidation reaction. Another variant extracts the soot with light gas oil in the form of carbon pebbles. These are screened off and recycled to the heavy hydrocarbon feed. The extracted water is returned to the soot scrubbing section. Heavy metals such as nickel and vanadium (introduced with the feedstock) are suspended as oxides and are partially also present as salts in the soot water circuit. To prevent an accumulation of these compounds in the water circuit, some of the extracted water has to be drained. The drained water is cleaned by flocculation, applying settlers and/or filters, and disposed off after a biological treatment. A vanadium and nickel containing paste is recovered and sold to the metallurgical industry.

Gasification of coal

For ammonia production, there are presently two gasifier types commercially used, the "entrained flow gasification" and the "moving bed gasification". The applied pressures range from 30 to 80 bar.

The entrained flow gasification corresponds basically to the partial oxidation concept of heavy hydrocarbons and takes place in an empty pressure vessel. The differences from the partial oxidation route are mainly in the method of introduction of the feedstock into the gasifier. The coal is fed to the gas generator either as dry dust via lock hoppers and rotary feeders or introduced as concentrated water/coal slurry by means of a reciprocating pump. Flow direction and use of waste heat boilers or quench and their degree of process integration may differ in the individual processes as well as the provisions to collect and remove the slag at the bottom of the gasifier. The separation of entrained coal dust from the raw gas, also contains some fly ash, is very similar to carbon removal in the gasification of heavy hydrocarbons. Reaction temperatures are around 1500 °C. The raw gas has a low methane content (0.4 %), a moderate CO_2 content and CO/H_2 ratios larger than 1.

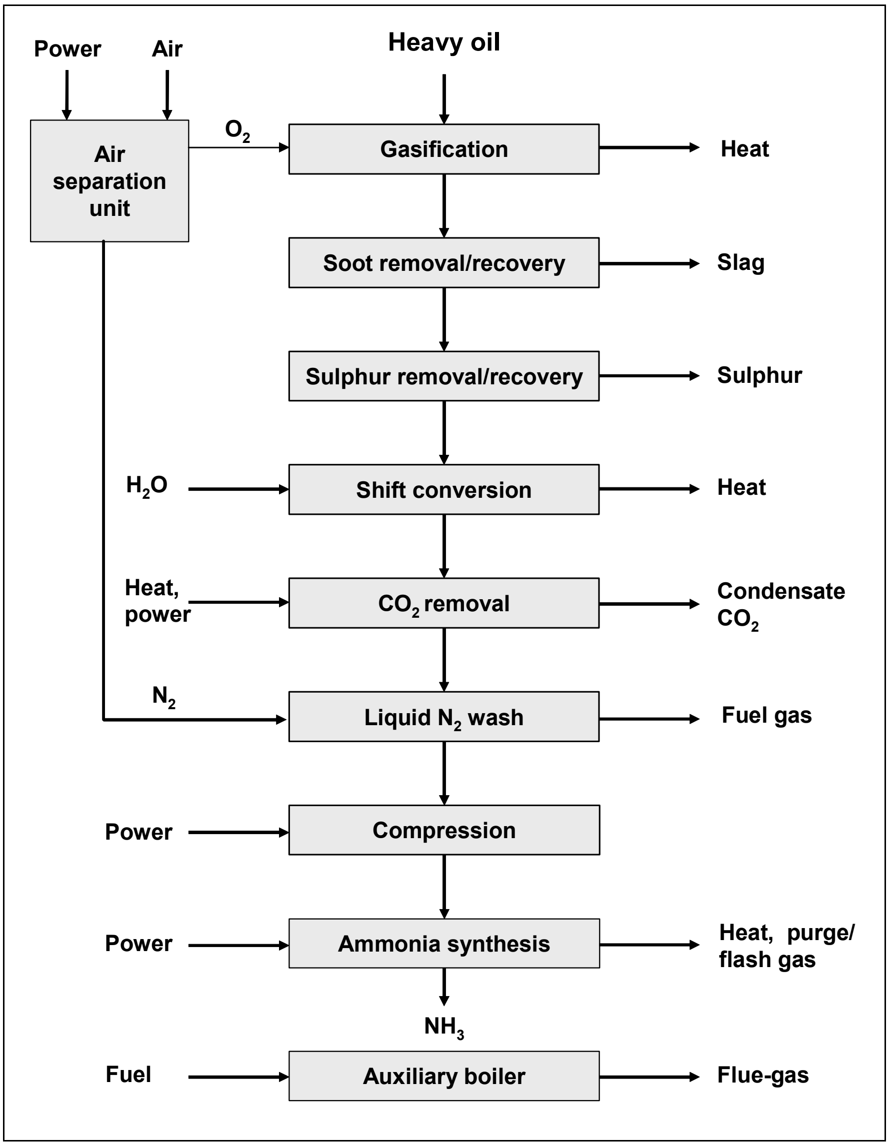


Figure 1.4: Ammonia production by partial oxidation
[13, EC, 1997]

In the moving bed process, coarse grained coal (4 to 30 mm) enters at the top of the gasifier via a lock hopper and is evenly distributed over the cross-section of the surface of the coal bed. The coal moves very slowly downward, and the gas leaves at the top of the gasifier at flowrates smaller than the minimum fluidising velocity. Ash is removed at the bottom of the gasifier using a revolving grid with slots through which the gasifying agents, oxygen and steam, are introduced. The temperatures are lower than in the entrained flow gasification: 1000 °C in the lower section of the bed and around 600 °C at the top where the gas leaves. Compared to the entrained flow gasification, the raw gas contains a higher amount of CH_4 and CO_2 and a lower CO/H_2 ratio because of the higher amount of steam, which causes the water gas reaction to proceed parallel to the partial oxidation reaction:

$$C + \frac{1}{2} O_2 \rightarrow CO \qquad \Delta H_o = -100.6 \text{ kJ/mol}$$
$$C + H_2O \rightarrow CO + H_2 \qquad \Delta H_o = 175.4 \text{ kJ/mol}$$

The hot reaction gas (raw gas) is first quenched with recycled gas condensates from the subsequent waste heat boiler. Because of the lower gasification temperature (a feature which saves oxygen) the raw gas contains a higher amount of impurities, e.g. tars, phenols and some higher hydrocarbons, which are normally recovered from the gas condensates. Additional adsorptive pre-cleaning is necessary before the gas can be fed to subsequent process steps such as sulphur removal.

Sulphur removal

Sulphur originating from the feedstock (up to 7 %) is present in the raw gas, mainly as H_2S. Depending on the process configuration the raw gas is cooled further under waste heat recovery and scrubbed with a solvent, usually chilled methanol at -30 °C, whereby a CO_2/H_2S fraction is separated and fed to a Claus plant. In this unit, H_2S is converted to elemental sulphur by combustion with air using alumina catalysts. Claus plants need an abatement system to reduce SO_2 emissions.

In an alternative process, the raw gas is sent directly to the subsequent shift conversion without prior sulphur removal. In this case, H_2S is removed after the shift conversion together with the total CO_2 formed there.

Shift conversion

Depending on the gasification design, i.e waste heat boiler or quench, additional steam has to be supplied ahead of the shift conversion by saturation and direct injection. The conversion takes place step-wise over iron-chromium oxide shift catalysts with intermediate heat removal. A residual CO content between 2 and 3 % can be attained. Over the past twenty years sulphur resistant cobalt-molybdenum-containing catalysts have in part replaced iron-chromium oxide catalysts. These catalysts are active at temperatures ranging from 230 to 500 °C and allow shift conversion without prior sulphur removal. In this case, the sulphur is recovered simultaneously with the CO_2 after the shift conversion. For the performance of the cobalt-molybdenum catalyst the presence of sulphur compounds in the gas is essential.

CO_2 removal

After cooling the exit gas from the shift conversion, the process condensate is separated. The gas is chilled and scrubbed with chilled methanol, which absorbs CO_2 and H_2S. Stripping regenerates the loaded methanol. In the process version without sulphur removal ahead of the shift conversion, two fractions are received in the regeneration: one is pure CO_2, which may be used for urea or other purposes, the other contains H_2S/CO_2 and is fed to a Claus plant.

Liquid nitrogen wash

For the final purification, normally liquid nitrogen at about –185 °C is used to remove residual CO, CH_4, and most of the argon. At the same time nitrogen is added to the synthesis gas. To prevent blocking of the cryogenic unit the traces of CO_2 are separated from the inlet gas by molecular sieve adsorption. The resulting synthesis gas is highly pure and purging in the synloop is minimised. The rejected waste gas fraction serves as a fuel.

Ammonia synthesis

The ammonia synthesis loop is identical to the synthesis for steam reforming.

Compression, steam and energy system

The degree of energy integration is lower than in the conventional steam reforming process. Separate auxiliary boilers are necessary to provide steam for mechanical energy and power generation, because of the absence of hot reformer flue-gases. The NO_X emitted in this process mainly originates from the flue-gas of the auxiliary boiler and fired preheaters. Centrifugal compressors are used to compress make-up gas and recycle gas, for air, the oxygen needed in the gasifier, nitrogen used in the liquid nitrogen wash and the ammonia synthesis loop. Steam turbines and occasionally electrical energy are used to drive these compressors.

1.1.1.6 Ammonia production using hydrogen from water electrolysis

The production of hydrogen and oxygen by the electrolysis of water has been carried out on an industrial scale since the beginning of the 19th century. Electrolytically produced hydrogen can be used directly for the production of ammonia, and such operations exist today in Egypt, Iceland and Peru.

In this process, hydrogen from the water electrolysis plant and nitrogen from the air separation plant pass to separate storage vessels, providing a buffer capacity and a stabilised gas pressure. Water electrolysis gives an extremely pure feed gas, containing only a very small amount of oxygen (0.1 – 0.2 %), compared to the synthesis gas generated from a hydrocarbon feedstock. Oxygen acts as a poison to the ammonia converter catalyst and has therefore to be removed. This is done by means of catalytic combustion, which takes place immediately after the mixing of hydrogen and nitrogen. A small amount of hydrogen reacts with the oxygen present producing water. The purified mixed gas (make-up gas) is then passed to a storage vessel that serves as a buffer for the ammonia synthesis stage. The synthesis loop is the same as for fossil fuel-based ammonia plants.

Ammonia production based on water electrolysis is carried out in small-scale plants of up to 500 t/d. The process is generally not considered economically viable. However, under certain circumstances, it can still be an interesting and competitive technology, in particular when cheap hydroelectric power is abundantly available.

Direct emissions from this process are minimal compared to the steam reforming and partial oxidation process.

1.1.1.7 Storage and transfer equipment

Liquefied ammonia from production plants is either used directly in downstream plants or transferred to storage tanks. Road tankers, rail or ships are used to transport stored ammonia to other users.

Ammonia is usually stored by using one or other of the following methods [2, EFMA, 2000]:

- fully refrigerated storage in large tanks with a typical capacity of 10000 to 30000 tonnes (up to 50000)
- pressurised storage spheres or cylinders up to about 3000 tonnes
- partially refrigerated tanks.

A well designed, constructed, operated and maintained installation has a very low probability of an ammonia leak of hazardous proportions. However, even though the residual risk is small, the effect of a major leak on areas of high population density can have a serious consequence. It is sensible practice therefore to build ammonia storage and handling installations at a safe distance from domestic housing, schools, hospitals or any area where substantial numbers of people may be present.

It is undesirable for ammonia storage tanks to be sited close to installations where there is a risk of fire or explosion, since these could risk the integrity of the tank and increase the possibility of an accidental release of ammonia into the environment.

1.1.1.7.1 Storage vessels

Anhydrous ammonia is stored in three types of vessels as outlined above:

- fully refrigerated at a temperature of about -33 °C, these tanks are provided with refrigeration equipment
- non-refrigerated tanks in which the ammonia is stored under pressure at ambient temperature
- semi-refrigerated spheres are at a temperature of about 0 °C to -5 °C at a pressure close to 5 bars absolute.

Refrigerated storage is preferred for the storage of large quantities of liquid ammonia [2, EFMA, 2000], as the initial release of ammonia in the case of a line or tank failure would be much slower than with pressurised ammonia.

There are several construction types for the storage of fully refrigerated liquid products. The most important types are:

Single wall tanks, which are tanks with one steel bottom and wall designed to contain the full liquid level of ammonia.

Double wall tanks, which are tanks with double steel bottom and wall, each designed to contain the full liquid level of ammonia.

For reasons of better understanding the difference between single and double wall, and the meaning of full containment, one or more of the following containment systems may be considered:

1. inner steel tank designed for the full containment of liquid ammnia
2. outer steel tank designed for the full containment of liquid ammonia, the roof may be separate for each inner or outer tank or common
3. concrete or steel wall designed as extra tank protection, not designed for containing liquid ammonia
4. bund wall (or dike) with height and distance designed to contain liquid ammonia that may be released from the ammonia tank in an accidental situation.

In general tanks must be constructed in conformity with an agreed code for the construction of pressure vessels or storage tanks taking account of the pressure and operating temperature. The storage tank must be safeguarded against high pressure and in the case of refrigerated liquid ammonia, also against a pressure below the minimum design pressure. Under certain conditions, warm liquid ammonia can be temporarily blocked in an unstable equilibrium under colder layers of liquid. The raising of hot liquid can induce an intensive vaporisation and an excessive pressure that may be hazardous for the storage vessel. It is important to use appropriate equipment that eliminates the risk of introducing or trapping hot product at the bottom of the vessel. All storage tanks should be equipped with two independent level indicators, each with a high level alarm.

An automatic cut-off valve, operated by a very high level alarm instrument, should be fitted when filling rates are high relative to capacity, such as when importing from a ship.

If a leak occurs, it should be possible to detect it with an alarm. It should be possible to pump the spill out from the containment bund. Covering the liquid with polyethylene sheeting can be beneficial; containment of the vapour with foam is also a possibility [14, EA, 1999]. Properly composed foam will not contain so much water that the heat of solution substantially increases the evaporation rate of the ammonia. A quantity of water in the foam is claimed to be beneficial, however, in capturing that part of the ammonia, which evaporates, and in providing vapour warming, thereby aiding buoyancy and dispersion.

In cases of refrigerated liquid ammonia, storage tanks must be equipped with a recompression installation to liquefy the boil-off. There should be at least two refrigeration units to allow proper maintenance and to prevent the emission of ammonia via the relief valves. Furthermore, an installed alternative power supply may be necessary. An automatic discharge system to a flare or to safe location may be located at a suitable distance from the tanks.

Relief valves should be provided, appropriate for the duty, using an adequate margin between operating and relief pressure.

1.1.1.7.2 Transfer equipment

Liquid or gas pipelines may be fitted with isolation valves. Remotely operated valves may be installed to back up the main isolation valves. The remote systems are designed of such a type that closure is automatic in case of a power failure. Liquid ammonia has a high thermal coefficient of expansion and, therefore, some means of safe venting is recommended on pipelines in which any significant quantity can be trapped between valves etc.

Liquid ammonia pipelines are normally fitted with remotely operated valves at suitable intervals to minimise the loss in the event of a line failure.

Ammonia can be transported in road tankers or rail tank cars (both pressurised) and ships (pressurised or refrigerated).

1.1.2 Current emission and consumption levels

The descriptions which follow are for typical plants. Plant configuration will vary from plant to plant. Operating parameters such as temperatures, pressures, compositions will also vary considerably from the values quoted.

The ammonia production process needs certain energy inputs to sustain the operations but the main purpose is to utilise the energy generated and either use this in the proces and/or export the excess to other users co-located on the site. The energy management in an integrated site is crucial to ensure an efficient use of energy in the form of steam/electricity.

1.1.2.1 Input

1.1.2.1.1 Feedstock

The typical feedstock requirements for modern plants are (approximately):

Conventional reforming	22.1 GJ (LHV)$t^{-1}NH_3$
Excess air reforming	23.4 GJ (LHV)$t^{-1}NH_3$
Autothermal reforming	24.8 GJ (LHV)$t^{-1}NH_3$
Partial oxidation	28.8 GJ (LHV)$t^{-1}NH_3$
LHV= Lower heating value	

Table 1.6: Ammonia feedstock energy requirements
[2, EFMA, 2000]

1.1.2.1.2 Fuel to generate heat

Assuming an efficient stand-alone plant with no energy export and no other import other than feedstock and fuel, the fuel requirements are (approximately):

Conventional reforming	9.2-9.0 GJ (LHV)$t^{-1}NH_3$
Excess air reforming	5.4-7.2 GJ (LHV)$t^{-1}NH_3$
Autothermal reforming	3.6-7.2 GJ (LHV)$t^{-1}NH_3$
Partial oxidation	5.4-9.0 GJ (LHV)$t^{-1}NH_3$

Table 1.7: Ammonia fuel requirements
[2, EFMA, 2000]

The unpredictabiliy in autothermal reforming is mainly due to the type of compressor drives.

1.1.2.1.3 Water and air

Process steam is taken from the plant steam system in the steam reforming processes, usually from an extraction turbine. The net consumption of steam according to the stoichiometic conversion is 0.6 - 0.7 kg/kg NH_3, and the total supply at a S/C ratio of 3.0 will be about 1.5 kg/kg NH_3. Much less steam is fed to the gasification reactor in partial oxidation, but additional steam is needed in shift conversion (1.2 kg/kg NH_3 in total) [2, EFMA, 2000].

Process air supply

In conventional reforming the nitrogen supply equals the ammonia nitrogen content plus the purge losses, i.e. about 0.85 kg N_2/kg NH_3 or about 1.1kg air/kg NH_3. The process air requirements are about 50 % and 100 % higher in the excess air reforming and gas heated reformer cases, respectively. The amount of air fed to the air separation unit is approximately 4kg/kg NH_3, based on the oxygen requirement in the partial oxidation process [2, EFMA, 2000].

Boiler feed-water

Only the process steam consumption has to be replenished by outside water, assuming all steam condensates are recycled. This amounts to 0.7 – 1.5 kg/kg NH_3 depending on whether the process condensate is recycled or not. Small additional losses and potential import/export of steam have to be allowed for in practice. Air and/or water for cooling will differ from one site to another.

1.1.2.1.4 Solvents and additives

Solvent consumption in the CO_2 removal unit should not normally exceed 0.02 – 0.04 kg/t NH_3, [2, EFMA, 2000] or about 2 kg/h for an optimum capacity plant. Solvent losses are caused mainly by leaks.

Standard treatment additives and regeneration agents are used in the boiler feed-water treatment units. Consumption figures should not differ from those of a standard steam boiler plant at the same location.

1.1.2.1.5 Catalysts

Approximate consumption figures, based on average filling volumes and normally recommended operating periods, for a gas based conventional reforming plant, are given in the table below. The usage refers to a 1500t/d capacity.

Catalyst use	Typical replacement m^3/year
Hydro-desulphurisation	1
Sulphur removal	5
Primary reforming	5
Secondary reforming	4
High temperature shift	10
Low temperature shift	20
Methanation	2
Synthesis	10

Table 1.8: Actual usage of catalysts
[2, EFMA, 2000]

Actual usage in existing plants may differ considerably from the guidance figures above.

1.1.2.1.6 Energy requirements

The total energy requirement in the reforming processes is 28.5 – 31.5 GJ(LHV)/tonne for a stand-alone plant with no energy export and no import other than feedstock and fuel. When using process waste heat in a gas heated reformer, the process itself will not produce sufficient steam to drive all the compressors. It may be necessary therefore to import power from a more efficient energy supply from outside the plant but within the integrated energy management complex of adjacent process plants. Alternatively energy may be imported from the electricity supply grid if this is more economical. In such cases the total energy consumption may be lowered to approach the present practical minimum of 36.9 (35.1-37.8) GJ (LHV)/tonne.

The total energy requirement is about 41 (39 – 42) GJ (HHV)/tonne in partial oxidation plants. This includes imported power and/or auxiliary steam for driving the machinery.

1.1.2.2 Output

1.1.2.2.1 Ammonia

Ammonia production in a typical optimum sized plant is 1000 – 1500 t/d (300000 - 500000 tonnes/yr) [2, EFMA, 2000]. Product is stored if not utilised.

Commercial anhydrous ammonia has two grades of purity:

- anhydrous ammonia min. 99.7 wt %, water content (about 0.2 % wt)
- anhydrous ammonia min. 99.9 wt %.

1.1.2.2.2 Carbon dioxide

Carbon dioxide is produced in accordance with stoichiometric conversion and can be recovered for further use as feedstock in a urea plant, in the beverage industry or as a coolant gas in nuclear reactors. There is however an inevitable excess of CO_2 which is released as an emission from the process. The carbon dioxide production in the steam/air reforming of natural gas is 1.15 - 1.30 kg/kg NH_3, dependent on the degree of air reforming. A CO_2/NH_3 mole ratio of 0.5 (weight ratio 1.29), the stoichiometric ratio for urea production, is obtainable in the heat exchange reformer concepts. CO_2 production is 2 – 2.6 kg/kg NH_3, dependent on the feedstock C/H ratio in partial oxidation of residual oils [2, EFMA, 2000].

1.1.2.2.3 Sulphur

In partial oxidation most (87 – 95 %) of the sulphur content of the gasifier feed is recovered in the Claus unit.

1.1.2.2.4 Steam export

Modern steam reforming processes can be designed with no steam export or with some export if this is favourable for the site energy balance of low/medium pressure steam. Surplus steam is usually produced in reforming processes where the process air compressor is driven by a gas turbine and in cases when electric power is used for the main compressors and can be used as export.

Processes with gas heated primary reforming may be designed for zero steam export even though some power import or gas turbine drive steam input is needed.

The partial oxidation process will have a steam deficit if all of the compressors are driven by steam.

1.1.2.3 Emission sources

1.1.2.3.1 Emissions during operation

Desulphurisation

The hydrocarbon feedstock is usually preheated to around 350 °C, normally by using either convection section flue-gases or a fired heater. Another option is to preheat the feedstock with the primary reformer flue-gases by indirect heat exchange, depending on the plant design. A low temperature desulphurisation system could operate with steam heating.

The quality of the flue-gas depends on the fuel used if a fired heater is used. This fuel is often the same as the feedstock, depending on the design of the combustion system. The concentration of SO_2, NO_X, CO and particulates in the flue-gas is equivalent for any fired heater operating with a comparable fuel.

Primary reformer

The major continuous atmospheric emission from an ammonia plant is flue-gas from the primary reformer. The total amount depends on the process efficiency and on the reformer design. The design of the reformer can take into account the excessive use of process air by distributing the air usage with the secondary reformer.
The main constituents of the flue-gas are atmospheric nitrogen, oxygen, carbon dioxide, water, carbon monoxide, nitrogen oxides, sulphur oxides, unburnt hydrocarbons and particulates.

Process condensate

Process condensate is produced throughout the process. The majority condenses out as the process gas cools from the low temperature shift exit temperature of around 230 °C. Other major sources are from the condensers removing water from the CO_2 regenerator top exit stream.

Process condensates contain ammonia and other compounds formed as by-products of the LT shift and other reactions. This includes methanol, acetic acid, formic acid, methylamines, dimethylamines and trimethylamines. Much of the methanol is produced in the LT shift reactor. The methanol concentration in the condensate is highest when the catalyst is new.

The following Table 1.9 shows the typical composition for the condensates on a 1000 t/d plant. This data is illustrative only.

	Units	Outlet HTS	Outlet LTS	Inlet CO_2 absorber	CO_2 regenerator
pH		8.2	8.8	7.6	6.8
NH_3	ppm w/w	895	455	1490	500
CO_3^{2-}	%	0.26	0.10	0.47	0.21
CH_3OH	ppm w/w	20	300	840	1100
HCOOH	ppm w/w	30	20	30	15
CH_3COOH	ppm w/w	29	<3	<3	<3
Methylamines	ppm w/w	<0.5	27	21	4
Dimethylamines	ppm w/w	<0.5	13	9	<0.5
Trimethylamines	ppm w/w	<0.5	5	23	<2.5
Flow	t/h	-	17	35	37

Table 1.9: Type of catalyts and temperature influence on condensate compositions
[14, EA, 1999]

Carbon dioxide removal

Carbon dioxide is released from the desorption unit of the carbon dioxide removal process. In some plants water vapour is normally condensed by indirect heat exchange, which also entrains ammonia vapour. Absorption liquid entrainment in the carbon dioxide stream is typically a few milligrams per cubic metric.

The carbon dioxide from ammonia plants is quite often used in other plants, either completely or in part. Some examples of uses include urea and/or methanol production or liquefaction. Liquid carbon dioxide is used in gas cooled nuclear power stations and in the beverage industry.

There are occasional effluents from the absorption liquor system itself, depending on the specific process used. In some cases, such as old MEA units, the reagent tends to degrade and requires regeneration, which leaves sludge for disposal. In some cases, the corrosion inhibitors contain vanadium, which will also be present in any leaks and purges. One of the carbonate systems, Vetrocoke, involves the use of arsenic oxide. However this is generally now being phased out globally because of water contamination risks [14, EA, 1999].

Benfield carbon dioxide removal systems have had problems with foaming which results in liquor entrainment up the desorber and out through the vent. A small bunded concrete area is sometimes installed to contain this overflow liquor. The risk of this foaming occurring can be minimised by installing a liquor cooling system.

Compression

A small quantity of condensate is removed during synthesis gas compression. This is substantially free of soluble organics such as methanol as the gas passes through the wet CO_2 absorption system. The lubricating oils can often contaminate the compressor condensate. To solve this the condensate is normally passed through an oil/water separator, perhaps as part of a common site effluent treatment, before discharge to sewer.

Oil from the compressors is a possible source of effluent. Compressor seals are generally of the oil film-oil bushing type with vented traps. Gas from the seals can be treated in a number of ways. Direct return to the process stream is one option. Scrubbing with water is another alternative. The liquor can also be used together with the process condensate feed to the stripper. Gross contamination of the lubricating oil can be minimised by proper design and operation.

Pollution control on the compression in the refrigeration systems will be the same as for the synthesis loop circulator.

Purge gas

The total quantity of purge gas taken from the synthesis loop can be significantly reduced if the inerts are separated from the raw synthesis gas in a cryogenic unit before it enters the loop. This is usually applicable where the process makes deliberate use of excess air in the secondary reformer, so a large loop purge is unnecessary.

Purge gas contains mainly ammonia, nitrogen and hydrogen, along with gases such as argon and methane. The purge is designed to remove these gases. Ammonia is recovered from the purge gas leading to a minimisation of the NO_X produced in the primary reformer when purge gas is used as fuel. Hydrogen may also be recovered using selective permeable membranes of pressure swing adsorption (PSA). More elaborate cryogenic schemes can recover most components from the purge gas; this may be economically justified if recovered argon is to be sold. Ammonia removed from the purge gas by chilling will be anhydrous, and can be sent to storage. Aqueous ammonia will be produced if a wet scrubbing is used. The concentration and quantity of ammonia generally makes it economically viable to recover by steam stripping, for re-use.

Utilities

Waste heat in the conventional ammonia plant is used to raise steam. This process steam can be used to drive the process compressors and larger pumps.

The steam/power system is of environmental interest as increased thermal efficiency generally results in a reduced use of fuel and a consequently lower emission [14, EA, 1999].

Boiler blowdown is typically one or two per cent of steam production and might contain, for example, sodium phosphate and sodium hydroxide. It is usually sent after flashing and cooling, to the site effluent disposal. Occasionally, the boilers will be chemically cleaned, which will also result in a liquid effluent.

Water treatment units produce effluents from the regeneration of the ion exchange by caustic (sodium hydroxide solution) and either sulphuric acid or hydrochloric acid. At the end of their life, the ion exchange resins must be removed and replaced. Also sludge is often produced from the preliminary softening of the raw water precipitation of calcium and magnesium compounds.

Cooling water is also a source of effluent. Cooling water blowdown contains treatment chemicals such as chromates and fungicides. This blowdown is usually sent to the site effluent treatment for, pH adjustment.

The effluents from the waste heat boilers, the auxiliary boilers, the water treatment plant and the cooling towers will be virtually the same as for these units on any process plants. The pollution control techniques will also be similar.

Steam is used as a process fluid in the reforming reaction. Any contaminants in the steam could find their way into other effluents such as the process condensate, the CO_2 vent, or the product. No evidence of any such contamination, such as by hydrazine, is reported by producers.

It is possible that ammonia or other process components may enter the cooling water, either if the stripped process condensate is used as cooling tower make-up or if there is a minor equipment leakage. Some ammonia may be stripped into the air in the evaporative cooling tower. Control precautions are needed which include stripping the process condensate as far as practical and maintaining the integrity of the equipment by proper maintenance.

If stripped process condensate is treated to produce boiler feed-water, then there is a possibility that remaining contaminants could enter the regeneration stream or pass to atmosphere from the degasifier. Once again, producers do not report this and the quantities would in any case be very small. Saturation of the natural gas with the process condensate avoids any of these possibilities, but requires a significant change in the steam/heat/power balance.

1.1.2.3.2 Periodic releases

Start up and shutdown

The ammonia plant is started up in stages. Nitrogen, heated by the primary reformer furnace is circulated and then steam is fed to the reformer from an auxiliary boiler. The feed gas is passed initially through the desulphuriser and then to the reformer. The product gases are vented, subsequent parts of the process are then started-up, with a subsequent venting of each stage. The converter in the synthesis loop is usually brought up to temperature using a fired start-up heater.

The full start-up sequence may take one or two days. Shutdown is a reverse of the start-up procedure. Usually the ammonia plants run continuously for several years with only minor interruptions that require a partial shutdown.

These procedures need atmospheric venting of large volumes of gases, usually containing hydrogen, carbon monoxide, methane and perhaps ammonia. The flows are usually less than half the full capacity flowrate. The main question of pollution control is how to dispose of these gases. One practice is to vent to a safe location. If loop purge gas is vented, it is usual to first remove the ammonia by scrubbing or other means. The alternative to venting at a safe location is to flare the vent gases. The vent gases are strongly combustible as they contain hydrogen, carbon monoxide, and methane. If not flared, spontaneous ignition may occur at the top of the vent.

Catalyst replacement

All the catalysts in the plant require replacement at the end of their useful life. The life of each catalyst varies from four years to, in the case of the methanator, twelve years [14, EA, 1999].

Catalysts are used for desulphurisation, primary and secondary reforming, shift reactors, methanation and the synthesis converter. If zinc oxide is used as a desulphurisation guard bed, the resulting zinc sulphide will also need periodic disposal. With essentially sulphur free natural gas the zinc oxide charge life may exceed 15 years.

These solids are normally removed from the site at a cost by a specialist contractor and taken for valuable metal recovery and controlled final disposal.

1.1.2.3.3 Vents and leaks

Pressure relief

Pressure relief valves are essential in, for example, situations where liquid ammonia may be contained by valving in an enclosed system. As is generally the case, the setting between the operating pressure range and the relief pressure needs to be set so that the relief system is actually used only in substantially abnormal conditions.

Vent flaring is currently used by a number of companies. Ammonia in particular is difficult to fully combust as it has a narrow range of flammability in air of 15 to 25 % by volume. This must be taken into account in the design of the burners and in the use of a continuous pilot flame.
Releases of ammonia to atmosphere due to emergency venting could give rise to a mist if acid gases are also present in the locality.

Leaks

Other sources of ammonia emmissions could be leaks probably through flanges, valve packing or pump seals. Pumps, flanges and valves used in handling of CO_2 absorption liquor are potential sources of liquid leaks. Such leaks are of less concern than ammonia leaks, because the liquid can be contained and handled without evaporation but design features such as mechanical pump seals are common practice.

Maintenance

Where possible significant quantities of liquid ammonia should be recovered, e.g. by sending to storage and vapour must be vented at a height for safe dispersion to the environment. This includes venting to the site flare system or to the storage tank vent system.

Ammoniated liquor spills, perhaps resulting from the washing down of minor ammonia spills, must be sent to a tank or sump with contained vents quickly, prior to treatment by stripping.

Containment of the CO_2 absorption liquor is needed during maintenance.

1.1.2.3.4 Emissions to air/steam reforming process

The main emission source in the ammonia production process is from the primary reformer section. This is usually a fired reactor, often backed by auxiliary boilers. The main pollutant is NO_X. Other pollutants in relatively low amounts, such as SO_2, CO, and particulates, are also released. CO_2 is also released due to the use of fossil fuels. Energy efficiency improvements to the process will automatically lead to lower CO_2 releases. The lowest NO_X levels reported are achieved by application of low-NO_X burners in addition to standard practices such as purge gas treatment and process optimisation.

The CO_2 removal unit is an important source of CO_2. Here nearly pure CO_2 is vented to the atmosphere. Traces of the solvents used, usually amines, are also released. CO_2 is used as feedstock for the production of urea in some plants, thus utilising the CO_2 rather than releasing it to the environment.

1.1.2.3.5 Discharges to water

Process condensates, mainly surplus steam from the shift conversion and minor quantities from other operations (CO_2 removal regenerator, compressor), are the main sources of pollution to water. The main pollutants are ammonia and methanol. Other compounds occurring in lesser amounts are acetic acid, formic acid, methylamines, dimethylamines and trimethylamines. Compressor condensates are likely to be contaminated by lubricated oils. Depending on the applied techniques the stripping operation can lead to air pollution. Medium-pressure steam stripping is preferable to minimise pollution when compared to air stripping.

1.1.2.3.6 Solid wastes

Solid wastes arise from spent catalysts in nearly all process steps (primary reforming, secondary reforming, shift conversion, methanation and synthesis). Specialised companies recover valuable materials from these spent catalysts.

1.1.2.3.7 Periodic releases

Periodic releases can occur during start-up/shutdown operations, trip-conditions, flaring, venting, and from leaks and fugitive sources. The initial start-up is usually the most severe because of its duration. The normal vent points are the desulphuriser's outlets, the high-temperature shift reactor outlet, the CO_2 absorber inlet, the methanator inlet and outlet, the ammonia converter outlet and the purge from the synthesis loop and refrigeration system. The pollutants comprise NO_X, SO_2, CO, H_2, and natural gas. Releases of NO_X during synthesis gas flaring at start-up or trips is estimated to be 10 - 20 kg/hour as NO_2 [13, EC, 1997].

Emissions summary

The following table shows the emission levels of existing steam reforming plants in the EU:

Emission sources	Pollutants	Emission Levels		
		Air	Water	Land
Desulphurisation	Catalyst			6 m^3/yr
Primary reformer	NO_X	0.2 - 0.4 g/Nm^3 0.6 – 1.3 kg/te NH_3		
	SO_2	0.1 - 2 mg/Nm^3 <0.01 kg/te NH_3		
	CO_2	500 kg/te NH_3		
	CO	5 - 10 mg/Nm^3 <0.03 kg/te NH_3		
	Particulates	5 mg/Nm^3		
	Catalyst			5 m^3/yr
Secondary reformer	Catalyst			4 m^3/yr
Shift reactors	Catalyst			30 m^3/yr HT 10 m^3/yr LT 20 m^3/yr
CO_2 removal	CO_2	1200 kg/tonne NH_3		
	Amines	5 mg/Nm^3		
Methanation	Catalyst			2 m^3/yr
Synthesis section	NH_3	75 mg/Nm^3 <40 g/tonne NH_3		
	Catalyst			10 m^3/yr
Process condensates	NH_3	0.4 - 2 kg/t NH_3 35 - 75 mg/Nm^3	0.4 - 1.5 kg/te NH_3 10 g/te NH_3	
	CH_3OH		0.6 - 2 kg/te NH_3	
	All organics		20 mg/l BOD	
	Others		50 g/te NH_3	
These figures correspond to plant sizes in the range of 1200 - 1500 t/d.				

Table 1.10: Emissions summary of existing steam reforming plants in the EU [13, EC, 1997]

1.1.2.4 Emissions/partial oxidation

Generally the partial oxidation process is considered to have similar emission sources as the steam reforming process apart from the primary reformer flue-gas.

The auxiliary boiler, superheater and thermal post-combustion (includes and treats the emissions from the Claus plant, carbon-wash, carbon-water treatment, and pelletisation) are the main emission sources to air. The main pollutants of these sources are the following:

- **auxiliary boiler**: NO_X, SO_2, particulates, CO and hydrocarbons
- **superheater**: NO_X, CO, CH_3OH and H_2S
- **thermal post-combustion**: NO_X, SO_2, particulates, CO and hydrocarbons.

Other emission sources are process condensates, CO_2 removal and intermittent operations.

The main sources of water releases are from the scrubbing/stripping of process gases, cooling waters and surface water from the plant area. The key parameters considered in permits for waste water treatment in partial oxidation plants are the following: nitrogen, COD and BOD. [13, EC, 1997]

The shift reactors and synthesis section are charged with catalysts, which are replaced every 3 to 6 years. The used catalysts are disposed off. In many cases specialised companies recover the valuable metals.

The main source of continuously produced waste (filter sludge) is from the central waste water treatment plant. Other sources of solid wastes are from maintenance operations at the gasifier, which results in used bricks for disposal to landfills and solid oils to incinerators.

Emissions summary

The following table shows the emission levels of existing partial oxidation plants (feedstock: heavy hydrocarbons) in the EU:

Emission Sources	Pollutants	Emission Levels		
		Air	Water	Land
Gasifier	Carbon and slag		Traces	
Superheater	NO_X	200 - 450 mg/Nm^3		
	SO_2	0.1 - 2 mg/Nm^3		
	CO	10 ppmv		
Shift reactors	Catalyst			30 m^3/yr
CO_2 Removal	CO_2 (heavy HC_x)	2.5 te/te NH_3		
	CO_2 (coal)	4 te/te NH_3		
	Amines	5 mg/Nm^3		
	CH_3OH	100 ppmv		
	H_2S	0.3 ppmv		
Synthesis section	Catalyst			10 m^3/yr
Process condensate	NH_3	0.4 – 2 kg/te NH_3 35 – 75 mg/Nm^3	0.4 - 1.5 kg/te NH_3 10 g/te NH_3	
	CH_3OH		0.6 - kg/te NH_3	
	All organics		20 mg/l BOD	
	Others		50 g/te NH_3	
Auxiliary boiler	NO_X	700 mg/Nm^3		
	SO_2	1700 mg/Nm^3		
	CO	10 ppmv		
	Particulates	traces		
Syngas compressor	NH_3	traces		
Claus unit	SO_2	2 % of the S-content in fuel		

Table 1.11: Emissions summary of existing partial oxidation plants in the EU
[13, EC, 1997]

1.1.2.5 Emissions monitoring

As outlined already, the emissions of pollutants to be expected from ammonia production are mainly:

- CO_2, NO_X, SO_2, and CO in the flue-gas from steam reforming processes with a fired primary reformer and/or auxiliary boilers
- SO_2 from the sulphur removal and recovery systems in partial oxidation processes
- CO_2 and traces of removal solvents and synthesis gas in vent streams from the CO_2 removal system
- small non-continuous and fugitive emissions
- NH_3 and methanol in process condensates (if not recycled).

The following emissions into air should be monitored as part of a proper supervision:

- NO_X in flue-gases
- SO_2 in flue-gases (may be calculated by mass balance instead of monitoring emission, if S input is known)
- SO_2 and H_2S from sulphur removal/recovery systems in partial oxidation processes.

The other emissions into air do not need to be monitored. The CO_2 emission can be calculated from the fuel specification and energy consumption, The CO emission is fixed by the operating conditions and is usually stable and low. Non-continuous and fugitive emissions are difficult to measure. The frequency of monitoring depends on local circumstances and the operating stability of the actual plant. Under normal operating conditions, measurements once a month are usually sufficient.

Methods for discontinuous and continuous measurements of NO_X, SO_2 and H_2S are available and are to a large extent standardised at national level (Norme Belge/Belgische norm, British Standard, AFNOR, Verein Deutscher Ingenieure, Nederlands Normalisatie Instituut).

Chemiluminescence or photometry are the most widely used methods for NO_X. SO_2 is determined by Infra Red (IR) absorption techniques. Traces of H_2S are measured by lead acetate.

Emissions into water from new plants are virtually zero as process condensates are recycled and monitoring is not normally required. In existing plants without any recycling of process condensate, the ammonia and methanol content should be monitored.

1.2 Nitric acid

Nitric acid is a strong acid that occurs only in nature in the form of its nitrate salts. When the large-scale production of nitric acid first began, sodium nitrate (soda saltpetre, Chile saltpetre) was used as the feedstock but it has now been replaced by the oxidation of ammonia. Ostwald developed the crucial step in nitric acid production, the catalytic combustion of ammonia, around the turn of the 20th century. The most important design parameters for a nitric acid plant were determined first in laboratory tests and later in a pilot plant. The first production facility employing the Ostwald process came on stream in 1906 at Gerthe in Germany. Most of the nitric acid produced is used for inorganic fertilisers; it is mostly neutralised with ammonia to form ammonium nitrate [33, Ullmann`s, 2000]. Nitric acid is one of the most important inorganic chemicals. Quantitatively it is one of the top ten industrial chemicals. The European production capacity is 18384 kt/yr, most of it for fertilisers. Production has levelled off in the 1990s because of the increased use of urea. Other uses for nitric acid are in the manufacture of polyurethanes, fibres, explosives and the treatment of metals. Ammonia oxidation has become nowadays the basis of all commercial nitric acid production. A weak acid (relating to the greater part of the production of nitric acid) or strong acid can be produced depending of the application required: Weak acid (50 – 65 wt % acid) is suitable for use in the production of fertilisers, but stronger acid (up to 99 wt % acid) is required for many organic reactions.

1.2.1 Applied processes and techniques

At the end of 1992 a tentative survey of the type of plants still in operation within the European Community gave the following results. Plants are classified by oxidation pressure and absorption pressures.

Process type	No of plants
Dual pressure processes:	
Low pressure/medium pressure	9 (oldest plants)
Medium pressure/high pressure	36 (newest plants)
Single pressure processes:	
Medium pressure/medium pressure	22
High pressure/high pressure	11
Total number of plants	78

Table 1.12: Number of European single and dual-pressure plants
[32, EFMA, 2000]

These plant numbers are probably optimistic as the European industry is currently engaged in substantial rationalisation.

The various processes used in Europe are discussed below and further details can be found in CEC report EUR 13004 EN (1990).

1.2.1.1 Process basis

The description which follows is for a typical plant. Details will vary from plant to plant:

Raw material preparation

The liquid ammonia (NH_3) is evaporated and filtered. Air is purified by using two or three stage filtration and is pressurised. The ammonia and air filter should both remove all particles as effectively as possible. The air is split in two streams: one stream is led to the catalytic reactor, while the other stream is led to (the bleaching section of) the absorption column

Ammonia oxidation

The evaporated ammonia (NH_3) is mixed with the purified air in a ratio of c. 1:10 and (optionally) filtered. Ammonia is reacted with air on a catalyst in the oxidation section. Nitric oxide and water are formed in this process according to the main equation:

$$4NH_3 + 5O_2 \leftrightarrow 4NO + 6H_2O \qquad (1)$$

Nitrous oxide, nitrogen and water are formed simultaneously in accordance with the following equations:

$$4NH_3 + 3O_2 \leftrightarrow 2N_2 + 6H_2O \qquad (2)$$
$$4NH_3 + 4O_2 \leftrightarrow 2N_2O + 6H_2O \qquad (3)$$

The yield of nitric oxide depends on pressure and temperature as indicated below:

Pressure (bar)	Temperature (°C)	NO yield (%)
Below 1.7	810 - 850	97
1.7 to 6.5	850 - 900	96
Above 6.5	900 - 940	95

Table 1.13: NO dependence on pressure and temperature

The reaction is carried out in the presence of a catalyst. The catalyst typically consists of several woven or knitted gauzes formed from wire containing about 90 % platinum alloyed with rhodium for greater strength and sometimes containing palladium. Air pollution and contamination from the ammonia can poison the catalyst. This effect, as well as poor ammonia-air mixing and poor gas distribution across the catalyst may reduce the yield by 10 %. Some of the platinum and rhodium vaporises during the reaction process and in most cases a platinum recovery system is installed below the catalyst. In this system a palladium alloy sometimes used with gold and known as a “getter” or catchment, allows a 60 to 80 % recovery of the total catalyst losses.

The enthalpy of the hot reaction gases is used to produce steam and/or preheat the waste gas (tail gas), as shown in Figure 1.5 Figure 1.6.

The combustion gas after this heat transfer for energy recovery has a temperature of 100 to 200 °C, depending on the process and it is then further cooled with water. The water produced in reactions (1) to (3) above is condensed in a cooler-condenser and transferred to the absorption column.

Oxidation of nitric oxide

Nitric oxide is oxidised to nitrogen dioxide as the combustion gases are cooled, according to the equation:

$$2NO + O_2 \leftrightarrow 2NO_2 \qquad (4)$$

For this purpose, secondary air is added to the gas mixture obtained from the ammonia oxidation.

Absorption of nitrogen dioxide

Demineralised water or steam condensate is added at the top of the absorption column. The weak acid solution (approx. 43 %) produced in the cooler condenser is also added to the absorption column. The nitrogen dioxide (NO_2) in the absorption column is contacted countercurrently with flowing water (H_2O), reacting to give nitric acid (HNO_3) and nitric oxide (NO).

The absorber is operated with a countercurrent flow of water. The absorption of the nitrogen dioxide and its reaction to nitric acid and nitric oxide take place simultaneously in the gaseous and liquid phases according to equations (4) and (5). These reactions to a large extent depend on pressure and temperature and are favoured by higher pressure and lower temperature.

$$3NO_2 + H_2O \leftrightarrow 2HNO_3 + NO \qquad (5)$$

Reaction (5) is exothermic and continuous cooling is needed within the absorber. As the conversion of NO to NO_2 is favoured by low temperature, this will be the significant reaction taking place until the gases leave the absorption column. The nitric acid produced in the absorber contains dissolved nitrogen oxides and is then bleached by the secondary air.

An aqueous solution of nitric acid is withdrawn from the bottom of the absorption tower. The acid concentration can vary from 30 to 70 % $^v/_v$ nitric acid, depending on the temperature, pressure, the number of absorption stages and the concentration of nitrogen oxides entering the absorber. The gases that are not absorbed in the nitric acid solution leave the absorption column at the top, at a temperature of approx. 20 - 30 ºC. This gas mixture is commonly referred to as tail gas and is heated in the heat recovery section. The hot tail gas is in certain cases led through a NO_X abatement system and through a tail gas expander for energy recovery. The resulting expanded tail gas (with a temperature >100 °C to prevent the deposition of ammonium nitrate and ammonium nitrite) is vented through a stack.

In general, two types of nitric acid plants can be distinguished: mono pressure and dual-pressure plants. In mono pressure (single pressure) processes, ammonia oxidation and NO_2 absorption take place at the same pressure. In the past, nitric acid plants worked at atmospheric pressure or low pressure (mono pressure below 1.7×10^5 Pa). Nowadays, mono pressure/low pressure plants hardly exist anymore. Mono pressure/medium pressure plants (pressure between 1.7×10^5 and 6.5×10^5 Pa) and mono pressure/high pressure plants (pressure between 6.5×10^5 and 13×10^5 Pa) are commonly used Figure 1.5 gives a simplified scheme of a possible mono-pressure plant.

Since reaction (1) is favoured by low pressures and the reactions (2) and (3) are favoured by higher pressures, many plants operate with a dual pressure (or split pressure) process. Older plants operate with low pressure/medium pressure, while more modern plants operate with medium pressure/high pressure. To make a higher pressure in the absorption section possible, a compressor is installed between the cooler condenser and the absorption column. The heat of compression is removed by heat exchange with the tail gas and/or by heat recovery in a steam boiler. A second cooler condenser reduces the temperature to 50 °C by cooling with water gives a simplified scheme of a dual-pressure plant Figure 1.6. Table 1.14 summarises the different existing plants.

Type of plant	Possible pressures	Pressure oxidation (bar)	Pressure absorption (bar)
Mono	Low	<1.7	
	Medium	1.7-6.5	
	High	6.5-13	
Dual	Low-medium	<1.7	1.7-6.5
	Medium-high	1.7 - 6.5	6.5 - 13

Table 1.14: Different existing plants
[32, EFMA, 2000]

1.2.1.2 Medium pressure, single pressure plants

A typical plant is represented in the block diagram in Figure 1.5 and includes:

1.2.1.2.1 Ammonia evaporation section

Liquid ammonia from storage is evaporated using water or condensates and then superheated to prevent any liquid carry-over.

1.2.1.2.2 Ammonia filtration section

Gaseous ammonia is filtered to remove any rust from carbon steel equipment. Some plants also use a magnetic filter on the liquid ammonia.

1.2.1.2.3 Air filtration section

High purity air is obtained by using two or three stage filtration. In some plants there is additional filtration of the air/ammonia mixture.

1.2.1.2.4 Air compression section

An air compressor is driven by a tail gas expander and by a steam condensing turbine.

1.2.1.2.5 Mixing section

Modern plants use static mixers to give the high quality mixture, which is essential to maintain good catalyst operation.

1.2.1.2.6 Catalytic reactor section

The catalytic reactor is designed to give a uniform distribution of the air/ammonia mixture over the catalyst gauzes. Maintenance of the catalyst operating temperature is very important for the NO yield. This is achieved by adjusting the air/ammonia ratio and ensuring that the lower explosive limit for ammonia in air is not exceeded.

1.2.1.2.7 Heat recovery sections

The catalytic reactor is typically mounted on the upper part of a vessel which contains the first heat recovery section (steam superheater and steam generator). A set of gas/gas heat-exchangers transfers the energy from the gas leaving the boiler to the tail gas.

1.2.1.2.8 Cooling section

The gas leaving the heat recovery section is cooled. Condensate is passed to the absorption tower.

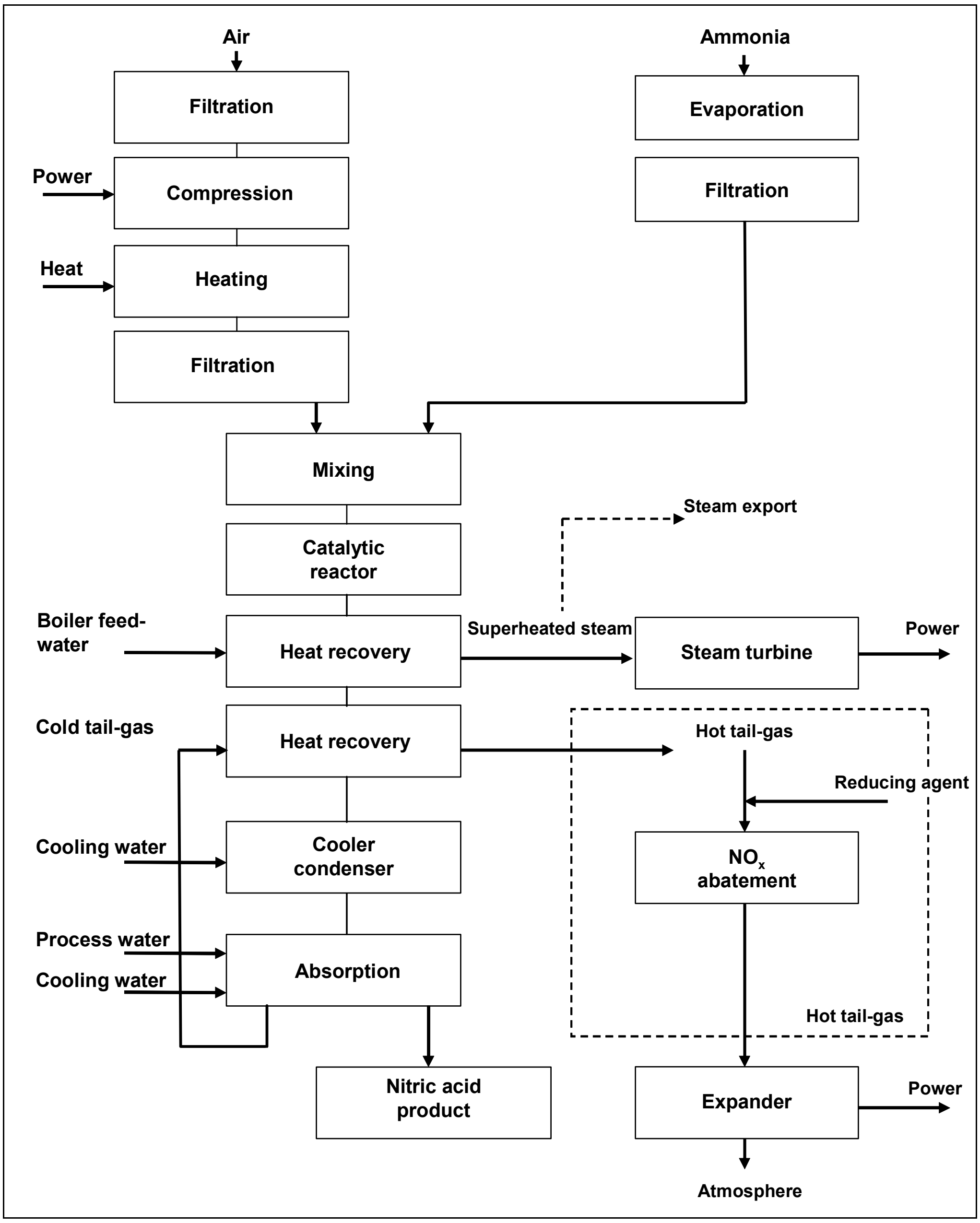


Figure 1.5: Nitric acid production - Single pressure plant
[32, EFMA, 2000]

1.2.1.2.9 Absorption section

The modern absorber design uses countercurrent flow circulation with high efficiency trays, usually sieve trays or bubble cap trays. The tray spacing increases progressively from the bottom to the top of the absorber. Many of the trays are fitted with internal cooling coils to remove the heat of reaction. The absorption section consists of one or more columns in series.

Demineralised water or steam condensate is added at the top of the tower as make-up water. The acid solution leaving the absorption section is rich in dissolved nitrogen oxides and is passed to a bleaching tower where it is contacted with a countercurrent flow of secondary air. The secondary air and the nitrogen oxides stripped out, are mixed with the gases leaving the cooling section and are recycled to the absorption section. The gas leaving the absorption section is commonly known as tail gas.

1.2.1.2.10 Expander section

The tail gas from the absorber is passed through the heat recovery and the expander sections for energy recovery and is then passed to the stack.

1.2.1.2.11 Steam turbine section

The expander generates insufficient energy to drive the air compressor. A steam turbine using part of the superheated steam generated in the plant makes up the deficiency. The steam turbine is also used for plant start-up. In some plants the energy make-up comes from an electric motor and the generated steam is exported.

1.2.1.3 Dual-pressure plants

A typical plant is represented in the block diagram in Figure 1.6. It is similar to the single pressure plant with regards to the cooling section. After the cooling section the plant layout is as follows:

1.2.1.3.1 NO_X compression section

In dual-pressure plants, the gases leaving the cooling section are mixed with the air and nitrogen oxides from the bleaching of the acid solution and compressed to a higher pressure for the absorption stage. The heat of compression is removed from the compressed gases by heat recovery into the tail gas or the boiler feed-water.

1.2.1.3.2 Cooling section

A second cooler condenser reduces the temperature of the gases to about 50 °C and the acid solution formed is mixed with the product acid.

1.2.1.3.3 Absorption section

The acid solution from the absorption section is passed to a column working at the pressure of the air compressor discharge, where it is stripped of the nitrogen oxides by a flow of air from the air compressor. The air and the stripped nitrogen oxides return to the NO_X gas compressor.

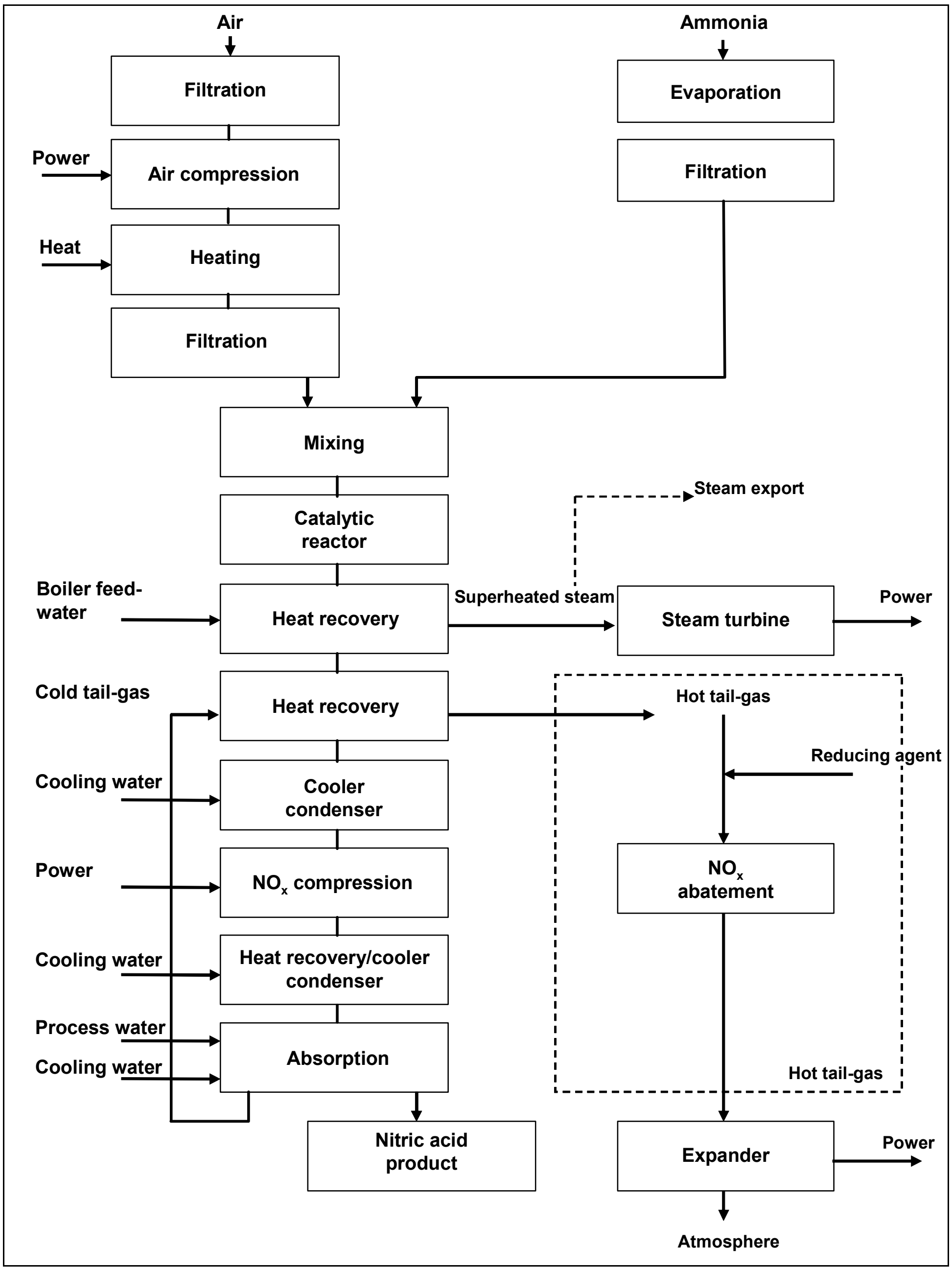


Figure 1.6: Nitric Acid Production – Dual-Pressure Plant

1.2.1.4 High pressure, single pressure plants

A typical high pressure, single pressure plant is similar in layout to the medium pressure single pressure plant Figure 1.5. The process parameters differ due to the higher operating pressure. The main differences are:

- a higher operating catalyst temperature and pressure with a lower NO yield, higher N_2O emissions and a greater loss of catalyst
- a higher inlet pressure to the gas expander allowing a higher inlet temperature and thus more energy to be recovered in the expander and the use of a smaller steam turbine
- a higher operating pressure in the absorber with a lower tail gas NO_X content.

.

1.2.1.5 Storage and transfer equipment

Storage of Nitric Acid

Nitric acid is normally stored in flat bottomed, roofed tanks, made from low carbon austenitic stainless steel, installed in areas provided with suitable containment facilities. The acid level in the tank is monitored by means of a level indicator. A vent to the atmosphere allows the escape of gas which comes from liquid movement and thermal effects. It is normal to earth the tanks.

Transfer Equipment for Nitric Acid

Nitric acid is transported using rail tank cars, road tankers and less frequently, ships. Additionalinformation can be found in EFMA's Guidelines for Transporting Nitric Acid in Tanks. Transfer is made by pumping or by gravity. Unloading large quantities by pressurization should be avoided. The recommended material for tanks, vessels and accessories is low carbon austenitic stainless steel.
[32, EFMA, 2000]

1.2.2 Current emissions and consumption levels

1.2.2.1 Inputs

The description which follows is for a typical plant. Details will vary from plant to plant.

The reactions taking place in nitric acid production are exothermic to a great extent. The reaction from ammonia to 60 % nitric acid theoretically releases 28.5 GJ/t N-HNO_3 corresponding to about 6.3 GJ/t HNO_3 (100 %). A nitric acid plant produces as well as nitric acid, steam or mechanical energy.

Nitric acid production with state-of-the-art technology is characterised by a high degree of energy regeneration. A modern nitric acid plant operating with a dual pressure process has a net energy export of 11 GJ/t HNO_3-N as high-pressure steam [1, UBA, 2001], corresponding to about 2.4 GJ/t HNO_3 (100 %). The average net energy export for Europe is assumed at 7 GJ/t N [1, UBA, 2001], corresponding to about 1.6 GJ/t HNO_3.

Production of high-pressure steam

The highly exothermic catalytic conversion of ammonia takes place in the **catalytic reactor** at temperatures between 840 and 950 °C. Waste heat arising from ammonia oxidation is recovered in a **waste heat boiler** arranged below the ammonia burners and used for high-pressure steam production. Part of the high-pressure steam produced in the waste heat boiler is used to supply compression energy (mechanically or electrically). Excess steam is exported for use elsewhere.

Recovery of low level energy

A set of **gas/gas heat-exchangers** recover low level energy from the NO_X gases leaving the waste heat boiler. The energy is transferred to the waste gas from the absorption column. Waste heat arising from the NO_x gas compression (dual-pressure plant) can also be used for preheating the waste gas leaving the absorption column. Reheating of the waste gas is carried out in the adiabatic operation of the waste gas expansion turbine and enables operation of a selective catalytic reduction (SCR) process without the need for additional heating to achieve the SCR working temperature.

Waste heat arising from the compression of secondary air is used in an **ammonia superheater** for preheating ammonia, resulting in the cooling of the secondary air. The low level energy of the NO_X gas stream can also be used for preheating primary air and for preheating boiler feed-water. Low-pressure steam (e.g. from electric power generation) can be used for evaporating or stripping ammonia (e.g. in an **ammonia evaporator**) and for the deaeration of the boiler feed-water.

Compression energy supply

A waste gas expansion turbine and a steam turbine usually supply drive power for the compressors (air compressor and/or NO_X gas compressor)**,** that are coupled mechanically to the compressors. The waste gas expansion turbine recovers part of the compression energy, depending on the degree of preheating of the cold waste gas downstream of the absorption stage. The remaining drive power is usually supplied by the steam turbine running on process steam. If the process steam is all exported (e.g. for electric power generation), an **electric motor** is used for the driving the compressors instead of the steam turbine.

Cooling water demand

In a **cooler condenser,** the NO_x gas stream is cooled down with cooling water, to condense water formed during ammonia oxidation. The reaction heat released in the **absorption column** is water-cooled as both the oxidation of NO into NO_2 and the absorption of NO_2 are favoured by low temperatures. Part of the heat absorbed by the cooling water can be used for evaporating ammonia [1, UBA, 2001]

In Table 1.15, the energy input and output of nitric acid plants at Linz are given. The specific energy input for compression is given for steam actuation and for actuation with electric energy.

	Line E M/H process	**line F N/M process**
Energy consumption for compression	~ 5	
Compression with electric actuation (MWh/h)		~ 20 (2)
Compression with steam actuation (tonne steam/h)		~ 0.60
Consumption except compression (MWh/h)	~ 0.55	
Steam production (tonne steam/h)	~ 43 (1)	~25 (2)
Notes: 1) 42 bar/520 °C 2) 23 bar/350 °C		

Table 1.15: Energy input and output of the nitric acid plants at Linz
[1, UBA, 2001]

1.2.2.2 Outputs

Nitrous oxide (N_2O) and NO_X are the most significant process emissions to air. These process emissions are vented through a stack. In addition, there may be fugitive emissions of NO_X, ammonia (NH_3) and nitric acid vapours (HNO_3).

1.2.2.2.1 Nitrous oxide (N_2O)

93 – 98 % of the feed ammonia in a nitric acid plant passing over a suitable catalyst can be converted to nitrogen monoxide. The remainder gives unwanted side reactions of nitrous oxide and nitrogen. A higher pressure and a lower temperature favour the formation of N_2O during the ammonia oxidation. Due to the high temperatures (850 – 950 ºC) present during the ammonia oxidation, N_2O is very unstable and partly reduces to N_2 and O_2. Concentrations of N_2O in the tail gas of nitric acid plants may range from 300 – 1700 ppm (580 – 3300 mg N_2O/m^3) [11, InfoMil, 1999] but higher concentrations varying from 300 - 3500 ppm (580 – 6860 mg N_2 $O)/m^3$) are also mentioned [32, EFMA, 2000]. The formation of N_2O is very much dependent on the quality and condition of the catalyst used.

1.2.2.2.2 Nitrogen oxide gases (NO_X)

The reaction of nitrogen dioxide (NO_2) with water is part of the nitric acid process.

The nitric oxide (NO) must be oxidised to NO_2, which is absorbed in water as N_2O_4:

$$2NO + O2 \leftrightarrow 2NO2 \leftrightarrow N2O4 \qquad (1)$$

Two limiting factors are present. Firstly, oxidation of NO to NO_2 is a very slow reaction. Secondly, increased temperature due to the exothermic absorption reaction tends to reverse the reaction. Only active cooling can counteract this. These factors impose economic limits on the absorption efficiency [11, InfoMil, 1999].

N_2O_4 reacts with water and forms in two steps nitric acid, water and nitrogen monoxide:

$$N_2O_4 + H_2O \leftrightarrow HNO_3 + HNO_2 \qquad (2)$$
$$3HNO_2 \leftrightarrow HNO_3 + H_2O + 2NO \qquad (3)$$

As a result of these reactions, one mole of NO is produced for every three moles of NO_2 absorbed, making complete absorption impossible, especially as the absorption of NO_2 is an equilibrium reaction.

Critical parameters for the absorption of nitrogen dioxide in water are as follows:

- gas volume in the absorption tower decreases as the absorption reaction proceeds. Furthermore, completion of the reaction is aided by increased **pressure**

- low temperature is a key factor for achieving high absorption efficiency. The temperature rises due to the addition of reaction heat. Continuous cooling with water is necessary

- nitric acid plants are designed for a **specific production rate**. Operating outside the optimal production rate affects the level of NO_X emissions. Increasing the production rate decreases the **residence time** in the absorption tower. The oxidation of NO diminishes and the absorption of NO_2 decreases, resulting in higher NO_X emissions. Operating below the design rate increases the residence time, and lower NO_X emissions would then be expected. However this technique for NO_X reduction would not be economically viable

- the **efficiency of the absorption tower** depends on various parameters such as the design, the number of trays, the kind of trays used (normally sieve trays or bubble cap trays) and the number of columns

- as a result of the continuously repeated and interconnected reactions of NO, NO_2 and N_2O_4, the **partial pressures of NO and NO_2** are steadily reduced. However, as they are formed from equilibrium reactions they maintain finite values.

A higher pressure and a lower temperature, in particular have a positive effect on both the oxidation of NO and the absorption of NO_2. The laws of chemistry however, prevent complete absorption, and some residual emissions are unavoidable. The NO_X concentration at the outlet of the absorber may vary [11, InfoMil, 1999] between 100 and 2000 ppm (205 - 4100 mg NO_X /m^3), expressed as NO_2. With the exception of nitric acid plants with high absorption pressures (>12 bar) nitric acid plants are usually equipped with secondary emission reduction processes.

The production of nitric acid is a continuous process, so start-up and shutdown should be regarded as exceptional events. NO_X emissions increase during start-up and shutdown periods caused by repairs and catalysts replacements.

Plant	Start-ups/ year	Start-up		Shutdown	
		Amount NO_X (kg/event)*	Period (min)	Amount NO_X (kg/event)*	Period (min)
DSM Geleen SZF4	±6	200 (est)	90	25 (est)	10
DSM Geleen SZF5	±6	70 (est)	60	31 (est)**	20**
DSM IJmuiden SZF4	--	--	--	--	--
DSM IJmuiden SZF5	--	--	--	--	--
Hydro Agri Sluiskil 6	2 - 3	--	--	15 (est)**	20**
Hydro Agri Sluiskil 7	2 - 3	--	--	15 (est)**	20**
Kemira Agro Pernis	±4	45 (est)	30	43 (est)	15
Kemira Agro Rozenburg	<10	254 (est)	100	50 (est)	30

* (me) = measurement; (est) = estimation. NO_X expressed as NO_2.

** During a planned stop (e.g. change of catalyst), the compressor unit prevents an extra emission; values mentioned are extra emissions during a technical malfunction.

Table 1.16: Extra NO_X concentrations in the Dutch nitric acid plants due to start-up/shut-down [11, InfoMil, 1999]

Note: Pernis has been shut down and Rozenburg relocated to Tertre, Belgium.

During normal operation the percentage of NO_2 in the NO_X is in the range 25 – 40 %. The NO_2 emission is larger than the NO emission, especially during start-up, and colours the stack gas reddish-brown or yellow.

1.2.2.2.3 Fugitive emissions

Differences in plant design and other factors, such as good maintenance and careful control of operations, affect the level of uncontrolled emissions from plant to plant.

NO_X and HNO_3 emissions may occur at HNO_3 storage. Atmospheric venting allows the escape of gases due to tank breathing losses, liquid movements, and from thermal effects. Water present in the liquid ammonia (typically 0.2 %) concentrates in the ammonia vaporiser and periodic blow-down of the water generates a small gaseous ammonia release [32, EFMA, 2000]. Fugitive emissions are very difficult to determine, but some values have been measured or estimated.

Plant	NH_3 (kg/yr)	NO_X (kg/yr)
DSM Geleen SZF4	1550	<600 (est)
DSM Geleen SZF5		
DSM IJmuiden SZF4	<1500	2000 (est)
DSM IJmuiden SZF5		
Hydro Agri Sluiskil 6	567 (est)	366 (est)
Hydro Agri Sluiskil 7	2031 (est)	185 (est)
Kemira Agro Pernis	2000 * (est)	--
Kemira Agro Rozenburg	600 (me)	≈0 (est)

(ME)=MEASUREMENT; (EST)=ESTIMATION. NO_X EXPRESSED AS NO_2.

* Based on calculation method by TNO

Table 1.17: Fugitive emissions in Dutch nitric acid plants [11, InfoMil, 1999]

Note: Pernis has been shut down and Rozenburg relocated to Tertre, Belgium

1.2.2.2.4 Discharges to water

The cooling water blowdown represents the major liquid discharge flow from the process. Due to the highly exothermic nature of the the process, large amounts of cooling water are required. In addition, some small liquid emissions are possible, for instance:

- **Boiler blowdown:**

The dissolved salt content of the boiler water is controlled by a blowdown of the water in the steam drum. Normally, the blow-down should be cooled prior to discharge.

- **Ammonia vaporiser blow-down:**

The build-up of water (and traces of oil) in the liquid ammonia vaporiser is controlled by a periodic blow-down. The ammonia dissolved in this water should be vaporised and reprocessed. The contamination (oil/water mixture) is led to an oil/water separator or to the sewage. The waste oil remaining should be reprocessed in the same way as used lubricating oil.

- **Purging and sampling:**

Purges and samples of nitric acid solutions are usually recycled to the process. Occasional emissions do occur from the purging and sampling of nitric acid solutions.

- **Lubricating oil:**

Periodic replacement is needed of the lubricating oil in rotating machines such as compressors, turbines and pumps.

1.2.2.2.5 Wastes

Some solid waste is generated from nitric acid production [11, InfoMil, 1999].

Ammonia oxidation catalyst

The catalyst (most of the time the catalyst will be based on platinum) will at some point need to be replaced due to losses from evaporation of platinum due to the high temperatures and due to slow poisoning from air pollution or from ammonia impurities. Precious metal loss increases with temperature and gas flow rate, which again increases with pressure. The frequency of replacements depends on the catalyst used (but usually 2 - 4 replacements will be carried out each year). All manufacturers of catalysts collect the old catalyst materials for re-use.

Catchment

The catchment or “getter” allows a more than 80 % recovery of the total catalyst losses. The efficiency of the catchment will reduce in time, so it needs to be replaced each campaign (i.e. every 90 – 180 days).

Filter cartridges

Replacement of the cartridges as a result of the pressure drop build-up in the various elements used for ammonia, air and air/ammonia mixture filtration. Filter cartridges can often be cleaned and re-used. However, after a number of re-uses the cartridges will need to be disposed of.

Solid deposits

Solid deposits containing significant catalyst content can be recovered from some parts of a nitric acid plant (e.g. piping of the heat-exchanger or on the waste heat boiler). Deposits are recovered and sent for reprocessing to a precious metals refiner.

1.3 Sulphuric acid

More sulphuric acid is produced than any other chemical in the world. In Western Europe in 1997 over 19 Mt were produced, the total production worldwide being estimated at around 150 Mt. About half of the world output is produced in North America, Western Europe and Japan [3, ESA, 2000].

By far the most important user is the phosphate fertiliser industry. Other important applications of sulphuric acid are found in petroleum refining, pigment production, steel pickling, non-ferrous metals extraction and the manufacture of explosives, detergents (organic sulphonation processes), plastics and man-made fibres. The chemical industry also uses varying amounts of sulphuric acid in specialised production applications for dyes, pharmaceuticals and fluorine chemicals.

Year	1992	1993	1994	1995	1996	1997
World sulphuric acid production	145.7	132.5	137.9	148.9	151.3	155.6
World sulphuric acid consumption	147.1	132.8	138.8	150.1	153.3	157.5

Table 1.18: World production and consumption in Mt sulphuric acid
[3, ESA, 2000]

Sulphuric acid is manufactured from sulphur dioxide. The primary process for producing sulphur dioxide is the combustion of elemental sulphur. A large producer of sulphur dioxide is the non-ferrous metals industry. The roasting and smelting processes produce off-gases with a sufficiently high concentration of sulphur dioxide to allow direct processing to sulphuric acid as a supplementary product. In recent years a significant number of sulphuric acid facilities have been installed in metallurgical plants for the recovery of SO_2, as environmental abatement units. The roasting of metal sulphides such as pyrite to produce SO_2 is still an important feedstock in several countries for sulphuric acid production, but production rates are no longer significant compared to the other sources. The thermal oxidising process of spent acids used as raw materials is also a way to produce SO_2 and sulphuric acid.

Year	1992	1993	1994	1995	1996	1997
Belgium/Luxembourg	1.836	1.535	1.515	2.174	2.067	2.160
Finland	1.351	1.361	1.373	1.376	1.479	1.570
France	3.132	2.515	2.227	2.382	2.263	2.242
Germany	3.800	3.515	3.380	3.530	3.978	3.496
Greece	0.620	0.588	0.630	0.515	0.615	0.675
Italy	1.725	1.423	1.228	1.344	1.588	1.590
Netherlands	1.080	1.000	1.073	1.113	1.060	1.040
Norway	0.587	0.564	0.585	0.609	0.594	0.666
Spain	2.420	2.176	2.348	2.265	2.786	2.810
Sweden	0.567	0.497	0.518	0.485	0.620	0.630
United Kingdom	1.568	1.269	1.225	1.293	1.196	1.205

Table 1.19: Production of sulphuric acid of countries in the European Community in Mt of sulphuric acid
[3, ESA, 2000]

The oxidation of sulphur dioxide over a suitable catalyst to produce SO_3, i.e. in the contact process, is the process used today for almost all sulphuric acid. This technology is well developed, although optimisation of the conversion and absorption stages were introduced commercially in the 1960s to increase the sulphur dioxide conversion efficiency. The improvement also meant that releases to the environment were minimised. The achievable conversion rate strongly depends on the process type and the starting conditions but some plants can now be designed for a sulphur dioxide conversion efficiency exceeding 99.8 % [33, Ullmann`s, 2000].

Modern plants can be designed to be very efficient in terms of sulphur dioxide conversion and energy recovery. For many years it has been good practice to recover 60 % or more of the total energy generated in sulphuric acid production, as high-pressure steam. Recently, the additional recovery of low-level heat from the acid system has substantially improved the energy efficiency of some plants.

Sulphur dioxide gas streams containing higher SO_2 concentrations are preferable to low concentration sources, reducing the capital and operating costs and further increasing high-temperature energy recovery. At the same time, quality requirements have become more stringent for commercial acid. It will be necessary to develop new processes to ensure quality for large quantities of "metallurgical acid" now available on the market. [33, Ullmann`s, 2000]

The reprocessing of acid wastes from user industries is a feedstock that needs to be taken into account by the sulphuric acid industry. This waste acid had been disposed of previously by alternative techniques. Concentration and decomposition to provide a source of sulphur dioxide as a feedstock for sulphuric acid production now recover this waste. Many uses also result in so-called spent acid: sulphuric acid in varying states of dilution, as well as contaminated with organic and inorganic impurities. Further developments are expected in the use of recovered heat from sulphuric acid plants but the technology in this area is quite extensive.

1.3.1 Applied processes and techniques

Conversion of SO_2 into SO_3

The design and operation of sulphuric acid plant are based on the following gas phase chemical equilibrium reaction using a catalyst:

$$SO_2 + 1/2\ O_2 \leftrightarrow SO_3 \qquad \Delta H_o = -99 \text{ kJ/mole}$$

This reaction can be characterised by the following conversion rate:

$$\text{Conversion rate} = \frac{SO_{2\,in} - SO_{2\,out}}{SO_{2\,in}} \times 100\ (\%)$$

Both thermodynamic and stoiochiometric considerations are taken account of by maximising the formation of SO_3. The Lechatelier-Braun principle, which states that when an equilibrium system is subjected to stress, the system will tend to adjust itself in such a way so as to partly relieve the stress, needs to be taken into account for optimisation of the equilibrium. The stresses are, for instance, variations of temperature, pressure, or the concentration of a reactant.

For SO_2/SO_3 systems, the following methods are available to maximise the formation of SO_3:

- as this is an exothermic process, so a decrease in temperature by removal of the heat will favour the formation of SO_3
- increased oxygen concentration
- SO_3 removal (as in the case of the double absorption process)
- increased pressure
- catalyst selection, to reduce the working temperature (equilibrium)
- longer reaction time.

Optimising the overall system behaviour requires a balance between reaction velocity and equilibrium. However, this optimum also depends on the SO_2 concentration in the raw gas and on its variability. Consequently, each process is more or less specific for a particular SO_2 source.

Absorption of SO_3

Sulphuric acid is obtained from the absorption of SO_3 and water into H_2SO_4 (with a concentration of at least 98 %).

The efficiency of the absorption step is related to:

- the H_2SO_4 concentration of the absorbing liquid (98.5 – 99.5 %)
- the temperature range of the liquid (normally 70 °C – 120 °C)
- the technique of acid distribution
- the raw gas humidity (mist passes the absorption equipment)
- the mist filter
- the temperature of incoming gas
- the co-current or countercurrent character of the gas stream in the absorbing liquid.

SO_3 emissions depend on:

- the temperature of gas leaving the absorption
- the construction and operation of the final absorber
- the equipment for separating H_2SO_4 aerosols
- the acid mist formed upstream of the absorber through the presence of water vapour
- the overall efficiency of the absorption step.

Many processes for sulphuric acid production have been developed over the years. These developments were dependent on the large number of sources of raw material which generate SO_2, which is the basic chemical needed for the production of sulphuric acid. The SO_2 is converted to SO_3, which is then absorbed to produce sulphuric acid and oleum.

The following sections describe the various stages to produce sulphuric acid starting from raw material preparation, followed by material processing through to product finishing.

1.3.1.1 Raw material preparation (including storage and handling)

1.3.1.1.1 Sulphur storage and handling

Liquid sulphur is a product of the desulphurisation of natural gas by the Claus-Process and raw oil. It can also be obtained from the cleaning of coal flue-gas. A third route is the melting of naturally occurring solid sulphur (Frash-process). This third option is not commonly used as there are many difficulties removing contaminants.

A typical analysis of molten sulphur (quality: bright yellow) from the Claus process is the following:

- ash: max. 0.015 % weight
- carbon: max. 0.02 % weight
- hydrogen sulphide: c. 1 – 2 mg/kg
- sulphur dioxide: 0 mg/kg
- arsenic: max. 1 mg/kg
- mercury: max. 1 mg/kg
- water: max. 0.05 % weight.

Ship, railcars and mild steel road tankers are used to transport liquid sulphur. Specialised equipment is used at all loading and unloading facilities.

Liquid sulphur is stored in steam heated insulated mild steel tanks. Dip-legs are used for filling to minimise static charges and to avoid disturbing the tank contents. The tanks are vented to atmosphere. This filling method minimises releases of hydrogen sulphide and sulphur dioxide. All pipes and pumps are steam heated and insulated. The normal temperature of storage and the handling is around 125 – 145 °C.

1.3.1.1.2 Ores storage and handling

Pyrite

A flotation process is normally used to produce pyrite. The resultant solid concentrate is quite fine with a moisture content governed by energy usage during drying. Analyses of the concentrate are variable and are within the following ranges:

Element		Content	Content in one specific pyrite
Sulphur	weight %	30 - 52	50 – 52
Iron	weight %	26 - 46	45
Copper	weight %	up to 2.7	max. 0.10
Zinc	weight %	up to 3.0	max. 0.10
Arsenic	weight %	up to 10.0	max. 0.06
Water	weight %	5 - 9	5

Table 1.20: Pyrite concentrate analysis

The far right column shows the analysis of a particular pyrite along with trace metals. Storage and transporting of pyrite should be enclosed to minimise dust arisings. If outside storage is needed the following problems are likely:

- dust problems can be expected under dry conditions. A dusty atmosphere, especially inside buildings could under certain conditions lead to a fire or an explosion
- water in contact with pyrite becomes acidic under wet conditions. The run-off water will thus need to be collected and treated before discharge. The pyrite internal transport system at the plant is liable to give problems with blockages if the moisture content of the ore is too high.

Metal sulphide ores

Approximately 85 % of primary copper is produced from copper ores with high sulphur content and sulphur can be regarded as a by-product of the majority of copper processes.

Copper ore concentrates are produced in a flotation process using mainly copper pyrites or chalcopyrite ($CuFeS_2$), which may also contain pyrite, chalconite, burnite, cuprite and other minerals. A typical copper ore concentrate composition is 26 – 30 % Cu, 27 – 29 % Fe and 28 - 32 % S.

The roasting of copper concentrates is the usual processing route. Ores and concentrates are delivered to site by road, rail or sea. Copper concentrates are usually enclosed in a storage building. Silos are used for the intermediate storage and the blend preparation Abatement systems for dust collection are used extensively for the unloading storage and distribution of solid material.

Zinc and lead are produced from ores with high sulphur content. The by-product sulphur dioxide is used to produce sulphuric acid.

These basic ores are treated similarly in a flotation process to produce concentrates. The concentrates are then shipped to smelters to produce the basic metal. Desulphurisation of concentrates is the primary process used for producing these metals. Ores and concentrate are delivered to site by road, train or sea. The storage on site, depending on local situations, is outside or in covered building storage. Silo systems and dust collections systems, such as bag filters, are extensively used for intermediate storage and blend preparation.

1.3.1.1.3 Other sources of SO_2 or spent acids

Spent sulphuric acids from operations such as steel pickling, titanium dioxide production or organic sulphonation reactions have such a variety of compositions that it is not possible to set out general rules for preparation, storage and handling. Most spent acids originate from the production of organic chemicals. Sulphuric acid is mostly used as a catalyst and can also be used as a raw material in the thermal oxidising process. Alkylation processes in refineries, nitration and sulphonation processes for chemical industry generate large amounts of spent acids. These spent acids are used as a raw material source of SO_2 to produce virgin acid via the thermal oxidising process, and can be recycled in any process.

Storage and handling

Barges, road and rail tankers are used to transport spent acids. Chemical analysis and physical tests are carried out before unloading to ensure that the product is within the contract specification and to avoid any chemical reaction in the storage when mixing spent acids arising from different processes. Storage vessels are located within containment bunds. The storage gas vents are connected to a thermal decomposition furnace, through non-flammable protection systems because of the risks associated with the organics, some dissolved sulphur containing products and to NO_X potential emissions. Nitrogen is used for inert blanketting to exclude oxygen.

The spent acid strength will determine the type of construction material used for equipment. Pumps and pipework for the furnace feed use corrosion-resistant materials.

1.3.1.1.4 H_2S or other sulphur containing gases

The production of textile fibres made by the viscose process releases H_2S and CS_2, and H_2S or SO_2 depending on the process. These are also formed during the production of synthesis gas using a fuel oil feedstock and may also be used as a feedstock.

1.3.1.1.5 SO_2 gases from different sources

Gases containing up to 90 % SO_2 from the production of organic compounds such as sulphonates, sulphites or from the combustion of gases containing H_2S, can also be used, after the removal of organic compounds, as a source of SO_2.

1.3.1.1.6 Sulphate salts

Ferrous sulphate is obtained in large quantities as its heptahydrate **($FeSO_4$. 7 H_2O)** during the regeneration of pickling liquors or as a side product in the TiO_2 process via the sulphate route.

Material processing

Since the technique of conversion of SO_2 to SO_3 and of absorption of SO_3 depends on the concentration of SO_2 in the feed gas entering the installation and on the variability of SO_2 concentration, the general presentation of the technique of production of sulphuric acid is divided into two parts:

Sources of SO_2

1. sulphur burning
2. pyrite roasting
3. metal sulphide roasting and smelting
4. sulphuric acid regeneration
5. metal sulphate roasting
6. combustion of H_2S or other sulphur containing gases
7. other processes.

1.3.1.1.7 Sulphuric acid production

The acid production will be divided in two different processes: <3 Vol.% SO_2 and >3 Vol.% SO_2, poor gas processes and tail gas processes leading sulphuric acid.

Poor gas processes with >3 Vol. % SO_2:
- single contact process
- double contact process
- wet Contact Process (WCP).

Tail gas processes with <3 Vol. % SO_2:
- modified Lead Chamber Process (MLCP)
- H_2O_2 process
- activated Carbon
- other processes.

1.3.1.2 Overview of techniques applicable to sources of SO_2

Table 1.21 gives an overview of techniques that reduce emissions from sulphur dioxide manufacture.

Techniques	Process control	Fuel selection	ESP	Filters	SOx
Sulphur burning	X			X	X
Ores roasting/smelting	X	X	X	X	X
H_2SO_4 Regeneration	X	X	X	X	X
Sulphates roasting	X	X	X	X	X
Combustion of H_2S	X	X		X	X

Table 1.21: Techniques reducing emissions
[3, ESA, 2000]

1.3.1.2.1 Sulphur burning

Combustion of sulphur, from either natural deposits, desulphurisation of natural gas or crude oil, is carried out in one stage or two stage sulphur combustion units between 900 °C and 1800 °C. The combustion unit consists of a combustion chamber followed by a process gas cooler. The SO_2 content of the combustion gases is generally as much as 18 % by volume and the O_2 content is low (but higher than 3 %).

The gases are generally diluted to 10 – 11 % before entering the conversion process. In the inlet-gas to the converter the ratio of SO_2/O_2 should not be higher than 0.8 to achieve a high conversion efficiency. This means that the highest percentage of SO_2 should not exceed 11 % in a 4-bed double contact (no Caesium) to achieve a conversion rate of 99.6 % average.

1.3.1.2.2 Pyrite roasting

Nowadays fluidised bed roasters are the preferred equipment for pyrite roasting. They are much superior to other types of equipments in term of process technology, throughput rates and economy. When roasting pyrite to get SO_2-gas, two by-products are also produced: iron-oxide and energy 1 tonne acid needs 0.5 tonne pyrite.

The SO_2 content of the gases is generally 6 – 14 %, and O_2 free.

The gases are always treated in 3 - 4 cleaning steps, cyclones, bag filters, scrubbers and electrostatic precipitators with a high efficiency. Waste water from the scrubbing has to be treated before discharge. The clean gas is diluted with air to 6 – 10 % and dried before entering the conversion process.

Due to the heterogeneous character of the raw material (pyrite), the SO_2 content in the gases is slightly variable over time.

1.3.1.2.3 Metal sulphide roasting and smelting

Many metal sulphides (other than pyrite), when roasted during metallurgical processes, produce gases containing SO_2. It is necessary to distinguish the main ores as indicated in Table 1.22.

Metal Sulphide		**Raw Gases**	**Process Gases**	**Variability in time**
	SO_2 %	O_2 %	SO_2 %	
ZnS containing ores	6 - 10	6 - 11	6 - 10	Relatively low
CuS containing ores	1 - 20	8 - 15	1 - 13	Can be very high
PbS containing ores				
- sintering	2 - 6	≈ 15	2 - 6	Relatively high
- other lead smelters	7 - 20	≈ 15	7 - 13	Low to very high (Batch process)

Table 1.22: Principal metal sulphides producing SO_2

The concentration of SO_2 in gases entering an acid plant, determines the amount of gas that must be treated per tonne of fixed sulphur. The concentration of SO_2 decreases as the size of the plant and the cost of fixing sulphur increase. Furthermore, there is a minimum concentration of SO_2 that can be treated without increasing the number of stages in the plant.

Copper production

For copper, it is typical to find not only fluctuations in the concentration of SO_2 in converters, but also important fluctuations in the gas flow. The reason for these effects of converter operation on the concentration of SO_2 is the fact that about 30 % of the converter operating time is used for charging and slag tapping.

Pyrometallurgical copper extraction is based on the decomposition of complex iron-copper sulphide minerals into copper sulphides, followed by selective oxidation, separation of the iron portion as slag, and finally oxidation of the remaining copper sulphide.

These steps are known as roasting, smelting and converting (the present-day tendency is to carry out the first two in a single process). The 'Flash Smelting' process is currently one of the most widely used pyrometallurgical processes.

Converters are used extensively, to blow air, or oxygen-enriched air through the copper matte to produce blister copper. Virtually all the sulphur from the concentrates finishes as SO_2. A concentrate of $CuFeS_2$ produces almost one tonne of sulphur (2 tonne of SO_2) per tonne of copper extracted. These gases are processed to obtain sulphuric acid, oleum or liquid SO_2, ensuring that releases to the environment are avoided.

The development of copper recovery processes has been dominated by two objectives. One is to economise on energy, making the maximum use of reaction heat obtained from the processes. The other has been the need to decrease the gas volume, and increase the concentration of SO_2 in metallurgical gases by the use of oxygen enrichment, to improve environmental controls. The final gas cleaning is where the gas is cooled and the dust and SO_3 eliminated by scrubbing, cooling and electrostatic cleaning. After that, the clean SO_2 gases are converted to sulphuric acid through the contact process.

Zinc production

Zn production is based on the treatment of Zn-concentrates, mainly sulphides, with an average composition of sulphide sulphur: 30 – 33 %, Zn: 50 – 60 %, Fe: 1 – 12 %, Pb: 0.5 – 4 % and Cu: 0.1 – 2 %. These concentrates are desulphurised in a first step.

After the desulphurisation step the product (calcine) is treated for Zn-recovery mainly in a 'Hydrometallurgical process' and for a minor part in a 'Pyrometallurgical process'. The Hydro way consists of leaching this calcine, thus purifying the enriched Zn-solution, with subsequently pure Zn-metal recovered by electrolysis.

In the Pyrometallurgical way, conditioned calcine is reduced in a shaft furnace (ISF) with the condensing of Zn-vapours in a splash condenser. This crude Zn is further refined in a distillation column.

More specifically the preliminary desulphurisation step takes place mainly in a fluidised bed roaster or alternatively in a sinter plant. The SO_2 content of the gases is about 5 to 10 %. After heat recovery in a waste heat boiler with the production of steam, the gases are dedusted in an ESP, cooled in scrubbing towers, and subsequently demercurified in a specific scrubbing-process. In a double contact process, a single one for older plants, the cleaned SO_2 gases are treated and converted to sulphuric acid.

Lead production

Primary lead is produced predominantly from Pb- and Pb-Zn concentrates and to a lesser extent from other sources, such as complex Pb-Cu concentrates. Concentrate compositions may vary between rather wide ranges: 10 – 80 % Pb, 1 – 40 % Zn, 1 – 20 % Cu, 1 – 15 % Fe, 15 - 35 % S. Different processes have been developed, and are used to obtain an optimum recovery of the various metals present in the feed. Whichever smelting technique is used, desulphurisation is always one of the objectives of the early treatment stages. This is carried out on belt sinter equipment in cases where a shaft furnace is the actual smelting step or in flash or bath smelting furnace in the other processes.

From this variety of feed materials and consequently of techniques, it should be clear that the characteristics of the SO_2-containing gas will differ largely from case to case. In continuous operations, such as with sinter machines, the SO_2-concentration can be kept fairly constant. It can be between 6 and 9 % depending on the actual feed mix. It will obviously be very variable, between 0 and 15 %, from batch operations depending on the process stage. Average concentrations may be among 2.5 and 10 %, depending on the actual feed mix and on the applied technique.

The gas cleaning stage will always include ESP and scrubbers. Energy recovery can be practised in some cases of bath smelting; a specific mercury removal step, either carried out on the gas or on the acid, may be necessary in others. The double absorption process is largely used, especially when SO_2 concentrations are high and constant. When low and very varying

SO_2-concentrations are inevitable, or where those streams cannot be integrated in more steady gas streams from other processes on the site, single absorption will be more appropriate.

1.3.1.2.4 Sulphuric acid thermal oxidising process using spent acid as a raw material

The thermal decomposition of spent sulphuric acids to sulphur dioxide is achieved in a furnace at a temperature in the range of 1000 °C. Spent acids arise from processes where H_2SO_4 or oleum is used as a catalyst (alkylation, nitration, sulfonation, etc.) or from other processes where H_2SO_4 is used to clean, dry, or eliminate water.

The gas phase thermal decomposition of sulphuric acid is represented by the overall equation:

$$H_2SO_4 \rightarrow SO_2 + H_2O + \frac{1}{2} O_2 \qquad \Delta H = +202 \text{ kJ/mole}$$

Spent acids are atomised into small droplets to achieve good thermal decomposition. The combustion of the organics from the spent acids provides energy and this is supplemented by the combustion of natural gas, fuel oil or coke. Preheating the combustion air reduces the amount of supplementary fuel needed. Furnaces can be horizontal, fixed or rotating, or vertical.

The SO_2 content in the combustion gases depends mainly on the composition of the spent acids, and it can vary from 2 to 15 %. The water and organics content affect the gas composition. Sulphur, can normally be fed to adjust the SO_2 content and to minimise too high variations. Most of the energy from the combustion gases is recovered as steam in a ‘Heat Boiler’. The exhaust gases are cleaned downstream, demisted and dried before passing to the converter. Another solution is the production of sodium bisulphite as a co-product of the sulphuric acid plant.

The O_2/SO_2 ratio is important in achieving an optimum conversion ratio of SO_2 to SO_3. Upsteam of the converter, the gases are reheated to the ignition temperature through gas/gas heat-exchangers using heat from the converter. A double absorption process can be used only if the SO_2 content of the gases is sufficiently high (about 8 %) at the converter inlet.

Conversion rates

Single absorption:
- SO_2 content at the converter inlet **8** % with an O_2/SO_2 ratio of 1.1**: 98 %**
- SO_2 content at the converter inlet from **5 to 8 %** with an O_2/SO_2 ratio of 1.1**: 97 to 98 %**
- SO_2 content at the converter inlet below **5 %** with an O_2/SO_2 ratio of 1.1: **96 to 97 %.**

Double absorption:
When achievable, leads to conversion rates from **99 to 99.6 %.**
For new plants double absorption is considered the best technique. For existing plants, single absorption can be combined with an ammonia scrubber so the by-product can be either sold on the market or recycled to the furnace.

1.3.1.2.5 Sulphate roasting

The decomposition of sulphates, e.g iron sulphate, is carried out in multiple-hearth furnaces, rotary kiln or fluidised bed furnaces at over 700 °C with the addition of elemental sulphur, pyrite, coke, plastic, tar, lignite, hard coal or oil as the fuel compensator. The SO_2 content of the gases obtained is dependent on the type of fuel; after cleaning and drying, the SO_2 content will be about 6 %. The variability of the SO_2 over a period of time is high.

The heptahydrate is dehydrated at 130 - 200 °C by flue-gases in spray dryers or fluidised bed dryers to a monohydrate or mixed hydrate during the first step. In the second step, the material is decomposed at about 900 °C.

Gases from this process contain about 7 % by volume of sulphur dioxide. Today it is common practice for ferrous sulphate to be decomposed in a fluidised bed pyrite roasting furnace at 850 °C or more. Elemental sulphur, coal or fuel oil may be used as supplementary fuels. The sulphur dioxide containing gas leaving the furnace is cooled in a waste heat boiler to about 350 – 400 °C and is then passed to the gas cleaning system. The cleaned gases are fed to the sulphuric acid plant.

A mixture of metallic or ammonium sulphates and eventually sulphuric acid resulting from the concentration of acidic wastes of titanium oxide production or from organic sulphonations could also be processed in a fluidised bed reactor or a furnace.

In individual cases, ferrous sulphate is also decomposed in multiple-hearth furnaces with flue-gases from fuel oil or natural gas combustion.

1.3.1.2.6 Combustion of H_2S or other sulphur containing gases

The combustion of hydrogen sulphide (H_2S) or similar gases is achieved in a fixed furnace at about 1000 °C. The combustion heat is higher than with sulphur combustion.
Two different methods are used to process the gases to SO_3 and H_2SO_4:

- dry processes, where the water is eliminated by condensation and drying. The dried gases are then processed the same way as for the spent acid regeneration process
- wet processes, in which the gases are processed with all the water and steam. A condenser replaces the absorption tower at the final stage of the process and temperature control of the condensation enables 96 % H_2SO_4 to be produced. The resultant excess water is vented to atmosphere.

The conversion rates of 99.6 % average are comparable to sulphur burning plants.

Tail gas scrubbing

The scrubbing of the tail gas to remove residual SO_2 is achieved by contact in a contercurrent packed scrubber with an alkaline solution. The inlet concentration of the SO_2 will determine which type of scrubbing liquor is applicable: ammonia, caustic soda, magnesium or calcium hydroxides. One or two reaction steps may be needed. The scrubbing liquor is circulated from a tank and the pH is adjusted with fresh liquor controlled by the exit SO_2 concentration. Bleeding off a portion of the spent solution, which depending on the alkali used may contain ammonium, sodium, magnesium or calcium hydroxides, controls the circulation tank liquor level. This liquor can be sold or disposed of to a suitable outlet.

1.3.1.3 Product finishing

1.3.1.3.1 Dilution of absorber acids

The acid produced, normally 95.5 - 96.5 % or 98.5 - 99.5 %, is diluted with water or steam condensate giving commercial concentrations of: 25, 37, 48, 78, 96 and 98 % H_2SO_4. The dilution can be by batch process or continuously by inline-mixing.

1.3.1.3.2 SO_2-stripping

The warm acid produced is sparged with a little air in a column or in a tower to reduce the remaining SO_2 in the acid to <20 mg SO_2/kg. The SO_2 laden air is then returned to the process.

1.3.1.3.3 Purification

Sulphuric acid production may potentially be contaminated during start-up after an extended period for repair. Insoluble iron sulphate or silicate from the brickwork tends to cloud the product acid. Conventional filtration methods can be used to clean the acid. Filtration units are needed in the filling lines for tanker or railway loading to ensure quality control.

1.3.1.3.4 Denitrification

Several different methods exist for the denitrification of sulphuric acid and oleum. Chemicals are used to reduce nitrosylsulphuric acid ($NOHSO_4$) or nitrate to N_2 or N_xO_y. The reactant must be added in stoichiometric amounts. See the following Table 1.23.

Method of denitrification	Special conditions	Effect	In tail gas
Urea	Absorber/tanks	+/only <80 % acid	N_2
Dihydrazinedisulphate 40 %	Absorber/tanks	+++/acid and oleum	N_2,N_2O
Amidosulphonic acid 15 % Hydroxylammoniumsulfat	Absorber/tanks	+++/only 50 – 99.5 % acid	N_2
SO_2 saturated acid	78 % H_2SO_4/ separated tower	+++/only acid/ water balance	NO_X

Table 1.23: Denitrification methods

1.3.1.3.5 Decolourisation

Acid produced from smelter plants or from acid regeneration plants can contain hydrocarbons or carbonaceous material, which may be absorbed in sulphuric acid. This causes a ‘dark’ colour. Decolourisation of the acid is known as “acid bleaching”. The method used to remove the discolouration is as described in Table 1.24 below.

Method of decolourisation	Special conditions	Effect
Hydrogenperoxide-solution <60 %	Absorber/tanks	+++/acid and oleum

Table 1.24: Discolouration technique

1.3.1.4 Use of auxiliary chemicals/materials

Catalysts

When producing sulphuric acid by the contact process an important step is to produce sulphur trioxide, by passing a gas mixture of sulphur dioxide and oxygen over a catalyst.

$$SO_2 + {}^{1}/_{2}\, O_2 \leftrightarrow SO_3 \quad \Delta H = -99 \text{ kJ/mole}$$

Without a catalyst this reaction needs a very high temperature to achieve a realistic reaction rate as the equilibrium favours SO_2 formation at high temperatures, which makes the conversion very low.

Only vanadium compounds, platinum and iron oxide have proven to be technically satisfactory when tested for catalytic activity for sulphur dioxide oxidation. At present vanadium pentoxide is used almost exclusively.

Commercial catalysts contain 4 - 9 wt % vanadium pentoxide (V_2O_5) as the active component, together with alkali metal sulphate promoters. Under operating conditions these form a liquid melt in which the reaction is thought to take place. Normally potassium sulphate is used as a promoter but in recent years caesium sulphate has also been used. Caesium sulphate lowers the melting point, which means that the catalyst can be used at lower temperatures. The catalyst support is different forms of silica.

The catalyst support is mixed together to form a paste and then usually extruded into solid cylindrical pellets, rings or star-rings which are then baked at high temperatures. Ring (or star-ring) shaped catalysts, which are mostly used today, give a lower pressure drop and are less sensitive to dust build up.

The lower temperature limit is 410 – 430 °C for conventional catalysts and 380 – 390 °C for caesium treated catalysts. The upper temperature limit is 600 – 650 °C, above this, catalytic activity can be permanently lost due to internal surface area reduction. The average operating life for the catalyst is about 10 years. Operating life is generally determined as a result of catalyst losses during screening of the catalyst, which has to be done periodically to remove dust.

1.3.1.5 Intermediate and final product storage

There is minimal air pollution problems associated with the storage, handling and shipping of sulphuric acid at normal temperatures as the vapour pressure of H_2SO_4 is low. Safety and management procedures for the handling of pure SO_3 and oleum are needed to minimise the risk of atmospheric pollution in the case of accidental release.

The following are important considerations relating to the above ancillary operations:

- receipt, handling and the storage of powdered raw materials must be carried out in such a way that minimises the release of dust. Liquid and gaseous feeds must be contained to prevent the release of odorous fumes or gases
- oleum and SO_3 storage and handling operations, both integral to H_2SO_4 production, must be installed with fume emission control. Vents must go to acid tanks or scrubbing systems. Installations must be built according to best engineering practice. Potential releases, either accidental or otherwise can condense and solidify in cool areas. Care must be taken not to overpressurise storage tanks and design features incorporated to minimise the risk of solids build up
- leaks may occur during the storage and handling of sulphuric acid and may impact on the soil or on receiving waters. In order to minimise the possibility and consequence of such leaks precautions have to be taken, such as bund containment and acid treatment systems.

1.3.1.6 Energy generation/consumption, other specific ‘utilities’

The process steps: sulphur burning, sulphidic ores roasting, SO_2 conversion and SO_3 absorption are all exothermic processes. In the production of sulphuric acid energy recovery is essential. The removal and utilisation of this excess heat is intrinsically linked to the process strategy for the operation of other energy dependent downstream plants. The viability of the whole operation of these integrated operations is dependent on local conditions, and the interaction with other production units. The technical possibilities for energy optimisation are governed by the age of production units, as the construction materials and specific building configurations used could limit the scope for energy generation/consumption. The sulphur burning in conjunction with double absorption process has shown itself as the most energy efficient. The different energy utilisation techniques are:

- techniques raising steam for electrical power generation, which includes specialised equipment such as a super-heater, economiser, and a steam boiler for the sulphur burner
- steam generation from the inter-pass absorber at temperatures from 110 °C to 180 °C and steam pressures from 1.5 bar_{abs} to 11 bar_{abs}
- steam turbines, with power generation up to 15 MWh (1250 tonne H_2SO_4 100 % Plant/day)
- preheating the water from 40 °C to 80 °C from the final absorption
- the optimisation of the process using special programmes (e.g. saving costs and energy recovery).

An essential characteristic of a conventional cold-gas plant (metallurgical gases) is that almost all the energy is discharged as waste heat at low temperature. Double absorption processes based on metallurgical gases differ from hot-gas plants based on sulphur combustion in that cold feed gases must be heated to the converter-inlet temperature using the energy liberated in the oxidation of sulphur dioxide.

At a feed gas concentration of 8.5 % SO_2 and a dryer inlet temperature of 30 – 40 °C about 2.7 GJ of thermal energy is liberated per tonne of sulphuric acid (5.4 GJ in the case of sulphuric acid produced from elemental sulphur). This corresponds to a thermal output of 31 MW for a 1000 t/d plant. About 45 % of the total energy is discharged through the intermediate absorber acid cooling system, 23 % through the final absorber acid cooling system and about 22 % through the dryer acid cooling system in terms of heat recovery. There is no excess high temperature heat that can be used for the generation of high-pressure steam in a conventional cold-gas double-absorption plant for processing relatively low-grade sulphur dioxide containing feed gases. However, where the sulphuric acid plant is linked to a modern smelter, a high concentration of SO_2 is available. Low temperature heat from the absorber acid circuits can be utilised for preheating the boiler feed-water to increase the output of high-pressure steam.

1.3.1.7 Gas cleaning of metallurgical off-gases

SO_2 containing gases from all metallurgical processes are filtered clean before passing to the contact process of the following:

- fumes or aerosols formed by a condensation of volatile metal components such as Zn, Pb, Sb. Bi, Cd and their chlorides, sulphates and oxides
- volatile gaseous metals such as As, Se, Hg and their compounds
- the gaseous non-metallic compounds such as HF, HCl, SO_3, CO.

A small amount of contaminants are absorbed in sulphuric acid or released with the stack tail gas after filtration.

CO is oxidised to CO_2 in the contact process. All other gases are absorbed in sulphuric acid or released with the stack tail gas. CO_2 is also released from associated combustion processes.

Table 1.25 shows the different metallurgical off-gases, the main disposal routes and the clean-up system used.

Offgas from	Main disposal	Clean up system used
'CuS' smelters	Hg, HF	ESP, gas scrubber with $HgCl_2$ or $Na_2S_3O_3$/HgS
'PbS' smelters	Hg	ESP, gas scrubber with $HgCl_2$
'ZnS' smelters	Hg	ESP, gas scrubber with $HgCl_2$
'Ni' smelters	Se	gas scrubber

Table 1.25: Clean-up systems for metallurgical off-gases

1.3.1.8 Handling of waste gas/stack height

The dispersion of SO_2/SO_3 and ground level concentrations around a sulphuric acid plant depend on the height of the exhaust stack, the gas buoyancy, atmospheric conditions, the local topography and any nearby building effects. Dispersion conditions may vary due to the:

- vertical temperature and humidity profile
- wind speed and direction
- atmospheric turbulence
- the sunshine intensity, etc.

Stack height calculations need to take account of these factors.

At present every Member State has its own method for estimating the minimum height of stacks. It is anticipated that this situation will be regularised across the EU by the issue of a specific Guidance note [29, EIPPCB, Draft].

1.3.2 Current emission and consumption levels

The inputs and outputs for sulphuric acid production are based on either a single or double absorption plant in the first instance. The actual sources of raw material that provide the SO_2 for conversion to sulphuric acid are then analysed for the inputs and outputs.

1.3.2.1 Inputs and outputs

Emissions into air

CO_2, SO_x, NO_X.

SO_3 emissions

Origins

- bad absorption efficiency
- vapour pressure of sulphuric acid/oleum
- minimisation techniques
- absorption improvements
- absorbing tower design (velocity)
- acid distribution (flow and repartition)
- packing efficiency
- acid temperature (vapour pressure).

H_2SO_4 emissions

Origins

- tower design
- mist formation
- vapour pressure.

Minimisation techniques

- droplet carry-over
- absorbing tower design (gas velocity, acid distribution)/demisters (mesh pads or candles)
- mist filter.

Process control

- ESP efficiency
- drying tower efficiency
- gas temperature upstream absorption
- NOX content in the gases
- acid temperature at the bottom of absorption tower
- acid vapour pressure (temperature)
- high efficiency demisters 50 mg.Nm-3 (particles >0.5µ).

SO_2 emissions

Origins

- bad conversion efficiency
- gas bypassing (acid cross bleed or convector).

Minimisation techniques without additional process

Gases

- composition (O_2, SO2, inerts…)
- velocities through catalyst and repartition
- cooling quality (heat exchangers or air cooling)
- operating pressure
- acid cross-bleeds (SO_2 stripping, SO_2 gases drying processes)
- temperature.

Catalyst

- converter design
- number of beds
- catalyst quality and quantity
- converter loading.

SO_2-Minimisation techniques with additional process

- without by-product: Single absorption double absorption (if gases are higher than 6 % SO_2
- SO_2 weak H_2SO_4 possible to recycle: Activated carbon oxidation process.

H_2O_2 process

- with co- or by-product:
- NH3 scrubbing, co-product ammonium sulphate
- NaOH scrubbing, co-product sodium sulphate
- $Ca(OH)_2$ scrubbing, co-product calcium sulphate (gypsum)
- $Mg(OH)_2$ scrubbing, co-product magnesium sulphate
- other processes – neutralisation absorption, bioconversion – exist but are less developed and depend on the specific site.

Emissions into water

- energy release from cooling
- accidental leakage
- waste water treatment plants must be able to deal with heavy metals
- emissions of noise by air cooling
- water treatment for steam production.

Solid wastes

Sulphuric acid spent catalysts

Methods for disposing of spent catalyst are:

Metal recovery

The vanadium content of the catalysts can be reclaimed for further use. This service is usually provided by the catalyst manufacturer who will have access to a reclamation operation. The metal can be recycled as vanadium salts or as ferrovanadium for steel production. In all recycling cases it is very important that the spent catalyst has a low content of arsenic. A typical analysis for spent catalysts:

- V_2O_5: min. 3 % weight
- K_2O: max. 10 % weight
- P: max. 0.5 % weight
- Sn, Pb, As, Sb, Bi, Cu, Zn, Cd, Hg: max. 0.1 % weight.

Landfill Disposal

Two types of disposal are available:

- **Fixation**: The catalyst is ‘fixed’ in an inert matrix, usually concrete or glass (also known as vitrification) prior to a controlled deposit in a suitably licensed landfill site. The fixation process is designed to prevent metals leaching into the landfill site

- **Direct landfilling**: The catalyst is deposited directly into a suitably licensed landfill site in compliance with national legislation. It is common practice to mix the catalyst with lime to neutralise any residual acidity.

Wastes from packing and lining

Waste from the chemical industry is always handled with care. Waste from sulphuric acid production, packing, lining and scrap-iron is always handled in the same way as waste from other chemical production plants. That means that where necessary, the waste is checked for impurities before a decision is made on how to handle it. There are usually no problems in normal sulphuric acid production.

Consumption of water/energy and other resources

Sulphuric acid production is one of the few chemical processes where more energy is normally produced than is used in the process. In many cases, sulphuric acid plants are used as the energy source for the production processes for other chemicals that require energy. Sulphuric acid production also has the advantage that there is no formation of carbon dioxide compared with the use of fossil fuel or natural gas, and energy is considered “green” compared to other energy productions due to the fact that the energy is a by-product. Overall the process is a net producer of energy, although the amount of recovery possible is a function of the level of quality of this energy.

Consumption of water

All acid plants have measures in place to control the use of water for cooling and to adjust the concentration in the acid system. The cooling system is normally a closed water circuit or it includes a measurement of the pH before discharge to waste. The use of water in the acid system is important to ensure the right concentration in the absorption tower, to prevent acid mist in the stack. Boiler feed-water for steam production requires special pre-treatment depending on the different sources such as groundwater or drinking water. Treatments include anion and/or cation exchange and conditioning with ammonia, sodium hydroxide, hydrazine or phosphates. Water quality, including pH and conductivity, must be fully controlled. About 95 % of the water is used for steam production and the remainder of the boiler water, which is mostly alkaline, can be discharged to drain after neutralisation. In the interests of economy all uncontaminated water condensates should be collected and used for new steam production.

Energy consumption

Sulphuric acid production is always a net producer of energy. The quality of the energy produced is a function of the site requirements. Examples of the different kinds of energy produced are steam at different pressures for chemical plants, power generation or city heating; or hot water for use in greenhouses or fish farms.

Other resources

Regeneration, recycling and evaporation are different ways to prevent spent acid becoming a waste and a problem for the environment. A sulphuric acid plant to process the tail gas from metal roasting prevents the emission of sulphur dioxide to the atmosphere.

Accidental pollution

There is always a risk of accidental pollution when chemicals are produced and handled. The more common a chemical, the more information is available about the different hazards and the lower the risk of accidental pollution. The highest risk for accidental pollution is during the transportation of the product and that is covered under the different transport regulations, such as those of ADR/RID and IMO. There is also a risk of pollution from the storage of sulphuric acid and different plants have different systems to collect leaks and spillages depending on guidelines applicable for the storage of acid. Gas leaks are not normally a problem as they are handled by various monitoring and control systems, which measure the SO_2 content in the air.

Areas of concern

The most important issue is the transportation of the product and that is covered under the relevant regulations. There is a risk to personnel during the loading and unloading of sulphuric acid if it is mishandled. All producers are responsible for the personal safety of their employees and and will have different systems in place to ensure proper handling.

Multimedia complexity

Emissions of sulphur dioxide into the air may deposit on the soil and contribute to a lower pH. SO_2 scrubbing gives rise to a by-product disposal problem, which depends on the type of by-product. For example, gypsum may be disposed of to landfill and ammonium sulphate may be sold or recycled.

1.3.2.1.1 Other single absorption plants

	Amount	Units	Comments
Inputs			
SO_2	2 – 6	%	Degree of variability: Low
O_2	9 – 5	%	Degree of variability: Low
CO_2	0	%	Degree of variability: No
Water (in the gas)	10	mg/Nm	
Outputs			
Energy	2500	MJ	Net balance
Emissions to air:			
- SO_2 1)	4.5 – 13.3	kg/tonne 3)	
- SO_3 1)	0.03	kg/tonne 3)	
- H_2SO_4 1)	0.03	kg/tonne 3)	
- NO_X 2)	<30	mg/Nm³	
- CO_2	0	% (vol)	
Emissions to water	0		No emission to water
Solid emisions	10	g/tonne	Spent catalyst
Conversion rate	98 – 99.5	%	
Emission with the final product:			
As	<0.01	ppm	
Hg	<0.01	ppm	
Se	<0.01	ppm	
F	<0.01	ppm	
SO_2	<30	ppm	
NO_X	<30	ppm	
HCl	<1	ppm	
Organic carbon	<1	ppm	
1) Expressed as SO_2 2) Expressed in NO_2 3) In kg per tonne of 100 % sulphuric acid			

Table 1.26: Other single absorption plants

1.3.2.1.2 Sulphur burning plants with double absorption

	Amount	Units	Comments
Inputs			
- SO_2	6 – 12	%	Degree of variability: Low
- O_2	9 – 15	%	Degree of variability: Low
- CO_2	0	%	Degree of variability: No
- Water (in the gas)	10	mg/Nm³	
Outputs			
Energy	2500	MJ	Net balance
Emissions to air:			
- SO_2 1)	1.5 – 3.9	kg/tonne 4)	
- SO_3 2))	0.1	kg/tonnne 4)	
- H_2SO_4 2)	0.1	kg/tonne 4)	
- NO_X 3))	<30	mg/Nm³	
- CO_2	0	%(vol)	
Emissions to water	0		no emission to water
Solid emisions	10	g/tonne	spent catalyst
Conversion rate	99.2 – 99.6	%	
Emission with the final product: 5)			
- As	<0.01	ppm	
- Hg	<0.01	ppm	
- Se	<0.01	ppm	
- F	<0.01	ppm	
- SO_2	<30	ppm	
- NO_X	<30	ppm	
- HCl	<1	ppm	
- organic carbon	<1	ppm	

1) Expressed in SO_2
2)) Expressed in H_2SO_4
3)) Expressed in NO_2
4) In kg per tonne of 100 % sulphuric acid
5) Those values may not be met with certain raw material

Table 1.27: Sulphur burning plants with double absorption

	Amount	Units	Comments
Inputs			
- SO_2	8 - 10	%	Slightly over time
- O_2	8 – 11	%	
- CO_2	0	%	
- H_2O	0	%	
Outputs			
Energy	~4500	MJ/tonne $^{3)}$	Net balance incl. roasting process
Emission into air:			
- SO_{2*}	3.0	kg/tonne $^{3)}$	
- SO_{3*}	0.2	kg/tonne $^{3)}$	
- H_2SO_{4*}	n.a.	kg/tonne $^{3)}$	
- $NO_X^{2)}$	~210	mg/Nm^3	
- CO_2	0	%(vol)	
Emission into water			No emission into water
Solid emissions	~40	g/tonne $^{3)}$	Spent catalyst
Conversion rate	99.4 - 99.6	%	
Emission with the final product:			Dependent of the analyses of the pyrite The figures are examples from one specific pyrite.
- As	0.01	ppm	
- Hg	0.03	ppm	
- Se	0.005	ppm	
- F	n.a.	ppm	
- SO_2	13	ppm	
- NO_X	n.a.	ppm	
- HCl	n.a.	ppm	
- Organic carbon	0	Ppm	
$^{1)}$Expressed in SO_2 $^{2)}$ Expressed in NO_2 $^{3)}$ Per tonne of 100 % sulphuric acid			

Table 1.28: Pyrite roasting

1.3.2.1.3 Zn, Pb smelter sulphuric acid plants (ZnS-roasting)

Inputs	**Single Abs.**		**Double Abs.**	
- % SO_2	4 ~ 6		5 ~ 9	
- % O_2	6 ~ 12		6 ~ 11	
- % CO_2	x		x	
- % H_2O	x		x	
Variability in time	Low		Low	
Energy (1kWh = 3.6 MJ) MJ/tonne H_2SO_4			~ 600	
Outputs				
Air emission at stack	kg/t H_2SO_4	$mgNO_X/Nm^3$	kg/t H_2SO_4	$mgNO_X/Nm^3$
- SO_2	7 ~ 12	x	1.7 ~ 3.3	x
- SO_3	0.1 ~ 0.2	x	0.05 ~ 0.08	x
- NO_X		150		150
- H_2SO_4	0.05 ~ 0.1	x	0.05 ~ 0.08	x
Conversion SO_2/SO_3	98 ~ 99 %		99.5 ~ 99.7 %	
H_2O emission	No contaminants		No contaminants	
Spent Catalyst	20 ~ 40 g/tonne H_2SO_4 To recycle in process		20 ~ 40 g/tonne H_2SO_4 To recycle in process	
H_2SO_4:				
- Hg	max 1 ppm			
- As	max 0.5 ppm			
- Se	max 0.2 ppm			
- SO_2	<50 ppm			
- NO_2	5 ~ 30 ppm			
- Org C	max. 1 ppm			
Energy Steam in roasting process MJ/t.H_2SO_4	3500			
(Waste) heat in acid production: MJ/t.H_2SO_4	1000 ~ 2000			
Net Balance (In-Out)	3900 ~ 4900			

Table 1.29: ZnS roasting

1.3.2.1.4 Complex (Pb, Cu) S batch treatment

Inputs	**Single Abs.**		**Double Abs.**	
% SO_2	2.70 % on dry			
% O_2	2.50 % on dry			
% CO_2	20.00 % on dry			
% H_2O	45 %			
Variability in time	Extremely			
Energy (1kWh = 3.6 MJ) MJ/t.H_2SO_4	900			
Outputs				
Air emission at stack	kg/tonne H_2SO_4	mgNO_2/Nm^3	kg/tonne H_2SO_4	mgNO_2/Nm^3
- SO_2	6 ~ 10			x
- SO_3	see H_2SO_4			x
- NO_2		100		
- H_2SO_4	0.15			x
Conversion SO_2/SO_3	99.0 - 99.2 %			
H_2O emission	None			
Spent catalyst	20 ~ 40g/tonne H_2SO_4			
H_2SO_4				
- Hg	<1 ppm			
- As	<0.2 ppm			
- Se	<0.5 ppm			
- SO_2	90 ppm			
- NO_2	150 ppm			
- Org C.	40 ppm			
Energy				
Steam in production process: MJ/tonne H_2SO_4	Depending on S-content			
(Waste) heat in acid production: MJ/t.H_2SO_4	1000 ~ 2000			
Net balance (In-Out)	~1000 – 2000			

Table 1.30: Complex Pb, Cu sulphides batch treatment

1.3.2.1.5 Copper smelter sulphuric acid plant

	Units	Double Absorption	Single Absorption	Comments
Inputs				
- SO_2	%	5 - 13	3 - 10	Degree of variability: High
- O_2	%	8 - 16	11 - 18	Degree of variability: High
- CO_2	%	0 - 3	0 - 3	Degree of variability: High
Water (in the gas)	% (vol)	5 - 7	5 - 7	
Process water	m^3/tonne	0 - 0.2	0 - 0.2	
Outputs				
Energy	MJ	2000 - 2900	2000 - 2900	Net balance
Emissions into air				
- SO_2 1)	kg/tonne 3)	1.2 - 3.3	6.5 - 20	
- SO_3 1)+ H_2SO_4 1)	kg/tonne 3)	0.05 - 0.2	0.06 - 0.35	
- H_2SO_4 1)	kg/tonne 3)			
- NO_X 2)	mg/Nm^3			Variability: High, depending of smelter O_2 enrichment
- CO_2	%(vol)	0 - 4	0 - 4	
Emissions into water				No emission to water
Solid emisions spent catalyst	g/tonne	20 - 40	20 - 40	5 – 10 % of the installed catalyst and per screening operation
Conversion rate	%	99.5 - 99.8	97 - 99	
Emission with the final product:				
- As	ppm	<1	Similar to double absorption	
- Hg	ppm	<1	"	
- Se	ppm	<0.5	"	
- F	ppm	0 - 2	"	
- SO_2	ppm	<30	"	
- NO_X	ppm	<40	"	Variability: High, depending of smelter O_2 enrichment
- HCl	ppm	<5	"	
- Organic carbon	ppm	traces	"	Influenced by the smelter fuel combustion burner type (<50)
1) Expressed in SO_2 2) Expressed in NO_2 3) In kg per tonne of 100 % sulphuric acid				

Table 1.31: Copper smelter sulphuric acid plant

1.3.2.1.6 Spent acid regeneration

	Amount	Units	Comments
Inputs			
- SO_2	7	%	Degree of variability: 2 – 10 %
- O_2	8	%	Degree of variability: 5 – 15 %
- CO_2	5	%	Degree of variability: 1 – 10 %
Water (in the gas)	10	mg/Nm³	
Outputs			
Energy	2500	MJ	Net balance
Emissions into air			
SO_2 [1]	2.6 to 2.7	kg/tonne[3] DA: 2.6 to 6.6 SA: 10 to 27	
SO_3 [1]	0.03	kg/tonne[3]	
H_2SO_4 [1]	0.03	kg/tonne[3]	
NO_X[2]	0 to 50	mg/Nm³	
CO_2	4	%(vol)	
Emissions to water	0		No emission to water
Solid emisions	0	g/tonne	Spent catalyst
Conversion rate	96 to 99.6	% DA: 99 to 99.5 SA: 96 to 98.5	
Emission with the final product			
- As	<0.01	ppm	
- Hg	<0.01	ppm	
- Se	<0.01	ppm	
- F	<0001	ppm	
- SO_2	<30	ppm	
- NO_X	<30	ppm	Depends on the spent acid type
- HCl	<1	ppm	
- Organic carbon	<1	ppm	

[1] Expressed in SO_2
[2] Expressed in NO_2
[3] In kg per tonne of sulphuric acid 100 %
ND: not determined

Table 1.32: Spent acid regeneration

Emission levels before bed 1

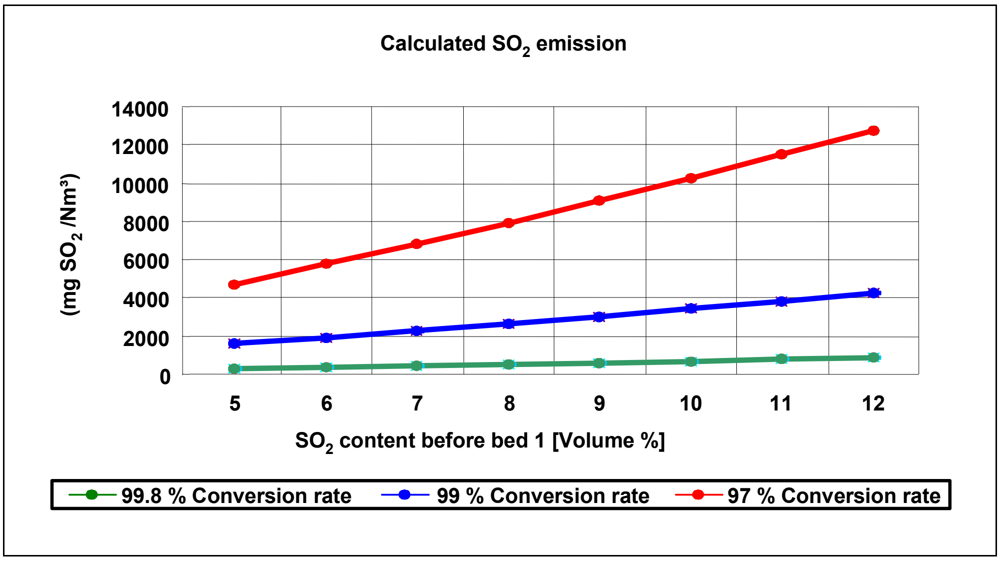


Figure 1.7: Calculated SO_2 emissions before bed 1

1.4 Phosphoric acid

In the late eighties and the early nineties fertiliser consumption in Western Europe reduced significantly, as a consequence of agricultural policy changes in the European Union. These policy changes have had a large impact on the structure of the European wet phosphoric acid industry. A large number of relatively small phosphoric acid plants in Europe have closed down, primarily because of unfavourable economics, and as a result the structure has increasingly moved towards a small number of large production plants. The number of plants in Western Europe has continued to reduce.

The list in the table below is the latest information on the units still producing phosphoric acid in the EU.

Plants		**Phosphoric Acid Capacity (kt P_2O_5)**
Belgium	Rhone-Poulenc Chemie	130
	Societe Chimique Prayon-Rupel SA	140
Finland	Kemira Chemicals Oy	235
Greece	Chemical Industries of Northern Greece SA	110
	Phosphoric Fertilisers Industry Ltd	65
Spain	Fertiberia S.L.	420
	FMC Foret, SA	130

Table 1.33: Overview of European phosphoric acid plants in 2003
[16, RIZA/Tebodin, 2000]

Note: Two plants in The Netherlands have now been shutdown and Grand Quevilly in France

Production routes and fields of application

Phosphoric acid is the most important mineral acid in terms of volume and value after sulphuric acid. Phosphoric acid is primarily used in the manufacture of phosphate salts and its direct use as an acid is secondary.

Two different processes using different raw materials can be used in the manufacture of phosphoric acid. The first process is known as the **thermal** process and uses elemental phosphorus as the raw material. Here elemental phosphorous is produced from phosphate rock, coke and silica in an electrical resistance furnace. The phosphoric acid that results from the thermal process is commonly called thermal acid. After this first step, elemental phosphorus is oxidised to P_4O_{10} after which the acid is generated by hydration of the oxide. Thermal acid is considerably purer than acid produced by the wet-process, but it is also more expensive, and is hence produced in much smaller quantities. About 80 – 90 % of the thermal acid produced is used for the production of industrial phosphates, especially the sodium, potassium, calcium and ammonium salts. Thermal acid is used in metal surface treatment and, as food grade quality, for the acidulation of beverages.

The second types of processes are those using phosphated minerals, which are decomposed with an acid. These types of processes are known as **wet processes**. There are three possible subgroups of wet processes depending on which acid is used for the acidulation i.e. nitric, hydrochloric or sulphuric acid. The wet digestion of phosphate rock with sulphuric acid is the preferred process in terms of volume [16, RIZA/Tebodin, 2000]. The wet-process involves the acid dissolution of the phosphate rock to produce phosphoric acid by double decomposition and is characterised by a relatively high production volume, low cost and low purity. The share of wet phosphoric acid amounts to 95 % of the total phosphoric acid in Western Europe. It is used primarily in the production of fertilisers (approximately 80 %) and animal feed supplements

(8 %). Part of the wet-process acid is purified for the manufacture of technical and food-grade phosphate salts, usually employing a solvent extraction process.

Economics have also had a very large impact on the production route used to produce technical grade acid. In Western Europe, the production of phosphoric acid using the solvent extraction-purifying route is preferred over the thermal route. The impact of the energy cost has caused the proportion of thermal acid to be largely reduced. Thermphos in Vlissingen, the Netherlands, at present are the only producers of phosphoric acid via the thermal route [16, RIZA/Tebodin, 2000]. The production capacity of this plant amounts to 155000 tonne/yr (the production in 1995 was 67000 tonne P_2O_5).

1.4.1 Applied processes and techniques

1.4.1.1 Raw materials for phosphoric acid production

Bones used to be the principal natural source of phosphorus but phosphoric acid today is produced from phosphatic ores mined in various parts of the world.

Phosphate ores are found in two major geological origins:

- igneous – found in, for example, Kola, South Africa, Brazil, etc.
- sedimentary – found in, for example, Morocco, Algeria, US, etc.

The phosphate minerals in both types of ore are of the apatite group, of which the most commonly encountered variants are:

- fluorapatite – $Ca_{10}(PO_4)_6(F,OH)_2$, and
- francolite – $Ca_{10}(PO_4)_{6-x}(CO_3)_x(F,OH)_{2+x}$.

Fluorapatite predominates in igneous phosphate rocks and francolite predominates in sedimentary phosphate rocks.

The most easily mined phosphate deposits are found in the great sedimentary basins. These sedimentary deposits are generally associated with matter derived from living creatures and thus contain organic compounds. These phosphates are interposed with sedimentary strata of the other materials interpenetrated by gangue minerals, and, thus sedimentary phosphate ores can have differing compositions even within the same source.

Most phosphate ores have to be concentrated or beneficiated before they can be used or sold on the international phosphate market. Different techniques may be used at the beneficiation stage, to treat the same ore for removal of the gangue and associated impurities. This gives rise to further variations in the finished ore concentrate product. Phosphoric acid technology has to rely on raw materials of variable consistency and needs to be constantly adapting the technology to meet raw materials variations.

	CEI Russia*	**S. AFRICA Phalaborwa***	**MOROCCO Khouribga**	**US Florida**	**SENEGAL**	**TOGO**
Grade (nominal) % BPL	84	80	73	75	80	80
Composition (WT-%)						
P_2O_5	38.9	36.8	33.4	34.3	36.7	36.7
CaO	50.5	52.1	50.6	49.8	50	51.2
SiO_2	1.1	2.6	1.9	3.7	5	4.5
F	3.3	2.2	4	3.9	3.7	3.8
CO_2	0.2	3.5	4.5	3.1	1.8	1.6
Al_2O_3	0.4	0.2	0.4	1.1	1.1	1
Fe_2O_3	0.3	0.3	0.2	1.1	0.9	1
MgO	0.1	1.1	0.3	0.3	0.1	0.1
Na_2O	0.4	0.1	0.7	0.5	0.3	0.2
K_2O	0.5	0.1	0.1	0.1	0.1	0.1
Organics		0.1	0.3	0.5		
Organ. C	0.1			0.2	0.4	0.1
SO_3	0.1	0.2	1.6	0.1		0.3
Cl			0.02			0.1
SrO	2.9	0.3	0.1			
Trace elements (ppm)						
Rare earth metals	6200	4800	900	600		
U_3O_8	11	134	185	101	124	
As	10	13	13	11	18	12
Cd	1.2	1.3	15	9	53	53
Cr	19	1	200	60	6	
Hg	33	0.1	0.1	0.02	0.2	0.6
Pb		11	10	17	5	
Ni	2	2	35	28		
Zn	20	6	200 - 400	70		
Cu	37	102	40	13		
* Igneous						

Table 1.34: Variation in chemical analysis of various phosphate rocks

1.4.1.2 Principles of the process

The basic chemistry of the wet process is very simple. The tri-calcium phosphate from the phosphate rock reacts with concentrated suphuric acid to produce phosphoric acid and the insoluble salt calcium sulphate.

$$Ca_3(PO_4)_2 + 3H_2SO_4 \longrightarrow 2H_3PO_4 + 3CaSO_4$$

The insoluble calcium sulphate is filtered from the phosphoric acid.

The reaction between phosphate rock and sulphuric acid is restricted by an insoluble layer of calcium sulphate which forms on the surface area of the rock. This restriction is minimised by contacting the phosphate rock with re-circulated phosphoric acid, thereby converting as much of it as possible to the soluble mono calcium phosphate, followed by precipitation as calcium sulphate with sulphuric acid.

$$Ca_3(PO_4)_2 + 4H_3PO_4 \longrightarrow 3Ca(H_2PO_4)_2$$

$$Ca(H_2PO_4)_2 + 3H_2SO_4 \longrightarrow 3CaSO_4 + 6H_3PO_4$$

Calcium sulphate exists in a number of different crystal forms depending particularly on the prevailing conditions of temperature, P_2O_5 concentration and free sulphate content as can be seen in Figure 1.8 and Figure 1.9.

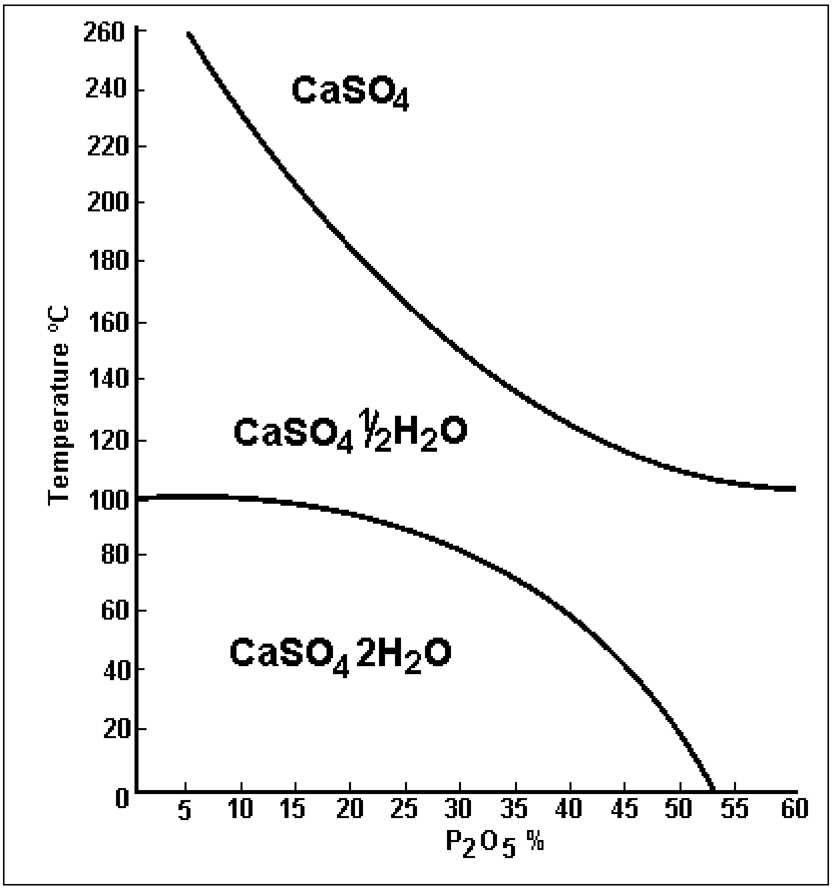


Figure 1.8: Dependance of calcium sulphate hydrate crystallisation on temperature [8, EFMA, 2000]

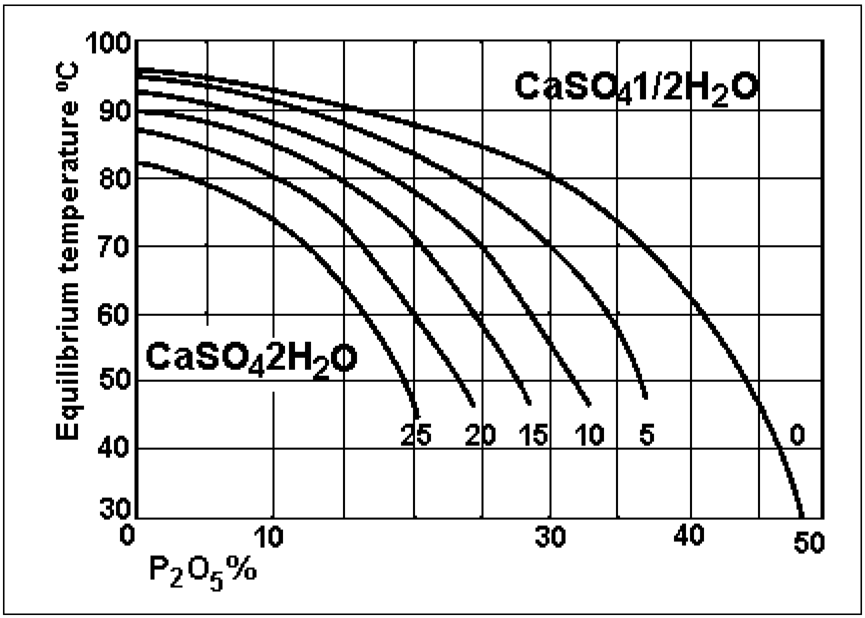


Figure 1.9: Dependance of calcium sulphate dihydrate/α-hemihydrate equilibrium on sulphuric acid concentration [8, EFMA, 2000]

The operating conditions are generally selected so that the calcium sulphate will be precipitated as the di or hemihydrate form, i.e. 26 – 32 % P_2O_5 at 70 – 80 °C for dihydrate precipitation and 40 - 52 % P_2O_5 at 90 – 110 °C for hemihydrate precipitation.

There are many impurities in phosphate rock, and in variable amounts. The adverse effects of these impurities appear in the reaction system, but others appear predominantly in the filtration or in the properties of the product acid.

Most phosphate rocks contain fluoride between 2 – 4 % w/w. This fluoride is released during acidulation, as hydrogen fluoride, but reacts readily with excess silica forming fluoro silicic acid (H_2SiF_6). Magnesium and aluminium compounds also react with HF forming $MgSiF_6$ and H_3AlF_6. A proportion of the fluoride is released in the vapour, the amount depending on the reaction conditions, with the rest remaining in the acid solution. Some of this residual amount may combine with other impurities at a sufficient rate for removal by filtration. The remaining amount will appear as sludge in the product acid. Volatile fluorine compounds can also be present in the release from the evaporator vent as a result of filter acid concentration.

Other impurities such as arsenic, cadmium, copper, lead, nickel, zinc and mercury, present in most phosphate rock can pass into the acid during acidulation and need to be taken into account when selecting the feedstock. Phosphate rocks contain naturally occurring uranium and the radioactive decay products from the uranium may also be contained within the phosphate feedstock. The uranium transfers into the product acid solution and any radioisotopes can be co-precipitated with the phosphogypsum.

Impurities such as iron, aluminium, sodium, potassium, chlorine, etc, also affect the phosphoric acid production and the product quality.

1.4.1.3 Production processes

Five process routes are discussed in this section and these represent the principal available process routes. These are:

1. dihydrate process
2. hemihydrate process
3. hemihydrate recrystallisation process
4. hemihydrate/dihydrate process
5. dihydrate/hemihydrate process.

1.4.1.3.1 Dihydrate process

This process offers a wide range of options and the advantages of dihydrate systems are:

- there is no phosphate rock quality limitation
- on-line time is high
- operating temperatures are low
- start-up and shutdown are easy
- wet rock can be used thereby saving drying costs.

The disadvantages are:

- relatively weak product acid (26 – 32 % P_2O_5)
- high-energy consumption in the acid concentration stage
- 4 – 6 % P_2O_5 losses, most of them co-crystallised with the calcium sulphate.

The dihydrate process consists of four stages, namely grinding, reaction, filtration and concentration. These are shown in Figure 1.10 and discussed below:

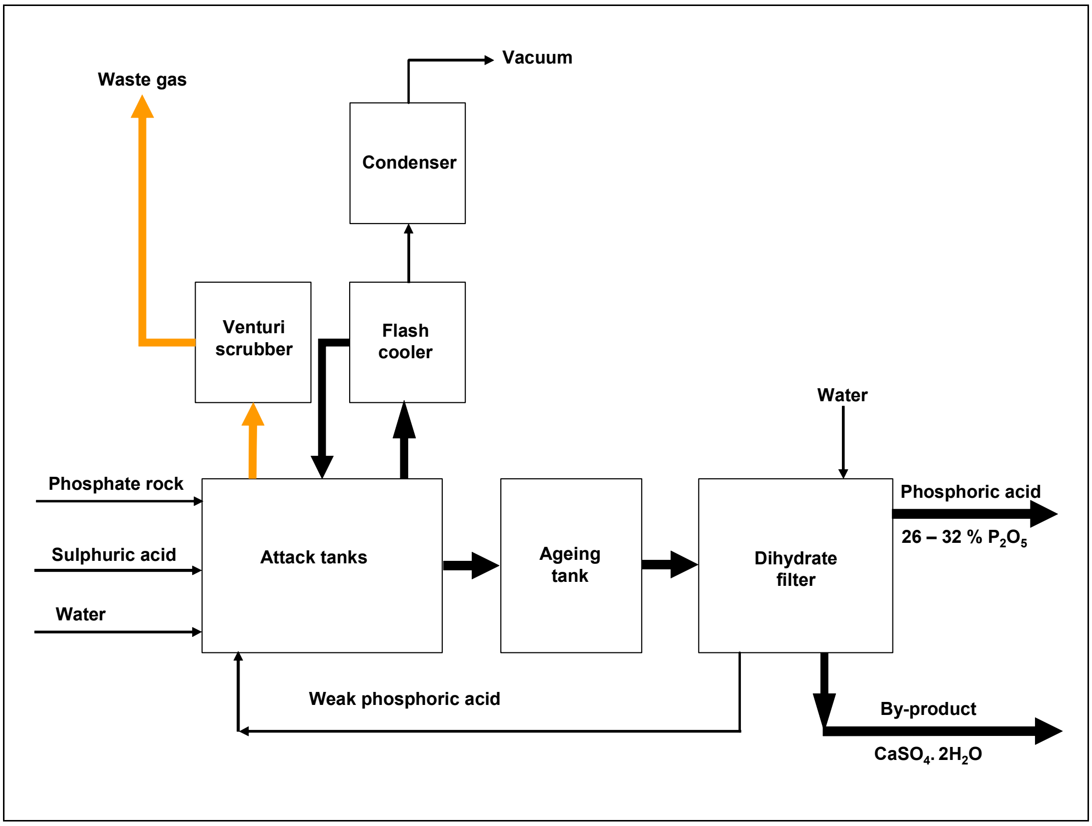


Figure 1.10: Dihydrate process

Grinding

Some grades of commercial rock do not need grinding, their particle size distribution already being acceptable for the dihydrate reaction section i.e. 60 – 70 % particles less then 150 µm. Most other phosphate rocks require particle size reduction, usually using ball or rod mills. Both types of mills can operate with wet or dry rock.

Reaction

Tri-calcium phosphate reacts with concentrated sulphuric acid producing phosphoric acid and insoluble calcium sulphate. Circulation of the reactor contents provides the necessary mixing. The reaction system consists of a series of separate agitated reactors. The multiple vessel reaction system is replaced by a single tank in some processes for economy of materials and space. Some of these single tanks may be divided into compartments, effectively creating separate reactors.

The optimum operating conditions for dihydrate precipitation are 26 – 32 % P_2O_5 and 70 - 80 °C. The slurry temperature is controlled by the use of a flash cooler. This also de-gases the slurry making pumping easier. The temperature may also be controlled, for instance, by using an air circulation cooler.

Filtration

This stage separates the phosphoric acid from the calcium sulphate dihydrate. Five tonnes of gypsum are generated for every tonne (P_2O_5 equivalent) of acid produced. The filter medium is moved in sequence through the various stages for continuous operation. The initial separation is followed by at least two stages of washing, which ensures that all the soluble P_2O_5 is recovered. It is only possible to achieve the required separation rate if the filtration is either pressure or vacuum assisted. In practice, vacuum is invariably used. At the end of the washing sequence the remaining liquid is taken out of the filter cake. The cake is then discharged and the cloth efficiently washed to avoid the filter blinding. The vacuum is released during the discharge of the cake. It is also beneficial at this point to blow air through in the reverse direction to assist in the solids dislodgement.

The filtrate and washings are then separated. They then have to be further treated under vacuum conditions to de-aerate the product so that it can be transport~~s~~ed under atmospheric pressure, as a product or for recycling to the process. The pressure difference is usually maintained by dip-legs into barometric tanks situated at a level below the separators to be adequate for the hydrostatic head to maintain a balanced vacuum.

The most common types of filtration equipment are the tilting pan, rotary table or travelling belt.

Concentration

There is a long history of direct contact concentrators, where evaporation is achieved by contacting the acid with hot combustion gas from a burner. This allows equipment walls to be made of selected materials and of a thickness that are suitable for efficient indirect heat transfer. Various patterns of direct-fired concentrators have been devised. Currently, almost all evaporators used today are of the forced circulation design as shown in Figure 1.11

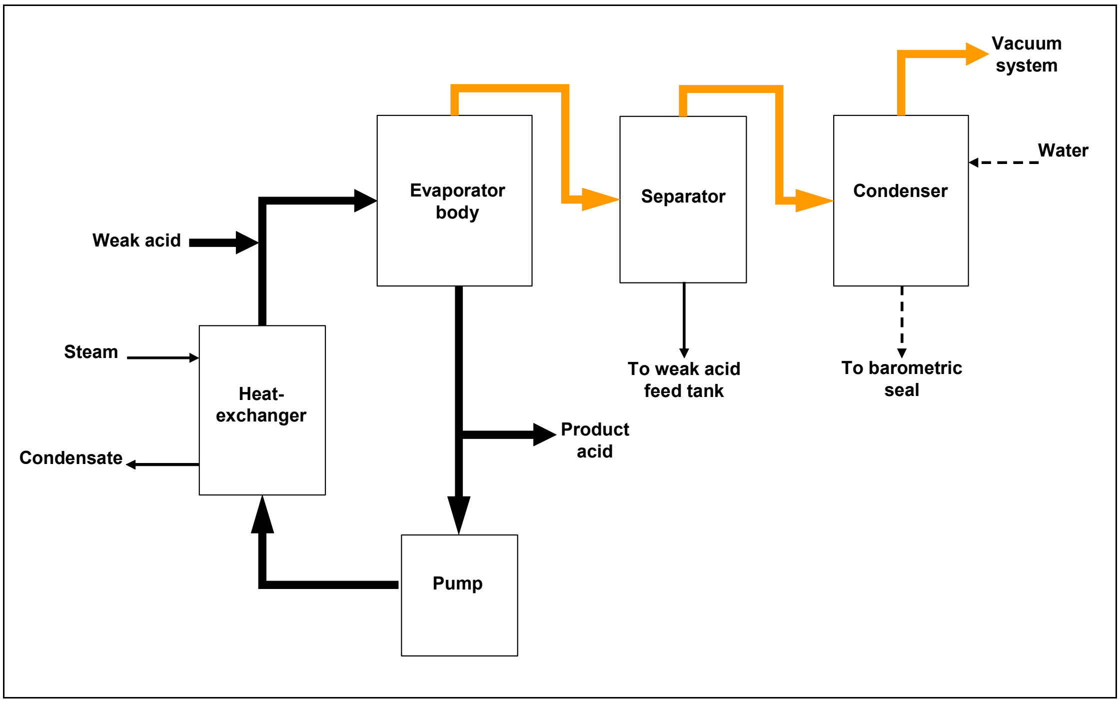


Figure 1.11: Concentration (forced circulation evaporator design)

The forced circulation evaporator consists of a heat-exchanger, vapour or flash chamber, condenser, vacuum pump, acid circulating pump and associated pipework. A fluorosilicic acid scrubber is usually included with a forced circulation evaporator system. All the evaporators in this service are generally of the single-effect design because of the corrosive nature of phosphoric acid and the very high boiling point of the process. The heat-exchangers are fabricated from graphite or stainless steel with the rest of the equipment made from rubber-lined steel.

All equipment designs need to be made using the best available engineering practices. A multiple effect evaporation system may be used depending on the concentration needed.

1.4.1.3.2 Hemihydrate (HH) process

The process operating conditions are set to enable calcium sulphate to be precipitated as the hemihydrate. In this way it is possible to produce 40 – 52 % P_2O_5 acid directly, enabling valuable savings to be made in energy usage. Figure 1.12 shows a simplified flow diagram of a HH process. The stages are similar to those of the dihydrate process although grinding may not be necessary.

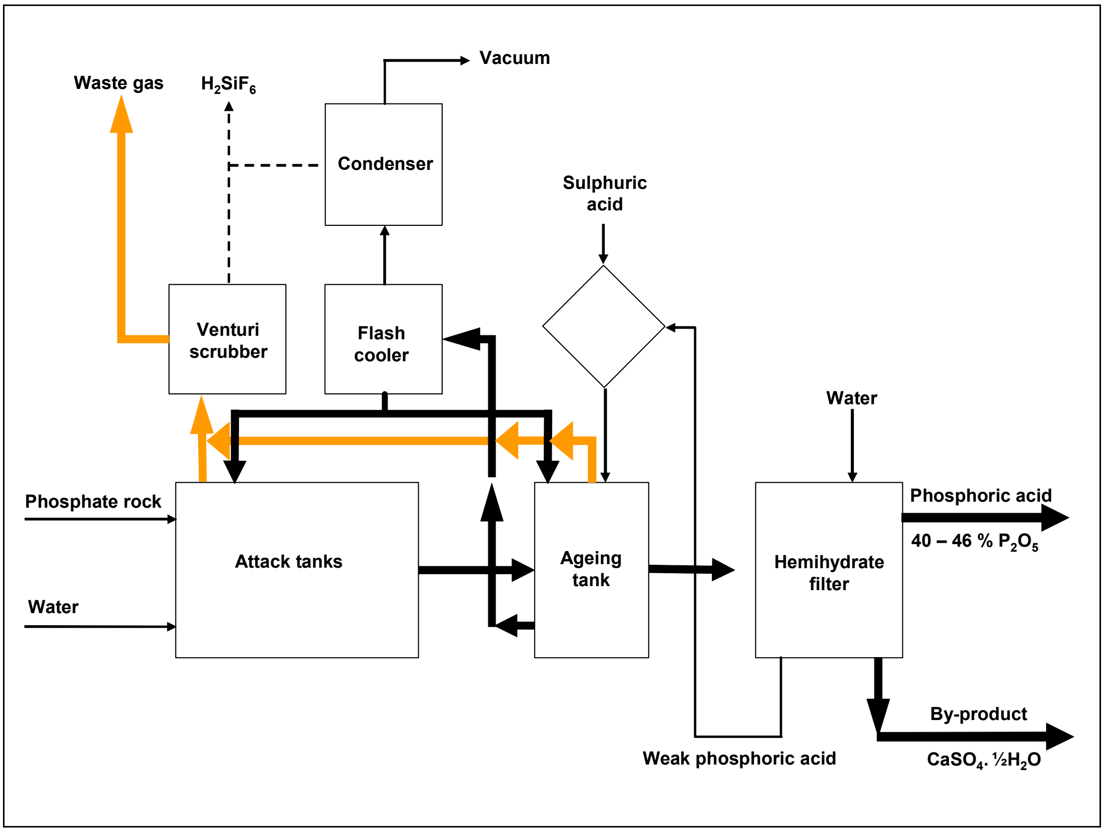


Figure 1.12: Hemihydrate process

Apart from the reduction or elimination of the need for evaporation heat the main **advantages** of this process are:

Capital savings

Purer acid

Acid from the HH process tends to contain much less free sulphate and suspended solids and lower levels of aluminium and fluorine than evaporated dihydrate process acid of the same strength.

Lower rock grinding requirements

A satisfactory rate of reaction can be achieved from much coarser rock than in the dihydrate process, because of the more severe reaction conditions in the HH process.

The **disadvantages** of HH systems are:

Filtration rate

Hemihydrate crystals tend to be small and less well formed than dihydrate crystals so hemihydrate slurries tend to be more difficult to filter than dihydrate slurries, unless crystal form modifiers are used to suppress excessive nucleation. With a good HH process however, there is no need to use modifiers.

Phosphate losses

The amount of wash-water that can be used is restricted by water balance needs. Additionally as a result of the higher P_2O_5 concentration of the slurry being filtered the amounts of both soluble and insoluble P_2O_5 remaining in the filter cake are greater. However despite these losses the simplicity of the HH plant and the absence of silicofluoride and chucrovite scaling in the HH filter may compensate for the higher insoluble P_2O_5 losses through the HH cake.

Scaling

Hemihydrate is not a stable form of calcium sulphate so there is a tendency for it revert to gypsum even before the acid has been filtered off. The conditions are even more favourable for re-hydration during washing. In a well run HH plant there is no conversion in the reactor train. A small quantity of anti-scaling agent may be required in a single-stage HH plant filter to minimise scaling.

Filter cake impurity

The cake is more acidic than gypsum filter cake because of the extra P_2O_5 losses. It also contains more fluoride and cadmium.

Corrosion

The demands on vulnerable items of equipment, particularly agitators and slurry pumps, are increased as a result of the higher temperature (100 ^{o}C) and acidic concentration (40 – 50 % P_2O_5) in comparison to a dihydrate plant.

1.4.1.3.3 Recrystallisation processes

The best P_2O_5 recovery efficiencies that could be expected in the single-stage dihydrate and hemihydrate processes considered up to now, are 94 – 96 % and 90 – 94 % respectively. Some residual P_2O_5 is retained in the filter cake and this can create disposal problems or with use of the by-product gypsum. Some of this residual P_2O_5 passes into solution and can be recovered when the calcium sulphate is finally separated, if the calcium sulphate is recrystallised as its other hydrate. This not only improves the overall efficiency of the process but also gives a much cleaner calcium sulphate.

Several manufacturing processes have been developed but in reality there are only three basic process routes:

1. acidulate under hemihydrate conditions; recrystallise to dihydrate without intermediate hemihydrate separation; separate product. (Hemihydrate recrysallisation (HRC) process)
2. acidulate under hemihydrate conditions; separate product; recrystallise hemihydrate to dihydrate; filter and return liquors to process. (Hemi-dihydrate (HDH) process)
3. acidulate under dihydrate conditions; separate product; recrystallise hemihydrate; filter and return liquors to process (Dihydrate-Hemihydrate (DH/HH) process).

1.4.1.3.4 HRC process

The flow diagram of this process is similar to the multiple reactor dihydrate process shown in Figure 1.10with the exception that the dissolution reactor operates under hemihydrate conditions. The reactors that follow operate under conditions favouring rehydration of the hemihydrate to gypsum. Dihydrate seed crystals in the recycled slurry from the filter feed initiate this rehydration. The product acid is the same concentration as from the dihydrate process but the gypsum is much purer. A flow diagram for this process is shown in Figure 1.13.

This process is also known as the hemi-dihydrate single stage filtration process (HDH-1 process).

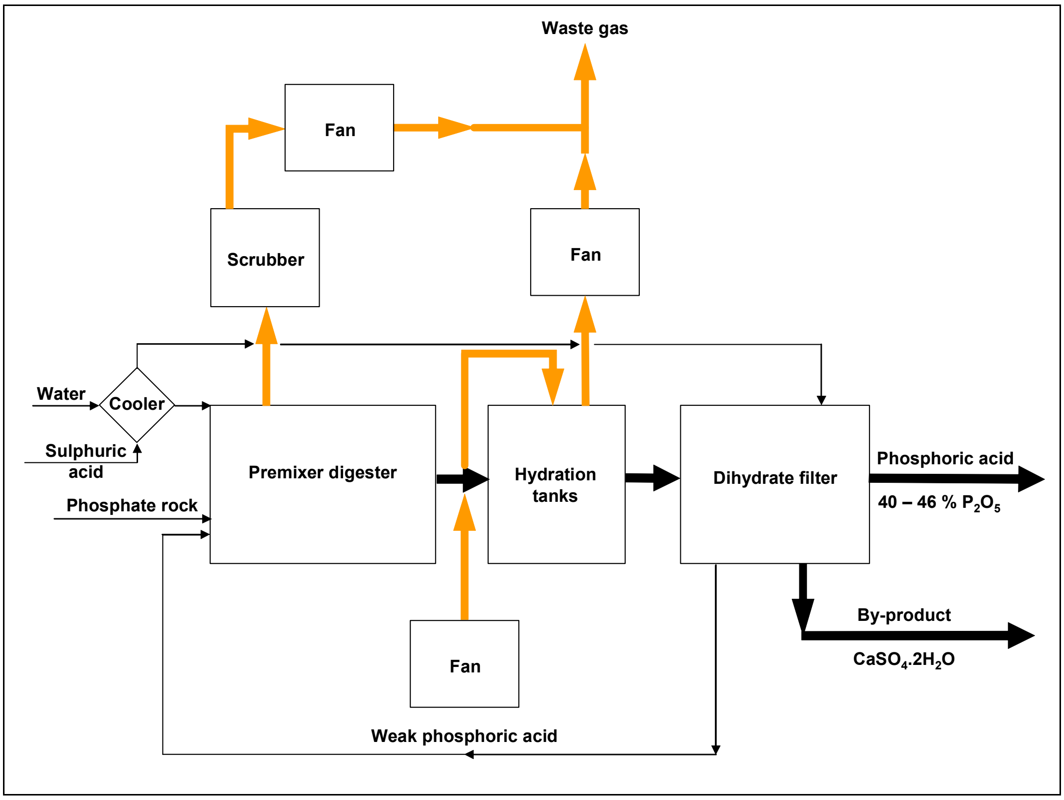


Figure 1.13: Hemihydrate recrystallisation process

1.4.1.3.5 HDH process

In this process it is possible to obtain 40 – 52 % P_2O_5 acid directly, by acidulating under hemihydrate conditions and separating the hemihydrate before recrystallising. The additional filter and the other equipment needed add to the capital cost of the plant but enable savings to be made on evaporation equipment. A flow diagram for this process is shown in Figure 1.14.

This process is also known as the hemi-dihydrate double stage filtration process (HDH-2 process).

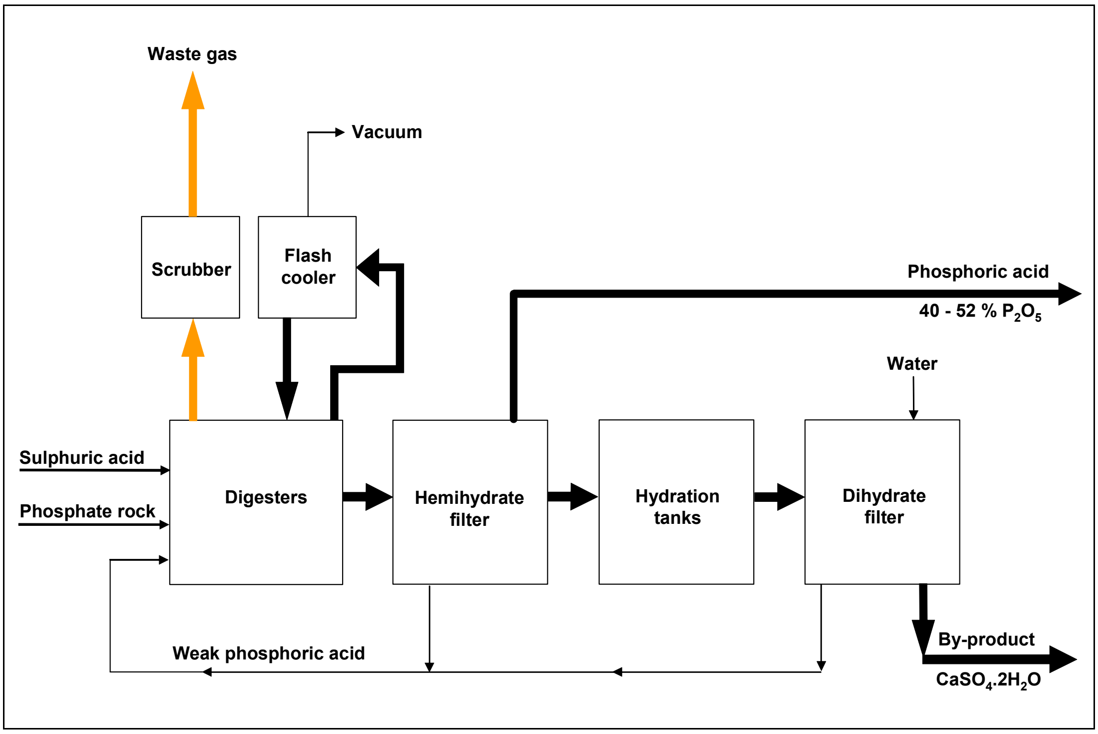


Figure 1.14: Hemidihydrate process

1.4.1.3.6 DH/HH process

In this process, although the reaction runs under dihydrate conditions, it is not necessary to obtain a high degree of P_2O_5 recovery during the separation of the acid from the dihydrate. The succeeding dehydration stage yields around 20 – 30 % P_2O_5 and 10 – 20 % sulphuric acid. The strength of the product acid is 32 – 38 % P_2O_5. A flow diagram for this process is shown inFigure 1.15.

This process is also known as the DHH process.

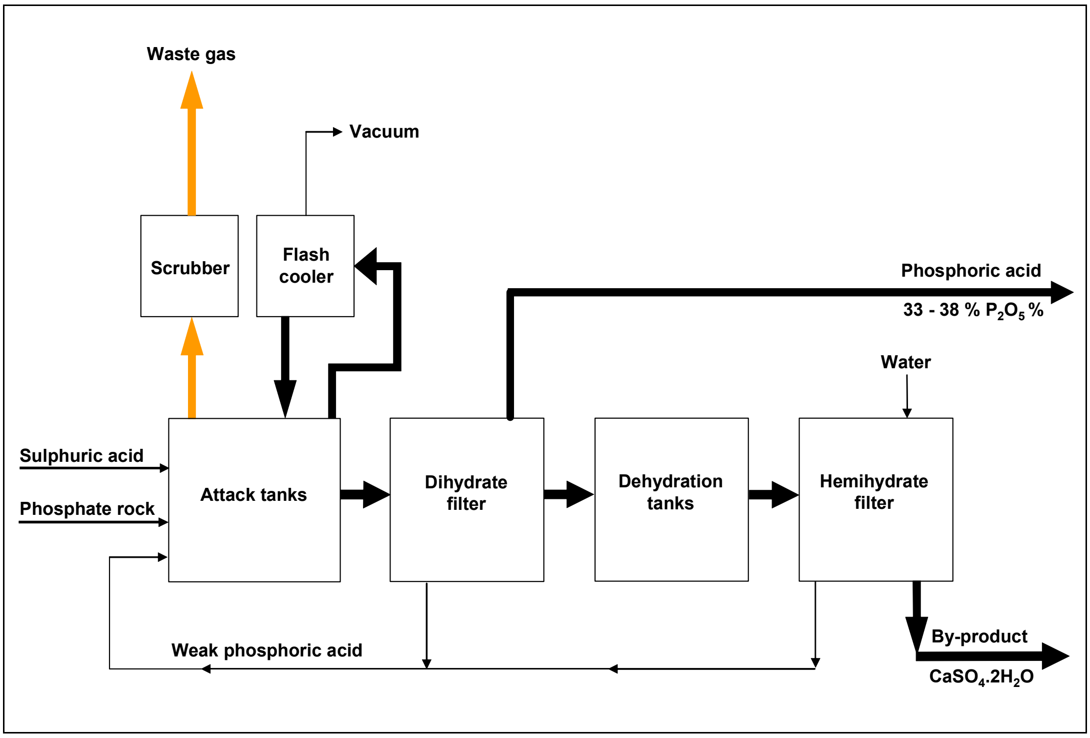


Figure 1.15: Dihemihydrate process

A further optimisation of the HRC process can be made by re-slurrying and washing the gypsum, followed by a second filtration step in the "Repulping Process". Most of the free acid which is not removed in the first filtration step, can be removed in this process and the efficiency can be improved by up to 1 % (depending on the amount of free acid).

The gypsum from the first filter is re-slurried in a tank and then pumped to a second filter where the gypsum is dewatered. The gypsum is then washed with the fresh water coming into the plant. The liquid obtained from the second filter is used on the first filter to wash the gypsum. The repulping process is actually an additional step in the countercurrent washing of the gypsum, using the water that enters the plant. The flow diagram for a repulping process is shown in Figure 1.16.

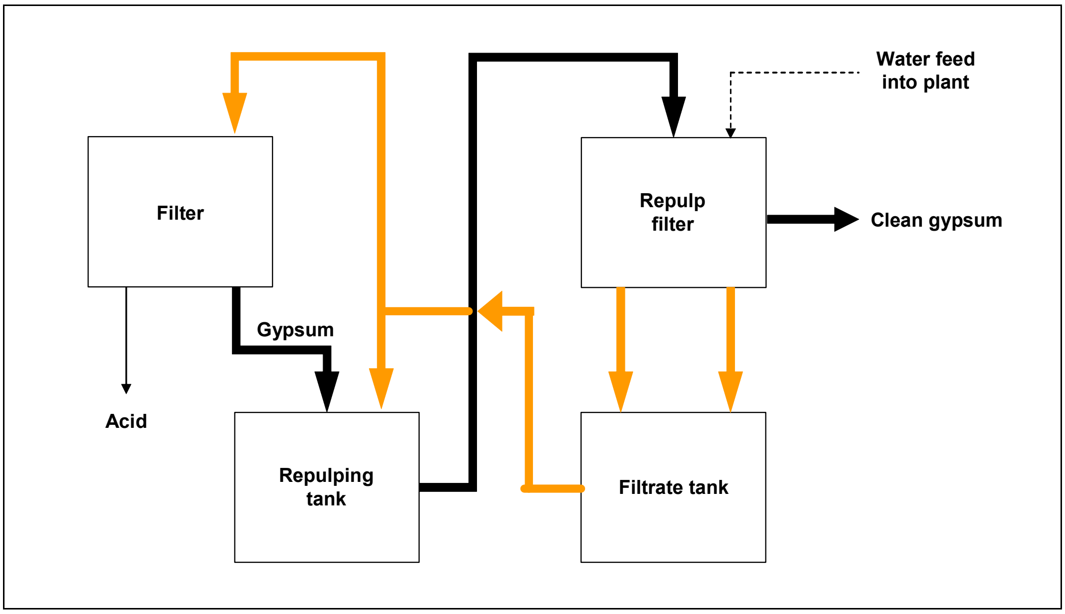


Figure 1.16: Repulp process

ADVANTAGES	DISADVANTAGES
Dihydrate process Single stage filtration. Simple design. Flexibility of rock source. Proven process. Ease of operation/shutdown. Requires lower grades of construction materials. Wet rock-grinding possible. Low maintenance cost and high operating factors. Easy transport of gypsum slurry.	Produces acid at 26 – 32 % P_2O_5. Normally requires steam for evaporation. Acid has high levels of F and Al. P_2O_5 efficiency 94 – 96 %. May require rock grinding. Requires weak acid storage and evaporation.
Hemihydrate process Single-stage filtration. Produces strong acid directly 40 – 48 % P_2O_5. No intermediate storage if acid is produced at user's strength. Uses coarse rock. Ease of operation.	Limited number of rocks processed industrially. Large filter area required for 48 % P_2O_5 acid. High lattice loss, low P_2O_5 efficiency (90 - 94 %) Produces impure hemihydrate. Tight water balance. Requires higher grade alloys. Care required in design and shutdown.
HRC process Single stage filtration. Proven process with sedimentary rock. Produces pure gypsum. Higher P_2O_5 efficiency (97 %). Slightly higher acid strength (30 – 32 % P_2O_5). Lower sulphuric acid consumption. Lower filter area.	Requires a fine rock grind. Requires sulphuric acid dilution. Large recrystallisation volume required. May dissolve more partially soluble impurities. Requires 32 % acid storage and evaporation. Post-precipitation before and after evaporation. Requires sophisticated materials of construction.
HDH process Produces strong acid directly (40 – 52 % P_2O_5). Produces purer acid (low SO_4, Al, F). Limited post- precipitation. Uses coarse rock. Low sulphuric acid consumption. High P_2O_5 efficiency (98.5 %). Produces a purer gypsum.	Two-stage filtration, lower utilisation. Limited number of rocks processed industrially. Care required in design and shutdown. High recrystallisation volume. High capital cost.
DH/HH process Flexible as to rock source. Proven process. Produces a pure hemihydrate. High P_2O_5 efficiency (98 %). Higher acid strength (32 – 36 % P_2O_5). Lower sulphuric acid consumption. Gypsum may be used directly for plasterboard, plaster or as a cement retarder, after the addition of lime and natural rehydration in a storage pile.	Two stage filtration, lower utilisation. High capital cost. Requires steam for conversion. Requires 35 % acid storage and evaporators. Rock slurry feed unacceptable. Requires final re-hydration of hemihydrate to gypsum. Normally, requires rock grinding. Care required in design and shutdown. Requires sophisticated materials of construction.
Additional techniques: repulping process Pure gypsum. High efficiency.	High capital cost.

Table 1.35: Advantages and disadvantages of various extraction processes

1.4.1.4 Storage and transfer equipment

Raw Materials Storage

Sulphuric acid

Reference should be made to [3, ESA, 2000] which covers the production of sulphuric acid.

Phosphate rock

Phosphate rock is generally loaded by crane from the ship and is transported to storage by belt conveyor or lorry. The unloading, handling and storage of these powdered materials should be carried out in such a way so as to minimise the emission of dust

Phosphoric Acid Storage

Phosphoric acid is most commonly stored in rubber-lined steel tanks, although stainless steel, polyester and polyethylene-lined concrete are also used. The types of rubber linings used include neoprene, butyl and natural rubber. Heating and insulation are not required in storage or during shipment since the impurities in wet-process acid promote supercooling and reduce the tendency for crystallisation. Merchant grade acid is usually shipped with a guaranteed solids content of less than 1 %. Storage tanks are normally equipped with some means of keeping the solids in suspension to avoid loss of product and costly cleaning of the tank.

Methods of agitation commonly used are:

- air injection
- agitation from the top
- jet mixing
- agitation from the side
- pump circulation and heating.

Leak-floors are provided underneath vulnerable equipment to prevent contamination of the soil from acid leaks. Any leaks or spills flow to special pits from where the fluid is pumped back into the system. Most acid storage tanks are bunded.

1.4.2 Current emissions and consumption levels

1.4.2.1 Input

The specific consumption of phosphate rock and sulphuric acid mainly depends on the composition of the rock used and the overall efficiency of the process. Phosphate rock usage is about 2.6 - 3.5 tonne/tonne P_2O_5 produced

The consumption of process water mainly depends on the concentration of the weak acid from the filter and whether the condensed water in the evaporation loop is recycled. The consumption of proces water is about 4 – 7 m^3/tonne of P_2O_5 produced, excluding scrubber water.

Cooling water is used in the reaction and concentration stages and during condensation of the vapours from the evaporators. The consumption of cooling water depends on the process used but is about 100 – 150 m^3/tonne of P_2O_5 equivalent as concentrated acid.

A phosphoric acid plant needs electrical power and steam. The power consumption depends on whether the process needs phosphate rock grinding. Consumption is about 120 - 180 kWh/tonne P_2O_5 equivalent. Steam is mainly used for the concentration stages at a rate of about 0.5 - 2.2 tonne/tonne P_2O_5 concentrated.

When the phosphoric acid plant is linked to a sulphuric acid plant, the high-pressure steam produced in the waste heat recovery boiler from the sulphuric acid is normally used to produce electric power and the low-pressure exhaust steam is used for phosphoric acid vacuum concentration. In addition it may be possible to reduce the steam consumption needed for the concentration by using waste heat originating in the sulphuric acid plant. This may be recovered as heated water and used in the process of concentrating weak acid to intermediate concentrations.

1.4.2.2 Output

The main product is phosphoric acid with a commercial concentration of 52 – 54 % P_2O_5. The production capacity is up to 1200 t/d P_2O_5 depending on the particular process route being used.

Fluosilicic acid with a concentration of 20 – 25 % H_2SiF_6 is obtained as a by-product and results from the F and Si impurities in the phosphate rock. The quantity of 100 % fluosilicic acid produced depends on the composition of the phosphate rock being used but is normally in the range 20 – 30 kg/tonne P_2O_5 produced.

1.4.2.3 Emissions

The main environmental aspects of wet process phosphoric acid production are:

- emission of gaseous fluorides to the atmosphere
- emission of dust
- discharge of effluent from off-gas treatment containing phosphorous and fluorine
- disposal of the waste gypsum
- radioactivity.

1.4.2.3.1 Fluoride emissions to air

Fluoride is present in most phosphate rocks at a level of 2 – 4 %, that is 20 – 40 kg/tonne rock or about 60 – 120 kg/tonne P_2O_5. Fluoride is distributed between the product acid, gypsum, vapours generated in the reactor and the acid concentration section during processing. Initially, fluoride is released in the reaction as hydrogen fluoride (HF), but in the presence of silica it reacts readily to form fluosilicic acid (H_2SiF_6) and compounds such as $MgSiF_6$ and H_3AlF_6. The fluosilicic acid may decompose with heating to give volatile silicon tetrafluoride and hydrogen fluoride.

In a DH process the temperature is usually too low to cause the decomposition of fluosilicic acid. The majority of fluorine compounds will be evolved with the evaporator vapours during concentration of the weak phosphoric acid. In the HH process most of the fluoride is released during the reaction. Fluoride leaves the reactor with the vacuum cooler condenser water or with the cooling air, depending on the cooling system used (flash cooler or air circulating cooler). A typical fluoride distribution in the DH and hemihydrate process is shown in the following table.

	DH Process (%)	HH Process (%)
Acid	15	12
Gypsum	43	50
Reactor off-gas	5	8
Flash cooler vapour	3	30
Concentrator vapour	35	-

Table 1.36: Typical fluorine distribution in DH and HH processes
[16, RIZA/Tebodin, 2000]

1.4.2.3.2 Dust emissions to air

Dust emissions begin with the unloading, handling and grinding of phosphate rock. Phosphate rock is normally supplied by ship. It is unloaded by cranes and transferred to storage and grinding sections by conveyor belts or trucks.

1.4.2.4 Discharges to water

Liquid releases mainly consist of the effluents originating from vacuum cooler condensers and gas scrubbing systems, which are used for cleaning and condensation of the vapours that evolve in the various process stages. These acidic condensed vapours contain mainly fluoride and a small amount of phosphoric acid.

The water from the slurry used to transport the phosphogypsum after settling is commonly recirculated in the process, therefore giving no liquid effluent. This water in some operations is discharged into a river or the sea and contains trace elements (Al, Ni, Cd, Pb, As) as well as fluoride and phosphoric acid.

1.4.2.5 Phosphogypsum

Gypsum is an inevitable by-product in wet phosphoric acid production; for every tonne of phosphoric acid (P_2O_5) produced around 4 - 5 tonne of gypsum are produced. In the process, the impurities associated with phosphate rock are distributed between the product and the calcium sulphate.

Type of Impurity	% impurity in gypsum	% impurity in acid
Cadmium	0 - 5	95 - 100
Mercury	100	0
Arsenic	0 - 5	95 - 100
Lead	100	0
Copper	30 - 60[2]	40 - 70
Zinc	0 - 5	95 - 100
Nickel	0 - 10	90 - 100
Chromium	0 - 5	95 - 100
Rare earth elements[1]	90 - 100	0 - 10
Uranium-238	0	100
Radium-226, Lead-210, Polonium-210	100	0

[1] The elements scandium, yttrium, lanthanum, cerium, praseodymium, neodymium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, lutetium; underlined are the elements that are the most abundant.

[2] The distribution of copper, zinc, nickel and chromium usually lies in the same range. However, deviations may occur as a result of the phosphate rock used

Table 1.37: Typical distribution of impurities between waste gypsum and product acid for an HRC process
[16, RIZA/Tebodin, 2000]

In HDH and DH/HH processes the amount of impurities that end up in the gypsum is slightly less, while in DH and HH processes the amount of impurities that end up in the gypsum is usually larger. In general, mercury, lead and the rare earth metals end up mainly in the gypsum. This also applies for the radioactive components radium-226, lead-210 and polonium-210. Arsenic and the other heavy metals such as cadmium, zinc, nickel and chromium end up mainly in the acid. Uranium-238 almost completely ends up in the acid. The distribution of these contaminants in the product and waste streams is more or less fixed and is difficult to re-distribute [16, RIZA/Tebodin, 2000].

1.4.2.6 Radioactivity

All natural materials contain naturally occurring radioactive nuclides. The sources of these radionuclides are uranium-238, uranium-235 and thorium-232, which all have long half-lives. These radionuclides, so-called mother radionuclides, decay through a chain of daughter radionuclides, which may have relatively long half-lives, to stable nuclides. uranium-238 is the most abundant one of the three mother radionuclides. There is 10 times as much uranium-238 present compared to the amounts of uranium-235 and thorium-232.

The radioactivity of phosphate rock is therefore mainly from radionuclides from the radioactive decay series of uranium-238. The radionuclides radium-226, radon-222, lead-210 and polonium-210 are part of the uranium-238 decay series.

The radionuclides content in phosphate rock is very dependent on the origin of the rock. Sedimentary rock contains more uranium-238 and its daughter radionuclides than igneous rock. During phosphoric acid production, the radionuclides will be divided mainly between the product acid and the by-product gypsum, although other emission sources may also contain limited amounts of radionuclides. For the by-product gypsum, the radionuclides radium-226, lead-210 and polonium-210 are important. Uranium-238, on the other hand, will almost completely end up in the product acid. Radon-222, as a decay product from radium-226, is generated as a gas, which is emitted to the air.

1.4.2.7 Dutch situation

Specific emissions 1996/97		
	Kemira per tonne P_2O_5	**Hydro Agri per tonne P_2O_5**
Emissions to air		
Fluorine	6.1 [1] g	2.8 g
Dust	12 [2] g	19 g
Liquid emissions to water		
Phosphate	1.3 kg	0.7 kg
Fluorine	15 kg	31 kg
Cadmium	0.003 [3] g	0 [4] g
Mercury	0 [3] g	g
Arsenic	0.02 [3] g	1.9 g
Heavy metals	1.9 [3] g	2.8 g
Solid emissions to water		
Gypsum	4000 kg	4700 kg
Phosphate	8.1 kg	5.8
Fluorine	33 kg	45 kg
Cadmium	0.5 g	1.4 g
Mercury	0.2 g	0.5 g
Arsenic	0.7 g	0 [4] g
Heavy metals [5]	53 g	27 g
Rare earth metals [6]	2200 g	360 g
Ra-226	1.4 MBq	2.3 MBq
Po-210	1.4 MBq	2.3 MBq
Pb-210	1.4 MBq	2.3 MBq

[1] Fluorine concentration $<1 mg/Nm^3$
[2] Dust concentration 30 mg/Nm^3
[3] Estimated values based on input-output calculations
[4] All values measured are below detection limit
[5] Lead, cooper, zinc, nickel and chromium
[6] Mainly lanthanum, cerium, praseodymium, neodymium.

Table 1.38: Actual emissions from the production of phosphoric acid [16, RIZA/Tebodin, 2000]

The plants referred to in the above table are now shut down.

Thermal phosphoric acid

1.4.2.8 Consumption levels

	Thermphos-1998[1] **per tonne P_2O_5**
Inputs	
Phosphate rock	3.0 - 3.4 tonne
Clay	0.2 - 0.3 tonne
Cokes	0.5 – 0.6 tonne
Process water	40 m^3
Cooling water	120 m^3
Electric power	5700 – 6000 kWh
Natural gas	n.a.
Steam	n.a.
Outputs: by-products	
Fuel gas	1500 - 1600[1] Nm^3
Phosphorous furnace slag	3.2 tonne
[1] In 1998 about 20 % of this gas was flared	

Table 1.39: Thermal phosphoric acid production process inputs and outputs
[16, RIZA/Tebodin, 2000]

1.4.2.9 Emissions and waste

The main sources of emissions and waste in the production of phosphorus and phosphoric acid from elemental phosphorus are:

- sintering of the phosphate rock pellets and drying of cokes in the sinter furnace. The off-gas from the sinter furnace contains a wide range of pollutants such as dust, fluoride, phosphate, heavy metals, radionuclides SO_2 and NO_X
- calcination of electrostatic precipator dust (gas phase produced in the phosphorus furnace contains a considerable amount of dust), flaring of fuel gas (after recovery of phosphorus from the gas, the remaining gas mainly consists of carbon monoxide) and drainage of liquid slag from the phosphorus furnace
- oxidation of phosphorus in the acid plant and removal of arsenic from the acid. The off-gas from the acid towers is contaminated with traces of P2O5 and phosphoric acid. Due to the specific fields of application (additive to foodstuff and beverages) traces of arsenic present in the phosphoric acid have to be removed. Sodium hydrogen sulphide (NaHS) is added to the acid, to remove the arsenic by precipitating arsenic sulphide (As2S3).

	Thermphos-1998[1] per tonne P_2O_5
Emissions to air	
Phosphate	0.6 kg
Fluorine	0.1 kg
Dust	0.4 kg
Cadmium	1.0 g
Lead	6.0 g
Zinc	5.9 g
Po-210	3.5 MBq
Pb-210	0.3 MBq
Emissions to water	
Phosphate	0.7 kg
Fluorine	0.7 kg
Cadmium	0.2 g
Mercury	<0.01 g
Arsenic	<0.07 g
Heavy metals	14 g
Po-210	0.05 MBq
Pb-210	0.06 MBq
Waste	
Cottrell dust	3.2 kg
Arsenic sulphide filter cake	0.1 kg

1) The figures presented in the table are based on the total emissions of the sinter plant, the phosphorus plant and the acid plant, and the amount of phosphate rock processed in 1998 assuming a P_2O_5 content of 33 % and an overall P-recovery efficiency of 94 %. In 1998 only about 20 % of the phosphorus produced was converted into phosphoric acid on site. The remaining was sold as phosphorus.

Table 1.40: Emissions factors realised during production of elemental phosphorus and phosphoric acid by Thermphos in 1998
[16, RIZA/Tebodin, 2000]

1.5 Hydrofluoric acid

Production capacity in the EU is around 300000 tonne of HF per year. Approximately 80 % of the production is in the anhydrous form and the rest aqueous.

Half of this output is used internally as an intermediate within the producing companies whilst the other half is sold on the open market. The major applications, in addition to its use as a raw material for fluorocarbons, are in the steel, glass and the alkylation industries. The market has been quite static in recent years.

HF is also used as a raw material for inorganic salts, hydrochlorofluorocarbons, and perfluorocarbons, as well as for fluoropolymers.

Different quality grades of HF are needed by the market, which may require different purification measures depending on requirements.

The EU plants are located in the UK, Germany, France, Italy, the Netherlands, Spain and Greece. The size of the plants varies from above 40000 tonne/year to below 5000 tonne/year. About 400 people are employed directly in the manufacturing of HF.

The majority of the plants were built between 1917 and 1989, but all have undergone major refurbishment during the last 12 years.

The producers have jointly prepared guidelines and recommendations on the safe handling and manufacturing of HF over the last 25 years taking account of the corrosive and toxic nature of the substance.

1.5.1 Applied processes and techniques

Hydrogen fluoride and hydrofluoric acid are produced by the conversion of dried fluorspar using concentrated sulphuric acid at elevated temperatures in accordance with the following reaction:

$$CaF_2 + H_2SO_4 \rightarrow 2HF + CaSO_4 \qquad \Delta H_R = 59\ kJ \qquad (1)$$

There are secondary reactions due to impurities contained in the fluorspar. These occur alongside the main reaction, forming e.g. silicon tetrafluoride, sulphur dioxide, hydrogen sulphide, carbon dioxide, water and elementary sulphur in accordance with the following reaction equations:

$$SiO_2 + 2CaF_2 + 2H_2SO_4 \rightarrow SiF_4 + 2CaSO_4 + 2H_2O \qquad (2)$$

$$CaCO_3 + H_2SO_4 \rightarrow CaSO_4 + CO_2 + H_2O \qquad (3)$$

$$R_2O_3 + 3H_2SO_4 \rightarrow R_2(SO_4)_3 + 3H_2O \qquad (R=Fe, Al) \qquad (4)$$

$$CH_3(CH_2)_nCOOH + (2n + 3)H_2SO_4 \rightarrow (n + 2)CO_2 + (3n + 5)H_2O + (2n + 3)SO_2 \qquad (5)$$

$$Fe\ (Reactor) + 2H_2SO_4 \rightarrow FeSO_4 + SO_2 + 2H_2O \qquad (6)$$

$$MS + H_2SO_4 \rightarrow MSO_4 + H_2S \qquad (M=Metals) \qquad (7)$$

$$2H_2S + SO_2 \rightarrow 3S + 2H_2O \qquad (8)$$

H_2S formed by reaction (7) is completely converted to sulphur according to reaction (8). Water formed by these reactions is removed from the reaction gases by absorption in sulphuric acid. Oleum is added, to provide the SO_3 reacting according to equation (9) to maintain the concentration of the sulphuric acid, being fed to the reactor, at a constant level.

$$H_2O + SO_3 \rightarrow H_2SO_4 \qquad (9)$$

1.5.1.1 Manufacturing process

1.5.1.1.1 Raw material preparation

The raw material for the preparation of hydrogen fluoride and hydrofluoric acid, is fluorspar, which is mined with a mass content of between 30 and 60 % CaF_2 in the crude ore. The crude ore is ground and the CaF_2 is separated from the other minerals by flotation. The flotation chemicals in current use are mainly saturated and unsaturated phytogenetic fatty acids. They remain in the fluorspar, which should ideally contain at least 97 % CaF_2 for use as “acid spar” [19, CEFIC, 2000]

Acid spar should not contain any fraction above 0.2 mm diameter. It is transported to the user as a bulk material with a water content of about 10 %, to minimise dust generation.

Component	Portion (mass content in %) Maximum acceptable values
CaF_2	>97.0
SiO_2	<2.0
$CaCO_3$	<2.0
Residual oxides (Fe and Al)	<2.0
$MgCO_3$	<1.0
$BaSO_4$	<1.0
Sulphides as S	<0.05
Phosphates as P_2O_5	<0.2
Flotation chemicals (saturated and unsaturated fatty acids)	<0.3

Table 1.41: Components in acid spar
[19, CEFIC, 2000]

The fluorspar needs to be dried before it is fed to the hydrogen fluoride plant. This is usually done in directly heated flue-gas dryers at about 120 ºC. There are also plants without spar drying equipment, but which purchase the spar already dried elsewhere.

1.5.1.2 Reactor systems

The HF processes in use are generally continuous in operation, using indirectly heated flue-gas rotary kilns. SO_3 is supplied as oleum, which is mixed with fresh concentrated sulphuric acid (95 to 99 % H_2SO_4) and water and solids containing sulphuric acid, which are recirculated after use as the scrubbing medium in the process gases scrubbing and condensing part of the plant. From this point the mixture is called "feed sulphuric acid", which has a concentration of 90 to 95 % H_2SO_4. The endothermic reaction energy is supplied by heating the steel shell of the kiln up to about 450 °C.

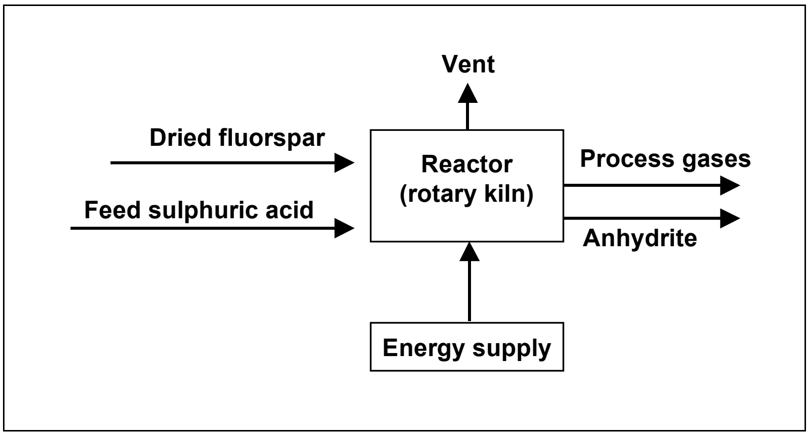


Figure 1.17: Principle of HF production
[19, CEFIC, 2000]

The heated kiln surface area needed to produce 1 tonne HF/d is about 5 to 10 m^2 with this arrangement. Dried fluorspar is not easily mixed with the sulphuric acid due to the flotation chemicals. There are several options possible to reach a higher HF production capacity for a given kiln:

- preheating the sulphuric acid feed
- mixing fluorspar and feed sulphuric acid in an indirectly heated pre-reactor before feeding the partially reacted mass to the rotary kiln. In the pre-reactor, the reaction mixture changes from liquid to a pasty and sticky consistency and is extremely corrosive and abrasive. It needs special knowledge regarding the materials of construction to reduce corrosion. The use of pre-reactors can significantly reduce the heated kiln surface area typically by 30 %
- another option is to calcine the dried fluorspar, heating it directly with oxygen containing flue-gases to 400 – 450 ºC. The calcined spar is free of organics; 95 % are burned to CO_2 and H_2O and 5 % are emitted as crack-products. This can be easily fed with the sulphuric acid. SO_2 formation is avoided and the heated kiln surface necessary to produce 1 t HF/d is only 2.5 – 3 m^2.

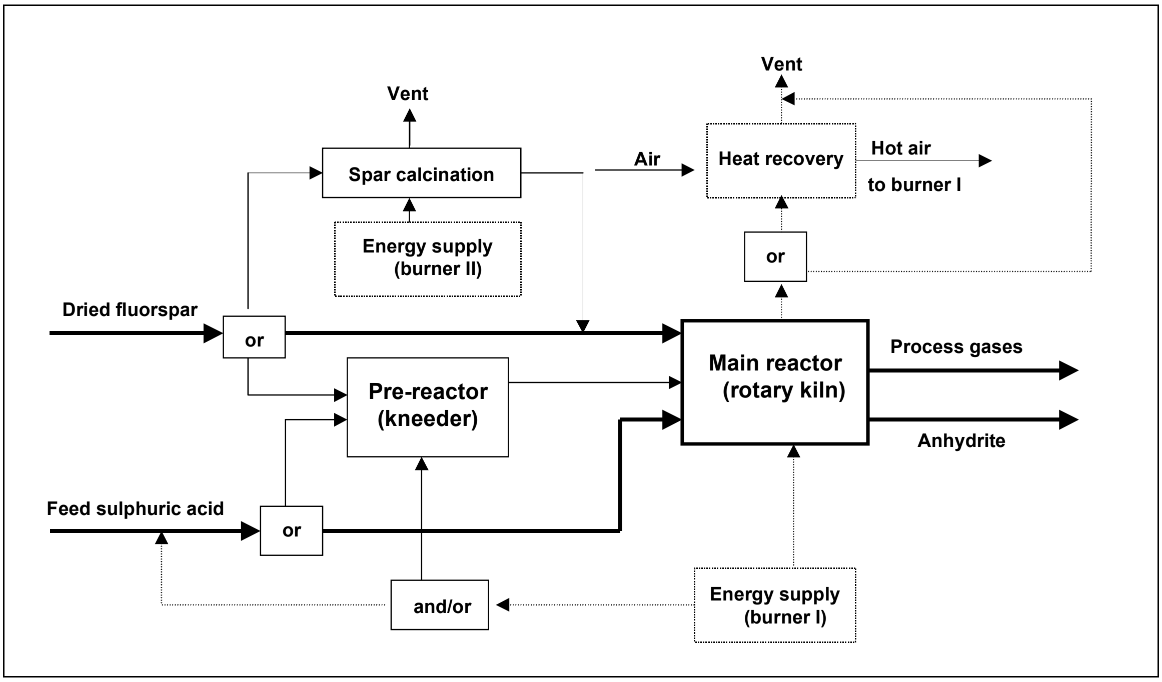


Figure 1.18: Different options for the production of HF
[19, CEFIC, 2000]

Process gases may be discharged either at the feed end or at the anhydrite discharge end of the kiln. In the first case the temperature of the process gases leaving the reactor system is about 150 °C and about 220 °C in the second case where the temperature of the anhydrite is in the range of 200 - 220 °C.

The whole HF plant is maintained under suction to minimise HF emissions. The reactors have to be carefully sealed to prevent air ingress in order to minimise the waste gas volume. [19, CEFIC, 2000]

Energy consumption is reduced by heat recovery in most plants, by preheating the air supplied to the main burner in a recuperator using the rotary kiln fluegas as a heat source.

1.5.1.3 Process gases scrubbing and condensation

Process gases leaving the reactor contain, besides dust and ingressed air, H_2O, SO_2, CO_2, sulphur gas, SiF_4 and others, the amounts depending on the quality of the fluorspar used. The main functions of this part of an HF plant Figure 1.19 are:

- to remove CaF_2 and $CaSO_4$ dust
- to condensate HF, and
- and to remove the low and high boiling impurities from the crude HF.

There are different possibilities available to achieve these objectives Figure 1.20.

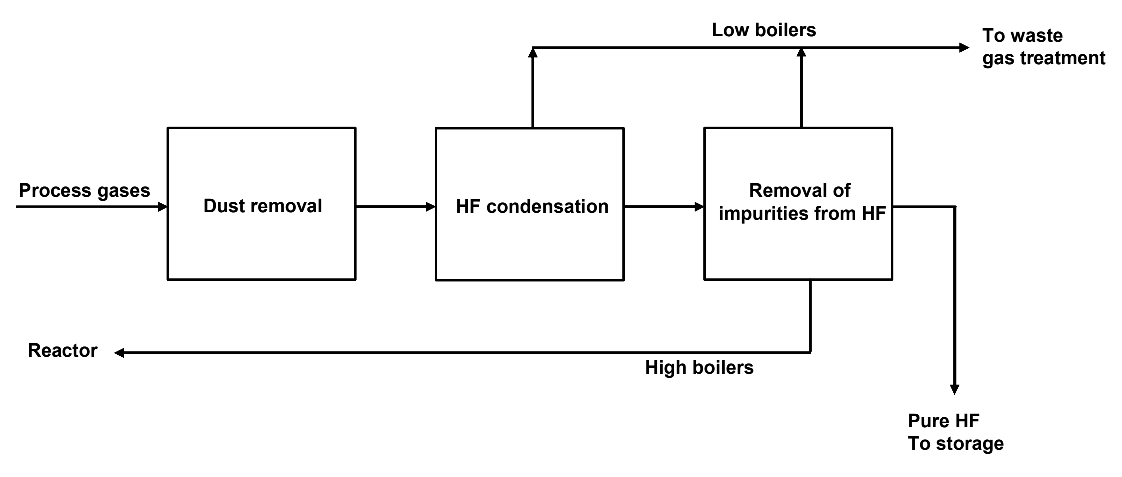


Figure 1.19: Process gas treatment

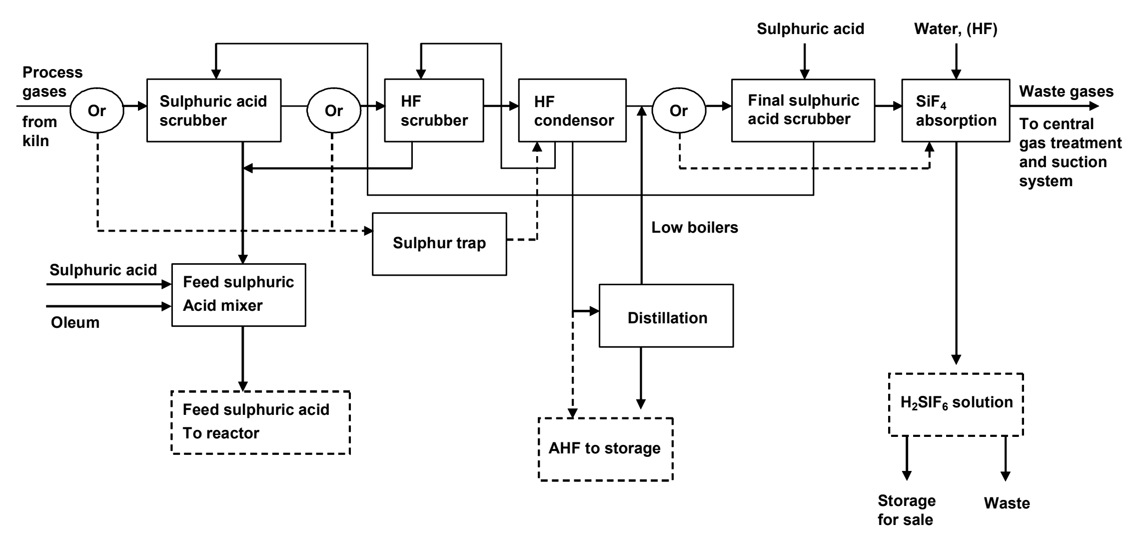


Figure 1.20: Process gas scrubbing and condensation

In most HF-plants, process gases are first scrubbed in a pre-purification column with concentrated sulphuric acid to remove dust and water and to cool the gas below 100 ºC. Secondary scrubbing and quenching is done with liquid HF to remove any remaining dust, H_2SO_4 and water and to cool the gas to about 20 ºC. In this HF scrubber, sulphur gas is partially desublimated. Alternatively it is possible to avoid using both scrubbers or only the second scrubber and pass the gases instead through a cooled sulphur trap. The HF scrubber and the sulphur trap have to be washed and cleaned periodically in order to remove any desublimated sulphur: the frequency of cleaning depends on the quality of the raw materials. The cooled and purified gases are then passed through condensers, using chilled water or brine as a cooling medium. Here most of the HF is liquified, part of the liquid HF is fed to the HF scrubber, and the other part, representing proper HF production, is passed to the storage or to a distillation column to remove the dissolved low boiling substances, mainly SO_2 and SiF_4. The low boilers leaving the column are gathered with the residual gases from the condensers and passed through a final sulphuric acid scrubber, where most of the HF is recovered. Thereafter residual gases pass through the SiF_4 absorber, where hexafluorosilicic acid is produced as an aqueous solution.

In plants without a final sulphuric acid scrubber, hexafluorosilicic acid with a relatively high HF content is produced. Cold sulphuric acid from the final sulphuric acid scrubber, which contains dissolved HF, passes to the first sulphuric acid scrubber (pre-purification column), where it is heated in contact with the process gases of the kiln. Acid from the scrubber is mixed in a vessel with fresh sulphuric acid and oleum to yield the feed sulphuric acid for the reaction process.

Depending on the quality of the HF after the low boilers distillation and on the end-use, there a second distillation may be required to remove any high boilers, mainly H_2O and H_2SO_4. This distillation requires more energy per tonne of HF than low boilers distillation, as all the HF has to be evaporated. The liquid HF leaving the head condenser is pure HF. Part of the HF is mixed with water to produce hydrofluoric acid of varying concentrations: 85, 73, 60 and 40 %. Mixing is strongly exothermic and sufficient cooling systems are necessary to avoid HF losses by evaporation. The production of high purity electronic grade HF out of technical grade HF requires special plants and sophisticated analytical techniques.

1.5.1.4 Product storage and handling

Anhydrous HF is a liquid, which boils at 19.5 °C. It is possible to keep liquid HF at low temperature, preferably below 15 °C, by cooling or by the installation of condensers in the vent storage pipelines which condense the evaporating HF.

Liquid HF is normally stored at atmospheric pressure in carbon steel tanks. A thin protective layer of FeF_2 is quickly formed which prevents further corrosion. Liquid velocity in the pipelines should be below 1 m/s to avoid erosion of the FeF_2 layer.

HF acid with a concentration of at least 70 % is stored in carbon steel tanks. Acid with concentrations of less than 70 % is stored in lined steel tanks or alternatively in polyethylene tanks.

1.5.2 Current emissions and consumption levels

1.5.2.1 Input

The raw materials used for HF production are fluorspar (CaF_2) and sulphuric acid. The typical consumptions, for 1 tonne of HF, are:

- 2100 – 2200 kg of CaF_2
- 2600 – 2700 kg of equivalent 100 % H_2SO_4.

Sulphuric acid is fed to the process in the form of 20 % to 35 % oleum and 95 % to 99 % H_2SO_4.

Chemicals used in the process include NaOH for alkaline scrubbing, and $Ca(OH)_2$ or CaO for anhydrite and liquid effluents neutralisation.

Utilities consumption

The following table shows the utilities consumption ranges, referenced to 1 tonne of HF.

Utilities	Consumption range (per 1 tonne of HF)
Steam	150 – 800 kg
Process water	0.5 – 25 m^3
Cooling water	30 – 100 m^3
Electric power	150 – 300 kWh
Refrigeration	2 – 3 x 10^9 J
Fuel	4 – 10 x 10^9 J

Table 1.42: Utilities consumption
[19, CEFIC, 2000]

Plant size and other factors can cause variations to these consumption ranges.

Distillation

One or two distillation columns can be used to give the correct specifications for the various product uses depending on the purity of the crude HF after gas scrubbing, and on the cooling and condensation. In some cases though, distillation may not be necessary. This in turn affects the utilities energy needs (mainly refrigeration and steam usage).

Kiln heating system

Utilities

The consumption of mainly natural gas, or other fuels used for the combustion with air for indirect kiln heating, is affected by the kiln dimensions, the HF production rate and the heating system design. For example, utilising heat recovery from discharged combustion gases after kiln heating has a beneficial effect on natural gas consumption, reducing it by about 20 % [19, CEFIC, 2000].

Cooling

Since anhydrous HF boils at 19.5 °C and needs to be cooled to prevent volatilisation, both the temperature of the cooling water available and its combination with a refrigerant system for crude gas cooling and condensation will influence the utilities consumption for refrigeration and cooling water.

1.5.2.2 Output

Anhydrite co-production

Anhydrite produced as a by-product contains between 0.2 to 2.0 % unreacted CaF_2 and less than 1.0 % H_2SO_4. It also contains the majority of the trace impurities contained in the fluorspar.

About 3.7 tonnes of anhydrite per tonne of HF are produced as by-product. This can be used as a marketable product but it needs further treatment. In cases where there is no market for the anhydrite, it will need to be treated as an effluent or as a solid waste.

The residual contents of CaF_2 and H_2SO_4 can be minimised by adjusting the feed ratio, residence time and heat supply.

1.5.2.3 Emissions

1.5.2.3.1 CaF_2 dust

CaF_2 dust emissions from the flue-gases of directly heated dryers and/or from pneumatic conveying gases are abated using cyclones and filters. Average dust emissions are typically in the range 0.05 - 0.10 kg/t HF, with a maximum average value of 0.50 kg/t HF, depending on the extent of pneumatic conveying and the number of storage silos [19, CEFIC, 2000]. Emissions will be lower if the plant does not include a drying section i.e. when the fluorspar has been predried, the range then will be between 0.01 and 0.05 kg/t HF, with a maximum value of 0.15 kg/tonne HF [19, CEFIC, 2000].

A small increase in dust emissions (typically 0.005 kg/t HF) and emissions of organic carbon compounds (about 0.1 kg/tonne HF) occurs in spar calcination, where an additional vent is needed.

1.5.2.3.2 $CaSO_4$ dust

When anhydrite is produced as a saleable product e.g. for the cement industry or for floor screed, the anhydrite neutralisation process and additional treatments generate dust, which is not avoided when landfilling or discharging to river or seawater.

Abatement equipment includes cyclones, filters and/or wet scrubbers.

The average dust emission levels are from 0.05 - 0.1 kg/tonne HF (max. 0.25 kg/tonne HF); depending on the different types of treatment, anhydrite disposal, or handling method and on the air transfer rates.

1.5.2.3.3 CaO and/or $Ca(OH)_2$ dust

Filtration equipment is used to reduce dust emissions which are generated during the handling of the CaO and/or $Ca(OH)_2$ needed in the anhydrite neutralisation.

Dust emission levels are below 0.001 kg/tonne HF [19, CEFIC, 2000].

1.5.2.3.4 SO_2

The whole plant is kept under a slight vacuum and wet scrubbers using either water or alkali treat the final vent tail gases. The wet scrubbers remove SO_2 from the flue-gas by absorption in the scrubbing liquid.

SO_2 emission values are from 0.3 to 0.5 kg/tonne HF, with a maximum of 1 kg/tonne HF, for water scrubbing. Typical values are from 0.001 to 0.01 kg/tonne HF, with a maximum of 0.065 kg/tonne HF for alkaline scrubbing.

1.5.2.3.5 Fluoride

The plant final vent and anhydrite treatment releases fluoride. The release levels depend on absorption and anhydrite treatment effectiveness and complexity. Typical values are from 0.005 to 0.015 kg/tonne HF, with a maximum of 0.1 kg/tonne HF [19, CEFIC, 2000].

1.5.2.4 Liquid effluents and solid wastes

1.5.2.4.1 Calcium sulphate (anhydrite)

The possible outlets of this co-product are:

- **marketable product:** Using calcium sulphate as a saleable product reduces the amount of waste/effluent. However, as it needs further (i.e. after neutralisation) treatments of varying complexity, more gaseous effluents, containing $CaSO_4$, F^- and dust will result.
- **landfilling**
- **dispersion in surface water or into the sea**

1.5.2.4.2 Liquid effluents

The quantity of tail gases needing treatment depends on the composition of the fluorspar. A water and/or caustic absorption treatment of tail gases produces a neutralised aqueous effluent containing sulphates and fluorides, e.g. silica impurities in the fluorspar will be contained in the anhydrite or released as SiF_4 in the tail gases. The water absorption of the SiF_4 produces aqueous H_2SiF_6, which in some cases may be sold or used as a feed material for the manufacture of fluorides or silicofluorides. H_2SiF_6 can also be chemically combined to produce CaF_2 and silica.

Liquid effluents contain the following contaminants [19, CEFIC, 2000].

- SO_4^{2-} 0.7 – 20 kg/tonne HF
- fluoride: 0.07 – 1 kg/tonne HF
- suspended solids: 0.1 – 1 kg/tonne HF.

The following are typical indicative values of the solid waste content in CaF_2 and $CaSO_4$ in the liquid effluents, depending on the complexity of anhydrite treatment [19, CEFIC, 2000].

- CaF_2: 6 - 70 kg/tonne HF
- $CaSO_4$: 5 - 50 kg/tonne HF.

1.6 NPK/MN fertilisers

Most producers of compound fertilisers in Western Europe produce nitrate based mineral compound fertilisers under the product name PK, NP, NK or NPK. These products contain nitrogen in ammoniacal (NH_4) and nitrate (NO_3) forms, phosphorous expressed as P_2O_5, and potassium normally expressed as K_2O. These types of fertilisers are often referred to as multinutrient (MN). Multinutrient fertilisers contain two or three of the elements N, P or K. Three numbers are used to indicate the percent of N, P_2O_5, and K_2O, which the product contains, for example NPK 24 - 6 - 12 indicates that this particulate grade contains 24 % N (expressed as nitrogen), 6 % P (expressed as P_2O_5) and 12 % K (expressed as K_2O). In addition the fertiliser may contain magnesium, boron, sulphur, micronutrients, and other elements. The typical content of nutrients ($N + P_2O_5 + K_2O$) will be between 40 - 60 %. There are two production routes used to produce NPK fertilisers. These are by the nitrophosphate route and the mixed acid route:

Nitrophosphate route

Phosphate rock is dissolved in nitric acid to produce nitrophosphoric acid and calcium nitrate tetrahydrate crystals (CNTH) which are then filtered out. The nitrophosphoric acid is then neutralised with ammonia, mixed with potassium/magnesium salts, sulphate and/or micro-nutrients and the product is then fed into a rotary granulation drum, fluidised bed, prilling tower or pug mill to obtain solid compound fertilisers containing nitrate.

Mixed acid route

Phosphate rock is transformed into phosphoric acid by means of sulphuric acid. The phosphoric acid obtained is then neutralised with ammonia. This can carried out in tank reactors and pipe reactors with gaseous or liquid ammonia. A wide range of grades, including ammonium phosphates, can be produced.

1.6.1 Applied processes and techniques

These compound fertilisers are made by one of the two following important production routes:

1. the nitric acid route or nitrophosphate process
2. the sulphuric acid route or mixed-acid process.

1.6.1.1 Nitrophosphate process

Note, this is also known as the nitric acid route.

1.6.1.1.1 Process chemistry

The integrated process starts with the dissolution of the phosphate rock in nitric acid.

$$Ca_5F(PO_4)_3 + 10HNO_3 \rightarrow 3H_3PO_4 + 5Ca(NO_3)_2 + HF$$

The mother liquor obtained contains too many dissolved calcium ions to guarantee the production of plant available P_2O_5. The solution is therefore cooled allowing calcium nitrate tetrahydrate (CNTH) to crystallise out according to the following reaction equation:

$$H_3PO_4 + HNO_3 + Ca(NO_3)_2 + 4H_2O \rightarrow H_3PO_4 + HNO_3 + Ca(NO_3)_2.4H_2O\downarrow$$

The solution of phosphoric and nitric acids, called nitrophosphoric acid, is separated from the CNTH crystals by filtration or centrifugation. The nitrophosphoric acid is then neutralised with ammonia and possibly mixed with potassium/magnesium salts, sulphate and/or micronutrients and converted in a rotary granulation drum, fluidised bed, prilling tower or pug-mill to obtain solid compound fertilisers containing nitrate.

The separated calcium nitrate crystals are dissolved in ammonium nitrate solution and treated with ammonium carbonate solution:

$$Ca(NO_3)_2 + (NH_4)_2CO_3 \rightarrow CaCO_3\downarrow + 2NH_4NO_3$$

This solution is filtered and the calcium carbonate crystals are separated and used in the production of granular calcium ammonium nitrate fertiliser. The resulting dilute ammonium nitrate solution is concentrated and also used to produce calcium ammonium nitrate fertiliser or NPK.

The calcium nitrate solution may also be neutralised and evaporated to obtain a solid fertiliser [9, EFMA, 2000].

A modern compound fertiliser plant, based on the nitrophosphate route, requires an integrated production complex of different units.

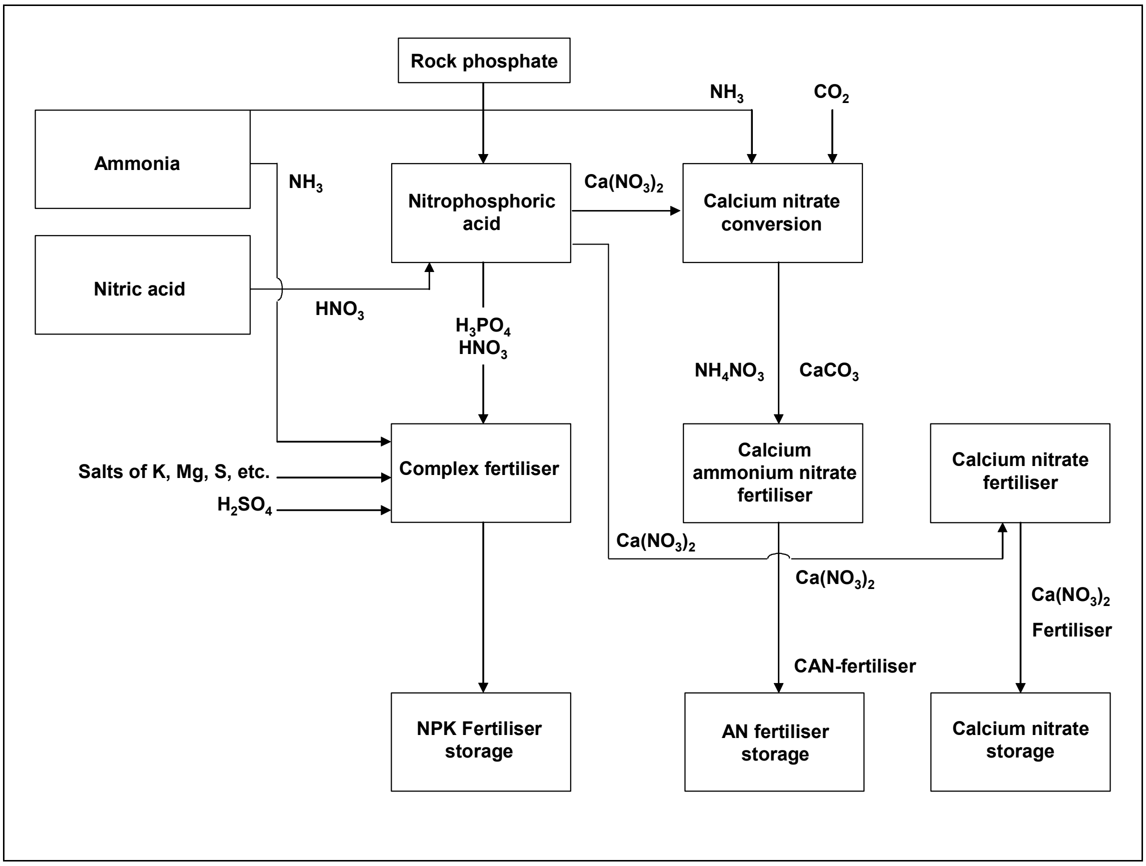


Figure 1.21: Integrated nitrophosphate process
[7, EFMA, 2000]

1.6.1.1.2 Ammonia plant

Ammonia is essential for the nitrophosphate process [7, EFMA, 2000], for instance:

- liquid ammonia is used in the nitrophosphoric acid section for cooling, as this is more economic than the use of refrigeration compressors which have high-energy consumptions
- gaseous ammonia is used for the neutralisation of the remaining acid
- the ammonia plant produces carbon dioxide for the conversion unit, which reduces the CO_2 emission from the ammonia plant. Other sources of CO_2 such as ethylene oxide or incineration plants can also be used.

1.6.1.1.3 Nitric acid plant

Nitric acid is essential for the nitrophosphate route. The nitric acid can be bought and stored for use in the process but the co-location with a production plant gives the following benefits:

- the nitric acid plant provides surplus steam for concentration purposes in the other units
- the nitric acid plant can, under certain conditions, also process waste waters from the neutralisation and evaporation stages of ammonium nitrate production, leading to a saving of expensive demineralised water.

1.6.1.1.4 Nitrophosphoric acid unit

The production of nitrophosphoric acid takes place in a special unit, in which natural rock phosphate, containing 30 – 40 % P_2O_5, is first dissolved in about 60 % HNO_3. The exothermic reaction releases off-gases containing NO_X resulting from the reaction of the nitric acid with reducing agents such as organic matter and ferrous salts in the rock.

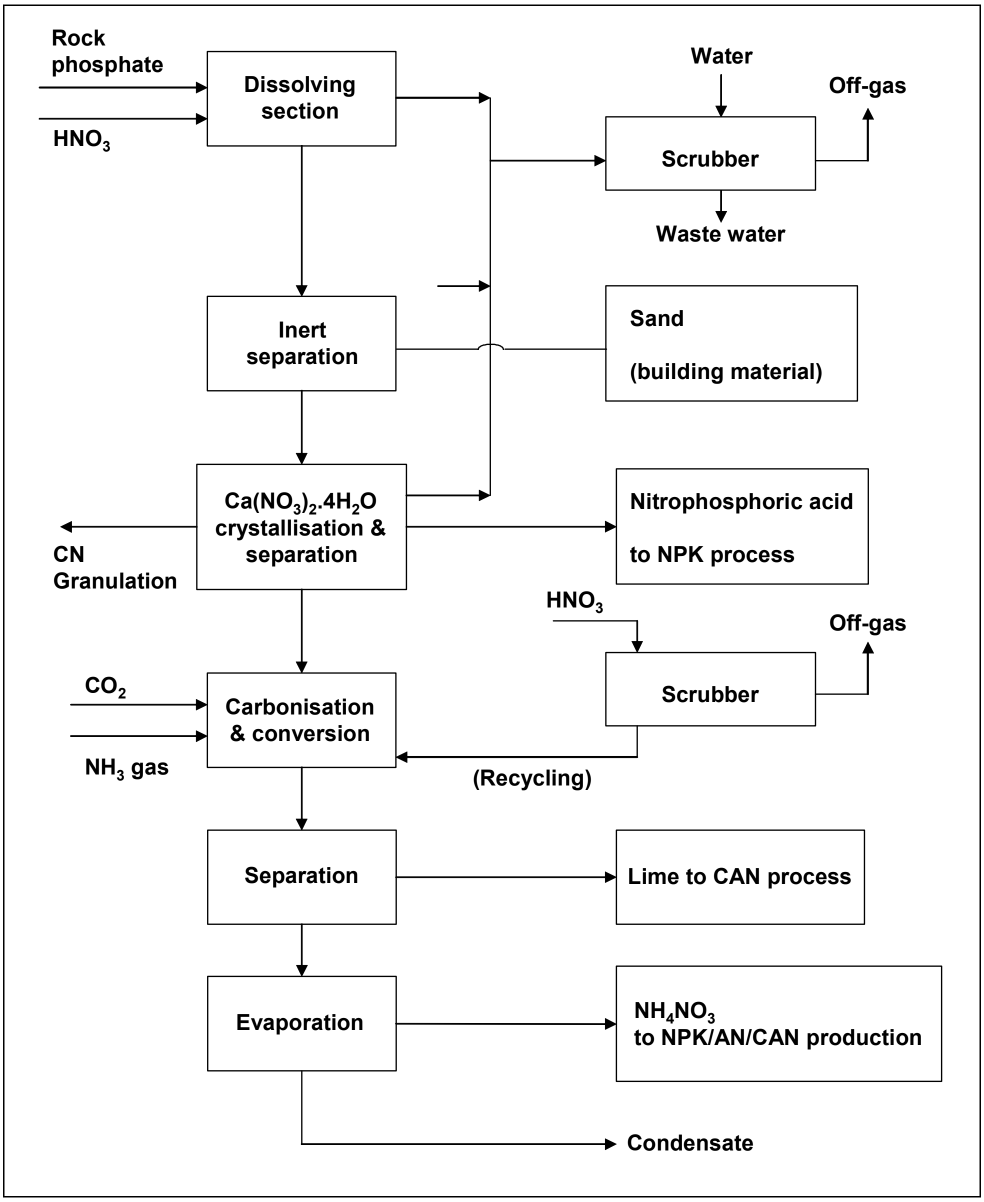


Figure 1.22: Process diagram of the production of nitrophosphoric acid
[7, EFMA, 2000]

The resultant dissolution liquor contains different amounts of suspended solids, mostly quartz sand. The actual amount depending on the origin of the different rocks. The liquor is then treated to remove most of this sand as this sand is an undesirable diluent of the nutrients in the final product and can cause equipment and piping erosion damage. Centrifuges, hydrocyclones or lamella separators are used to remove it. The overflow solution flows into a storage tank and the thickened inert slurry is further treated. The digestion solution is used in the crystallisation stage of the process and the sand is washed. The liquid effluent from this washing can be sent to a treatment plant and the neutral sand can be used, for example, in the building industry.

The digestion solution still containing minor amounts of sand is fed discontinuously to a number of standard batch-wise operating crystallisers. The solution is cooled with water and liquid NH_3 to the required final crystallisation temperature to allow most of the calcium to crystallise out as CNTH. These crystals are subsequently removed from the remaining solution by a centrifuge, rotating drum filter or, more recently, by belt filter techniques. The remaining nitrophosphoric acid ("NP solution") will have a CaO/P_2O_5 ratio varying between 0.21 and 0.65 (typical composition at a CaO/P_2O_5 ratio of 0.25 is 23 % P_2O_5, 5.8 % CaO, 6 % NO_3-N and 33 % H_2O), and is the basic starting material for the production of nitrate containing compound fertilisers.

1.6.1.1.5 The calcium nitrate tetrahydrate conversion unit

Production of calcium carbonate

The CNTH crystals, previously separated from the nitrophosphoric acid solution, are dissolved in an ammonium nitrate solution and pumped to a storage tank.

A solution of ammonium carbonate in dilute ammonium nitrate is bought or prepared in another section of the plant. Carbon dioxide from e.g. an ammonia plant and gaseous ammonia from e.g. the refrigeration section of the nitrophosphoric unit are the raw materials for the ammonium carbonate production. Around 1.0 tonne of CO_2 is used per tonne of P_2O_5 produced.

The ammonium carbonate solution is mixed with the calcium nitrate solution and calcium carbonate is formed according to the following reaction:

$$Ca(NO_3)_2 + (NH_4)_2CO_3 \rightarrow CaCO_3\downarrow + 2NH_4NO_3$$

The resulting reaction mixture passes to a belt filter where the precipitated $CaCO_3$ is filtered off. The calcium carbonate is sent to storage before being used in the production of granular calcium ammonium nitrate or in other applications. The remaining ammonium nitrate solution (50 – 56 % AN) is pumped to a storage tank and can be used for the production of compound fertilisers or for other applications of AN such as calcium ammonium nitrate.

This production stage has no liquid effluents since all the water used is recycled in the different production stages. Nevertheless, the carbonisation and conversion sections have off-gases which are treated in a scrubbing column and the scrubbing liquor is recycled. The off-gases, containing small amounts of NH_3 and F after scrubbing, are discharged to atmosphere.

Production of concentrated ammonium nitrate solution

The solution from the belt filter is treated in a second filtration step to remove the remaining $CaCO_3$ crystals. The excess ammonium carbonate is neutralised with nitric acid and the resulting neutral clean dilute ammonium nitrate solution is stored in an AN solution tank, from where it is pumped to the AN evaporation section. Typically the AN evaporation section consists of a series of falling film evaporators and involves a double or triple effect evaporation depending on the capacity and cost of energy at the given location.

The concentrated AN solution can be stored before use in the production of granular fertilisers and for other applications of AN.

1.6.1.1.6 Compound fertiliser production unit

Nitrate containing fertilisers can be produced from nitrophosphoric acid by carrying out a neutralisation with ammonia, with a possible addition of nitric acid, ammonium sulphate, or sulphuric acid, potassium and magnesium salts and micronutrients. This production is carried out in three stages: neutralisation, particle formation and conditioning.

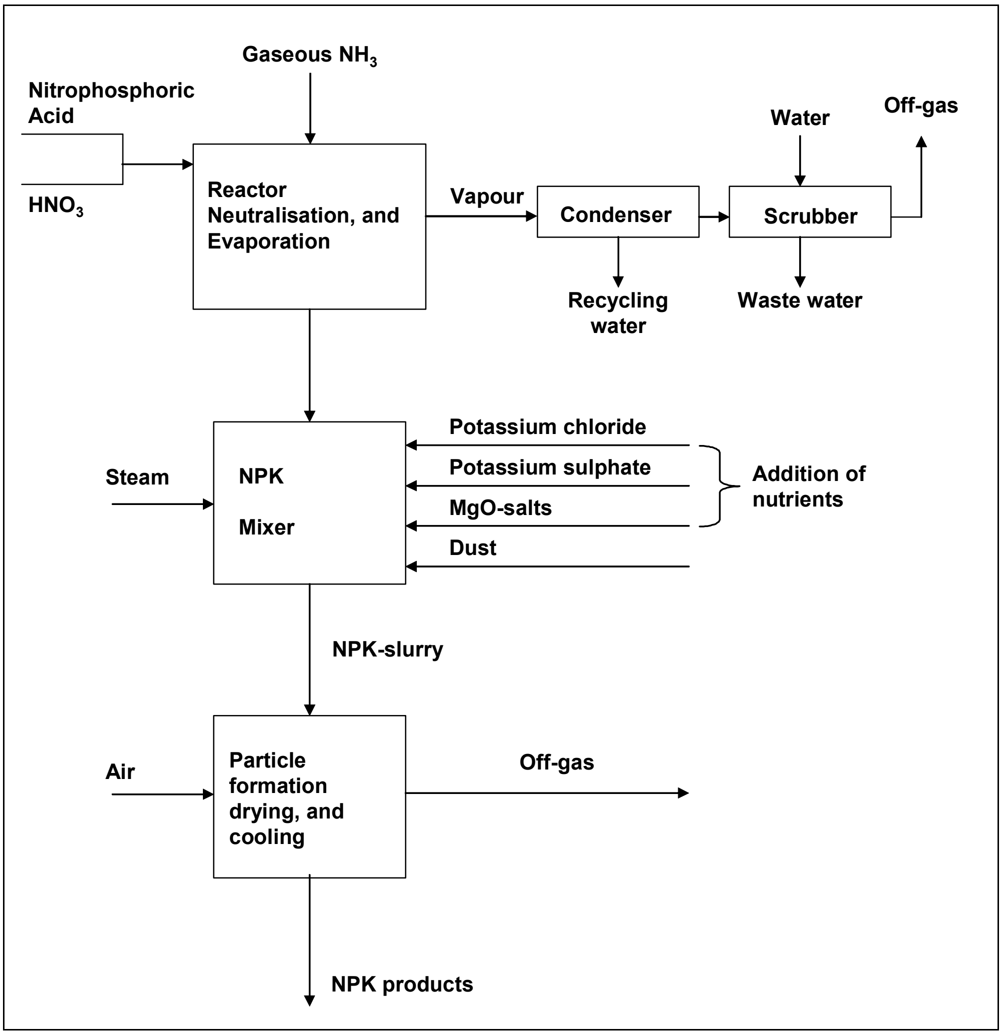


Figure 1.23: Process diagram of the production of nitrate containing compound fertilisers (NPK) by the nitrophosphate route
[7, EFMA, 2000]

Neutralisation

Nitrophosphoric acid (NP) solution with a CaO/P_2O_5 ratio of 0.21 – 0.65:1, is neutralised with gaseous ammonia in stainless steel reactors in a number of different stages. This reaction is very exothermic and the temperature rises to around the solution boiling point (125 – 145 ºC). The reaction heat is normally used for an economic evaporation of the slurry and for cooling the slurry.

In some processes the NP solution is neutralised to around pH 5 in successive stirred reactors, with the addition of potassium salts and/or other nutrients. This slurry normally has a temperature of about 120 °C and a water content of 12 – 22 %, depending on the type of process utilised and the type of fertiliser being produced. The resulting solution is pumped to the granulator. Other kinds of neutralisation systems may also be used, for example the NP solution may be neutralised in two stages: first being evaporated in circulating evaporators in series, before the final neutralisation. Here the pH is increased to 5 and the free water in the final NP liquor is 5 – 12 %. Potassium and other salts are added and the final slurry is pumped to the granulation drum. In a third system, the NP solution is neutralised with preheated gaseous ammonia in a pressurised reactor at 1.5 – 2.5 bar and 150 – 180 ºC.

If the NP liquor is to be prilled, the solution is finally concentrated in evaporators on top of the prilling tower. Concentration takes place in one or two stages under reduced pressure, and is done to give a final water content of about 0.5 %. Preheated potassium salts may also be added at the top of the prilling tower, for safety, to minimise the decomposition risk.

For neutralisation under pressure, the process vapour from the neutraliser reactor, containing 2 - 8 % ammonia is scrubbed by small amounts of process water to collect any carry over of P_2O_5, nitrates and insolubles. The scrubbing solution is then returned to the NP surge tank. The saturated process vapours leaving the NP scrubber are normally condensed in an indirect condenser system. Part of the process vapour is used to preheat the NP solution before neutralisation and part of the vapour heat is fed to a steam converter, producing low-pressure steam which can be used in the NPK production or other process units. Any remaining vapour is condensed in a water-cooled condenser. All condensates are collected in an ammonia condenser tank.

The ammoniated NP liquors from the neutralisation reactor are concentrated in evaporators. The off-gas contains ammonia together with some fluorine compounds. The ammonia is recovered by scrubbing. The main purpose of the scrubber is to collect the carry over of NP liquor from the evaporators and to reduce the ammonia and fluoride content of the vapours before indirect condensation. The scrubbing solution is recycled to the process.

The neutralisation and evaporation sections may be connected to a common ammonia condensate stripping system. Ammonia can be recovered by stripping, using 5-bar steam from the collected process condensate. The bottom flow from the ammonia stripper is, in some cases, the effluent leaving the NPK plant and contains ammoniacal N and traces of nitrate N.

The temperature (about 95 ºC) of the off-gases from the atmospheric neutralisation carried out without evaporation is too low for steam production. The off-gases can be condensed directly or treated in a scrubbing system. The condensates, as well as the scrubbing liquor, can be recycled.

The off-gases from the scrubber system will contain NH_3, HF and minor amounts of NO_X.

Particulate formation

Three types of processes are normally used for the production of NPK fertilisers; prilling, drum or pugmill granulation and spherodiser granulation. The three tways of forming particulates give different amounts of emissions to air and require different treatment systems.

Prilling

Evaporated NP liquor from the neutraliser is mixed with the required salts and recycled product. The final water content is about 0.5 %. The mixer overflows into a rotating prill bucket from which the slurry is sprayed into the prill tower. Fans at the top of the tower cause ambient air to flow countercurrent to the droplets formed by solidification. The solid prills fall onto a rotating tower bottom and are scraped off and forwarded to the dry handling system.

The product leaving the prilling tower is screened to meet product specifications. Over and undersize material is returned to the process and the ‘on-size’ NPK product is sent to the conditioning section.

Dust emissions from the prilling tower itself are very low. No special air treatment system is needed for the vast amounts of cooling air since the dust concentration is less than 5 mg/Nm^{-3}. The total dust emission is dependent on the ammonium nitrate content and is normally less than 2.5 kg/h as the total air volume passing through the prilling tower is more than 500000 Nm^3/h. The concentration of ammonia is also low, being typically 10 - 15 mg NH_3/Nm^3 (5 - 7.5 kg/h). The amount of ammonia which escapes is related to several process parameters, especially pH, high temperature and the NH_3/P_2O_5 ratio of the NP liquors. Effective recovery of this ammonia from such large volumes is unrealistic and the only way to minimise this ammonia loss is to control the pH. [10, infoMil, 2001]

Drum and pugmill granulation

The NP liquor, at approximately 135 °C and with a water content around 4 - 12 %, is mixed with the required salts and recycled products and is pumped and sprayed into a rotating drum granulator.

The water evaporated in the drum is carried away by a co-current flow of air. The granules which are formed are dried in a rotating drying drum with hot air. The water content of the granules is normally below 1.5 %. The air leaving the drums, about 100000Nm^3/h for the production of 55t/h 15 – 15 - 15, contains water vapour, dust, ammonia and combustion gases.

The air from the granulation and drying drums is treated in high performance cyclones, giving low dust levels (<50mg/Nm^3) after passing the cyclones. As with the prilling tower, the amount of ammonia lost in the granulation and drying drum depends on the operating temperature and the final pH of the neutralised slurry.

The average ammonia content is less than 150 mg/Nm^3 under normal conditions, if the final pH is maintained at about 5.0. The NPK product, after drying, is screened and the on-size hot product is sent to the conditioning section. The undersized and oversized granules, are returned to the granulator after crushing. Screens, crushers and conveyor discharge points are dedusted in one mode of operation using the air going to the drums.

Spherodiser granulation

The NP liquor, with a temperature of 115 - 120 °C, is mixed with the required salts and recycled products. The resulting slurry has a water content of 10 - 28 %, and is pumped and sprayed into a special rotating drum, called a spherodiser. Warm air, heated to 300 – 400 °C by gas or fuel, flows co-currently in the spherodiser evaporating the water from the NP liquor and building up dry granules with a water content of <1.5 %.

The air from a spherodiser, about 100000 Nm^3/h is treated in high performance cyclones. The remaining dust and NH_3-content is dependent on the grade, the operating temperature and the pH of the NP liquor.

The dry granules are screened and the oversize taken out, crushed and returned to the spherodiser together with the undersize. The on-size fraction passes to the conditioning process. The screen, crusher and conveyor discharges are dedusted using the air required for granulation.

Conditioning

The commercial product from the drying and screening is cooled in a fluidised bed, a bulk flow heat-exchanger or a rotating drum. Off-gases from these latter stages, containing minor amounts of dust and generally no ammonia, are dedusted. Finally, the product is cooled and coated before storage in order to minimise the subsequent caking of the material.

1.6.1.1.7 Calcium nitrate fertiliser production unit

The calcium nitrate crystals from the nitrophosphate process can be processed to a solid calcium nitrate (CN) fertiliser.

Neutralisation and evaporation

The CNTH crystals from the nitrophosphoric acid unit are heated to form a melt, which is pumped to a two-stage atmospheric reactor for neutralisation with gaseous ammonia. The reaction between the melt and the remaining acid in the CNTH melt is exothermic. The ventilation gases from the two reactors are scrubbed with water before being discharged to atmosphere.

The 60 % CNTH melt, containing small amounts of ammonium nitrate is evaporated in one or two stages to a final concentration of 85 % and this concentrated solution is then transferred to the prilling or granulation process.

The process steam containing ammonia is scrubbed with condensate and compressed for energy recovery for use in the evaporators. Part of the condensate is discharged into water and the remainder is returned to the process. The discharge of NO_3 and NH_4 nitrogen into water from a 100t/h CN plant is around 30kg/h, when a spillage collection system is installed in the wet part of the process. The collected spillage is returned to the process.

Pan granulation

The concentrated melt from the evaporator system is sprayed into the pan granulator together with the recycled fines. The granules are smoothed in a smoothing drum and air-cooled in a fluidised bed. The cooled product is screened in two stages and the correct size product is transferred to a coating drum and finally to storage. Any oversized material is crushed, mixed with the fines and recycled to the granulator.

The ventilation gases from the granulation and from the dry part of the process are scrubbed with water and process condensate from the wet part of the process, in a lamella separator before discharge to atmosphere. The emission of CN-containing aerosols to air is normally <4 mg NO_3-N.Nm^3 of off-gas. The volume of ventilation air from a pan granulator producing 50t/h of CN fertiliser is 170000Nm^3/h.

The condensate from the lamella separator, containing calcium nitrate, is mixed with collected spillage from the dry part of the process and returned to the neutralisation section.

There is no discharge of NO_3-N into water from the dry part of the process.

Prilling

The concentrated melt from the evaporators is mixed with recycled fines and fed to a rotating prill bucket. The melt leaving the bucket solidifies due to the heat exchange with countercurrent air in the prill tower. Air from the prill tower is discharged to atmosphere without dust removal. The volume of air from a 40t/h CN plant is 370000Nm^3/h, normally with a CN dust concentration of 20mg/Nm.

The prills from the base of the tower are cooled with air in a fluidised bed cooler and screened to remove off-size material. The product-size prills are coated before storage. Oversize material is dissolved in neutralised CN solution and returned to the evaporator feed tank. Undersize material is mixed into the evaporated melt before prilling.

1.6.1.2 The mixed acid route

1.6.1.2.1 Granulation with a pipe reactor system

The process works with a classical granulation loop but incorporates one or two pipe reactors. One pipe reactor is fitted in the granulator and another may be used in the dryer.

Phosphoric acid, or a mixture of phosphoric and sulphuric acids, is neutralised in the pipe reactors with gaseous or liquid ammonia. A wide range of grades, including ammonium phosphates, can be produced. The process is flexible and easy to operate and the pipe reactors can be operated with a high turn-down ratio.

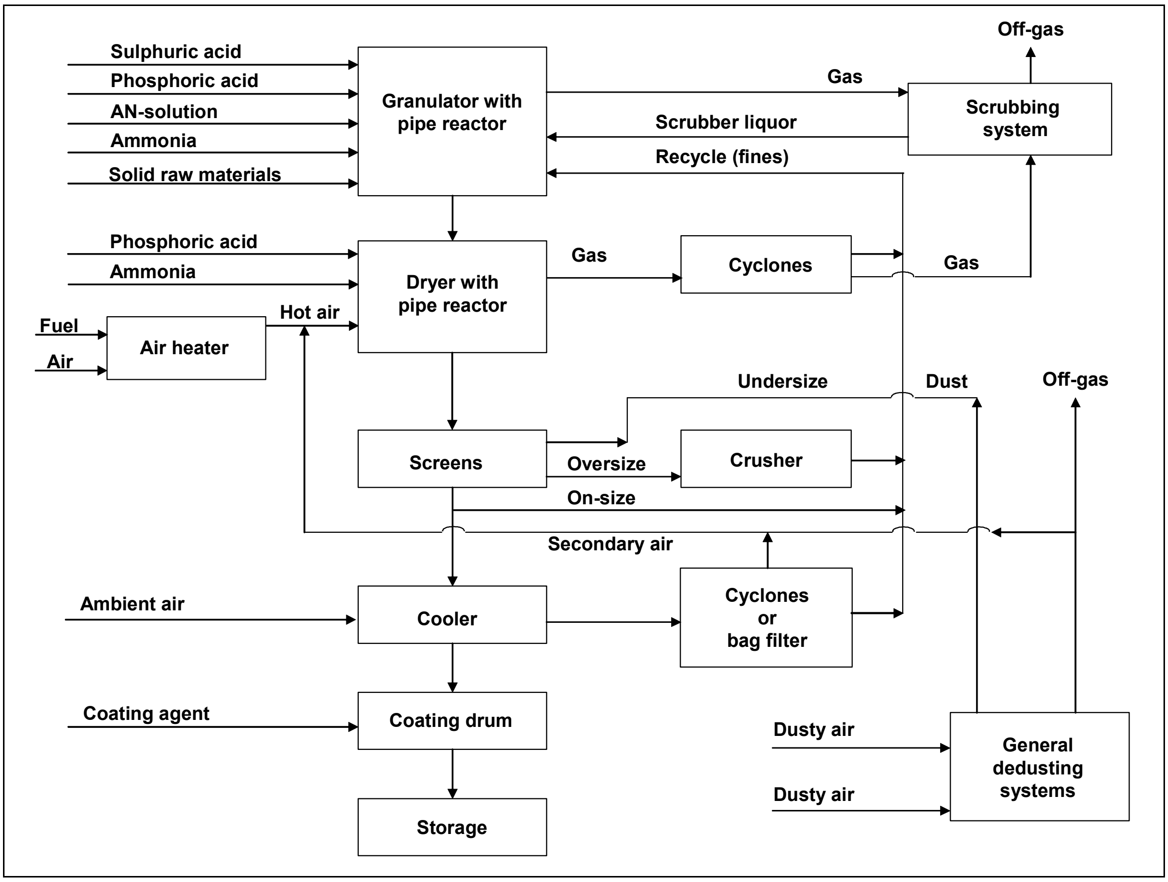


Figure 1.24: Granulation with a pipe reactor
[7, EFMA, 2000]

Granulation and drying section

The raw materials needed, such as potassium chloride, potassium sulphate, superphosphate, secondary nutrients, micronutrients and filler are metered and fed into the granulator together with the recycle material. The pipe reactor fitted in the granulator is designed to receive phosphoric acid, part of the ammonia, and all other liquid feeds such as sulphuric acid and recycled scrubber liquor.

Concentrated ammonium nitrate solution may be added directly into the granulator. Ammoniation rates in the pipe reactor vary according to the product. Further ammoniation may be carried out in the granulator.

Screening, crushing, cooling and coating

The dry granules are screened into three fractions. The oversized granules are removed crushed and, along with the fines, returned to the granulator. The correct sized fraction is removed with the possibility of returning part of this fraction to the granulator to stabilise the recycling loop.

Finally the correct specification fraction is cooled in a fluidised bed cooler, a cooling drum or a bulk flow cooler.

The cooled product is fed into a coating drum where a surface coating is applied to prevent caking.

1.6.1.2.2 Drum granulation with ammoniation

The process consists of a classical granulation loop using mainly solid raw materials. Ammonium nitrate solution and/or steam are/is fed into the granulator. The process is very flexible, and is able to produce a broad spectrum of grades including products with a low nitrogen content. [7, EFMA, 2000]

Granulation and drying

The required raw materials, such as potassium chloride, potassium sulphate, superphosphates, ammonium phosphates, secondary nutrients, micronutrients and filler, are metered and fed into the granulator together with the recycle material.

Ammonium nitrate solution is sprayed directly into the granulator and sulphuric acid may be fed into the granulator followed by ammoniation. For some NPK grades steam is also used to keep the temperature at the required level. The granules obtained are dried in a drying section using a heated air stream.

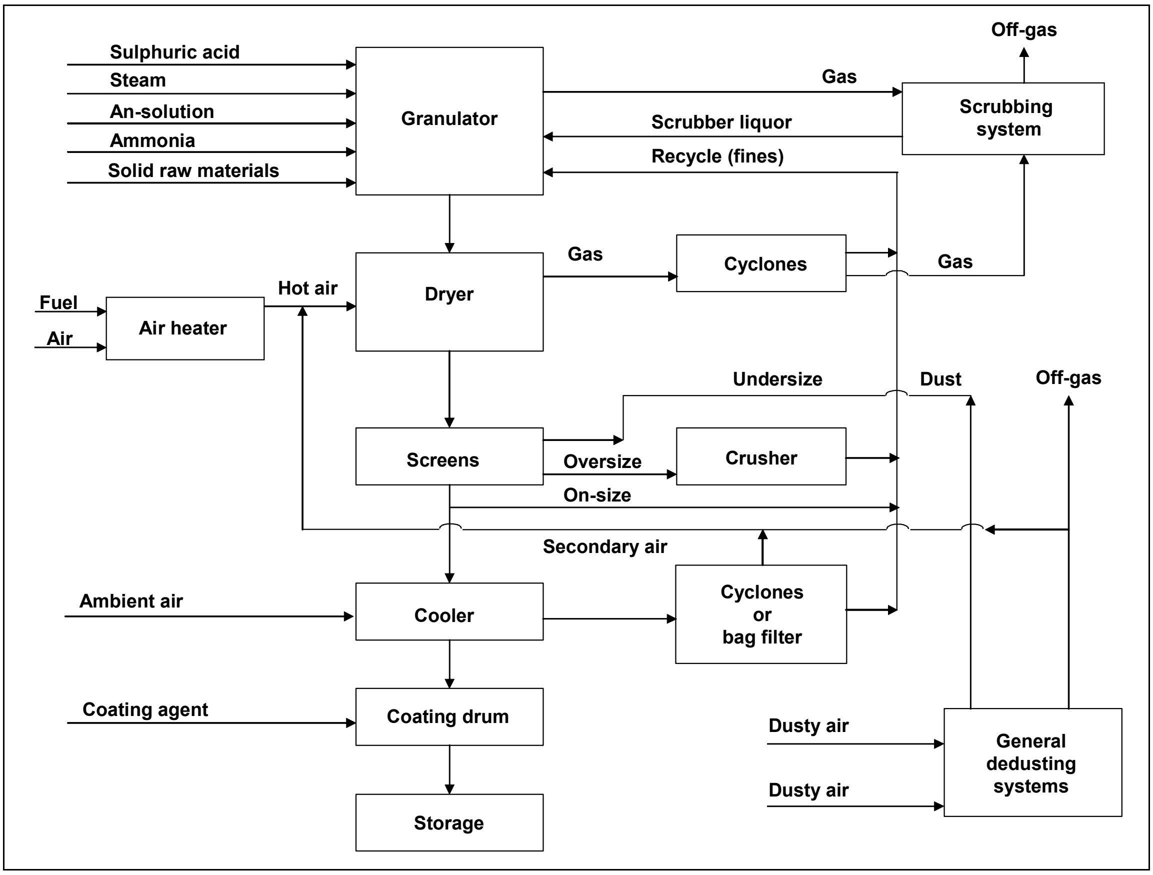


Figure 1.25: Drum granulation with ammoniation
[7, EFMA, 2000]

Screening, crushing, cooling and coating

The dry granules are screened into three fractions and the oversize is removed and returned via the crusher to the granulator, together with the fines. The product-size fraction is removed with the possibility of returning part of this fraction to the granulator to stabilise the recycling loop. Finally, the product fraction is cooled in classical cooling equipment, such as a fluidised bed cooler or a cooling drum, and the cooled product is fed into a coating drum, where a surface coating is applied to prevent caking.

Gas scrubbing and dust removal

Gases from the granulator and dryers are scrubbed in venturi scrubbers with recirculating ammonium phosphate or ammonium sulpho-phosphate solution. Make-up phosphoric and/or sulphuric acid are/is added for pH control if necessary. The scrubber liquor, which is recycled, is fed into the granulation drum.

The gases coming from the dryer are dedusted in high efficiency cyclones to remove the dust before scrubbing. The air from the cooling equipment is generally recycled as secondary air to the dryer after de-dusting.

1.6.1.2.3 Mixed acid process with phosphate rock digestion

The process is very flexible and produces grades with varying solubilities. The process is able to use relatively cheap raw materials, such as phosphate rock.

Phosphate rock digestion and ammoniation

The first step of the process is the digestion of phosphate rock with nitric or sulphuric acid, resulting in a solution of phosphoric acid and calcium nitrate. Acid gases, such as the oxides of nitrogen and fluorine compounds, are formed during the digestion, depending on the type of phosphate rock.

Other raw materials such as phosphoric, sulphuric and nitric acids or AN solution can be added after the digestion, which is an exothermic process. The acid slurry is ammoniated with gaseous ammonia and, after the neutralisation, other components are added such as ammonium phosphates, superphosphates, ammonium sulphate and compounds containing potassium and magnesium. Most of these materials may also be added before or during the neutralisation but if the raw material contains chloride the pH of the slurry should be 5 – 6 to avoid the production of hydrogen chloride.

The design of the reactor system can vary from a few large reactors to many smaller reactors. Common to all the reactor system designs is that the row of reactors ends with a buffer tank.

The water content of the slurry in the buffer tank can vary between 5 % and 30 % and the temperature from 100 °C to 140 °C, depending on the type of raw material, the amount of gas scrubber liquid to be recycled and the degree of ammoniation.

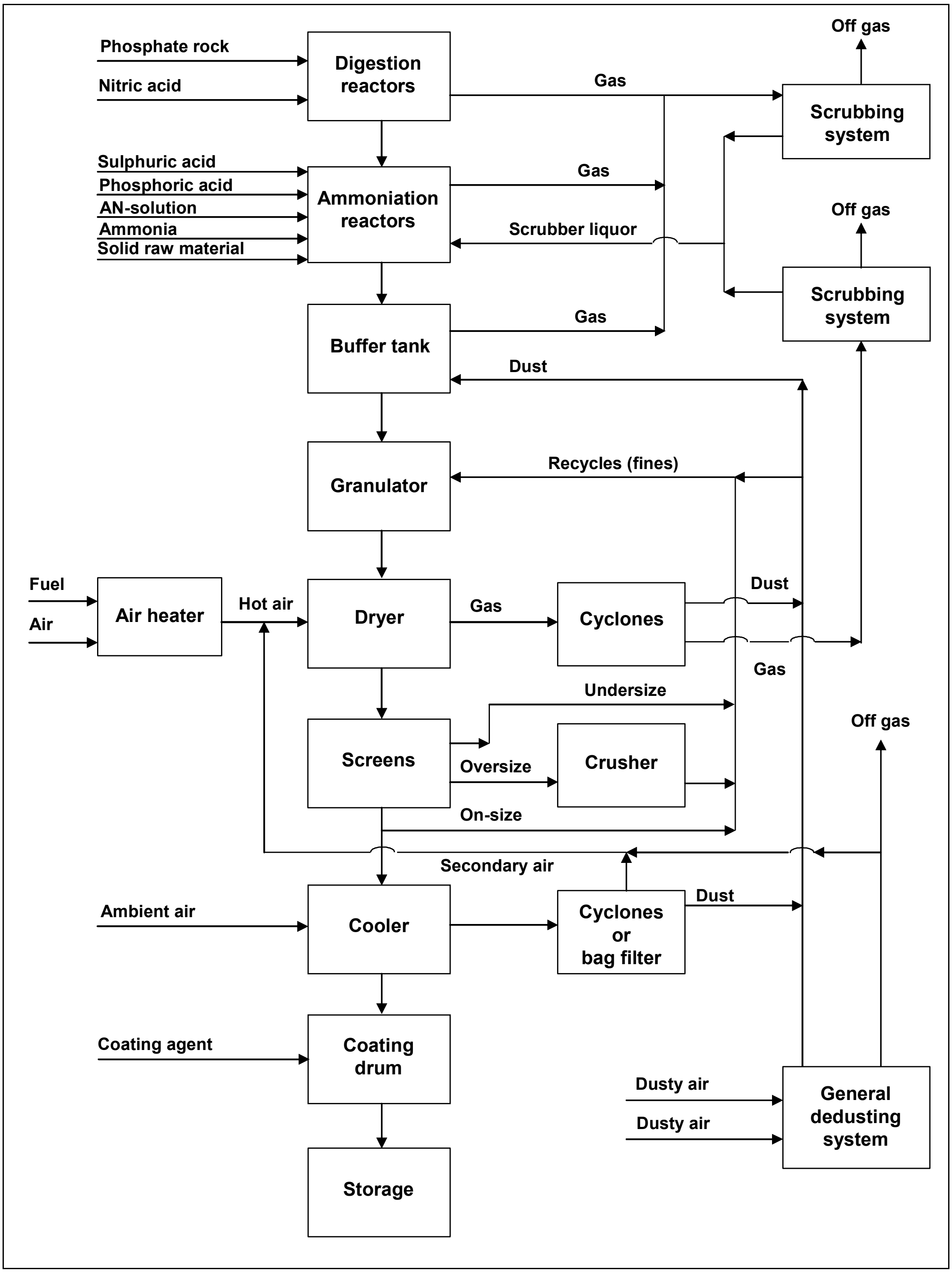


Figure 1.26: Mixed acid process with rock digestion
[7, EFMA, 2000]

Granulation, drying, screening, crushing, cooling and coating

The granulation can be carried out in different equipment such as drum, blunger and spherodiser. The drying operation is incorporated in the spherodiser granulation.

These processes can produce a broad spectrum of grades, although NPK fertilisers with a very low content of nitrogen are not suitable for the spherodiser process. This is because the high content of water needed for the slurry to be sprayed is unrealistic.

The off-specification fraction from the screening/crushing operation is recycled in all granulation processes.

All granulation processes, apart from the spherodiser process, need a drying stage after granulation. The drying is normally carried out in a drying drum. The fertiliser may be cooled and also coated to prevent caking, in a cooling drum, a fluidised bed cooler or in a bulk flow cooler. The coating can be a combination consisting of treatment with an organic agent and an inorganic powder.

1.6.1.2.4 Storage and transfer equipment

Solid raw materials

The main solid raw materials are potash and phosphate rock. The means of transport to site is by ship, trains or lorries.

Ship unloading

Grab cranes are normally used for ship unloading. This method is very dusty and dust may spread to the local harbour area. The use of closed unloading methods (screw or pneumatic ship unloading machines) minimises the dust risk.

Unloading of rail wagons or lorries

Raw materials from wagons and lorries are tipped into hoppers, which in turn transfer the materials to conveyors.

Storage

Raw materials are stored in enclosed buildings or silos. Payloaders, scrapers or cranes handle materials in storage.

1.6.1.2.5 Products

Bulk storage

Bulk storage is in enclosed buildings with separating walls for different product grades. Payloader or scrapers handle the materials.

Screening

For quality reasons fines and lumps must be screened out from the product after bulk storage. Separated over and undersize material is recycled before caking back to the NPK plant.

Bulk delivery

Bulk delivery should be carried out under cover in roofed areas. Some products may be supplied to customers in bulk. Bulk products are loaded onto lorries, rail wagons or ships. During this operation there is a risk of dust being released to the surrounding areas from the filling chutes. Dust collection systems are recommended to minimise waste. Rainwater run-off is collected from the asphalt areas near the bulk loading system and, in new plants, returned to the recycling system.

Bagging

Part of the product may be bagged in either 40 – 50 kg bags or 500 – 1200 kg big bags. Bagged products are normally stored under cover.

Solid waste products

Waste products, such as the undersize from screening, dust from the filters and spillages from the bagging and bag storage, are collected and recycled before caking to the NPK plant, using conveyors or container vehicles.

1.6.2 Current emissions and consumptions

1.6.2.1 Nitrophosphate route

1.6.2.1.1 Inputs and outputs

Emissions

The emission of NO_X and fluorides need to be controlled.

The washing and crystallisation section also produces off-gases, which contain NO_X and fluorides, which must be treated although the concentration of NO_X in the off-gases is low compared to that from the dissolving section [7, EFMA, 2000].

Nitrogen oxides

NO_X, mainly NO and NO_2, is released as a result of phosphate rock being dissolved in nitric acid. The organic and iron contents in the rock, as well as the reaction temperature, affect the amount released. Releases can be minimised by adding urea solution or by reactor cooling. [9, EFMA, 2000]

The off-gases are treated in scrubbers and emission values of <500 mg/Nm^3 result.

Fluorides

Phosphate rocks contain about 4 % fluorine equivalent and the majority of this passes through the process into the fertiliser, with only a small part being released in the tail gas. The fluorides are normally removed in scrubbers and emission values are of the order 5 mg F^-/Nm^3 [9,EFMA, 2000]

Chloride

When potassium chloride (KCl) is added to the powder, ammonium chloride (NH_4Cl) and hydrogen chloride (HCl) form in both the granulator and the dryer. Any ammonia present can react with HCl, forming aerosols of NH_4Cl. These aerosols can cause the so-called Tyndall-effect, creating a “blue mist” at the stack.

Plant	Installation	Capacity (kt/yr)*	Process step	Emission		End-of-pipe technology
				mg/m^3	g/t	
AMFERT	Drying drum	500	--	3.7(1)	<2.7*	Cyclones scrubber
Zuid-Chemie	Granulation 2***	180 - 220	Finishing (drum granulator)	<30	22	Cyclones, 2 scrubbers in series (one with acid)
			Dedusting shop floor, transportation, sieves etc.	<30	28	2 fabric filters
	Granulation 3***	250 - 275	Finishing (drum granulator)	15	21	2 scrubbers in series (one with acid)
			Drying			Cyclones/2 scrubbers in series (one with acid)

* based on a continuous process (± 860 hrs./year)
** led back to process
*** also production of SSP, TSP, CAN and MAN (Zuid-Chemie only)
(1) actual emission value

Table 1.43: Chloride emmissions to atmosphere Dutch MN fertiliser plants

Ammonia

Major ammonia emissions originate from the CNTH conversion, AN evaporation, the neutralisation of nitrophosphoric acid and partially from the granulation or prilling sections.

High process temperatures and the technical difficulties in overneutralising nitric acid with ammonia make it impossible to avoid NH_3 emission. Scrubbers remove the ammonia off-gases from the evaporation and nitrophosphoric neutralisation steps. The resulting ammonia in the exhausted air is 60 mg NH_3/Nm^3 wet. The ammonia emission from the granulation and drying sections is on average <150 mg NH_3/Nm^3. The actual emission depends on the nature of the fertiliser, the operating temperatures and in particular, the pH value. [9, EFMA, 2000].

Aerosols

Throughout the different production steps, there is a very high possibility of aerosol formation, with the main aerosols being NH_4NO_3 and NH_4Cl. It is important therefore to avoid contact between different NO_X and NH_3 containing waste gases.

Fertiliser dust

The main sources of dust are from the drying and granulation drums and/or prilling towers, with minor amounts also arising from the cooling drum, screens, crushers and conveyors. The best method way for de-dusting this waste air is to pass the off-gases through a battery of high performance cyclones with suitably sized air streams, velocity, temperature and pressure.

It is important to have well trained staff who continuously control the granulation step and the emissions. Generally the emission value for dust is 50 mg dust/Nm^3, but values may be up to 75 mg/Nm^3 when producing grades with a high solid or sulphate content of the slurry to be granulated. [9, EFMA, 2000]

The choice of starting materials strongly influences the overall dust emission due to grinding. Phosphate rock requires grinding, while AN does not.

Plant	Installation	Ground material(s)	Dust emission		End-of-pipe technology
			mg/m^3	kg/h	
AMFERT	Grinding mill 1	Phosphate rock			Fabric filter
	Grinding mill 2	Phosphate rock			Fabric filter
	Dedusting shop floor mill house	Phosphate rock			Fabric filter
	Pallman-mill 1	Various (incl. KCl)	--	--	--
	Pallman-mill 2	Various (incl. KCl)	--	--	--
DSM-IJ1	Exhaust system grinding PM-301*	Dolomite, bentonite, $CaSO_4$,	25	0.5	Cyclone/ fabric filter
	Exhaust system grinding PM-201**	Dolomite, bentonite, $CaSO_4$	25	0.5	Cyclone/ fabric filter
	Exhaust system grinding PM-101*	Dolomite, bentonite, $CaSO_4$,	25	0.5	Cyclone/ fabric filter
	Grinding mill Swelo-1	Phosphate rock			Cyclones/ceramic filter
Zuid-Chemie	Grinding mill Swelo-2	Phosphate rock			Cyclones/ ceramic filter
	Grinding mill P.M.-8	Phosphate rock			Cyclones/ ceramic filter

Table 1.44: Dust emissions to atmosphere in MN plant from grinding operations
[10, infoMil, 2001]

1.6.2.1.2 Discharges to water

The main effluent components are ammonia, nitrate, fluoride and phosphate. Ammonia emissions into water occur when not all the condensates of the ammonium nitrate evaporation or the neutralisation of the nitrophosphoric acid solution can be recycled. The main sources of the nitrate and fluoride emission are the scrubber liquor of the phosphate digestion and the sand washing. Phosphate emissions to water originate from the sand washing.

Two methods for the reduction of emissions have been demonstrated in nitrophosphoric acid plants. One reduces the P_2O_5 emission from 0.4 kg to 0.02 kg P_2O_5/t^1 P_2O_5 produced, by recycling the liquor of the sand washing. The other method reduces the emissions of N and F from 1.2 and 0.7 to 0.6 kg N/t P_2O_5 and 0.02 kg F/t P_2O_5 respectively, by recycling of the NO_X scrubber liquor. In theory, a reduction of N, P_2O_5 and F is possible when using nitric acid of more than 63 % strength but this has not yet been demonstrated. [9, EFMA, 2000]

1.6.2.1.3 Solid wastes

There is minimal solid waste. By-products are converted into commercial products and spillages and off-specification products are recycled into the NPK production.

1.6.2.2 Mixed acid route

1.6.2.2.1 Inputs and outputs

Emissions

Ammonia

The majority of the ammonia emissions originate from the ammoniation reactors and the granulation drum or pug mill. The actual amount depends on the pH, temperature, and slurry viscosity. Some ammonia evaporates at the inlet of the spherodisers, in the drying drums, and in the drums with ammoniation because of the high temperature and/or drying rate.

Nitrogen oxides

NO_X, mainly NO and NO_2, is released when phosphate rock is dissolved in nitric acid. The organic and iron contents in the rock and the reaction temperature affect the amount released. Releases can be minimised by adding urea solution or by reactor cooling [9, EFMA, 2000].

Fluorine compounds

The fluorine compounds originate from the phosphate rock and thus, indirectly, from the phosphoric acid. In practice, the main part of the fluorine compound passes through the process into the fertiliser and only a small part is released into the gaseous phase as ammonium fluoride.

Aerosols

The main aerosol components are ammonium nitrate, ammonium fluoride and ammonium chloride, which are formed in the gas-phase reaction between ammonia and acidic components, as well as by sublimation from the boiling reaction mixture.

Gas scrubbing and dust removal

Reactor gases

Vent gases from the nitric acid phosphate rock digestion reactors are separately treated in a spray tower scrubber to remove NO_X and fluorine compounds. The pH is adjusted by ammonia addition.

One option for gas scrubbing is the ammoniation reactor, where the gases are scrubbed in a number of countercurrent scrubbing stages. The pH is adjusted to optimum scrubbing condition, typically pH 3 – 4, with a mixture of HNO_3 and/or H_2SO_4 [4, EFMA, 2000]. The first stage is gas scrubbing; the second is a high-pressure venturi stage for the removal of aerosols. The other stages aim to improve the recovery efficiency, so that the final stage operates with the cleanest scrubbing liquid. A droplet separator is installed in the stack, or just before it.

Drying gases

Gases from the dryer (granulator/dryer) vent through cyclones and then a scrubber. The scrubber consists of a variable throat venturi followed by a two stage scrubbing. The last stage is operated with the cleanest liquid. After circulation, the solid separation from a part of the liquor is carried out in a settler. The settled part is fed to the reactors and the overflow returned. The pH is adjusted with acids to pH 3 – 4.

Cooling gases

One option for cooling the gases is to use a cooler which uses ambient or cooled conditioned air. The warm air from the cooler can then be recycled to the dryer inlet.

Gases from the granulator and the dryer are scrubbed in venturi scrubbers with recirculating ammonium phosphate or ammonium sulpho-phosphate solution. Make-up phosphoric and/or sulphuric acid(s) are/is added for pH control if necessary. The scrubber liquor, which is recycled, is fed to the pipe reactor in the granulator.

Finally, the gases are vented through cyclonic columns irrigated with an acidic solution. The particulates in the gases coming from the dryer are abated in high efficiency cyclones to remove the majority of the dust before scrubbing. The air coming from the cooling equipment is generally recycled as secondary air to the dryer after abatement.

The main sources of fertiliser dust are the granulator and the dryer. A smaller amount is also released from the cooling drum. Dust collection is needed for the classifiers, crushers and conveyors.

Carbon dioxide and sulphur dioxide

Hot air from the combustion of heavy fuel oil or natural gas is used for drying. The carbon and sulphur content in the fuel determines the amount of carbon dioxide and sulphur dioxide released. Sulphur dioxide is minimised by gas scrubbing. Fuel usage is minimised by using excess heat from the neutralising reactors to dewater the feed slurry. Energy savings are achieved by the re-circulation of the cooling gases to the drying drum and by utilising low pressure process steam from other plants to pre- heat the dryer inlet air.

1.6.2.2.2 Granulation with a pipe reactor system

Input requirements

	Water solubility of phosphates	
	85 %	**95 %**
Typical raw materials		
Nitric acid* kg/tonne (100 %)	280	242
Ammonia* kg/tonne	107	122
Phosphoric acid P_2O_5kg/tonne	105	154
SSP (21 % P_2O_5) kg/tonne	212	-
Potash (60 % K_2O) kg/tonne	250	250
Filler kg/tonne	-	150
Utilities		
Electricity kWh/tonne	30	30
Total energy for drying MJ/tonne	320	320
*Includes the part added as AN solution		

Table 1.45: Raw material input requirements with a pipe reactor

Output production

The production rate is fixed at 50 t/h (1200 t/d or 350000 t/yr). AMFERT (NL) has a production rate of 450000 t/yr.

There is no export of energy related to the process.

Emissions and waste

There are no solid and liquid wastes when these streams can be recycled to the process. Some liquid effluent will arise when manufacturing NPK grades containing high levels of ammonium nitrate. There are no measurable fugitive emissions and the total amount of air is estimated to be 120000Nm^3/h (wet).

Typical values for the emissions into air are listed below.

Component	Emission at 50t.h^{-1}		
	kg/h	kg/t NPK	mg/Nm^3 (-wet)
NH_3	3 (2.5 – 6)	0.06 (0.05 – 0.1)	25 (20 – 50)
Fluorides	0.3 (0.2 – 0.6)	0.0005 (0.004 – 0.01)	2.5 (1.5 – 5.0)
Dust	6 (5 – 9)	0.12 (0.1 – 0.2)	50 (40 – 75

Table 1.46: Typical release values to air

The ranges in brackets are the variations of the emissions which can be expected when different grades are produced.

1.6.2.2.3 Drum granulation with ammoniation

Input requirements

Typical raw materials	
Nitric acid* kg/tonne (100 %)	301
Ammonia* kg/tonne	101
Sulphuric acid kg/tonne (100 %)	32
SSP (18 % P_2O_5) kg/tonne	11
TSP (45 % P_2O_5) kg/tonne	329
Potash (60 % K_2O) kg/tonne	250
Utilities	
Electricity kWh/tonne	33
Total energy for drying MJ/tonne	300
*Including the part added as AN solution	

Table 1.47: Raw material input requirements for drum granulation with ammoniation

Output production

The water solubility of the phosphates is 85 %.
The production rate is fixed at 50 t/h (1200 t/d or 350000 t/yr).
There is no export of energy related to the process.

1.6.2.2.4 Mixed acid process with phosphate rock digestion

Input requirements

	Water solubility of phosphates	
	60 %	80 %
Typical raw materials		
Phosphate rock (38.5 % P_2O_5) kg/tonne	151	128
Nitric acid* kg/tonne (100 %)	298	282
Ammonia* kg/tonne	107	111
Phosphoric acid P_2O_5 kg/tonne	96	104
Sulphuric acid kg/tonne (100 %)	53	76
Potash (60 % K_2O) kg/tonne	251	251
Utilities		
Electricity kWh/tonne	50	50
Total energy for drying MJ/tonne	450	450
* Includes the part added as AN solution		

Table 1.48: Raw material input requirements for a mixed acid process with phosphate rock digestion

Output production

The production rate is fixed at 50 t/h (1200 t/d or 350000 t/yr). There is no export of energy from the process.

Emissions and wastes are the same as those given in Table 1.46. The total amount of air is estimated to be 200000 Nm^3/h (wet).

Typical levels for the emissions to air are listed below.

Component	Emission at 50t./h		
	kg/h	kg/t NPK	mg/Nm^3 (wet)
NH_4-N	6 (2.5 – 10)	0.1 (0.05 – 0.25)	30 (12 – 60)
NO_X as NO_2	16 (7 – 30)	0.3 (0.15 – 0.6)	80 (30 – 150)
Fluorides	0.5 (0 – 1)	0.01 (0 – 0.02)	2.5 (0 – 5)
Particulates	10 (5 – 15)	0.2 (0.1 – 0.3)	50 (25 – 75)

Table 1.49: Typical levels for releases to air

The ranges in brackets are the variations of the emissions which can be expected when different grades are produced.
[10, infoMil, 2001]

1.7 Urea/UAN

The take up in use of urea as a fertiliser at first was rather slow but it has since become the most used solid nitrogen fertiliser in the world, mainly because of its use for flooded rice. The biggest demand for urea is now in Asia. The annual global production has increased by about 30 Mt in the last 10 years. Current world output amounts to more than 100 Mt/year. [34, IFA, 2001]

Urea plant installations in Europe

62 urea plants were in operation in Western Europe in the year 2000. The total capacity in the fertiliser year 1999/2000 was about 5.8 million tonnes.

Urea is also used as a raw material for the manufacture of melamine and for various urea/formaldehyde resins adhesives and as a cattle feed supplement, where it is an inexpensive source of protein.

Ureas compounds are produced in some facilities by adding a sulphur compound (ammonium sulphate or aluminium sulphate) to the urea melt.

Urea ammonium nitrate

Ammonium nitrate (AN) and urea are used as feedstocks in the production of urea-ammonium nitrate (UAN) liquid fertilisers. Most UAN solutions typically contain 28, 30 or 32 % N but other customised concentrations (including additional nutrients) are produced. Plant capacities for the production of UAN solutions range between 200 and 2000 t/d. Most of the large-scale production units are located within integrated plants where either urea or ammonium nitrate or both are produced.

The addition of corrosion inhibitors or the use of corrosion-resistant coatings allows carbon steel to be used for storage and transportation equipment for the solutions. Western European consumption of UAN in 1998/99 was 3.72 Mt of solution, 41 % of which was imported.

A typical UAN solution analysis would show: N content 28 – 32 % by weight, pH 7 to 7.5, density 1280 - 1320 kg/m^3, and a salt-out temperature of 18 to -20 °C, depending on the N content, with it being at its lowest when the urea N/ammonium nitrate N ratio is about 1:1.

A large proportion of AN is applied as a straight fertiliser. However, in some European countries like the Netherlands and Germany, AN is not applied as a fertiliser. AN is also a raw material for many blended and complex fertilisers, such as calcium ammonium nitrate (CAN), magnesium ammonium nitrate (MAN), ammonium sulphate nitrate (ASN), and potassium ammonium nitrate.

Calcium ammonium nitrate (CAN)

CAN is Western Europe's most applied fertiliser product. To produce CAN, the concentrated AN solution (95 – 97 %) is mixed with a ground, dried filler, consisting of dolomite, limestone or calcium carbonate (by-product of a NP fertiliser plant). Minor amounts of by-product are formed during the manufacturing process of CAN via the reaction:

$$2\ NH_4NO_3 + CaCO_3 \rightarrow Ca(NO_3)_2 + 2\ NH_3 + CO_2 + H_2O$$

Applying a rapid mixing or using additives such as NH_4SO_4, $MgSO_4$ or $FeSO_4$ can prevent this reaction. The CAN slurry can be prilled or granulated.

CAN can also be produced as a by-product of NPK fertilisers produced by the so-called nitrophosphate process.

Magnesium ammonium nitrate (MAN)

The AN solution is mixed with magnesium containing compounds (dolomite with a relatively high magnesium content, magnesium carbonate, magnesium sulphate). Ammonium sulphate is sometimes also added. Prilling or granulation solidifies the solution. If dolomite is used, the calcium carbonate in dolomite might react with AN as described under CAN above to form urea ammonium nitrate (UAN).

UAN is a liquid fertiliser, produced by mixing a concentrated AN solution with a concentrated urea solution. Both continuous and batch processes are available.

Ammonium sulphate nitrate (ASN)

By adding ammonium sulphate to an approximately 95 wt % ammonium nitrate solution, or by neutralising HNO_3 - H_2SO_4 mixtures with ammonia, a solution of ASN can be produced. After prilling or granulation, the fertiliser hardens during storage, due to further reactions. The addition of salts of Mg, Fe or Al can prevent this.

Potassium ammonium nitrate

A potassium salt (KCl or K_2SO_4) is added to the ammonium nitrate solution before solidification (prilling or granulating).

1.7.1 Applied processes and techniques

Urea

The commercial synthesis of urea is achieved by the reaction of ammonia and carbon dioxide at high pressure forming ammonium carbamate, which is then dehydrated by applying heat, forming urea and water:

$$\begin{array}{ccccccccc} & & & 1 & & 2 & & & \\ 2\mathrm{NH_3} & + & \mathrm{CO_2} & \leftrightarrow & \mathrm{NH_2COONH_4} & \leftrightarrow & \mathrm{CO(NH_2)_2} & + & \mathrm{H_2O} \\ \text{Ammonia} & & \text{Carbon} & & \text{Ammonium} & & \text{Urea} & & \text{Water} \\ & & \text{Dioxide} & & \text{Carbamate} & & & & \end{array}$$

Reaction 1 is fast and exothermic and essentially goes to completion under the industrial reaction conditions used. Reaction 2 is slower and endothermic and does not go to completion. The conversion (on a CO_2 basis) is usually in the order of 50 – 80 %. The conversion increases with increasing temperature and NH_3/CO_2 ratio and decreases with increasing H_2O/CO_2 ratio.

Several side reactions may occur in urea synthesis. The most relevant are:

Hydrolysis of urea

$$\mathrm{CO(NH_2)_2 + H_2O \leftrightarrow NH_2COONH_4 \leftrightarrow 2NH_3 + CO_2}$$

Formation of biuret

$$\mathrm{2\ CO(NH_2)_2 \leftrightarrow NH_2CONHCONH_2 + NH_3}$$

Formation of isocyanic acid

$$\mathrm{CO(NH_2)_2 \leftrightarrow NH_4NCO \leftrightarrow NH_3 + HNCO}$$

The hydrolysis reaction is the reverse reaction of the urea formation and only takes place in the presence of water. This reaction is determined by temperature (high temperatures favour hydrolysis) and reaction kinetics. Furthermore, adding acids or alkaline solutions can also accelerate the rate of hydrolysis. In practice, residence times of urea-containing solutions at high temperatures must be minimised.

Excess ammonia is added to shift the hydrolysis reaction to the left. However, the high NH_3 concentration in the urea reactor also shifts the biuret reaction to the left. In downstream sections of the plant, NH_3 is removed from the urea solutions, creating a driving force for biuret formation. In practice biuret is only formed in concentrated urea solutions with a low ammonia content and in molten urea. Again, residence times of urea containing solutions and urea melts at high temperatures must be minimised. Biuret must be limited in fertiliser urea (preferably

<1 %), since biuret might cause crop damage, notably during folier spraying. In technical urea (e.g. used in the production of synthetic resins), the biuret may be higher (generally up to 1.5 %) or much lower (even <0.15 %) depending on customer requirements. Low NH_3 concentrations and high temperatures also favour the formation of isocyanic acid, especially in the evaporation section of the plant, the reaction forming isocyanic acid is shifted to the right.

The percentage conversion of NH_3 and CO_2 to urea per reactor pass can technically be maximised, but this would require a longer reaction time, which is less economical. Therefore, the aim is to attain the maximum quantity of urea per unit of time with due regard to the cost of recycling unconverted NH_3 and the cost of an increased reactor size and corrosion difficulties, which increase with temperature. As a result, the process design is mainly concerned with the most efficient ways to separate product urea from the other reaction components, to recover excess NH_3, and to decompose the residual ammonium carbamate (NH_2COONH_4) to NH_3 and CO_2 for recycling. The simplest way to decompose the carbamate to CO_2 and NH_3 is to depressurise and boil the reactor effluent.

The design of commercial processes also takes account of how to separate the urea from the other constituents, how to recover excess NH_3, and the decomposition of the carbamate for recycling. Studies have been conducted on the development of materials able to withstand the corrosive carbamate solution and construction materials have been identified. Studies have also looked at the optimisation of the heat and energy balances.

The earliest urea plants operated on a “Once Through” principle where the off-gases were used as the feedstock for other products. Subsequently “Partial Recycling” techniques were developed to recover and recycle some of the NH_3 and CO_2 to the process. Originally it was essential to recover all of the gases for recycling to the synthesis to optimise the raw material usage and since recompression was too expensive an alternative method was developed. This involved cooling the gases and re-combining them to form carbamate liquor, which was then pumped back to the synthesis. A series of loops involving carbamate decomposers at progressively lower pressures and carbamate condensers were used. This was known as the ‘Total recycle Process.’ The benefit of recycling the gases was that the NH_3/CO_2 molar ratio in the reactor increased, thereby increasing the urea yield.

Decomposing the carbamate in the reactor effluent has since lead to further improvements without needing to reduce the system pressure. This ‘Stripping Process’ dominates synthesis technology and provides capital/energy savings. Two commercial stripping systems have been developed, one using CO_2 and the other using NH_3 as the stripping gases.

Other processes have emerged which combine the best features of the ‘Total Recycle’ and ‘Stripping Technologies’ since the base patents on stripping technology have expired. For convenience, total recycle processes were identified as either **conventional** or **stripping** processes.

The urea solution from the synthesis/recycling stages of the process is concentrated to a urea melt for conversion to a solid prilled or granular product for use as a fertiliser. In some cases, urea is produced solely for melamine production.

Improvements in process technology have concentrated on reducing production costs and minimising the environmental impact. These have included boosting the CO_2 conversion efficiency, increasing heat recovery, reducing utilities consumption and recovering residual NH_3 and urea from plant effuents. At the same time the size limitation of prills and concern about the prill tower off-gas releases lead to an increased interest in melt granulation processes and prill tower emission abatement. Some or all of these improvements have been used in updating existing plants, with some plants also adding computerised systems for process control. New urea installations vary in size from 800 to 2000 t/d and are typically 1500 t/d units.

Modern processes have very similar energy requirements and nearly 100 % material efficiency. There are some differences in the detail of the energy balances but they are considered to be minor in effect.

Block flow diagrams for CO_2 and NH_3 stripping total recycle processes are shown in Figure 1.27 and Figure 1.28.

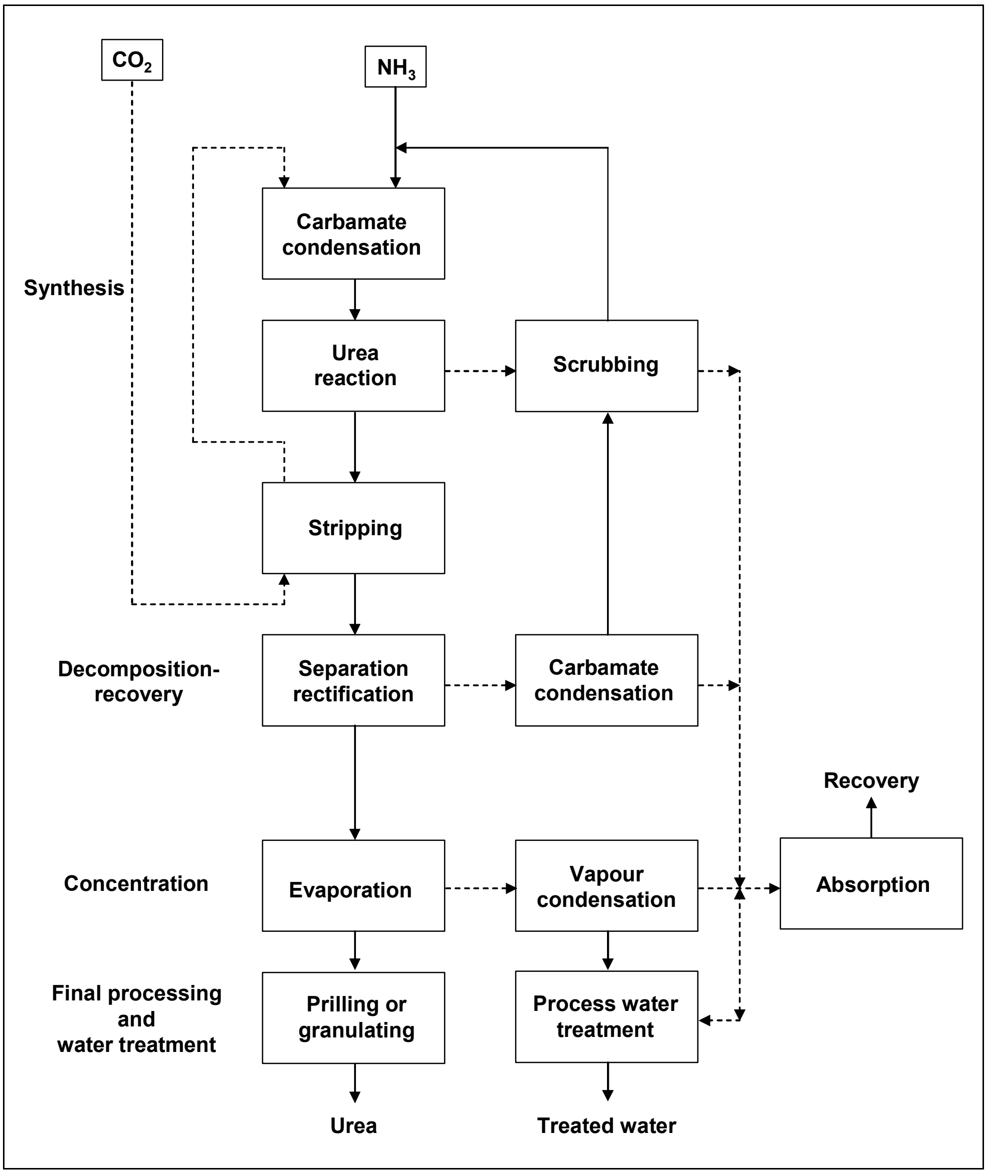


Figure 1.27: Block diagram of a total recycle CO_2 stripping urea process
[5, EFMA, 2000]

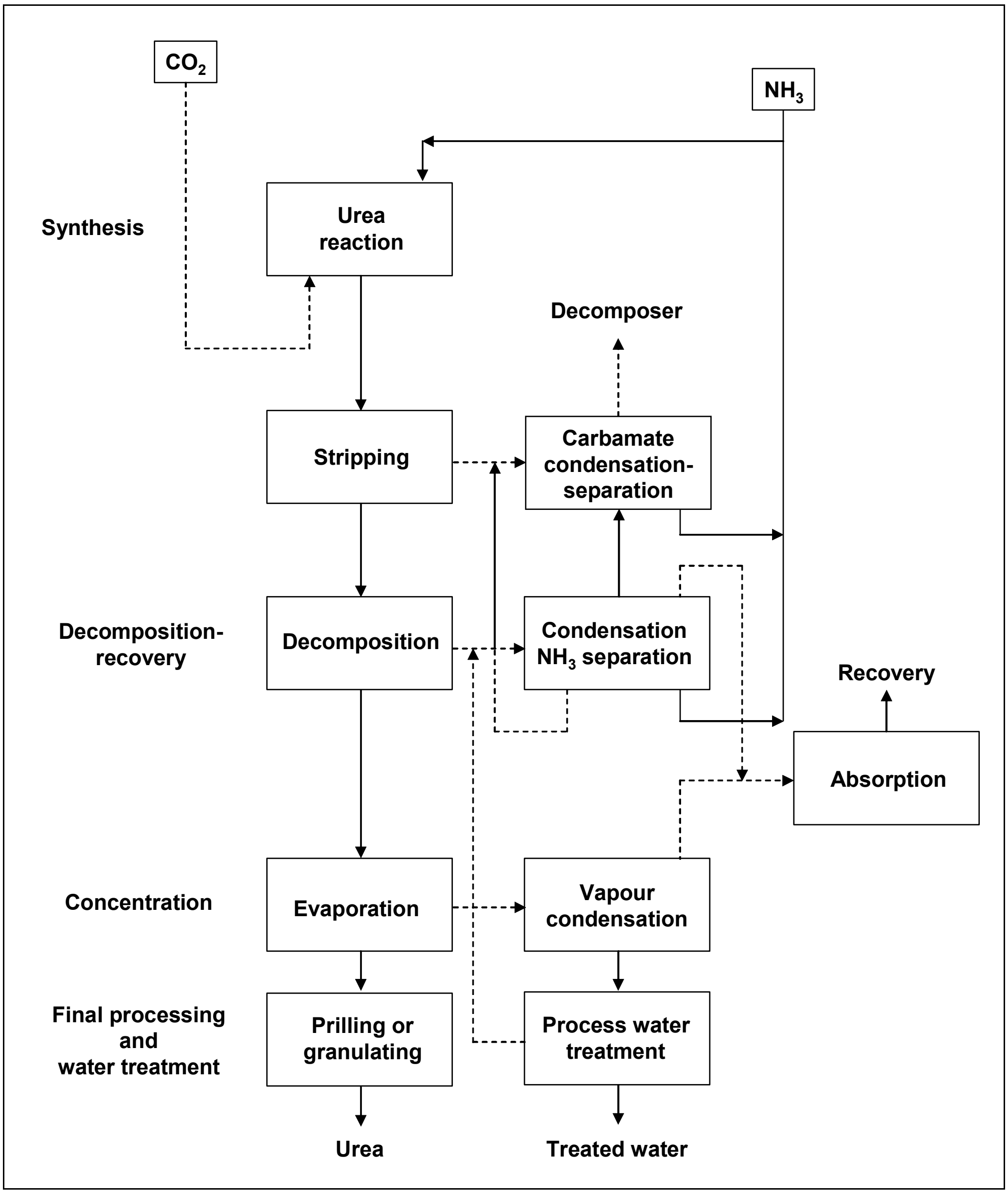


Figure 1.28: Block diagram of a total recycle NH_3 stripping urea process
[5, EFMA, 2000]

Description of production processes

The water produced from each process discussed in this section is purified by the recovery of dissolved urea, NH_3 and CO_2, which are recycled to the synthesis section through a low-pressure carbamate condensation system.

1.7.1.1 Carbon dioxide stripping process

NH_3 and CO_2 are converted to urea via ammonium carbamate at a pressure of approximately 140 bar and a temperature of 180 – 185 ºC. The molar NH_3/CO_2 ratio used in the reactor is 2.95:1. This results in a CO_2 conversion of about 60 % and an NH_3 conversion of 41 %. The reactor effluent containing unconverted NH_3 and CO_2 undergoes a stripping operation at essentially reactor pressure, using CO_2 as the stripping agent. The stripped NH_3 and CO_2 are partially condensed and recycled to the reactor. The heat evolved from this condensation is used to produce 4.5 bar steam that can be used, in part, for heating purposes in the downstream sections of the plant. Surplus 4.5 bar steam is sent for use in the CO_2 compressor turbine.

The NH_3 and CO_2 in the stripper liquor are vaporised in a 4 bar decomposition stage and then condensed forming a carbamate solution, which is recycled to the 140 bar synthesis section. The urea solution is further concentrated after the 4 bar decomposition stage in the evaporation section, where a 99.7 % urea melt is produced.

1.7.1.2 Ammonia stripping process

NH_3 and CO_2 are converted to urea through an ammonium carbamate intermediate at a pressure of 150 bar and a temperature of 180 °C. A molar NH_3/CO_2 ratio of 3.5 is used in the reactor, giving a CO_2 conversion of 65 %. Reactor effluent passes to the stripper where a large part of the unconverted carbamate is decomposed by the stripping action of the excess NH_3. Residual carbamate and CO_2 are recovered after the stripper in two successive stages operating at 17 and 3.5 bar respectively. NH_3 and CO_2 vapours from the stripper exit are mixed with the recovered carbamate solution from the High-Pressure (HP)/Low-Pressure (LP) sections, condensed in the HP carbamate condenser and fed to the reactor. The heat of condensation is used to produce LP steam. The urea solution leaving the LP decomposition stage is concentrated in the evaporation section to give the urea melt.

1.7.1.3 Advanced cost and energy saving (ACES) process

In this process the synthesis section operates at 175 bar with an NH_3/CO_2 molar ratio of 4 and a temperature of 185 to 190 °C.

The reactor effluent is stripped using CO_2 as the stripping agent at essentially reactor pressure. The overhead gas mixture from the stripper is fed to two carbamate condensers in parallel, where the gases are condensed and recycled under gravity to the reactor along with absorbent solutions from the HP scrubber and absorber. The heat generated in the first carbamate condenser is used to generate 5 bar steam and the heat formed in the second condenser is used to heat the solution leaving the stripper bottom after pressure reduction. The inerts in the synthesis section are purged to the scrubber from the reactor top for the recovery and recycling of NH_3 and CO_2. The urea solution leaving the bottom of the stripper is further purified in HP and LP decomposers operating at approx. 17.5 bar and 2.5 bar respectively. The separated NH_3 and CO_2 are recovered to the synthesis via HP and LP absorbers.

The aqueous urea solution is initially concentrated to 88.7 % wt in a vacuum concentrator and then further concentrated for prilling or granulating.

1.7.1.4 Isobaric double recycle (IDR) process

The reactor pressure is around 200 bar for the process. The molar NH_3/CO_2 ratio is 4.5 and the reactor product temperature is 185 to 190 °C. The urea conversion rate is 70 % CO_2 conversion per pass and 35 % for NH_3.

Most of the unconverted materials in the effluent from the reactor bottom are separated by heating and stripping in two consecutive strippers operated at reactor pressure and heated by 25 bar steam. Carbamate is decomposed/stripped by NH_3 in the first stripper, with the remaining NH_3 being removed in the second stripper using CO_2 as stripping agent. The overheads from the first stripper are fed directly to the reactor with the overheads from the second stripper being recycled to the reactor through the carbamate condenser. The heat of condensation is recovered as 7 bar steam and used further on in the process.

Whereas all the carbon dioxide is fed to the plant through the second stripper, only 40 % of the ammonia is fed to the first stripper. The remainder goes directly to the reactor for temperature control. The ammonia-rich vapours from the first stripper are fed directly to the urea reactor.

The carbon dioxide-rich vapours from the second stripper are recycled to the reactor via the carbamate condenser, irrigated with carbamate solution recycled from the lower-pressure section of the plant. The heat of condensation is recovered as 7 bar steam which is used downstream in the process. Urea solution leaving the IDR loop contains unconverted ammonia, carbon dioxide and carbamate. These residuals are decomposed and vaporised in two successive distillers, heated with low-pressure recovered steam. After this, the vapours are condensed to carbamate solution and recycled to the synthesis loop. The urea solution leaving the LP decomposition for further concentration is fed to two vacuum evaporators in series, producing the urea melt for prilling and granulation.

1.7.1.5 Process water sources and quantities

A 1000t/d urea plant generates on average approximately 500m^3/d process water containing 6 % NH_3, 4 % CO_2 and 1.0 % urea (by weight). The principal source of this water is the synthesis reaction where 0.3 tonnes of water is formed per tonne of urea, e.g.:

$$2NH_3 + CO_2 \rightarrow CO(NH_2)_2 + H_2O$$

The other sources of water are ejector steam, flush and seal water and the steam from the waste water treatment plant.

The principal sources of urea, NH_3 and CO_2 in the process water are from the evaporator condensate.

The NH_3 and urea in the evaporator condensate are attributable to:

- the presence of NH_3 in the urea solution feed to the evaporator
- the formation of biuret and the hydrolysis of urea in the evaporators, both reactions liberating NH_3.

$$2CO(NH_2)_2 \rightarrow H_2NCONHCONH_2 + NH_3$$

$$CO(NH_2)_2 + H_2O \rightarrow 2NH_3 + CO_2$$

- the direct carry over of urea from the evaporator separators to the condensers (physical entrainment)
- the formation of NH3 from the decomposition of urea to isocyanic acid

$$CO(NH_2)_2 \rightarrow HNCO + NH_3$$

- the reverse reaction which occurs on cooling the products in the condensers
- off-gases from the recovery/recirculation stage absorbed in the process water
- off-gases from the synthesis section absorbed in the process water
- flush and purge water from pumps
- liquid drains from the recovery section.

The purpose of the water treatment is to remove NH_3, CO_2 and urea from the process water and to enable the recycling of the gases to the synthesis. This ensures raw material utilisation is optimised and effluent is minimised.

Prilling and Granulation

In urea fertiliser production operations, the final product is in either a prilled or granular form. Production of either form from the urea melt requires the use of a large volume of cooling air which is subsequently discharged to the atmosphere. A block diagram of the prilling and granulation processes is shown in Figure 1.29.

Prilling

The concentrated (99.7 %) urea melt is fed to the prilling device (e.g. rotating bucket/shower type spray head) located at the top of the prilling tower. Liquid droplets are formed which solidify and cool on free fall through the tower against a forced or natural up-draft of ambient air. The product is removed from the tower base to a conveyor belt using a rotating rake, a fluidised bed or a conical hopper. Cooling to ambient temperature and screening may be used before the product is finally transferred to storage.

The design/operation of the prilling device exerts a major influence on the product size. Collision of the molten droplets with the tower wall as well as inter-droplet contact causing agglomeration must be prevented. Normally mean prill diameters range from 1.6 - 2.0 mm for prilling operations. Conditioning of the urea melt and ‘crystal seeding’ of the melt, may be used to enhance the anticaking and mechanical properties of the prilled product during storage/handling.

Granulation

Depending on the process a 95 - 99.7 % urea feedstock is used. The lower feedstock concentration allows the second step of the evaporation process to be omitted and also simplifies the process condensate treatment step. The basic principle of the process involves the spraying of the melt onto recycled seed particles or prills circulating in the granulator. A slow increase in granule size and drying of the product takes place simultaneously. Air passing through the granulator solidifies the melt deposited on the seed material.

Processes using low concentration feedstock require less cooling air since the evaporation of the additional water dissipates part of the heat which is released when the urea crystallises from liquid to solid.

All the commercial processes available are characterised by a product recycle, and the ratio of recycled to final product varies between 0.5 and 2.5. Prill granulation or fattening systems allow a very small recycle, typically 2 to 4 %. Usually the product leaving the granulator is cooled and screened prior to transfer to storage. Conditioning of the urea melt prior to spraying may also be used to enhance the storage/handling characteristics of the granular product.

Urea-ammonium nitrate production

Description of production processes

Continuous and batch type processes are used; in both processes concentrated urea and ammonium nitrate solutions are measured, mixed and then cooled. Block diagrams for UAN production are shown in Figure 1.29 and Figure 1.30.

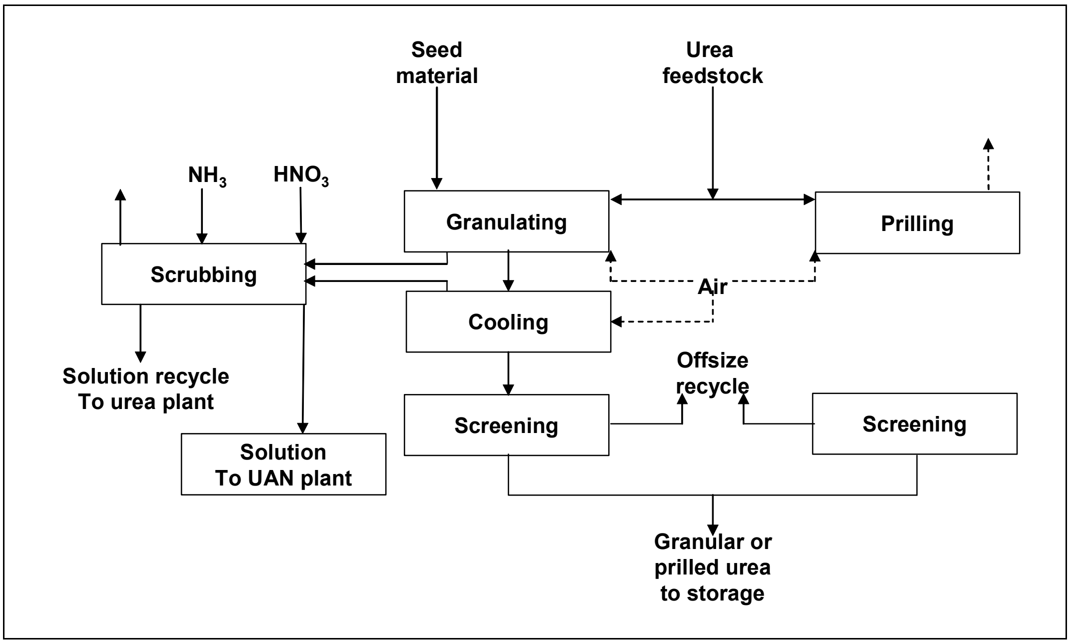


Figure 1.29: Block diagram for UAN process

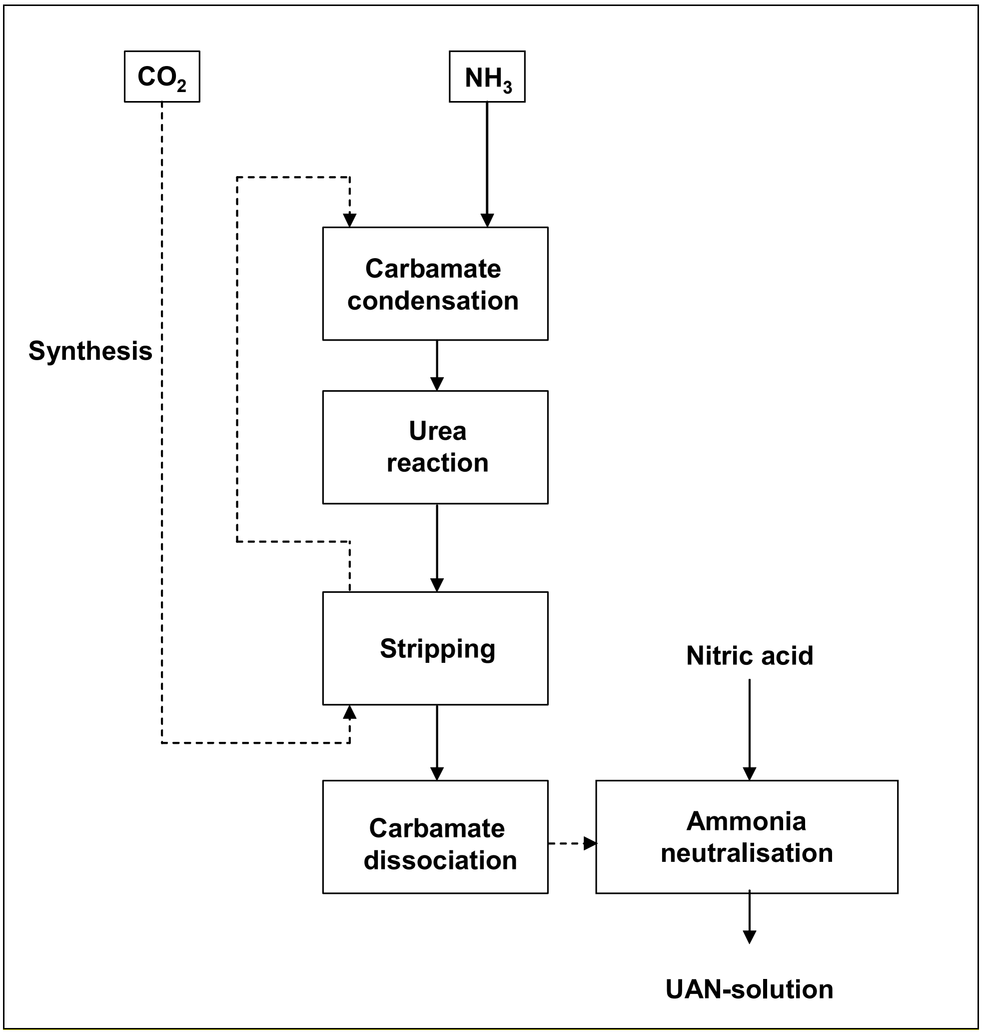


Figure 1.30: Block diagram of a Partial Recycle CO_2 Stripping Urea process for UAN Production

In the **continuous process,** the ingredients of the UAN solution are continuously fed to and mixed in a series of appropriately sized static mixers. Raw material flow as well as finished product flow, pH and density are continuously measured and adjusted. The finished product is cooled and transferred to a storage tank for distribution.

In the **batch process,** the raw materials are sequentially fed to a mixing vessel fitted with an agitator and mounted on load-cells. The dissolving of the solid raw material(s) can be enhanced by recirculation and heat exchange as required. The pH of the UAN product is adjusted prior to the addition of the corrosion inhibitor.

A partial recycle CO_2 stripping urea process is also suitable for UAN solution production. Unconverted NH_3 and CO_2 from the stripped urea solution, together with the gases from the water treatment unit, are transferred for conversion into UAN solutions.

Description of storage and transfer equipment

The physical form of the feedstock dictates the handling and storage system requirements. Bunded tank areas and collection pits allow any solution spillages to be collected for recycling. Air ducting and filtration helps in the recovery of air-borne dust.

Regulations specific to the storage and handling of solid or solutions of ammonium nitrate must be adhered to. Recommendations for the storage and transfer of ammonia and nitric acid are given in [2, EFMA, 2000] [32, EFMA, 2000]. Recommendations for the storage of solid ammonium nitrate can be found in [36, (EFMA), 1992].

1.7.2 Current emissions and consumptions

1.7.2.1 Input and output

Process energy consumption

The synthesis section of the urea plant operates at high pressure (140 – 250 bar). Energy is needed for gas compression. Most urea plants use stripping systems, which require energy to recover CO_2 and NH_3. Energy is sometimes recovered by generating low-pressure steam from the carbamate condenser(s). The overall energy consumption depends on the stripping system used and on local conditions.

Process	**NH_3 (t/tonne urea)**	**CO_2 (t/tonne urea)**	**CO_2 compressor***	**Steam***		**Cooling water */** (m^3/tonne urea)**	**Electricity* (MJ/tonne urea)**
				Amount (t/tonne urea)	**Pressure (bar)**		
CO_2 stripping	0.567	0.733	ST	0.770 - 0.920	120	70	54
			E	0.800	24	60	396
NH_3 stripping	0.567	0.735	ST	0.760 - 0.950	108	75 - 80	76 - 82
IDR process	0.57	0.74	ST	0.600	105	75	79
ACES process	0.57	0.74	ST	0.700 - 0.800	98	60 - 80	54 - 108
			E	0.570	24.5	51	436
			E	0.84	24	60	425

* Depending on whether the CO_2 compressor is driven by an electromotor (E) or steam turbine (ST)
** Temperature difference of 10 °C

Table 1.50: Typical inputs into modern urea plants (including concentrating and prilling operations)
[10, InfoMil, 2001]

Energy consumption due to product finishing

The total energy consumption given in Table 1.50 includes the energy needed to make granules from a urea melt, containing less than 0.5 % water. A significant proportion of the energy consumption for product finishing is used in drying the product. More energy is needed for granulation compared to prilling, to drive the equipment.

The energy consumption required for product finishing very much depends on local effects such as climate, end-product temperature and the requirements for pollution control. The design of the granulation equipment also has a significant influence on the energy consumption and varies considerably between designs. The electricity consumption can vary from 40 to 135 MJ/tonne urea, while steam consumption is in the range of 40 kg of low pressure steam per tonne urea up to 200 kg urea of 9 bar steam per tonne urea [10, infoMil, 2001].

1.8 Ammonium nitrate/calcium ammonium nitrate

Ammonium nitrate is used extensively as a nitrogenous fertiliser. It is made exclusively by the neutralisation reaction between gaseous ammonia and aqueous nitric acid. The resultant ammonium nitrate solution may be used in various ways:

- it can be stored as a solution and then used in downstream plants or sold in solution
- it can be made as solid ammonium nitrate by prilling or granulation
- it can be mixed with a solid filler such as calcium carbonate in the form of ground limestone, dolomite or calcium carbonate by-product from, for example, a nitrophosphate process, to make a product which is known in the industry as “Calcium Ammonium Nitrate” (CAN), which can then be prilled or granulated.

One of the important parameters in the production of ammonium nitrate is the nitric acid strength, which can vary from 50 to 70 %. Normally the ammonium nitrate is made from an adjacent nitric acid production unit but it may also be made from purchased nitric acid.

The final solid fertiliser product may leave the production site either as loose bulk or in a variety of pack sizes.

The main marketable products are: hot solution of ammonium nitrate, ammonium nitrate containing 33.5 % nitrogen and calcium ammonium nitrate containing less than 28 % nitrogen

Plants for the production of ammonium nitrate and CAN generally produce a few hundred t/d up to 3600 t/d.

Fertiliser regulations in the European Union place certain requirements on ammonium nitrate which is to be labelled as an EC Fertiliser. Fertiliser grade products produced at a plant must conform to these specifications in the application of BAT. In outline these requirements are as follows:

- no additions of substances are allowed which increase the sensitivity of the ammonium nitrate to heat or detonation
- the oil retention must pass a specified test
- the combustible material must be less than 0.2 % for a product containing 31.5 % N, and less than 0.4 % for a product containing between 28 and 31.5 % N
- the pH of a 10 % solution must be greater than 4.5
- less than 5 % of the product is allowed to be smaller than 1mm, with less than 3 % smaller than 0.5mm
- chlorine content must be less than 0.02 %
- heavy metals should not be added and trace amounts incidental to the process should not exceed the limit fixed by the Committee
- copper content should be less than 10 mg/kg
- the product must pass a specified detonation test (optional).

AN and CAN fertilisers containing an excess of the specified thresholds of ammonium nitrate are classified as oxidising substances under the UN Transport Regulations.

Ammonium nitrate declared as an EC Fertiliser may only be supplied to the end user in packages. The legislation of the appropriate country must be consulted for the precise details of local requirements. Conformance to these requirements ensures that the ammonium nitrate is safe for the customer. The manufacturer must select a process route that satisfies the specified limits and must take measures to control the raw materials which are to be used (i.e. in respect to the trace elements analyses) to ensure that all limits are met. This also applies to anticaking and conditioning additives, which are often used to improve the final product.

1.8.1 Applied processes and techniques

Ammonium nitrate (AN; NH_4NO_3) is produced mainly from ammonia (NH_3) and nitric acid (HNO_3). The process chemistry of AN production is relatively simple; AN is produced by neutralising 45 - 60 wt % aqueous HNO_3 with gaseous NH_3:

$$NH_3 + HNO_3 \rightarrow NH_4NO_3$$

The reaction is highly exothermic and proceeds rapidly. The heat produced is often used to generate steam. The obtained AN solution can be concentrated by evaporation. Most applied production processes comprise 3 main operations: neutralisation, evaporation and solidification (prilling or granulation).

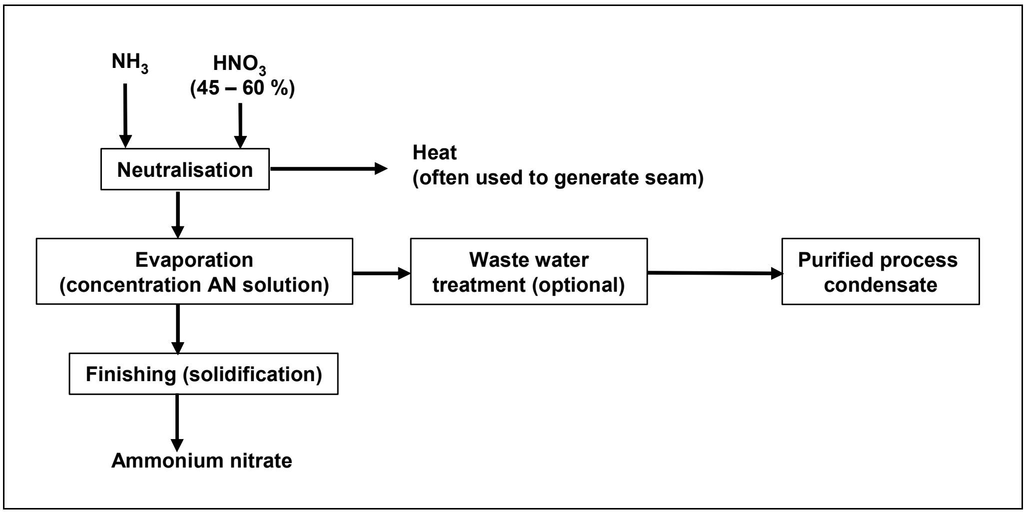


Figure 1.31: Production of solid ammonium nitrate
[10, infoMil, 2001]

1.8.1.1 Neutralisation

The exothermic neutralisation of nitric acid with ammonia gas produces ammonium nitrate solution and steam. The nitric acid is normally preheated in corrosion-resistant equipment, particularly if the concentration of nitric acid is at the lower limit of the 50 – 70 % range. Preheating using steam or hot condensate from the ammonium nitrate process is the most effective use of this excess heat.

The amount of preheat required can be estimated from an enthalpy energy balance using the concentration of the nitric acid and the concentration of ammonium nitrate from measured physical data. Neutralisation is carried out in a single stage or in two stages. A two-stage neutraliser operates with a low pH in the first stage (acidic conditions) and a neutral pH in the second stage. The equipment can operate at a variety of operating pressures and temperatures.

The pressure, temperature and concentrations in most neutralisers are linked by the boiling point characteristics of the ammonium nitrate solutions, with only two of these variables being independent.

Ammonia gas may contain small quantities of such as unreacted hydrogen and inert nitrogen. These are vented from the neutraliser system at a suitable point, depending on the characteristics of the particular process.

1.8.1.2 Neutralisers

Neutralisers may be free boiling vessels, circulating systems, or pipe reactors. The factors, which influence the choice of neutraliser are: [7, EFMA, 2000]

- a two-stage neutraliser produces most of the boil-off steam in the first stage and most of the ammonia emission in the second stage. This reduces the total ammonia emission
- a single stage neutraliser is simpler and cheaper
- neutralisation at an elevated pressure will produce steam at a higher temperature (and ammonium nitrate at a higher concentration). This steam is more usable for downstream processes such as evaporation and drying
- the control of the neutraliser is a critical parameter. The pH and the temperature must both be strictly controlled to limit losses from the neutraliser. All installations must therefore include pH and temperature controls, using reliable equipment, which must be tested on a routine basis
- the control of impurities has been mentioned above. At the operating temperature of the neutraliser, impurity control is of great importance because a safety incident would constitute a significant environmental incident. Some manufacturers do not recycle ammonium nitrate screenings to the neutraliser for this reason. Recycling is especially to be avoided if the screenings are contaminated by an organic anticaking additive. It should be noted that an acidic solution of ammonium nitrate is more unstable than an alkaline solution.

1.8.1.3 Steam purification

The steam leaving the neutraliser can be purified, or it can be condensed and then purified. The steam may be used in the evaporator (see below) or it may be used to preheat and evaporate ammonia, and also to preheat the nitric acid. The following techniques have been used commercially for the purification of the steam and should be considered to be “available”:

Droplet separation techniques

- knitted wire mesh demister pads
- wave plate separators
- fibre pad separators using, for example, PTFE fibres.

Scrubbing devices

- packed columns
- venturi scrubbers
- irrigated sieve plates.

Ammonium nitrate emissions from neutralisers are very difficult to remove because the particles are very fine. A combination of droplet separators and scrubbers can be used. For all the above, scrubbers would require the addition of acid, normally nitric acid, to neutralise any free ammonia and to optimise its removal. Process interchange is preferred where practicable for condensation of the steam. Alternatively, water or air cooled exchanger(s) are required.

1.8.1.4 Condensate treatment

Contaminated condensate can be re-used or purified using various techniques including:

- stripping with air or steam with the addition of alkali to liberate ionised ammonia if required
- distillation
- membrane separation techniques, such as reverse osmosis.

Another option is ion exchange but there are safety risks about using organic material that need to be taken into account. The recycling of organic resins to the ammonium nitrate process must be prevented, and the exchange resin must not be allowed to become nitrated [6, EFMA, 2000].

Condensate, arising from the steam, leaving the neutraliser, can be discharged in one of the following ways:

- to drain
- to a nitric acid plant for use as absorption water, if the quality is acceptable for production
- to other users on the site, such as in fertiliser solution manufacturing
- as boiler feed-water, after further purification
- to the scrubbing section of AN/CAN prilling or granulation.

Amonium nitrate solution is the product from the neutraliser. The concentrations are variable depending on the feed materials and/or operating conditions. The product solution may be sent to storage without further processing. If it is to be used in the manufacture of solid ammonium nitrate, CAN or NPK fertiliser, it is normally concentrated by evaporation.

1.8.1.5 Evaporation

The ammonium nitrate solution is normally concentrated in an evaporator to the water strength required by the particular manufacturing process before being used for the finished product. The water concentration is normally below 1 % for a prilled product and up to 8 % for some granulation processes.

Steam from the ammonium nitrate process (neutraliser) or from a steam raising facility on the site is used as the heat source for evaporation.

Steam at a controlled temperature must be used to avoid the decomposition of ammonium nitrate, as excessive temperatures may lead to decomposition. Evaporation may be carried out at atmospheric pressure or under vacuum. The latter allows for the re-use of neutraliser steam, but it is more capital intensive.

The steam, which is boiled off, will be contaminated with ammonia, along with droplets of ammonium nitrate, and must be removed.

There is a large variety of evaporator systems in industrial use; these include circulatory, shell and tube heat-exchangers and falling film evaporators. Falling film evaporators have the advantage of utilising a small working volume and a short residence time. Steam formed during the evaporation process might be contaminated, but any steam used is generally not contaminated.

Techniques for decontamination include:

- droplet separators, as used in the neutralisers
- scrubbers, as used for the removal of fine dusts and fumes in the production of solid product
- using steam, which can be condensed and used in the system to purify neutraliser condensate.

The AN solution produced must be kept at a concentration and temperature that prevents crystallisation of the AN. In order to minimise effluents from downstream equipment, the solution from the evaporator may need to be cooled.

1.8.1.6 Prilling and granulation

The prilling technique (the formation of spheres by the solidification of liquid droplets of fertiliser material) is used in many plants for the production of ammonium nitrate and in some plants for CAN. The granulation of ammonium nitrate may be carried out in a dedicated plant, or in one which can also produce CAN. CAN and NPK fertilisers can be produced in the same installation.

Tanks for the storage of high concentrated AN-solutions are generally equipped with pH-monitoring, temperature indicators, ammonia dosing for adjusting the pH-value and a dilution device.

1.8.1.6.1 Prilling

The ammonium nitrate feed to a prilling tower needs to be virtually anhydrous. To achieve this, the solution is sprayed through one-component nozzles, perforated plates, or perforated centrifuges at the top of the tower. Cold air is drawn through the tower countercurrently to extract the heat of crystallisation. The droplets solidify into round granules, as they fall through the tower, and are removed at the foot of the prilling tower, where they are then cooled and screened. When CAN is being produced, ground calcium carbonate (limestone or dolomite) is added before the solution is prilled.

Ammonia and ammonium nitrate (and calcium carbonate in CAN production) become entrained in the air discharged at the top of the prilling tower. A lower melt temperature can reduce emissions [6, EFMA, 2000]. Ammonia is usually removed by absorption in a wet scrubber. Small particles of ammonium nitrate (miniprills) are carried out with the air and these can be removed using comparatively simple equipment. Ammonium nitrate fume is also lost from the surface of the prills, which are submicron in size and more difficult to remove. An effective means of scrubbing ammonium nitrate fume is to use irrigated candle filters [6, EFMA, 2000]. Candle filters cannot be used for the abatement of CAN prilling towers effluent as the insoluble calcium carbonate can quickly blind the filters.

1.8.1.6.2 Granulation

Granulation, in contrast to the prilling technique, needs a more complicated plant and a variety of equipment, including rotating pans and drums, fluidised beds and other more specialised equipment. The main advantage of granulation, environmentally, is that, although the nature of the effluent is similar, the quantity of air to be treated is much smaller so typically the abatement equipment is more cost effective [6, EFMA, 2000]. The granular product can also be made in a wide range of particle sizes, which are larger than prills. Some granulation processes can use ammonium nitrate containing up to 8 % water but this water still has to be removed in the process. However as the temperature needed is lower a greater overall energy economy is possible.

Some examples of granulators used in AN/CAN plants include rotary pans and drums, spherodisers, pugmills and fluidised beds. The filler will normally be added in the process before the granulator if CAN is to be produced, with the ammonium nitrate being added to the granulator as a spray of hot concentrated solution. Further drying of the granules is unnecessary. The granules are screened and the oversized granules are crushed and, together with the fines, recycled to the granulator. CAN and CAN/NPK granulators include drums and pugmills, where the filler may be mixed with the ammonium nitrate solution before granulation or in the granulator itself. Granules from this process will normally require drying in a fluidised bed or rotary dryer. When drying CAN it might not be necessary to add any additional heat as the granules may have retained sufficient heat to provide the necessary driving force. Such a process is known as an autothermal process. The granules are screened after drying.

Gases from the granulator and from the dryer may be cleaned by a combination of dry cyclones or bag filters and wet scrubbers. Candle filters are most suitable if the emission contains a large proportion of submicron particles. Dry devices must be kept heated above the dew point of the air and below the critical relative humidity of the dust. Wet scrubbers normally use a circulating solution. A pH control with acid may be needed. The gases may be saturated with water in a separate unit before passing to the scrubber.

The solution from a wet scrubber will normally be recycled to the process but it might not always be possible for all the solution to be recycled without adversely affecting the granulation. Further concentration may then be needed. It is important that the wet scrubbers on a CAN plant are suitably designed to handle the inert solids without choking; a solid waste may then be produced from such scrubbers.

1.8.1.7 Cooling

Both granulators and prill towers normally produce a product which needs further cooling in rotary or fluidised bed coolers, with the air cleaned by high efficiency cyclones, bag filters or wet scrubbers. Air cleaned in a dry system can generally be re-used as secondary air to the dryer, after de-dusting (where possible).

A bulk flow heat-exchanger may be used. The product is cooled by transferring the heat to water from a cooling tower in a development of a plate heat-exchanger. This has minimal atmospheric effluents [6, EFMA, 2000].

1.8.1.8 Conditioning

Ammonium nitrate and CAN are prone to caking during storage and are therefore conditioned to prevent caking. Anticaking agents may be included as part of the product or applied as a coating to the outside. These additives can also minimise dust formation and moisture absorption during storage.

1.8.1.9 Storage

Solid ammonium nitrate in bags must be stored in a general warehouse which is approved for ammonium nitrate duty. The specific requirements vary between countries and the appropriate authorities must be consulted.

Bulk ammonium nitrate and CAN have to be protected from moisture, as both products are hygroscopic. Large bulk warehouses may need to be air-conditioned, depending upon the local climatic conditions and the anticaking additive used in the product. Some additives can reduce the water uptake rate.

Ammonium nitrate solution may be stored for use in downstream plants or before sale. It must be stored at a temperature above the crystallising temperature of the solution. Tanks may be lagged and/or heated; the solution may be circulated through a heat-exchanger or heated with an internal (steam) coil. Tanks are normally protected in case of overfilling and are either contained in a bund or located in an area with suitable containment facilities.

1.8.2 Current emissions and consumptions

The description which follows is for a typical plant. Details will vary from plant to plant.

1.8.2.1 Input

The **raw materials**, i.e. ammonia and nitric acid, are needed in virtually stoichiometric quantities. Nitric acid is typically around 45 - 60 % strength. The water present in the nitric acid is emitted from the process in one form or another or recycled to another plant.

The ammonium nitrate production process normally uses proprietary anticaking additives. The amounts needed are variable and the individual plant will determine the type/quantity depending on each specific marketing need.

Water may be imported as make-up water for the cooling towers, but on some plants the cooling towers are part of a centralised facility. Water is not normally needed for other process purposes. The water needed for process duties, for the washing and flushing of equipment to clear blockages and to prepare equipment for maintenance is normally available from the production process after treatement.

The electricity demand for new plants producing solid ammonium nitrate can range from 25 to 60 kWh/tonne of product. However, large amounts of electricity may be needed to retrofit existing facilities. This could mean up to 70 kWh/tonne over the quoted figures [6, EFMA, 2000]. The production of ammonium nitrate solution needs less electricity than solid ammonium nitrate e.g. 5 kWh/tonne of product [6, EFMA, 2000].

Steam is needed to evaporate the ammonium nitrate solution but the amount needed will depend on the nitric acid concentration and the product concentration needs. The evaporation process may, in some plants, use steam from the neutralisers but this may not be a practicable proposition as a retrofit to an existing process. Energy is needed to evaporate liquid ammonia in some plants. This is normally supplied from the process for example, by using the steam from the neutraliser. Steam requirements can be variable from zero to 50 kg/tonne of product. If the plant only makes ammonium nitrate solution steam can be exported at a rate of up to 170 kg/tonne of ammonium nitrate and some plants can export hot water. The production of an AN solution with approx. 95 % AN is achievable without an additional energy demand for evaporation by carrying out a pressure neutralisation. Plants that make solid CAN also need around 150 – 200 kg steam per tonne of product, together with electrical power of 10 - 50 kWh/tonne of product [6, EFMA, 2000].

1.8.2.2 Output

There are no by-products or co-products normally associated with the production of ammonium nitrate or CAN. There are no plants which can export electricity and steam export is only possible at a small rate on a small number of plants. The export of steam condensate is common on plants which use a larger quantity of steam in the process. Contaminated condensate may be exported to other plants.

1.8.2.3 Emissions

Emissions from ammonium nitrate production plants consist of ammonium nitrate and coating materials as particulates, as well as ammonia and nitric acid from solution formation and the granulators.

The neutralisers and evaporators are the main emission sources for solution formation and concentration processes, primarily releasing nitric acid and ammonia. The neutralisation reactor off-gas is mostly steam with some ammonia and NH_4NO_3. These releases vary depending upon the operating characteristics of the specific plant and or the use of excess ammonia or acid in the neutraliser. Particulate emissions from these operations tend to be smaller in size than those from solids production and handling processes and are generally recycled back to the process.

Prill towers for high and low density prills, along with rotary drum and pan granulators are the main processes resulting in solid products. The main releases are ammonium nitrate particulate matter and ammonia. These fine particles arise as a result of microprill formation, prill attrition with each another and with the tower wall, and from rapid changes in the ammonium nitrate crystal states. Releases from high-density prilling are greater than from low-density prilling.

Partially plugged orifices of melt spray devices can increase the fine dust loading and the emissions from microprill formation. Designs and techniques such as spinning buckets and vibrating spray plates can help reduce the formation of microprills. Increased emissions can also occur as a result of entrainment at the higher airflows needed to cool the prills and result in an increased fume formation at the higher temperatures.

The airflow in granulation processes is lower than that in prilling operations. The design and operating parameters of granulators can affect the emission rates.

Cooling and drying is usually carried out in rotary drums or in fluidised beds. The design and operating parameters of the rotary drums can affect the emissions quantity in a similar way to granulators. Prill and granule temperature control is essential to limit potential releases from the solids breakdown as a result of changes in the crystal state.

Screening operations due to solid breakdown leads to releases. Screening operations in the ammonium nitrate manufacturing industry are nearly all totally enclosed. Screening equipment is located within a building, with any resulting emissions being ducted from the process for recovery or re-use.

Some ammonia is lost from the ammonium nitrate solution during evaporation and this must be replenished prior to solidification.

Process	**Particulate matter kg/tonne**		**Ammonia Uncontrolled[b] kg/tonne**	**Nitric acid kg/tonne**
	Uncontrolled	**Controlled[a]**		
Neutraliser	0.045 - 4.3	0.002 - 0.22	0.43 - 18.0	0.042 – 1[c]
Evaporation/concentration operations	0.26		0.27 - 16.7	
Solids formation operations				
High density prill towers	1.59	0.60	28.6	
Low density prill towers	0.46	0.26	0.13	
Rotary drum granulators	146	0.22	29.7	
Pan granulators	1.34	0.02	0.07	
Coolers and dryers				
High density prill coolers[d]	0.8	0.01	0.02	
Low density prill coolers[d]	25.8	0.26	0.15	
Low density prill dryers[d]	57.2	0.57	0 - 1.59	
Rotary drum granulator coolers[d]	8.1	0.08		
Pan granulator coolers[d]	18.3	0.18		
Coating Operations[e]	≤ 2.0	≤ 0.02		
Bulk Loading operations[e]	≤ 0.01			

[a] Based on the following control efficiencies for wet scrubbers, applied to uncontrolled emissions: neutralisers, 95 %; high density prill towers, 62 %; low density prill towers, 43 %; rotary drum granulators, 99.9 %; pan granulators, 98.5 %; coolers, dryers and coaters, 99 %

[b] Given as ranges because of variation in data and plant operations. Factors for controlled emissions are not presented due to conflicting results on control efficiency

[c] Based on 95 % recovery in a granulator recycle scrubber

[d] Factors for coolers represent combined precooler and cooler emissions, and factors for dryers represent combined predryer and dryer emissions

[e] Fugitive particulate emissions arise from coating and bulk loading operations

Table 1.51: Emission factors for process in ammonium nitrate manufacturing plants (some ammonium nitrate emission factors are based on data gathered using a modification of EPA method 5)

Typically prills and granules are coated in a rotary drum. The mixing action leads to some suspension of the coating material, which creates particulate emissions.

Bagging and bulk loading operations are a source of particulate emissions. Dust is emitted from each type of bagging process during the final filling when dust-laden air is displaced from the bag by ammonium nitrate. The potential for emissions during bagging is greater for coated than uncoated material. Emissions from bagging operations are expected to be primarily kaolin, talc or diatomaceous earth coating material [12, EIPPCB, 2000].

1.8.2.4 Discharges to water

Unabated releases to water can be up to 5000 mg AN N/l and 2500 mg NH_3 N/l (6 and 3 kg/tonne of product respectively). Condensed exhaust vapours and process effluents may be used in other areas of fertiliser production, such as in nitric acid production.

1.9 Production of superphosphates

Superphosphates, i.e. single superphosphate (SSP) and triple superphosphate (TSP), account for one quarter of the world phosphate fertiliser production. Superphosphates are used as straight fertilisers, but are also a feedstock for mutinutrient fertilisers.

Superphosphates are all derived from phosphate rock. The final product depends on the acid used; with sulphuric acid, the reaction produces normal superphosphate; with a mix of sulphuric acid and phosphoric acid, the reaction produces concentrated superphosphate; with phosphoric acid, the reaction produces triple superphosphate. All the products are marketable. The content of P_2O_5 varies as follows:

- **normal superphosphate** 16 - 24 %
- **concentrated superphosphate** 25 - 37 %
- **triple superphosphate** equivalent or up to 38 %.

The content of $CaSO_4$ is:

- **normal superphosphate** 50 - 38 %
- **concentrated superphosphate** 37 - 21 %
- **triple superphosphate** 20 - 30 %.

1.9.1 Applied processes and techniques

1.9.1.1 Production of single superphosphate (SSP)

Single superphosphate (SSP) is a widely used fertiliser. According to EC Directive 76/116, SSP must contain at least 16 % of P_2O_5 soluble in neutral ammonium nitrate, of which at least 93 % needs to be water soluble. It is manufactured as follows: phosphate rock is ground very finely and mixed with 65 – 75 % sulphuric acid, giving the following overall reaction:

$$Ca_{10}F_2(PO_4)_6 + 7\ H_2SO_4 + H_2O \rightarrow 3\ Ca(H_2PO_4)_2 \cdot H_2O + 7\ CaSO_4 + 2\ HF$$

Phosphoric acid is formed from the reaction between phosphate rock and H_2SO_4 in the first part of this reaction. An important factor in the production of SSP and triple superphosphate (TSP) is the amount of aluminium (as Al_2O_3), iron (as Fe_2O_3) and magnesium compounds in the phosphate rock; impurities of these elements above 5 % cause the product to be too viscous. Two sources of H_2SO_4 used in SSP production are virgin acid and spent acid. Virgin acid is produced from sulphur dioxide derived from burning elemental sulphur (sulphur-sulphuric acid), pyrite (pyrite-acid) or as a by-product acid from non-ferrous metal smelters processing sulphide ores (fatal acid). Spent acid is recycled from various industries (e.g. non-ferrous metal smelters) that use large quantities of sulphuric acid.

The remaining rock reacts with the phosphoric acid formed as an intermediate to Ca $(H_2PO_4)_2$ in the second part of the reaction. The first part of the reaction is rapid, as is the second part (more than 96 % yield). The reaction can continue for several days as the remaining free acid continues reacting with the excess phosphate rock. This process retains the calcium sulphate ($CaSO_4$) in the product unlike the similar reaction producing phosphoric acid.

Ground phosphate rock and sulphuric acid are mixed in a reaction vessel. The reaction begins in the reactor, and is exothermic, reaching temperatures of 90 – 100 °C. The slurry is fed on to a slow moving conveyor belt or to a holding vessel and held for a period of 10 – 20 minutes. The cured SSP is fed to a clod breaker and afterwards to a granulation line (direct granulation) or to storage (pile). The SSP can be fed to the granulation line (indirect granulation) or sold without further processing from the storage facility.

As well as SSP, partially acidulated phosphate rock (PAPR) can also be produced. PAPR is a mixture of superphosphate ($Ca(H_2PO_4)_2$) and phosphate rock. PAPR contains $Ca(H_2PO_4)_2$ in a form insoluble in water but available to vegetation. This product can be made in an SSP or TSP plant using a lower proportion of H_2SO_4 to phosphate rock.

1.9.1.2 Production of triple superphosphate (TSP)

TSP or concentrated superphosphate, is the most concentrated straight phosphate fertiliser that exists with 44 – 48 % available P_2O_5, of which at least 93 % is water-soluble. Ground phosphate rock is mixed with 50 – 55 % phosphoric acid to produce TSP:

$$10\ CaF_2(PO_4)_6 + 7\ H_3PO_4 + 10\ H_2O \rightarrow 10\ Ca(H_2PO_4)2{\cdot}H_2O + 2\ HF$$

The production is quite similar to the production of single superphosphate (SSP). The slurry is fed on to a slow moving conveyor belt or to a holding vessel and held for a period of 10 - 20 minutes. The cured TSP is then fed to a clod breaker and afterwards to the granulation line (direct granulation) or to storage (pile). The TSP can be fed to the granulation line (indirect granulation) or sold without further processing from the storage facility. From the storage pile, the cured TSP is ground and granulated. Steam, water and acid may be added to help granulation.

Direct granulation after curing has some advantages in comparison to run-of-pile (ROP) granulation; production costs are usually lower and the granules are denser and stronger. Some disadvantages of direct granulation are the need to use reactive phosphate rock and the possibly of greater losses of soluble P_2O_5 due to the incomplete reactions.

1.9.2 Current emissions and consumptions

1.9.2.1 Input

The main energy demand in the production of superphosphates, amounting to 750 MJ/tonne product, is from air heating for the drying process. About 55 kg steam per tonne of product is needed for granulation. The electrical energy demand amounts to 19 kWh/tonne for the powdery product and rises to 34 kWh/tonne product for granulated superphosphate. Specific energy demands for electric energy, steam and fuel are shown in Table 1.52.

Characteristics/Demands	Units	Manufacture of superphosphate	
		Powdery	Granulated
P_2O_5-share in the product	%	18	18
Electric energy	kWh/tonne product	19	34
Process water (for off-gas scrubbers)	m^3/tonne product	0.1	2.0
Steam	kg/tonne product	-	55
Fuel (for heating air)	MJ/tonne product	-	750
Off-gas	Nm^3/tonne product	350	3000

Table 1.52: Process data of the continuous manufacture and granulated superphosphate

Single superphosphate (SSP)

This is produced from 65 - 75 % sulphuric acid and phosphate rock. To increase reactivity, the phosphate rock is ground very finely, which requires energy. The reaction takes place at an elevated temperature of 90 - 100 °C due to the exothermic nature of the process.

The production of granular SSP (via direct granulation) requires 1.4 GJ of energy/tonne of SSP produced, of which 0.4 GJ is needed for the powder production and 1.0 GJ for granulation. The production of one tonne of granular SSP (using 96 % sulphuric acid and phosphate rock containing 33 % P_2O_5) requires 34 kWh of electricity, 55 kg of steam and 180 kcal of fuel. The production of powdered SSP (using 96 % sulphuric acid and phosphate rock containing 33 % P_2O_5) requires less energy, i.e. 19 kWh of electricity. SSP ROP only requires energy for grinding the phosphate rock and the acidulation process.

Triple superphosphate(TSP)

To produce triple superphosphate (TSP), ground phosphate rock is mixed with 50 - 55 % phosphoric acid. Most TSP is produced run-of-pile (ROP); TSP powder is produced in the first step, where the main energy input is for rock grinding. The ROP powder is granulated with steam in the second step. The total energy consumption based on 48 % phosphoric acid is 2.0 GJ/t TSP produced of which 0.7 is used for evaporation, 0.3 for powder production and 1.0 for granulation. A process based on 42 % acid would have a 20 % lower energy consumption, but this would require very soft rock and might experience problems with unreacted rock in the product. The direct granulation of TSP requires less recycle, water and steam, due to the plasticity and heat content of fresh TSP which makes it much easier to granulate than cured TSP. However, direct granulation has disadvantages too. Table 1.53 and Table 1.54 provide information about the energy consumption of both methods.

Inputs	Consumption
Cured TSP	1.02 tonne/t TSP
Steam	75 kg/t TSP
Cooling water	250 kg/t TSP
Fuel	0.67 GJ/t TSP
Electrical energy	29 kWh/t TSP
Operating labour	0.3 workhours
* Based on 52 % phosphoric acid	

Table 1.53: Production of TSP by granulation with intermediate storage (ROP) values

Process data	Value
Phosphoric acid concentration	>50 %
Ratio of recycle	1.0 - 1.25
Steam consumption	50 - 60 kg/t TSP
Water consumption	60 - 65 kg/t TSP
Power consumption*	38 kWh/t TSP
Operating labour	0.25 workhours/t TSP
* Including rock grinding (10 kWh/t TSP)	

Table 1.54: Production of TSP by direct granulation values

1.9.2.2 Output

1.9.2.2.1 Emissions

Off-gas emissions

Off-gas emission sources include from decomposition products, granulation and drying operations. Powdery superphosphate manufacturing gives rise to an off-gas volume of 350 Nm³/tonne product whereas for granulated final product, the off-gas volume is much higher at 3000 Nm³/tonne.

The decomposition reaction gas containing fluoro-compounds and those from the storage, granulation and drying are extracted and abated by an off-gas water scrubber. Gaseous silicon tetrafluoride (SiF_4) reacts with the water to produce hexafluoro silicic acid (H_2SiF_6) and SiO_2 according to the reaction equation:

$$3SiF_4 + 2H_2O \leftrightarrow SiO_2 + 2H_2SiF_6$$

The off-gases from decomposition, granulation and drying are scrubbed and then discharged through a stack to atmosphere. The fluoride and dust concentrations in the total off-gas stream amount to 0.5 - 4 mg fluoride/m³ and 30 - 50 mg dust/m³ (half hour values), respectively.

Quoting specific concentrations per tonne product is difficult, as there are many product changes.

Different salts, such as potassium chloride, are added during granulation and then later released. Average half-hour emission concentrations are 19.1 mg/m^3. This is only true when superphosphates are used to produce PK.

The raw phosphate also contains organic substances, leading to releases of organic carbon, which can give rise to odour emissions. Investigations to reduce odours by biofilter systems have so far been unsuccessful, due to the low pH. [10, InfoMil, 2001]

To prevent emissions to air, especially emissions of HF and SiF_4, many plants use scrubbers. Scrubber water then becomes contaminated with phosphate, calcium oxide, fluoride, various compounds (such as SO_4) and trace elements (such as As, Cd, Hg and heavy metals).

Part of the SiF_4 reacts with HF and with water according to the following reactions:

$$SiF_4 + 2HF\ (aq) \rightarrow H_2SiF_6\ (aq)$$
$$3SiF_4\ (g) + 2H_2O \rightarrow 2H_2SiF_6 + SiO_2$$
$$3SiF_4\ (g) + 4H_2O \rightarrow 2H_2SiF_6 + SiO_2.2H_2O\ (aq)$$

Due to the presence of water, these reactions especially take place in the scrubber. The fluorosilicic acid (H_2SiF_6) can be recovered and used as scrubber liquid or sold. Fluorosilicic acid is processed to synthetic cryolite, aluminium fluoride and various fluorsilicates. None of the Dutch sites recover H_2SiF_6.

Also other contaminants from the phosphate ores end up in the scrubber water. Variations in the rock composition have only a limited effect on the overall emissions of the fertiliser plant. End-of-pipe technology is often necessary to reduce emissions to acceptable values.

1.9.2.2.2 Releases to water

The main emission source in the production of single and triple superphosphate is the scrubbing liquor arising from waste gas scrubbing. Scrubbing liquor is contaminated with phosphates, fluorine compounds (in particular H_2SiF_6), sulphates, heavy metals, such as Cd and Hg, and As.

In particular the discharge of highly toxic fluosilicic acid, which arises in considerable amounts, is a major environmental issue of the phosphate fertiliser manufacture. This waste water arising from the off-gas scrubber is discharged after treatment directly to an outfall.
[10, infoMil, 2001]

2 TECHNIQUES TO CONSIDER IN THE DETERMINATION OF BAT

This chapter describes in detail the techniques that are considered to be most relevant for determining BAT. This chapter should be seen as the main background information for the determination of best available techniques in the LVIC-AAF sector (Chapter 3). Techniques that are generally seen as obsolescent are not included. Moreover, it does not include all the techniques applied in the LVIC-AAF sector and described in Chapter 1. Only techniques with good environmental performance are included here.

Production, prevention, control, minimisation and re-cycling procedures/techniques are considered in this chapter. This can be done in many ways, such as using production techniques that pollute less than others, changing the operating conditions, reducing material inputs, re-engineering processes to re-use by-products, improving management practices or employing the substitution of toxic chemicals. This chapter provides information on some both general and specific pollution prevention and control advances that have been implemented within industry in general and in the LVIC-AAF industry in particular.

As in previous chapters, each section of this chapter deals with a LVIC-AAF process or activity and contains the process and abatement techniques to be considered in the determination of BAT. If different techniques may be applicable for a particular process/activity, they are discussed in some section. Sections from this chapter have been structured internally in the same way. Each of those sections contain first the pollution prevention techniques applicable in the process/activity section referred to and secondly the end-of-pipe techniques that may be applicable to reduce the emissions coming from the process/activity. Those end-of-pipe techniques are grouped in media/pollutant bases to clarify the sequence of techniques applicable as, in some cases, the number of EOP techniques that may be used is quite extensive.

Each technique (both preventive (including process techniques) and control) is well documented and includes information on the consumption and emission levels considered achievable by using the technique, some idea of the costs and the cross-media issues associated with the technique and the extent to which the technique is applicable to the range of installations requiring IPPC permits, for example new, existing, large or small installations. Each technique in this chapter is analysed in the same way in order to give a good background for the determination of BAT for LVIC-AAF. That determination is done in the next chapter.

When possible, this chapter provides information from real activities that can be, or are being, implemented by this sector, including the associated costs. When possible, information provided gives the context in which the technique can be used effectively.

2.1 Ammonia

2.1.1 Screening of available techniques

Table 2.1 shows an overview of the identified techniques for the steam reforming ammonia production route. Most of the identified techniques do not apply only to single process units but are integrated into the whole plant. Similarly, the identified emission sources and the achieved input-output levels depend on the synergy of many of the identified techniques. In this context and mainly because of the difficulty to single-out the environmental performance data of isolated techniques, consideration has been given to "whole plant" concepts which contain the identified single techniques in several possible combinations and arrays.

The first two columns of Table 2.1, refer to the single techniques and to their application areas. The third column aggregates the single techniques into process families, the so-called "whole plant" concepts that produce the same product but follow intrinsically different production routes. The achieved environmental benefits are presented in the fourth column.

The identification of available techniques for the partial oxidation production route are presented in Table 2.2.

Identified single techniques	Main application area (in brackets the main benefits)	Technique considerd under “whole-plant concepts”	Achieved environmental benefits
• Ammonia removal from purge and flash gases (see 2.3.2.1) • Low-NO_X burners (see 2.1.3.2.5) • Stripping process condensates and recycling to boiler feed-water (see 2.1.3.2.8) • CO_2-removal systems with improved solvents (see 2.1.3.2.11) • Indirect cooling of ammonia synthesis reactor (see 2.1.3.2.13) • Use of smaller catalyst particles (see 2.1.3.2.14) • Non-iron based ammonia synthesis catalysts (see 2.1.3.2.17) • Hydrogen recovery from purge gas (see 2.1.3.2.23) • Preheating of combustion air (see 2.1.3.2.21) • Metal recovery and controlled disposal of spent catalysts (see 2.1.3.2.9)	Synthesis gas section (NO_X emission reduction) Primary reformer (NO_X emission reduction) Condensates from shift converter (reduction of NH_3 discharge) CO_2 removal unit (energy eff. improvement) Synthesis section (energy eff. improvement) Synthesis section (energy eff. improvement) Synthesis section (energy eff. improvement) Synthesis section (energy eff. improvement) Synthesis section (energy eff. improvement) Handling of solid wastes (reduction of waste disposal by recycling)	Advanced conventional process(es)	These processes are characterised by a lower energy consumption and lower NO_X emissions. The liquid wastes are virtually eliminated by scrubbing – recycling
• Transferring duty from primary to secondary reformer using excess air (see 2.1.3.2.3) • Prereformer (see 2.1.3.2.2) • Low-NO_X burners (see 2.1.3.2.5) • Ammonia removal from purge and flash gases (see 2.1.3.2.1) • Supplying process steam by feed gas saturation (see 2.1.3.2.15) • Stripping process condensates and recycling to boiler feed-water (see 2.1.3.2.8) • Preheating of combustion air (see 2.1.3.2.21) • CO_2-removal systems with improved solvents (see 2.1.3.2.11) • Indirect cooling of ammonia synthesis reactor • (see 2.1.3.2.13) • Use of co-promoted Iron catalyst for ammonia synthesis (see 2.1.3.2.20)	Primary and secondary reformer (NO, emission reduction) Reforming (energy eff. improvement and NO_X reduction) Primary reformer (NO_X emission reduction) Synthesis gas section (NO_X emission reduction) Primary reformer (energy eff. Improvement) Condensates from shift converter (NH_3 emission reduction) Primary reformer (energy eff. improvement) CO_2 removal unit (energy eff. improvement) Synthesis section (energy eff. improvement) Synthesis section (energy eff. improvement)	Process(es) with reduced primary reformer	Lower NOx emissions demonstrated. The liquid wastes are virtually eliminated through scrubbing recycling

• Non-iron based ammonia synthesis catalysts (see 2.1.3.2.17) • Hydrogen recovery from purge gas (see 2.1.3.2.23) • Use of gas turbine to drive the process air compressor (see 2.1.3.2.22) • Metal recovery and controlled disposal of spent catalysts (see 2.1.3.2.9)	Synthesis section (energy eff. improvement) Synthesis section (energy eff. improvement) Total plant (energy eff. improvement) Handling of solid wastes (reduction of waste disposal by recycling)		
• Exchanger reformer (see 2.1.3.2.4) • Ammonia removal from purge and flash gases (see 2.1.3.2.1) • Supplying process steam by feed gas saturation (see 2.1.3.2.15) • Low-temperature desulphurisation (see 2.1.3.2.10) • Isothermal shift conversion (see 2.1.3.2.16) • CO_2 -removal systems with solid adsorbents (see 2.1.3.2.12) • Use of co-promoted iron catalyst for ammonia synthesis (see 2.1.3.2.20) • Non-iron based ammonia synthesis catalysts (see 2.1.3.2.17) • Hydrogen recovery from purge gas (see 2.1.3.2.23) • Metal recovery and controlled disposal of spent catalysts (see 2.1.3.2.9) • Combination of heat exchange reforming with autothermal reaction in one vessel (see 2.1.3.2.6)	Primary and secondary reformer (NO, emission reduction) Synthesis gas section (NO_X emission reduction) Primary reformer (energy eff. improvement) Desulphurisation unit (energy eff. improvement) Shift Conversion of synthesis gas (energy eff. improvement) CO_2 removal unit (energy eff. improvement) Synthesis section (energy eff. improvement) Synthesis section (energy eff. improvement) Synthesis section (energy off. Improvement) Handling of solid wastes (reduction of waste disposal by recycling) Reforming section (NO_X emission reduction)	Process(es) with heat exchange reformer.	Lower NO_X emission levels is achieved by eliminating the primary reformer. Energy consumption may increase The liquid wastes are reduced by recycling. Start-up times are reduced.
"Whole plant concepts" correspond to the "system boundaries" of the specific techniques			

Table 2.1: Results of the screening of available techniques for steam reforming ammonia production plants

Identified single measures	Main application area (in brackets the main benefits)	Technique considered under“whole-plant concepts”	Achieved environmental benefit
• Claus unit (see 2.1.3.2.7)	Sulphur removal (emission reduction into the air, saving of raw materials)	Partial Oxidation of heavy hydrocarbons	Lower NO emissions are achieved
• Ammonia removal from purge and flash gases (see 4.1.3.2.1)	Synthesis gas section (NO_X emission reduction)		
• Low- NO_X burners (see 2.1.3.2.5)	Auxiliary boiler (NO_X emission reduction)		
• Stripping process condensates and recycling to boiler feed-water (see 2.1.3.2.8)	Condensates from shift converter ((NO_X emission reduction)		
• Use of sulphur resistant catalyst for shift reaction of synthesis gas from partial oxidation (see 2.1.3.2.8)	Shift conversion of synthesis gas (energy eff. improvement)		
• CO_2 removal system with solid adsorbent (see 2.1.3.2.12)	CO_2 removal unit (energy eff. improvement)		
• Indirect cooling of ammonia synthesis reactor (see 2.3.1.2.13)	Synthesis section (energy eff. improvement)		
• Non-iron based catalysts for the ammonia synthesis (see 2.1.3.2.17)	Synthesis section (energy eff. improvement)		
• Use of smaller catalyst particles in ammonia converters (see 2.1.3.2.14)	Synthesis section (energy eff. improvement)		
• Use of co-promoted ammonia synthesis gas catalsyts (see 2.1.3.2.20)	Synthesis section (energy eff. improvement)		
• Liquid N., wash (see 2.1.3.2.19)	Final synthesis gas purification (energy eff improvement)		
• Metal recovery and controlled disposal of spent catalysts (see 2.1.3.2.9)	Handling of solid wastes (reduction of waste disposal by recycling		

Table 2.2: Results of the screening of available techniques for ammonia partial oxidation plants (feedstock: heavy hydrocarbons)

2.1.2 Environmental performance of various techniques

2.1.2.1 Steam reforming

For the steam reforming process the following "whole-plant" concepts are identified as available techniques

1. advanced conventional processes
2. processes with reduced primary reforming
3. processes with heat exchange primary reforming

2.1.2.1.1 Advanced conventional processes

The different process steps described in Chapter 2 for the conventional steam reforming process are integrated together with respect to mass and energy flow. During the years of development a considerable reduction in energy consumption has been achieved by improving the existing components in the process. In addition, today's equipment and machinery can achieve a considerable thermodynamic efficiency and a high degree of reliability. Online availability exceeding 93 % is not uncommon in such plants.

Description
Advanced conventional process plants are usually characterised by the following features: high duty primary reformer using high pressures of up to 40 bar equipped with low-NO_X burners, stoichiometric air in secondary reforming (stoichiometric H/N ratio), and a low energy CO_2 removal system.
Differences in the configurations offered by the various engineering contractors generally result from the optimised arrangements that they utilise and from using different well developed equipment designs. Specific examples of some applied techniques are:

- increasing the temperatures of the mixed feed and process air in line with the current limits for metallurgical standards for construction. This in turn allows for a reduced reformer firing and an increase in the reformer operating pressure, which also saves in the energy needed for compression of the synthesis gas
- utilising the recovered heat after the secondary reformer to raise steam and for the superheat
- applying improved designs of high temperature shift reactors for lower steam to carbon ratio
- utilising ammonia converter designs which use small size catalysts for higher conversions
- ensuring the efficient recovery of a large proportion of reaction heat energy from the ammonia synthesis. This is achieved by extracting the heat in the ammonia synthesis and using it to raise high-pressure steam
- applying a high efficient ammonia condensation and refrigeration system.

The high levels of NO_X emissions of the conventional process are mainly due to the particular firing conditions in the primary reformer. The use of low NO_X burner techniques minimises the level, but relatively high NO_X emissions still remain. These techniques are generally applicable in new and existing plants. The currently known achieved input-output levels using the advanced conventional concept are shown Table 2.3.

2.1.2.1.2 Processes with reduced primary reforming

Designs using a reduced primary reforming process are characterised by the shifting of a proportion of the reforming duty to the secondary reformer or to a prereformer. In this way the modified reformer design requires less firing at lower temperatures compared to the conventional process. The main advantage of this procedure is the reduced NO_X formation and the lower flue-gas flowrates. At the same time the total energy consumption, as well as emissions to water and land, can be limited to the lowest achievable levels.

Description
Reducing primary reforming by shifting a part of the conversion to the secondary reformer
The main characteristics of this concept are the following:

- transferrance of the reforming duty to the secondary reformer, and as a aconsequence a reduction in the firing in the primary reformer
- greater reforming duty carried out in the secondary reformer using excess air
- remove the surplus nitrogen, introduced by excess air, by cryogenic final purification. The cryogenic separation may lead to a lower inert gas level in the synthesis gas.

The excess process air used in the secondary reformer can be up to 50 % or greater than that used in conventional concepts. Lower temperatures in the primary reformer also allow a lower steam to carbon ratio i.e. 2.8 and lower. An alternative is to feed a portion of the feed gas directly to the secondary reformer as opposed to feeding the whole amount to the primary reformer.

Using a Prereformer
Pre-reforming proceeds in an adiabatically operated catalytic reactor, prior to the primary reformer. The gas cools down as a result of the endothermic reaction(see Chapter 1.1.1) and so has to be reheated before feeding into the primary reformer utilising medium grade excess process heat. The primary reforming duty is decreased which leads to less firing, less NO_X emissions and a lower S/C ratio. This in turn allows further steam savings to be made elsewhere in the process.

Further measures that can contribute to NO_X reduction are the use of low-NO_X burners and removal of the ammonia that would be normally be recycled to the reformer along with purge or flash gases from the synthesis section. These techniques are available for both new and existing plants. The currently known achieved input-output levels for the reduced primary reforming route are shown in Table 2.4.

Input-output parameters	Achieved values	Reference to applied techniques with major contribution to the demonstrated input-output levels
NO_X emissions to air (primary reformer)	157 mg/Nm^3 320 g/t NH_3	Ammonia removal from purge and flash gases in the ammonia synthesis section (see 2.1.3.2.1). Low-NO_X burners (see 2.1.3.2.5)
NH_3 emissions to water	28 g/tonne NH_3	Stripping of process condensates and recycling to boiler feed-water (see 2.1.3.2.8)
Emissions to land		Metal recovery and controlled disposal of spent catalysts by specialised companies (see 2.1.3.2.9)
Net energy consumption (LHV)	29.2 GJ/tonne NH_3	CO_2 removal systems with improved solvents (AMDEA) (see 2.1.3.2.1). Indirect cooling of ammonia synthesis reactor (see 2.1.3.2.13). Use of smaller catalyst particles in ammonia converters (see 2.1.3.2.14). Preheat of combustion air (see 2.1.3.2.21). Hydrogen recovery from the purge gas of the ammonia (see 2.1.3.2.23).

Table 2.3: Achieved input-output levels using the advanced conventional ammonia process [13, EC, 1997]

Achieved environmental benefits

Installing the advanced conventional process configuration leads to higher NO_X emissions than other concepts. However, the total energy consumption and releases to water and land are minimised.

Input-output parameters	Values achieved	Reference to applied techniques with major contribution to the demonstrated input-output levels
NO_X emissions to air (primary reformer)	90 mg/Nm^3 270 g/tonne NH_3 [1]	Low-NO_X burner (see 2.1.3.2.5) Ammonia removal from purge and flash gases in the ammonia synthesis section (see 2.1.3.2.1) Shifting reformer duty from primary reformer to secondary reformer by use of excess process air (see 2.1.3.2.3)
Emissions to water	negligible emissions	Stripping of process condensate and recycling to boiler feed-water (see 2.1.3.2.8)
Emissions to land		Metal recovery and controlled disposal of spent catalysts by specialised contractors (see 2.1.3.2.9)
Net energy consumption (LHV)	28.9 GJ/tonne	Indirect cooling of ammonia synthesis reactor (see 2.1.3.2.13) Use of gas turbine to drive the process air compressor (see 2.1.3.2.22) CO_2 removal systems with improved solvents (AMDEA) (see 2.1.3.2.1) Shifting reformer duty from primary reformer to secondary reformer by use of excess process air (see 2.1.3.2.3)

[1] According to this technique NO_X emission levels in the range of 300 g/tonne are achieved only if air preheat is carried out with waste gas from a gas turbine where low O_2 and high CO_2-concentrations exist. If considerable air preheat is applied and no gas turbine waste gases can be used, the NO_X emission is in the range of 130 mg/Nm^3 or 390 g/tonne NH_3.

Table 2.4: Achieved input-output levels by using reduced primary reforming ammonia production design
[13, EC, 1997]

Installing the reduced primary reformer concept results in relatively low NO_X emissions compared to the conventional ammonia process. Energy consumption and releases to water and land are minimised.

2.1.2.1.3 Processes with heat-exchange primary reforming

This process route simplifies ammonia production by introducing new process steps which replace the fired steam reformer. The number of purification steps is also reduced.

The key consequence of the elimination of the reformer firing is that no firing at all takes place at typical reformer conditions. In this way, reformer flue-gas is eliminated totally. Flue-gases containing NO_X are generated only in the preheater and boiler. The overall NO_X load is reduced in comparison to other processes. The total energy consumption of the plant is relatively higher than the levels currently achieved by other ammonia production concepts. Another important aspect that needs special consideration is the fact that relatively small capacities, i.e. in the range of 400 t/d, can be constructed and operated with favourable input-output levels, compared to the reference data. According to [32, EFMA, 2000] the capacity limits are presently 1000 t/d. Recent information shows that this concept can be used up to a capacity of 1800 t/d with a single line exchanger reformer. Two plants of this size are presently under construction.

Description
The achieved input-output levels, summarised in Table 2.5, are based on the operation of 450 t/d plants.

Heat for the reform reaction is supplied to the reforming tubes by hot process gas from the secondary reformer. In a heat-exchange primary reformer, excess air has to be supplied to the secondary reformer to ensure a heat balance between these two steps, and this results in an overstoichiometric amount of nitrogen in the gas. The high temperature shift reactor and the low temperature shift reactor are, in this technique also replaced by a single isothermal medium temperature shift reactor using heat from the shift conversion for the saturation of process gas with steam and recycling process condensates. A 'Pressure Swing Adsorption' (PSA) system is used to remove carbon dioxide and residual carbon monoxide and methane, to produce a purified synthesis gas. A cryogenic purification system may need to be incorporated in the process to remove the surplus nitrogen. A modified synthesis converter using an improved catalyst with a total resulting in a lower overall synthesis pressure further simplifies the process.

Other configurations of the heat-exchange primary reformer concept use alternative steps for the shift reaction and syngas purification and ammonia synthesis compared to the above. In one of these alternatives, only one third of the feed passes through the exchanger reformer with the residual amount being sent directly to the secondary (autothermal) reformer, which uses enriched air (30 % O_2) instead of excess air. The ammonia synthesis uses the new ruthenium based catalyst.

This concept allows the building of a plant which can be started up quickly, and which gives emissions much lower than from comparable conventional concepts.

Input-output parameters	**Achieved values**	**Reference to applied techniques with major contribution to the demonstrated input-output levels**
NO_X emissions to air	Process air heater: 80 mg/Nm^3 Aux. boiler: 20 mg/Nm^3 175 g/tonne NH_3 (total, including equivalent from el. import)	Heat exchange reforming (see 2.1.3.2.4) Ammonia removal from purge and flash gases in the ammonia synthesis section (see 2.3.2.1)
NH_3 emissions to water	80 g/tonne NH_3	Supplying process steam by feed gas saturation with process condensates (see 2.1.3.2.15)
Emissions to land		Metal recovery and controlled disposal of spent catalysts by specialised contractors (see 2.1.3.2.9)
Net energy consumption (LHV)	31.8 GJ/tonne	Low-temperature desulphurisation (see 2.1.2.3.10) Isothermal shift conversion (see 2.1.3.2.16) Use of co-promoted ammonia synthesis gas catalyst (see 2.1.3.2.20) CO_2 removal systems with solid adsorbents (see 2.1.3.2.12) Supplying process steam by feed gas saturation with process condensates (see 2.1.3.2.15)

Table 2.5: Achieved input-output using the heat exchange primary reformer ammonia production concept
[13, EC, 1997]

Achieved environmental benefits
Installation of the exchanger reformer concept results in the lowest achievable NO_X emissions. Energy consumption is more than other processes. The preferred capacities of about 450 - 1000 t/d could lead to potential safety improvements as the need for ammonia storage capacity could then be reduced. This does not mean however that ammonia storage will always be reduced overall, as the actual storage capacity depends on overall site requirements. Another benefit is the lower ammonia inventory for the plant.

2.1.3 Partial oxidation

The partial oxidation of heavy hydrocarbons is the only partial oxidation "whole plant" concept presently applied in Europe for the ammonia production.

2.1.3.1 Partial oxidation of heavy hydrocarbons

Partial oxidation for ammonia production is the preferred process route when heavy hydrocarbons are the selected feedstocks. This is because heavy hydrocarbons cannot be converted to synthesis gas by catalytic steam reforming, as they cannot be easily vaporised, they contain high amounts of sulphur which could be poisonous for a catalyst and as they tend to decompose at high temperatures, thus blocking catalyst pores and reformer tubes. Synthesis gas is produced by converting heavy hydrocarbons by partial oxidation with oxygen or air enriched with oxygen (instead of steam).

Description
This process is called partial oxidation because the amount of oxygen present is insufficient to anable the total combustion of the feedstock to CO_2. The result is raw synthesis gas that contains a high degree of CO and carbon dust from the heavy hydrocarbons. Carbon dust and some slag that is formed, need to be removed by water scrubbing, recovered and then be recycled to the process.

In several commercial processes the reaction is carried out in a reactor chamber lined with high heat resistance bricks, with oil and oxygen being fed into the chamber by nozzles. A small amount of steam is usually added to moderate the combustion reaction and to atomise the hydrocarbons. The gasification can operate at a pressure of up to 75 bar. The hot reaction gas, which is at about 1200 - 1400 °C, is cooled either in a waste heat boiler generating steam or by direct water quench. First soot is removed and recycled and then the CO in the gas needs to be converted stepwise with intermediate cooling to hydrogen. Either standard HTS catalysts or sulphur tolerant shift catalyst are used, depending on the process configuration. A scrubbing process is used for CO_2 removal that can produce a product which is rich in H_2S and another which gives sulphur free CO_2, usually by chilled methanol scrubbing. Normally a liquid nitrogen wash is applied for the final purification, this removes residual CO and $CH_{4,}$ resulting in a practically inert free synthesis gas, which saves energy removing the process need to purge the gas loop. An air separation plant is needed to supply oxygen for gasification and nitrogen for the synthesis fed after or in the liquid nitrogen wash. The synthesis section may use standard ammonia converter designs.

Input-output parameters	Achieved values	Reference to applied techniques with major contribution to the demonstrated Input-output levels
Emissions to Air Auxiliary boiler:	NO_X: 560 mg/Nm^3, 1040 g/tonne NH_3 SO_2:1060 mg/Nm^3, 1980 g/tonne NH_3 Particulates: 4 mg/Nm^3, 8 g/tonne NH_3 CO: 8 mg/Nm^3, 16 g/tonne NH_3 Hydrocarbons: 9 mg/Nm^3, 17 g/tonne NH_3	Low-NO_X burners (see 2.1.3.2.5)
Superheater:	NO_X: 185 mg/Nm^3, 410 g/tonne NH_3 CO: 7 mg/Nm^3, 16 g/tonne NH_3 H_2S: 0.03 mg/Nm^3, 1 g/tonne NH_3 Methanol: 94 mg/Nm^3, 210 g/tonne NH_3	Low-NO_X burners (see 2.1.3.2.5)
Thermal post-combustion:	NO_X: 350 mg/Nm^3, 56 g/tonne NH_3 SO_2:1340 mg/Nm^3, 2180 g/tonne NH_3 Particulates: 4 mg/Nm^3, 8 g/tonne NH_3 CO: 5 mg/Nm^3, 1 g/tonne NH_3 Hydrocarbons: 9 mg/Nm^3, 1 g/tonne NH_3	Claus unit (see 2.1.3.2.7)
Emissions to water	130 g NH_3/tonne NH_3	
Emissions to land	Waste water treatment sludge: 4.4 kg/tonne NH_3 Spent catalysts	Controlled disposal Metal recovery and controlled disposal of spent catalysts by specialised companies (see 2.1.3.2.9)
Net energy consumption (LHV)	38.7 GJ/tonne NH_3	Use of sulphur resistant catalyst for shift reaction of synthesis gas from partial oxidation (see 2.1.3.2.18) Liquid nitrogen wash for final purification of synthesis gas from N (see 2.1.2.3.19)
Materials	Production of sulphur: 26 kg/tonne NH_3 Argon: 32 kg/tonne NH_3 (as by-products)	Claus unit (see 2.1.3.2.7) Liquid nitrogen wash for final purification of synthesis gas from partial oxidation (see 2.1.2.3.19)

Table 2.6: Achieved input-output levels by the partial oxidation of heavy hydrocarbons for ammonia production
[13, EC, 1997]

Achieved environmental benefits

The partial oxidation of heavy hydrocarbons has the advantage of making effective use of a variety of feedstocks that would otherwise be wastes and would pollute the environment. Extremely viscous hydrocarbons and plastic wastes may also be used as fractions for the feed. This route of producing ammonia offers an alternative for the future utilisation of such wastes on a larger scale.

Partial oxidation leads to significant SO_2 emissions into the air and substantially higher emissions of NO_X compared to the steam reforming process. On the other hand, it saves raw materials by recovering elemental sulphur.

The energy consumption is considerably higher compared to steam reforming.

2.1.3.2 Technical information of specific techniques

The following list indicates the techniques described in this section and applicable for:

1. ammonia removal from purge and flash gases in the ammonia synthesis section
2. prereformer
3. shifting the reformer duty from the primary reformer to the secondary reformer by the use of excess process air
4. heat exchange reforming
5. low-NO_X burners
6. combination of heat exchange reforming with autothermal reaction in one vessel
7. claus unit
8. stripping of process condensate and the recycling of it as boiler feed-water
9. metal recovery and controlled disposal of spent catalysts by specialised companies
10. low-temperature desulphurisation
11. CO_2 removal systems with improved solvents
12. CO_2 removal systems with solid adsorbents
13. indirect cooling of ammonia synthesis reactor
14. use of smaller catalyst particles in ammonia converters
15. supplying process steam by feed gas saturation with process condensates
16. isothermal shift conversion
17. non-iron based catalyst for ammonia synthesis
18. use of sulphur resistant catalyst for shift reaction of synthesis gas from partial oxidation
19. liquid nitrogen wash for final purification of the synthesis gas from partial oxidation
20. use of cobalt-promoted ammonia synthesis gas catalyst
21. preheat of combustion air
22. use of gas turbine to drive the process air compressor
23. hydrogen recovery from the ammonia synthesis purge gas.

2.1.3.2.1 Ammonia removal from purge and flash gases in the ammonia synthesis section

Description

Recovering ammonia from purge and vent gases reduces NO_X emissions. Purge and vent gases are usually burnt in the reforming section. Ammonia present in these gases significantly increases NO_X formation.

An integrated technique primarily applicable in new and existing conventional steam reforming plants. Ammonia is removed from purge and flash gases by water scrubbing. Compression of low pressure flash gases is achieved by a mechanical compressor or by an ejector, and is carried out in order to feed them to a water scrubbing system.

Achieved environmental benefits

See Table 2.3, Table 2.4, Table 2.5.

Cross-media effects

To avoid aquatic pollution the recovered NH_3 solution can be recycled either in other process sections or it can be distilled to recover pure NH_3.

Operational data

Applicability

Economics

Driving force for implementation

Example plants

Reference literature
[13, EC, 1997]

2.1.3.2.2 Prereformer

Description
A prereformer installed prior to the primary reformer reduces NO_X emissions and energy consumption. Integrated technique applicable in new and existing conventional steam reforming plants. Pre-reforming takes place through an adiabatically operated catalyst bed, before the primary reformer. The cooled gas needs to be reheated before it is passed to the primary reformer. Low and medium grade process heat can be used to reheat the gas. The primary reforming duty is reduced as less firing and hence is needed (less NO_X emissions), allowing at the same time a lower S/C ratio (energy saving) to be achieved.

Achieved environmental benefits
As less firing is needed in the primary reformer, with up to 5 – 10 % heat load reduction, emissions to the air are reduced.

Cross-media effects
Combined improvements in NO_X reduction and the usage of surplus steam from an adjacent source leads to an overall cost saving.

Operational data

Applicability

Economics

Driving force for implementation

Example plants

Reference literature
[13, EC, 1997]

2.1.3.2.3 Use of excess process air to shift the primary reformer duty to secondary reformer

Description
Integrated technique applicable to conventional steam reforming plants and to concepts with reduced primary reforming duty. Transferring some of the duty to the secondary reformer reduces the primary reforming duty. This results in less firing and lowers NO_X formation, although the methane concentration in the reacted gas leads to higher methane emissions. Overall the heat supply to the primary reformer can be reduced and the process outlet temperature can be lowered to about 700 °C. This increases the firing efficiency and reduces the size and cost of the primary reformer furnace. The less onerous operating conditions allow catalyst and reactor tubes to last longer.

Achieved environmental benefits
See Table 2.3, Table 2.4.

Cross-media effects
Combined energy saving and reduction of flue-gas generation from fired primary reformer.

Operational data

Applicability

Economics

Driving force for implementation

Example plants

Reference literature
[13, EC, 1997]

2.1.3.2.4 Heat-exchange reforming

Description
An integrated technique in steam reforming plants eliminates firing and flue-gas generation in the primary reformer. It is also proposed as a revamp for existing plants. It is wasteful to generate steam using the high-level heat of the secondary reformer outlet gas and the primary reformer flue-gas from a thermodynamic point of view, both at temperatures around 1000 °C. Recent developments allow this heat to be used in the primary reformer instead of firing it. This eliminates the fired furnace and its emissions. Surplus air or oxygen enriched air is needed in the secondary reformer to meet the heat balance. NO_X emissions are generated only through auxiliary combustion in the plant and amount to less than 50 % of the emissions of the conventional design. So far only 3 installations of small capacity (about 500 tonne per day each) have been built and operated: two in the UK, one in the US Capacities of about 1000 t/d seem to be feasible for single stream units.

Achieved environmental benefits
See Table 2.5. The energy use and emissions during start-up are reduced due to the shorter start-up period. Fuel use is typically 2 x 10^3 GJ per start-up for this kind of plant (conventional plants use 12 x 10^3 GJ).

Cross-media effects
No cross-media effects are known.

Operational data

Applicability

Economics

Driving force for implementation

Example plants

Reference literature
[13, EC, 1997]

2.1.3.2.5 Low-NO_X burners

Description
NO_X emissions are reduced in the flue-gases from the fired primary reformers and auxiliary boilers by modification of the combustion section. Integrated technique applicable to new and existing steam reforming and partial oxidation plants. The peak flame temperature, the availability of oxygen and the residence time in the combustion zone, all influence the

formation of NO_X. Low-NO_X burners reduce the formation of NO_X by controlling these factors through the staged addition of combustion air and/or fuel gas, they may also include partial flue-gas recirculation.

Achieved environmental benefits
See Table 2.3, Table 2.4.

Cross-media effects
No cross-media effects are known.

Operational data

Applicability

Economics

Driving force for implementation

Example plants

Reference literature
[13, EC, 1997]

2.1.3.2.6 Combination of heat-exchange reforming with autothermal reaction in one vessel

Description
NO_X emissions are reduced by substituting a fired primary reformer with a combination of exchange reforming and partial oxidation in a single vessel. An integrated technique applicable in new and existing steam reforming plants involves a combination of heat exchange reforming and partial oxidation in a single vessel. A steam-feed-gas mixture is passed through catalyst filled tubes of the heat-exchange reforming part. These tubes are heated externally by the hot reformed gas returning from the partial oxidation section below the tubes, using oxygen and/or air.

Achieved environmental benefits
Information not available although it is thought that the NO_X reduction is similar to that from using the heat exchange primary reformer concept.

Cross-media effects
No cross-media effects are known.

Operational data

Applicability

Economics

Driving force for implementation

Example plants

Reference literature
[13, EC, 1997]

2.1.3.2.7 Claus unit

Description
This technique is applicable to new and existing partial oxidation plants. In a Claus plant, a part of the H_2S is burnt to SO_2 which then reacts with the remaining H_2S on a catalyst to yield elemental sulphur condensed from the gas phase. Claus processes in various concepts are state-of-the-art for sulphur recovery from H_2S containing streams. Thermal post-combustion techniques are used to treat tail gases.

Achieved environmental benefits
See Table 2.6.

Cross-media effects
Recovers sulphur.

Operational data

Applicability

Economics

Driving force for implementation

Example plants

Reference literature
[13, EC, 1997]

2.1.3.2.8 Stripping of process condensate and the recycling of it as boiler feed-water

Description
This technique is applicable to new and existing steam reforming and partial oxidation plants. The condensation of the steam surplus in the gas downstream of the shift conversion forms process condensate. This condensate contains NH_3 and CH_3OH as contaminants, which can be removed by stripping with process steam and then recycled to the primary reformer. The stripped condensate, which may still contain minor amounts of impurities, can be recycled to the boiler feed-water after further cleaning by an ion exchange.

Achieved environmental benefits
Eliminates emissions to water completely. See Table 2.4.

Cross-media effects
No cross-media effects are known.

Operational data

Applicability

Economics

Driving force for implementation

Example plants

Economics
EUR 2.9 - 3.3 million for retrofit in existing plants with a capacity of 1500 t/d [2, EFMA, 2000].

Reference literature
[13, EC, 1997]

2.1.3.2.9 Metal recovery and controlled disposal of spent catalysts by specialised companies

Description
This management concept is applicable to all ammonia plants. Several companies currently offer services for the correct handling of catalysts when unloading spent catalysts, with a subsequent transport to environmentally safe deposition sites or to metal recovering facilities.

Achieved environmental benefits
See Table 2.3, Table 2.4, Table 2.6.

Cross-media effects
Allows the recovery and re-use of materials.

Operational data

Applicability

Economics

Driving force for implementation

Example plants

Reference literature
[13, EC, 1997]

2.1.3.2.10 Low-temperature desulphurisation

Description
An integrated technique applicable in the desulphurisation section of existing and new plants (all steam reforming plant concepts). In standard desulphurisation units, the energy required for heating the feed gas originates from the fired reformer flue-gas. However, in concepts using an exchanger reformer heated by the effluent of the secondary reformer an independent energy source is needed to preheat the feed gas, which may be a gas fired heater with additional NO_X emissions. Using desulphurisation catalysts with a lower operation temperature can utilise the low temperature steam to heat the feed gas, then needing instead of direct firing. In this way NO_X emissions from the desulphurisation unit are avoided.

Achieved environmental benefits
See Table 2.5.

Cross-media effects
No cross-media effects are known.

Operational data

Applicability

Economics

Driving force for implementation

Example plants

Reference literature
[13, EC, 1997]

2.1.3.2.11 CO_2 removal systems using improved solvents

Description
This integrated technique applies to all new and existing steam reforming ammonia plants. The CO_2 formed in the gasification and in the shift conversion is normally removed by scrubbing with a solvent. In the processes, mechanical energy is needed to circulate the solvent and in most cases heat is needed to regenerate the solution. In this way almost pure CO_2 is recovered which is typically vented, although it could be used in other processes, e.g. urea production. CO_2 removal systems using improved solvents, e.g. MDEA, consume substantially less energy than other systems. The energy consumption of a CO_2 removal system also depends on the way it is incorporated in the ammonia plant, and is affected by the syngas purity and CO_2 recovery.

A simple, relatively inexpensive technique to improve the energy consumption of 'Hot Potassium Carbonate CO_2' removal systems is the addition of special catalysts such as Flexsorb, ACT-1 and LRS-10.

Achieved environmental benefits
Energy saving of 30 - 60 MJ/kmol CO_2 is possible. See Table 2.3, Table 2.4.

Cross-media effects
No cross-media effects are known.

Operational data

Applicability

Economics

Driving force for implementation

Example plants

Reference literature
[13, EC, 1997]

2.1.3.2.12 CO_2 removal systems using solid adsorbents

Description
This integrated technique is applicable to new steam reforming plant concepts. A PSA system can be used in an ammonia plant to replace CO_2 removal and methanisation and to simplify the shift conversion from a two step to a one step configuration. The process can be applied in plants which have no secondary reformer, as well as in plants with an exchanger/autothermal reformer system. When applied to a plant with no secondary reformer, nitrogen from an air separation unit is needed to supply the stoichiometric requirements for the synthesis. Pure CO_2 can be recovered by adding a conventional CO_2 removal system using solvents from the fraction containing impurities from the PSA unit. Residual CH_4 and CO from the remaining gas fraction are used as a fuel.

Achieved environmental benefits
See Table 2.5.

Cross-media effects
No cross-media effects are known.

Operational data

Applicability

Economics

Driving force for implementation

Example plants

Reference literature
[13, EC, 1997]

2.1.3.2.13 Indirect cooling of the ammonia synthesis reactor

Description
This is an integrated technique applicable to new and existing steam reforming and partial oxidation plants. In the ammonia synthesis reactor, the catalyst is divided into several layers and the heat is removed by heat-exchangers instead of by injecting cold synthesis gas. The reaction heat can be used for the production of high-pressure steam, or for the boiler feed-water preheat, as well as to heat the incoming syngas to the desired inlet temperature of the catalyst beds. Energy is saved in this way since a higher ammonia conversion rate per pass is achievable. In addition the volume of catalyst necessary can be reduced.

Achieved environmental benefits
See Table 2.3, Table 2.4.

Cross-media effects
No cross-media effects are known.

Operational data

Applicability

Economics

Driving force for implementation

Example plants

Reference literature
[13, EC, 1997]

2.1.3.2.14 Use of smaller catalyst particles in ammonia converters

Description
This is an integrated technique applicable to new and existing steam reforming and partial oxidation plants. The higher activity of smaller catalyst particles results in a reduced circulation rate and/or reduced synthesis pressure. Another consequence is that a lower catalyst volume is

needed. To compensate for the increased pressure drop resulting from the smaller catalyst particles, converters with radial flow, axial/radial flow, or with cross-flow (horizontal converter) have been developed.

Achieved environmental benefits
See Table 2.3.

Cross-media effects
Possible increased pressure drop.

Operational data

Applicability

Economics

Driving force for implementation

Example plants

Reference literature
[13, EC, 1997]

2.1.3.2.15 Supplying process steam by feed gas saturation with process condensates

Description
This is an integrated technique applicable to new steam reforming plants. In special cases it can be retrofitted to existing plants. The process steam needed for the reforming reaction is usually generated in waste heat boilers and sometimes additionally in an auxiliary boiler. However a portion of the process steam may be obtained by saturating the feed gas with process condensate using low-grade heat from the process, e.g. from the shift conversion. This concept saves energy and avoids water pollution, since it allows for a complete recycling of the process condensates. The saturation can be performed using a saturator or by a direct injection of the process condensate into the hot feed gas.

Achieved environmental benefits
Energy savings up to 1.28 GJ/tonne NH_3 in revamps.

Cross-media effects
Energy saving combined with the prevention of emissions to water.

Operational data

Applicability

Economics

Driving force for implementation

Example plants

Reference literature
[13, EC, 1997]

2.1.3.2.16 Isothermal shift conversion

Description
This is an integrated technique applicable to new steam reforming plants. In special cases it can be retrofitted to existing plants. Lower temperatures favour the strong exothermic shift conversion. Therefore, heat has to be removed to achieve a low residual CO concentration. In conventional plants this is performed in two stages: high-temperature shift conversion (360 - 440 °C) and low temperature shift conversion (200 - 250 °C), using different types of catalysts. The gas is cooled down between the two steps.

Alternatively a single step system can be used to the two-step approach. Here the conversion is performed isothermally by continuously removing the heat from the catalyst bed, by using cooling tubes. In this way the need for a chromium-containing conventional high-temperature shift catalyst is avoided. As the isothermal shift occurs without a chromium-based catalyst, the Fisher-Tropsch reaction does not take place in the shift reactor, thus allowing a lower steam to carbon ratio.

Achieved environmental benefits
See Table 2.5

Cross-media effects
Energy saving and no necessity for the disposal of chromium spent catalyst. The start-up time of the one-step isothermal shift is reduced compared to the conventional two-steps shift systems, resulting in lower emissions.

Operational data

Applicability

Economics

Driving force for implementation

Example plants

Reference literature
[13, EC, 1997]

2.1.3.2.17 Non-iron based catalyst for ammonia synthesis

Description
This is an integrated technique applicable to new and existing steam reforming and partial oxidation plants. A new ammonia synthesis catalyst containing ruthenium and an alkali promoter on a graphite support has recently been developed which as a much higher activity per volume compared to the conventional iron-based catalyst. This allows energy savings to be made in the ammonia synthesis reactor, since lower operation pressures can be used and a higher conversion rate per pass can be obtained. The catalyst volume can also be reduced.

Achieved environmental benefits
An energy reduction up to 1.2 GJ/tonne NH_3 can be achieved.

Cross-media effects
No cross-media effects are known.

Operational data

Applicability

Economics

Driving force for implementation

Example plants

Reference literature
[13, EC, 1997]

2.1.3.2.18 Use of sulphur resistant catalyst for shift reaction of synthesis gas from partial oxidation

Description
This is an integrated technique applicable in new partial oxidation plants. The technique allows for the removal of CO_2 and sulphur compounds, traditionally carried out in separate steps, to be combined into one step. In an ammonia plant using partial oxidation for syngas production, two basic process configurations can be used. In one configuration, the syngas is cooled after the gasifier in a waste heat boiler. The H_2S is subsequently recovered from the syngas in a cold methanol wash unit. The cleaned gases are saturated with steam before entering the high-temperature shift reactor, using a conventional iron-based catalyst. After the shift reactors, CO_2 is removed in a conventional CO_2 removal unit, for instance in a second stage cold methanol wash unit.

In the second configuration, cooling of the syngas after the generator is carried out by a direct water quench, which also provides the steam needed for the shift conversion. In this case the cold methanol washing unit is placed after the shift conversion, removing CO_2 and H_2S in two separated fractions. In this configuration, the feed for the shift conversion still contains all the sulphur in the syngas and so a sulphur tolerant shift catalyst is needed. Energy savings may be achieved in the second configuration, as it is not needed to reheat the syngas before the high-temperature shift.

Achieved environmental benefits
See Table 2.6.

Cross-media effects
No cross-media are known.

Operational data

Applicability

Economics

Driving force for implementation

Example plants

Reference literature
[13, EC, 1997]

2.1.3.2.19 Liquid nitrogen wash for final purification of the synthesis gas from partial oxidation

Description

This is an integrated technique applicable to new partial oxidation plants. The synthesis gas is scrubbed countercurrent with liquid nitrogen at a temperature of around –185 °C. The CO_2, CO and CH_4 impurities are dissolved in the liquid nitrogen and recovered by flashing and distilling, for subsequent use as a fuel. In the liquid nitrogen wash, the nitrogen for the ammonia synthesis reaction is also supplied. The process produces practically inert free synthesis gas. As the synthesis gas is of such a high purity, the purge gas is unecessary and a high conversion rate per pass is achievable.

Achieved emission levels

See Table 2.6. Eliminates purge gas and increases the efficiency of the synloop.

Cross-media effects

No cross-media effects are known.

Operational data

Applicability

Economics

Driving force for implementation

Example plants

Reference literature

[13, EC, 1997]

2.1.3.2.20 Use of cobalt promoted ammonia synthesis gas catalyst

Description

This is an integrated technique applicable to new and existing steam reforming and partial oxidation plants. The activity of the traditional iron synthesis catalyst is increased considerably by promotion with cobalt. A lower pressure in the ammonia synthesis reactor and/or a lower recycle rate can also be achieved.

Achieved environmental benefits

See Table 2.5.

Cross-media effects

No cross-media effects are known.

Operational data

Applicability

Economics

Driving force for implementation

Example plants

Reference literature

[13, EC, 1997]

2.1.3.2.21 Preheat of combustion air

Description
This is an integrated technique applicable to new and existing steam reforming plants. Combustion air is normally heated with waste heat from the primary reformer or auxiliary boiler flue-gases. The increased flame temperatures in the air preheat leads to higher NO_X emission levels. In this instance, a gas turbine is used to drive the process air compressor for combustion, so the hot exhaust gases may be used as preheated combustion air. This gas turbine exhaust has more inerts (CO_2, H_2O, N_2O) than normal air but has a higher temperature than normally preheated combustion air [13, EC, 1997]. These two opposing effects influence the flame temperature in the primary reformer, and hence the NO_X concentration will depend on the specific site requirements and layout.

In one instance where this particular technique is used, energy is saved while the flame temperature in the primary reformer is decreased. The reason for the reduced flame temperature is the low O_2 and high CO_2 -concentrations in the waste gas from the gas turbine. If considerable air preheat is applied and no gas turbine waste gases can be used, a value of 100 mg/Nm^3; 300 g/tonne NH_3 could be raised to 130 mg/Nm^3; 390 g/tonne NH_3.

Achieved environmental benefits
See Table 2.3 and [13, EC, 1997].

Cross-media effects
No cross-media effects are known.

Operational data

Applicability

Economics

Driving force for implementation

Example plants

Reference literature
[13, EC, 1997]

2.1.3.2.22 Use of a gas turbine to drive the process air compressor

Description
This is an integrated technique applicable to new steam reforming plants. When using a condensation steam turbine to drive the air process compressor, more than half of the energy contained in the steam is transferred to the cooling medium and lost. An alternative is to install a gas turbine for driving the process air compressor and using the hot exhaust gases, which still contain sufficient oxygen, as preheated combustion air in the primary reformer. An overall efficiency for the driving and preheat operations in excess of 90 % can be achieved using this technique. The preheating of the combustion air saves in fuel consumption for the firing of the reformer but the higher flame temperatures increase NO_X formation.

Achieved environmental benefits
See Table 2.4.

Cross-media effects
Increase of NO_X emissions.

Operational data

Applicability

Economics

Driving force for implementation

Example plants

Reference literature
[13, EC, 1997]

2.1.3.2.23 Hydrogen recovery from the ammonia synthesis purge gas

Description
This is a technique applicable to new and existing steam reforming plants. A continuous purge gas stream has to be withdrawn to remove inerts from the ammonia synthesis loop. In older designs, this extracted purge gas was usually added directly or after water scrubbing to the reformer fuel. As a consequence the intrinsic heating value of the gas was used but the additional energy to generate and purify the hydrogen was lost. In more recent designs, the hydrogen is recovered from this purge gas and recycled to the synloop.

This hydrogen recovery can be performed using different technologies, such as cryogenic separation, membrane technology or pressure swing adsorption (PSA).

Achieved environmental benefits
See Table 2.3.

Cross-media effects
No cross-media effects are known.

Operational data

Applicability

Economics

Driving force for implementation

Example plants

Reference literature
[13, EC, 1997]

2.2 Nitric acid

In general, process-integrated measures are the first measures to consider when emission reduction and energy efficiency are pursued.

The description which follows is for a typical plant. Plant configuration will vary from plant to plant. Operating parameters such as temperatures, pressures, and compositions will also vary considerably from the values quoted.

2.2.1 Optimisation of the oxidation step

Description

The aim of optimising the oxidation step is to get an optimum NO yield. This means that the formation of unwanted side products such as N_2O is lower. The NO yield in the oxidation step is highest at an optimum NH_3/air ratio of 9.5 – 10.5 % ammonia. A good mixing of ammonia and air, good distribution of the ammonia-air mixture across the catalyst, low pressure (as low as possible), optimum temperature (750 – 900 °C) and good quality and condition of the platinum catalyst are also needed.

Ammonia-air ratio

From an engineering standpoint, the combustion of ammonia is one of the most efficient catalytic industrial reactions (maximum possible conversion of 98 %). The ammonia-air reaction mixture should contain 14.38 % ammonia according to the equation stoichiometry. However a lower NH_3/air ratio is used for a variety of reasons, the most important being that the conversion efficiency decreases at a high NH_3-air ratio. In addition, ammonia and air can form an explosive mixture. The ‘Lower Explosion Level’ (LEL) drops with pressure so high-pressure burners can only safely operate with up to 11 % ammonia, whereas 13.5 % ammonia is possible in low-pressure systems. A safety margin is necessary to deal with locally higher ratios as a result of imperfect mixing, so many plants add ± 10 % ammonia [11, InfoMil, 1999].

Mixing of ammonia and air

A good mixing of air and ammonia is essential to obtain a NO yield as high as possible. Local ammonia excesses in the burner are a plant safety risk (based on LEL) and could also cause the catalyst gauze to overheat. Only static mixers are used [11, InfoMil, 1999].

Distribution of the gas across the catalyst

Good distribution of the gas across the catalyst is a necessity to optimise the NO yield. For this reason, the burner head often contains a perforated plate or honeycomb grid to ensure good distribution. The gas velocity over the catalyst gauze must be steady [11, InfoMil, 1999].

Pressure

Operating at low pressure increases the conversion of NH_3 to NO according to the laws of thermodynamics. [11, InfoMil, 1999]

Temperature

A high reaction temperature enhances ammonia combustion, but decreases the conversion efficiency due to the increased by-products generation of N_2 and N_2O. The oxidation generally takes place at temperatures between 850 and 950 °C, resulting in NO-yields above 96 %. Temperatures above 950 °C are possible, but catalyst losses, mainly due to vaporisation, then greatly increase. The reaction mechanism tends to be more selective towards nitrogen and nitrous oxide (N_2O) formation at lower catalyst temperatures.

Nitrous oxide (N_2O) is unstable at these temperatures (i.e. 850 – 950 °C) and partly reduces to N_2 and O_2. A long residence time and a high temperature in the catalytic reactor promote this reduction.

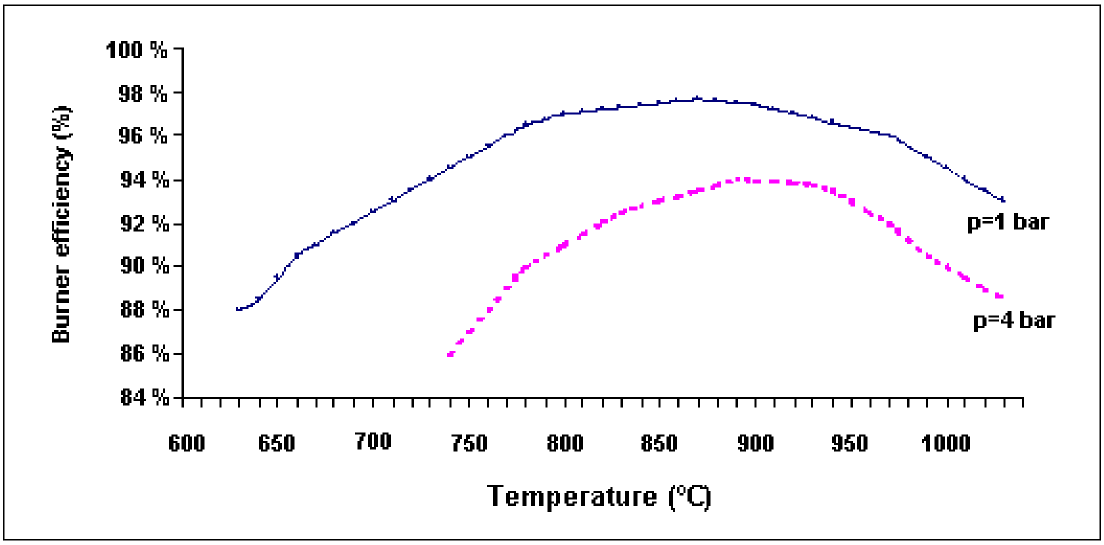


Figure 2.1: Possible conversion of NH_3 to NO on a platinum gauze as a function of temperature [11, InfoMil, 1999]

The reaction temperature is directly related to the ammonia-air ratio: a 1 % increase in the proportion of ammonia increases the temperature by c. 68 °C. [11, InfoMil, 1999]

Catalyst quality and condition

Currently platinum catalysts are almost exclusively used. Non-noble metal oxide catalysts can also be used and cost less than platinum catalysts, but conversion is lower and the non-noble metal catalysts are more quickly poisoned. In the republics of the CIS, two-step catalysts are widely used. One or several platinum gauzes are used in the first step, and a bed of non-platinum oxide catalyst is used as the second step. The platinum step offsets the drawbacks of the non-platinum step, reducing platinum usage by 40 – 50 % and reducing platinum losses by 15 - 30 % under equal conditions. [11, InfoMil, 1999]

Since the introduction of the industrial production of nitric acid by the Ostwald process, several hundred materials have been tested as catalysts for ammonia combustion. Research into replacing platinum catalysts by catalysts made of less expensive materials which may give the same or better results still continues, but at present no references of commercial exploitable alternatives are available.

Platinum is usually alloyed with rhodium to improve its strength and to reduce catalyst loss. In the past rhodium was more expensive than platinum increasing the cost. A rhodium content of 5 – 10 % has been shown to be optimal. If a low reaction temperature, i.e. <800 °C, is chosen, a pure platinum catalyst should be employed. Otherwise, rhodium(RI)oxide could accumulate at the catalyst surface and decrease catalytic activity [11, InfoMil, 1999]. Palladium is also used in catalyst alloys to reduce costs. Adding up to 5 % palladium, resulting no significant differences in the nitrogen monoxide yield, and has the benefit that palladium costs are lower than platinum or rhodium

The NO yield decreases and there is some formation of undesired side-products due to vaporising and slow poisoning of the catalyst as the level of N_2O increases. To maintain a high NO yield, the catalyst gauzes have to be replaced regularly at least 2 - 4 times a year [11, InfoMil, 1999].

Achieved environmental benefits

By optimising the NH_3-air-ratio, the pressure, and the temperature, an NO conversion close to 98 % is possible. There are limitations for changes in existing plants but in new plants adaptation is easier. Improvements however are only marginal.

Cross-media effects
No significant cross-media effects occur.

Operational data

Applicability
The above parameters; NH_3-air-ratio, mixing, distribution, temperature, pressure, quality and condition of the catalyst, affect production rates and product quality As a result, these parameters are usually set up to be as close to the optimum as possible within the technical limitations of the plant.

Economics
No information available

Driving force for implementation

Example plants
All plants throughout the world can be expected to optimise the operating conditions for maximising an NO yield. The NO yield affects the production rate and the quality of the end-product: as a result, the NO yield must be as high as possible within the technical and economical possibilities of the plant, however the conversion of NO is limited to 98 % maximum, with the remaining conversion being to N_2O and N_2.

Reference literature

2.2.2 Reduction of N_2O

Description
The formation of N_2O is unavoidable. From an environmental point of view, emissions of N_2O need to be prevented; N_2O has a greenhouse effect 310 times greater than CO_2.

Achieved environmental benefits
A theoretical N_2O reduction of 70 – 85 % is claimed. Achieved results in the Porsgrunn plant is an N_2O emmission of 300 - 400 ppm, which is a reduction of approx. 70 %. Comparing the Porsgrunn plant with plants of similar capacity, an N_2O emission of approx. 200 ppm is expected (= 392 mg N_2O/m^3). No effects on the NO yield or the NO_X emission are measured [11, InfoMil, 1999].

Hydro Agri has installed this system successfully in a new 2000 t/day nitric acid plant in Porsgrunn (Norway) in 1992, giving an N_2O reduction of approx. 70 % without any measurable effects on the NO yield and the NO_X concentration [11, InfoMil, 1999].

Cross-media effects
No significant cross-media effects occur.

Applicability
This process is more suitable for new plants, as the reactor chamber has to be replaced. It is possible to retrofit existing nitric acid plants but the successful retrofit depends on the plant layout [11, InfoMil, 1999].

Economics
The costs of the oxidation reactor are approximately 5 % higher in comparison to a conventional reactor when applied to a new nitric acid plant. The cost of installation in an existing nitric acid plant is very dependent on the plant design, but is expected to be much higher because of engineering limitations.

Driving force for implementation

Example plants
Hydro Agri has developed an oxidation reactor that gives lower N_2O emissions. The oxidation reaction zone has been extended in comparison to other nitric acid plants. This gives a longer gas residence time, so that the unstable N_2O in the reactor is reduced to N_2 and O_2 [11, InfoMil, 1999].

Reference literature
[11, InfoMil, 1999]

In general, developments in the nitric acid industry to reduce nitrous oxide (N_2O) can be divided into the following classificators:

1. **First stage:** This covers activities that affect the formation of nitrous oxide during the catalytic oxidisation of ammonia
2. **Second stage:** This covers activities related to the process gas stream, produced in the process from the oxidisation catalyst, to the absorption tower treatment.
3. **Third stage:** This covers activities related to the process between the absorption tower and the expansion turbine
4. **Final stage:** This covers the process gas beyond the expansion turbine (atmospheric conditions) [35, InfoMil/novem, 2001].

These techniques are not necessarily available on a commercial scale.

2.2.2.1 First stage

2.2.2.1.1 Optimising conventional platinum-based catalysts

Description
Platinum catalysts are almost exclusively used today. Modifications to the geometry of the catalysts can lead to a higher ammonia conversion to NO and/or to a reduction in the production of N_2O [35, InfoMil/novem, 2001].

Achieved environmental benefits
Advantages:
A 30 % reduction in N_2O emission is considered achievable.

Disadvantages:
No significant disadvantages are anticipated.

Cross-media effects
No significant cross-media effects are anticipated.

Operational data

Applicability
If optimised platinum catalysts become available on the market, it can be anticipated that these catalysts will be suitable for all nitric acid plants, both new and existing, operating at any pressure.

Economics
Other advantages such as higher nitric acid yield and lower catalyst costs are likely to occur, along with a reduction of the N_2O emission [35, InfoMil/novem, 2001].

Driving force for implementation

Example plants
Both suppliers and nitric acid producers are continuously researching catalyst optimisation. No specific reference plants are available.

Reference literature
[35, infomil/novem, 2001]

2.2.2.1.2 Alternative oxidisation catalysts

Description
N_2O emissions can be reduced when alternative catalysts are used. In the republics of the former CIS, two step catalysts are used extensiveley. One or several platinum gauzes are used as the first step, and a bed of non-platinum oxide catalyst is used as the second step [35, InfoMil/novem, 2001].

Achieved environmental benefits
Advantages:

- it has been demonstrated that alternative oxidisation catalysts produce less N_2O than platinum based catalysts of up to 80 – 90 % approximately 1.9 kg N_2O/tonne HNO_3 [35, InfoMil/novem, 2001]
- some sources claim higher ammonia conversion efficiencies (94 – 95 %), whilst others say this is only 88 – 92 % in a high-pressure plant. Normally, NO-yield in an existing nitric acid plant will be approximately between 93 % and 98 % [35, InfoMil/novem, 2001]
- lifetime of the catalyst is longer, reducing the number of plant shut-downs [35, InfoMil/novem, 2001]
- lower pressure drop [35, InfoMil/novem, 2001]
- the use of two-step catalysts reduces the amount of platinum used by up to 40 – 50 % and platinum losses are reduced by 15 – 30 % under similar conditions [35, InfoMil/novem, 2001].

Disadvantages:

- high temperatures and reduction of Co_3O_4 to CoO leads to catalyst deactivation [35, InfoMil/novem, 2001]
- the yield of ammonia to nitric acid is claimed to be lower, making the process less efficient, especially in high-pressure plants [35, InfoMil/novem, 2001].

Cross-media effects

Operational data

Applicability
When alternative oxidation catalysts become available on the market, it is expected that these catalysts will be suitable for all nitric acid plants, both new and existing, operating at any pressure, although some modification of existing plants will be necessary. At least one plant, Incitec in Australia, already uses a cobalt oxide (Co_3O_4) based catalyst.

Economics
For new plants alternative catalysts can be an option. For existing plants retrofit costs are reported to be USD_{1999} 1.5 – 2 million ($Euro_{2001}$ 1425000 - 1900000) [35, InfoMil/novem, 2001]. The lower NO-yield should also be taken into account as it has a significant cost effect.

Driving force for implementation

Example plants

Incitec (Australia) uses a cobalt oxide catalyst [35, InfoMil/novem, 2001]. Two-step catalysts are widely used in the republics of the former CIS [35, InfoMil/novem, 2001].

Reference literature

2.2.2.2 Second stage

2.2.2.2.1 Homogeneous decomposition

Description

Norsk Hydro has developed and patented a technology that reduces the production of N_2O by increasing the residence time in the reactor at high temperatures (850 – 950 °C). This technology consists of an 'empty' reaction chamber of approx. 3.5 m extra in length between the platinum catalyst and the first heat-exchanger. Due to the longer residence time of 1 – 3 seconds, a N_2O reduction of 70 – 85 % is obtained, since N_2O is metastable at higher temperatures and decomposes to N_2 and O_2.[35, InfoMil/novem, 2001]

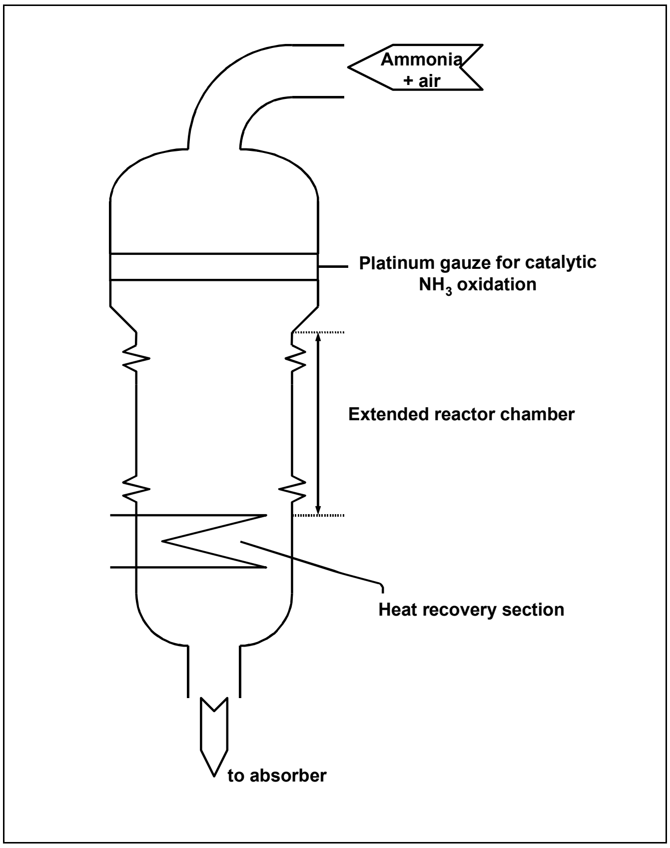


Figure 2.2: Homogeneous decomposition by extended reactor chamber

Achieved environmental benefits

Advantages:

- a reduction of N_2O of approx. 70 % has been achieved using this technology. No additional operational costs
- no NO losses.

Disadvantages:

- low conversion levels in low-pressure plants, and, as a consequence this technique is not applicable in low pressure plants [35, InfoMil/novem, 2001].

Cross-media effects

No significant cross-media effects occur.

Operational data

Applicability

This process is more suitable for new plants, as the reactor chamber will usually have to be replaced in existing plants, hence applicability in existing plants is dependant on plant layout [35, InfoMil/novem, 2001].

Economics

High investment costs, especially in existing plants due to revamp.

This technology opens up possibilities for new nitric acid plants, as additional investment costs are relatively low. The additional investment cost for a new nitric acid plant will only be approximately 5 % higher. Investments for existing plants will be much higher and mainly depend on retrofit costs. Depending on the local situation, these costs can differ considerably. The main advantage of this technology is the negligible operational costs. [35, InfoMil/novem, 2001]

Driving force for implementation

Example plant

Hydro Agri has installed this system successfully in a new 2000-t/day nitric acid plant in Porsgrunn (Norway) in 1992. Reduction of N_2O is approx. 70 % without measurable effects on the NO yield and the NO_X concentration. Installation of an extended oxidation chamber will result in an N_2O emission of of 3 - 400 ppm if operating conditions are similar to the plant in Porsgrunn. [35, InfoMil/novem, 2001]

Reference literature

2.2.2.2.2 High temperature catalytic decomposition

Description

As already stated, N_2O is formed as an undesirable by-product of the catalytic ammonia combustion. Various catalysts are available to promote the decomposition of N_2O to N_2 and O_2.

Within a nitric acid plant, there are two suitable locations for catalytic N_2O decomposition:

- in the oxidation chamber, directly after the ammonia combustion catalyst at a temperature of 850 – 950 °C, which can allow high temperature catalytic decomposition.
- just before the tail gas expander at a temperature of 200 – 350 °C (mono-pressure plants and older dual-pressure plants) or 400 – 500 °C (relatively new dual-pressure plants) (low temperature catalytic decomposition. [35, InfoMil/novem, 2001]

For high temperature catalytic decomposition, a catalytic bed is installed directly after the platinum catalyst in the oxidation chamber. Nitrous oxide is decomposed to N_2 and O_2. At least two different catalysts are available: a Cu-Zn-Al spinelle-based catalyst (patent owned by BASF) and a catalyst with unpublished composition (patent owned by Norsk Hydro). [35, InfoMil/novem, 2001]

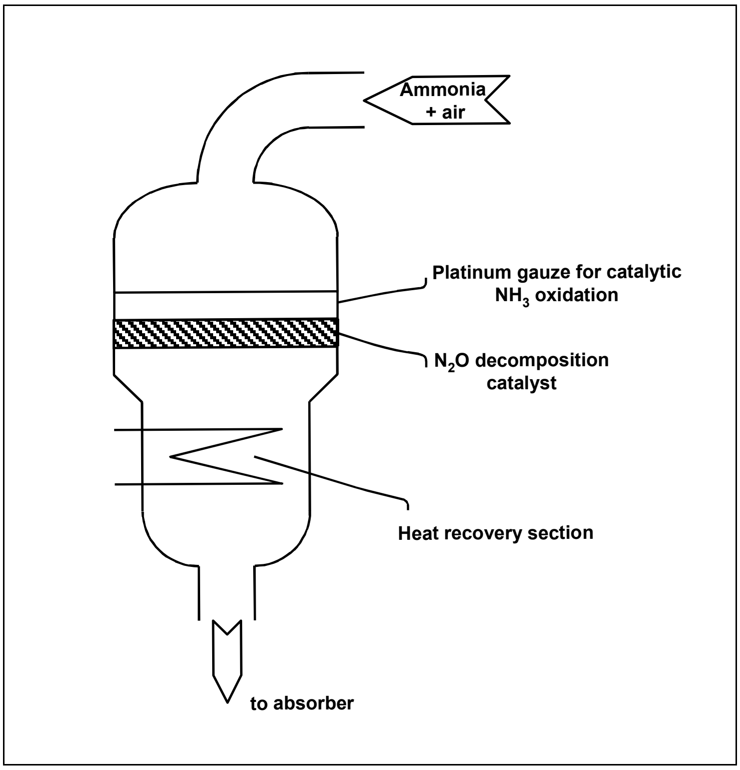


Figure 2.3: High temperature catalytic decomposition

Achieved environmental benefits

Advantages:

- reduction of N_2O emissions by up to 80 – 90 % [35, InfoMil/novem, 2001]
- applicable in most nitric acid plants
- relatively simple implementation

Disadvantages:

- the BASF catalyst and the second-generation catalyst of Norsk Hydro include a considerable pressure drop of 15 mbar. In some cases, special catalyst support has to be used to compensate for this pressure drop, thereby increasing the costs of the system. The exact pressure drop depends on the burner design and space velocity. BASF and Norsk Hydro are working on this problem and it is anticipated that the pressure drop will be soon much lower [35, InfoMil/novem, 2001]
- due to the high temperatures, the catalyst lifetime may be limited but with a proven lifetime over 2 years, and small particles of the catalyst may end up in the product. Nitric acid is an important feedstock for the production of ammonium nitrate, a widely used fertiliser. This contamination may act as a catalyst, causing decomposition or even detonation of ammonium nitrate [35, InfoMil/novem, 2001].

Cross-media effects

Operational data

Applicability

High temperature catalytic decomposition may be a good option in mono pressure and older dual-pressure plants. In these plants (approximately 2/3 of the number of European nitric acid plants), low temperature catalytic decomposition is not applicable, since due to the rather low tail gas temperatures, the activity of the N_2O decomposition catalyst is too low.

Both high temperature catalytic decomposition systems (BASF and Norsk Hydro) are available and applicable in both new and existing nitric plants, operating at any pressure and temperature.

However, both systems involve rather high pressure drops (see disadvantages). Installing the BASF system might, depending on the burner configuration, require adjustment of the burners [35, InfoMil/novem, 2001].

Economics

Assuming that the effect on the NO-yield is negligible and that the pressure drop is reduced, the cost effectiveness of the technique can be estimated at EUR 0.3 – 0.5/tonne CO_2-equivalent This will lead to an increase in production costs for nitric acid of EUR 0.7 – 1.5 Euro/tonne HNO_3. Expected lifetime of the catalyst is 2 – 5 years. For a 500000 t/d nitric acid (100 %) plant with a combustion pressure of 5 bar (medium pressure), this catalyst will cost approximately EUR 250000 (including licence fee, but excluding engineering). The costs of the BASF catalyst are strongly determined by the long research carried out and the small amounts of catalyst being made. Large-scale production of the catalyst would reduce the costs. [35, InfoMil/novem, 2001]

Driving force for implementation

Example plants

The BASF catalyst has been successfully installed in at least 3 nitric acid plants and is being installed in at least one more. In 1999, the catalyst was installed in an atmospheric (mono) pressure plant in Ludwigshaven (Germany). The N_2O concentration of about 1000 ppm decreased to 100 - 200 ppm (reduction of 80 – 90 %), depending on the space velocity setting of the combustion chamber. The lifetime is proven to be over 2 years [35, InfoMil/novem, 2001].
In July 1999 and January 2000, the catalyst was also installed in 2 of the 4 nitric acid plants of BASF Antwerpen (Belgium). All these plants are dual-pressure plants: the oxidation step takes place at 5 – 5.5 bar, while the adsorption step takes place at 10 bar. In the first plant (catalyst operational since July 1999), the N_2O emission was reduced from approximately 1200 ppm to 500 ppm, i.e. a reduction of 60 %. In the other plant, the reduction of N_2O is over 80 %, from approximately 1400 ppm to approximately 250 ppm. [35, InfoMil/novem, 2001]

DSM Geleen (the Netherlands) intends to install the BASF catalyst in one of their two nitric acid plants. and is testing the catalyst support system now. DSM are also investigating the potential risk of product contamination.

The first-generation catalyst of Norsk Hydro was installed in a medium-sized nitric acid plant at Landskrona, Sweden. This plant is now closed. The plant had been running without any noticeable operational problems at a more or less constant N_2O reduction level of 90 %. This was the combined result of the catalyst and an extended reaction chamber. No losses in the NO yield and no significant increase in pressure drop had been measured during the 9 month test period. [35, InfoMil/novem, 2001]

Reference literature

2.2.2.3 Third stage

2.2.2.3.1 Low temperature catalytic decomposition

Description

A catalytic bed is installed in the energy recovery section, between the absorption tower and the expander. Nitrous oxide is decomposed to N_2 and O_2. Several catalysts have already been tested on a laboratory scale and some will be tested on pilot scale.

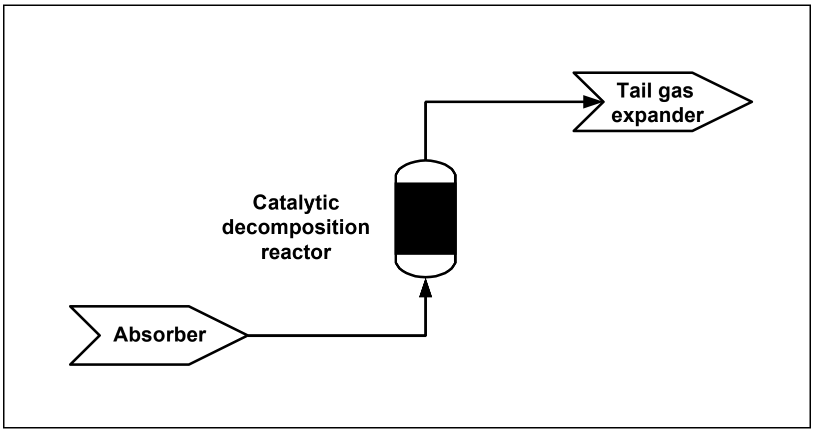


Figure 2.4: Catalytic decomposition

Achieved environmental benefits

Advantages:

- results from laboratory tests and pilot tests indicate that N_2O reductions of 80 – 90 % are achievable. However, lower reduction rates (<70 % have been mentioned).
- no risk of product contamination nor NO-losses.

Cross-media effects

Cross-media effects are not clear yet

Operational data

Applicability

Application of the technology seems to be limited to nitric acid plants with tail gas temperatures of over 400 °C. Scientific research indicates that it will not be possible to find a catalyst that has enough activity at lower temperatures. The reason for this limitation seems to be the formation of nitrates on the surface of the catalyst.

Disadvantages:

- not applicable in nitric acid plants with tail gas temperatures lower than 400 °C
- still in pilot stage

Economics

Costs per tonne N_2O removed would be approximately EUR 0.5 - 1/tonne CO_2-equivalent or EUR 1-2 /tonne 100 % HNO_3.

Driving force for implementation

Example plants

Results are available from tests on the laboratory scale and from some pilot tests.

Reference literature

2.2.2.3.2 Selective catalytic reduction with hydrocarbons, possibly combined with NO_X reduction

Description

A catalytic bed can be installed in between the energy recovery section in the absorption tower and the expander. Nitrous oxide reacts with a hydrocarbon to form N_2 and CO_2. Several catalysts have already been tested on a laboratory scale. The most promising catalysts are iron-zeolite based [35, InfoMil/novem, 2001].

In order to lower the costs for this measure, different combinations with NO_X reduction are currently under investigation. [35, InfoMil/novem, 2001].

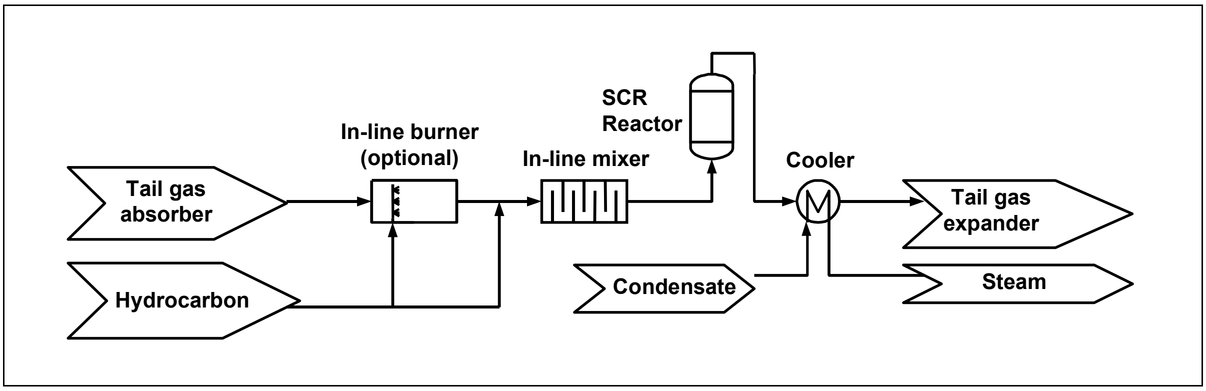


Figure 2.5: SCR with hydrocarbons as reagent

Achieved environmental benefits

Advantages:

- results from laboratory tests and pilot tests indicate that N_2O reductions of 80 – 90 % are achievable
- no risk of product contamination nor NO-losses
- simultaneous NO_X removal may be possible.

Disadvantages:

- the use of hydrocarbons as a reagent results in emissions of carbon monoxide (CO), carbon dioxide (CO_2) and hydrocarbons (C_xH_y) and an increase in energy consumption
- still in the pilot stage.

Cross-media effects

A surplus of heat is generated.

Operational data

Applicability

In principle, the technology can be applied to all kinds of nitric acid plants. Due to local circumstances, retrofit costs can be relatively high.

Economics

Costs per tonne N_2O removed would be approximately EUR 1.5 - 3/tonne CO_2-equivalent or EUR 3 - 6/tonne HNO_3. The use of reducing agent accounts for almost 50 % of these costs. The economic feasibility depends on local circumstances.

Driving force for implementation

Example plants

Until now no reference plant data has been available, but results are available from tests on a laboratory scale.

Reference literature

2.2.2.3.3 Non selective catalytic reduction (NSCR) of NO_X (with simultaneous N_2O reduction)

Description

The non-selective catalytic reduction of NO_X enables the reaction of a reducing agent (fuel) with nitrogen oxides, to produce nitrogen and water. Although developed as a $DeNO_X$ system, NSCR also considerably reduces the emissions of N_2O. This process is called non-selective, because the fuel first depletes all the free oxygen present in the tail gas and than removes the NO_X and N_2O. The most used fuels are natural gas or methane (CH_4), hydrogen (H_2) or ammonia plant purge gas (mainly H_2) and naphtha. An excess of reducing agent is required to reduce nitrogen oxides and nitrous oxide to nitrogen [35, InfoMil/novem, 2001].

Catalysts for NSCR are usually based on platinum, vanadium pentoxide, iron oxide or titanium; catalyst supports are typically made of aluminia pellets or a ceramic honeycomb substrate. The fuel requirement is the stoichiometric amount needed to reduce all the oxygen present (free and in nitrogen oxides) plus an excess (c. 0.5 v % CH_4). As the catalyst ages, the amount of fuel is increased to maintain the same NO_X and N_2O reduction values in the tail gas [35, InfoMil/novem, 2001].

The tail gas must be preheated before the reaction on the catalyst proceeds. The required temperature depends on the fuel selected, varying from 200 - 300 °C (H_2) to 450 - 575 °C (natural gas). Due to the exothermic reactions in the NSCR facility, the tail gas temperature can become very high (>800 °C), exceeding the maximum for admission to the gas expander unit. To deal with these high temperatures, two methods of NSCR are developed: single-stage and two-stage reduction [35, InfoMil/novem, 2001].

Single stage units can only be used when the oxygen content of the absorber tail gas is less than 2.8 % (an oxygen content of 2.8 % will result in a tail gas temperature of ± 800 °C after the NSCR facility). The effluent gas from these units must be cooled by a heat-exchanger or quenched to meet the temperature limitation of the gas expander unit [35, InfoMil/novem, 2001].

Two stage units with an internal quench section are used when the oxygen content is over 3 %. Two systems of two-stage reduction are used. One system uses two reactor stages with an interstage heat removal. The other system involves preheating 70 % of the tail gas to ±480 °C, adding fuel, and then passing it over the first stage catalyst. The fuel addition to the first stage is adjusted to obtain the desired outlet temperature. The remaining 30 % of the tail gas, preheated to only ±120 °C, is mixed with the first stage effluent. The two streams, plus fuel for the complete reduction, are passed over the second stage catalyst. After the second catalyst, the tail gas passes to the gas expander [35, InfoMil/novem, 2001].

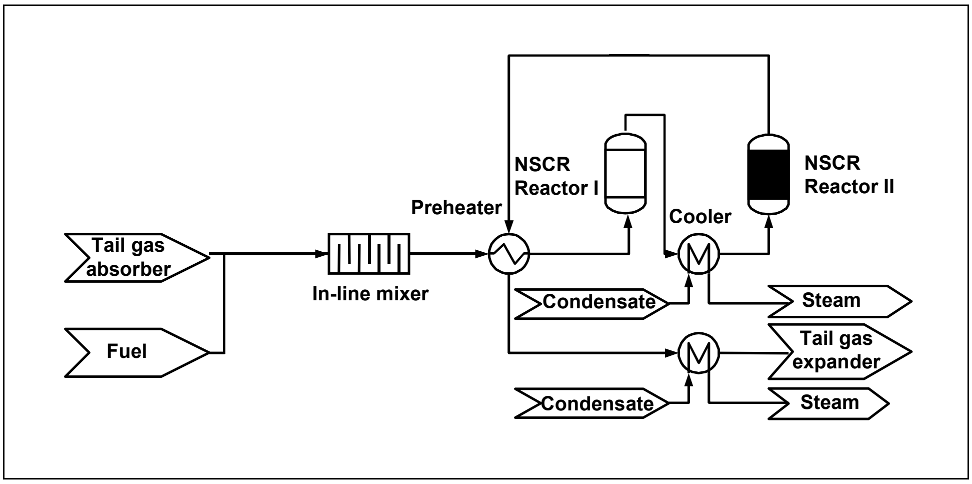


Figure 2.6: Two stage NCSR

Achieved environmental benefits

Advantages:

- reduction of N_2O of at least 95 %, reducing emissions well below 50 ppm N_2O (<100 mg N_2O/m^3)
- an NSCR facility also reduces the NO_X emission to 100 - 150 ppm (205 - 308 mg/m^3)
- availability and (often) low cost of the reducing agent (CH_4 or H_2) in an ammonia plant, if present [35, InfoMil/novem, 2001].

Cross-media effects

- when hydrocarbon fuels are used, emissions of carbon monoxide (CO), carbon dioxide (CO_2) and hydrocarbons (C_xH_y) will take place. Normally, the carbon monoxide emission will be less than 1000 ppm (1250 mg/m^3), but emissions of hydrocarbons can be up to 4000 ppm. Emissions of CO_2 can be over 6300 ppm (12348 mg/m^3) [35, InfoMil/novem, 2001]
- the tail gas needs a high preheat temperature, especially when hydrocarbon fuels are used. The tail gas needs heating from ± 50 °C to ± 250 - 300 °C (H_2) or to 450 - 550 °C (natural gas). The energy to use this abatement technique can be obtained from the process, but reduces the possible amount of exportable steam [35, InfoMil/novem, 2001]
- as a result of the high tail gas temperature after the NSCR facility, more expensive construction materials are necessary [35, InfoMil/novem, 2001]
- the NSCR facility cannot be started until the oxygen content has stabilised. To prevent temperatures that might cause inactivation of the catalyst (T>800°C), the oxygen content must be monitored. In an one-stage NSCR, problems might occur when the oxygen content exceeds 2.8 % [35, InfoMil/novem, 2001]]
- when hydrocarbon fuels are used, the expected lifetime of the catalyst is reduced to 3 - 5 years. When hydrogen is used as a fuel, the lifetime of the catalyst will be much longer.

Operational data

Applicability

In principle, NSCR facilities can be applied in both new and existing nitric acid plants, operating at any pressure. As stated above, the tail gas must be preheated to start the reaction. Energy is needed to heat the tail gas. Furthermore, high temperature equipment (e.g. a gas expander) is necessary as a result of the reaction in the NSCR. Application in an existing plant will demand major adjustments, making the installation of an NSCR less feasible [35, InfoMil/novem, 2001].

Several factors influencing the performance of the NSCR facility are described in [35, InfoMil/novem, 2001]

Economics

According to [35, InfoMil/novem, 2001], the price of an NSCR catalyst varies between USD 106000 and 143000/m^3 (≈ EUR 98000 – 131000/m^3). Technical and maintenance costs are excluded. A catalyst volume of 1.20 m^3 is required to treat a flowrate of 48235 m^3/h. Since this technology is not selective, N_2O is reduced too. In this example, 290 m^3 natural gas/h are necessary to reduce the NO_X concentration from 2000 ppm to 150 ppm (from 4100 to 308 mg/m^3). The reduction of N_2O is unknown, but will be considerable. As a result, fuel operating costs are USD 29.0/h (≈ EUR 26.8/h) or USD 1.95/tonne 100 % HNO_3 produced (≈ EUR 1.80). Note that this only covers the catalyst and fuel costs. Installation, maintenance and depreciation are excluded. Some of the costs of the natural gas may be offset by the increased power recovery. On the other hand, the high temperatures (T >800 °C) reduce the lifetime of the catalyst to 3 - 5 years.

Driving force for implementation

Example plants

Kemira Agro Rozenburg (the Netherlands) used a NSCR as a De-NO_X facility in their nitric acid plant. The plant had a capacity of 400 ktonne 100 % HNO_3/year and operated at 9 bar (mono-pressure). The plant was designed to be combined with a NSCR, reducing the emission of N_2O to 27 ppm (53 mg/m^3). Kemira Agro Rozenburg closed in December 2000. [35, InfoMil/novem, 2001]

Reference literature

2.2.2.3.4 Combined N_2O and NO_X abatement reactor - UHDE process

Description

The process comprises a combined N_2O and NO_X abatement reactor which is installed between the final tail gas heater and the tail gas turbine and operates at tail gas temperatures of about 400 - 480 °C. The combined N_2O and NO_X abatement reactor consists of two catalyst layers (Fe zeolite) and an intermediate injection of NH_3. Within the first catalyst layer (DeN_2O step) the decomposition of N_2O into N_2 and O_2 is carried out at full NO_X load, because the NO_X additionally promotes the decomposition of N_2O (co-catalysis). Within the second catalyst layer (DeN_2O/$DeNO_X$ step) NO_X is reduced by injection of NH_3. Further decomposition of N_2O also takes place. Figure 2.7 illustrates the process concept developed by UHDE, which has been realised at full commercial scale at Agrolinz Melamine International GmbH in autumn 2003 (cf. reference plant).

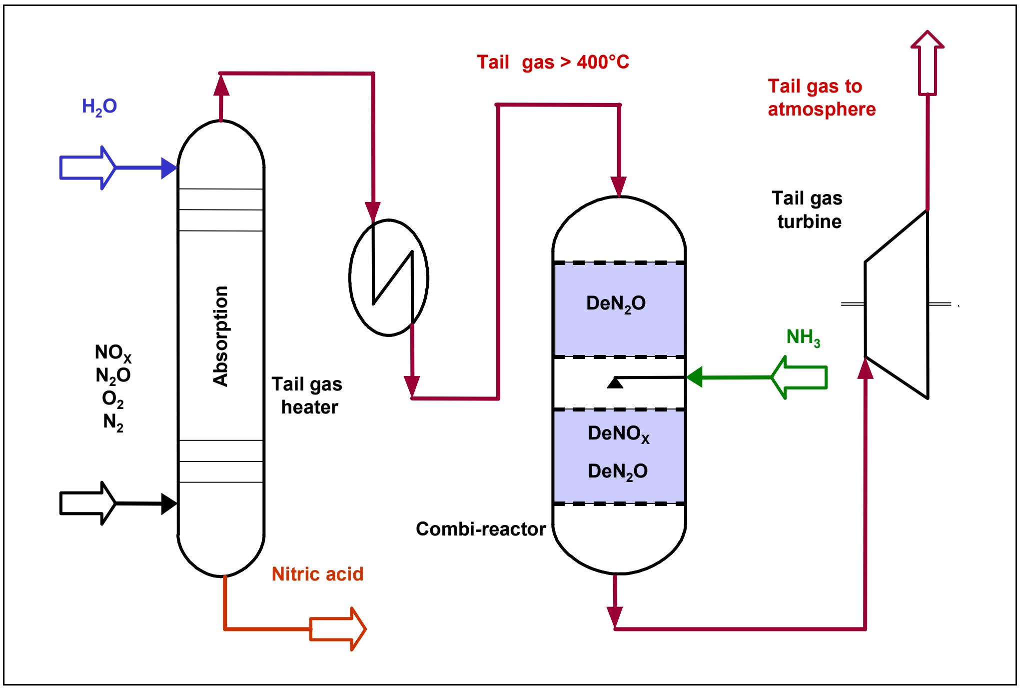


Figure 2.7: UHDE plant concept

Achieved environmental benefits

Advantages:

- simultaneous abatement of N_2O and NO_X emissions
- high N_2O removal rates: Mean N_2O removal rate over 2 years >90 % from miniplant results, N_2O abatement of ~ 99 % being maintained up to present in commercial scale reactor (3 months of operation, status mid-January 2004)
- high NO_X reduction efficiency (~0 ppm NO_X achievable, currently adjusted to ~30 ppm NO_X in commercial scale unit, status mid-January 2004)
- no ammonia slip
- no consumption of reducing agents for N_2O abatement
- no losses of NO that could otherwise be converted to product nitric acid.

Disadvantages:

- not applicable in nitric acid plants with tail gas temperatures below 400 °C
- no long term experience with catalyst lifetime in commercial scale installation (status mid-January 2004).

Cross media effects

No cross media effects are known

Applicability

The application of the combined N_2O/NO_X abatement reactor is possible in nitric acid plants with a tail gas temperature of about 400 - 480 °C. At temperatures beneath this the lower catalyst activity necessitates additional injection of reducing agents. This has been tested under realistic operating conditions in the Uhde miniplant, however, there is not yet a commercial scale installation. At higher temperatures oxidation of NH_3 might occur.

According to an estimate of about $^1/_3$ of the world's nitric acid plants are recent dual-pressure plants with tail gas temperatures in the range 450 - 500 °C. For the majority of these plants the technology would be applicable. The remaining are mono-pressure plants and old dual-pressure plants with tail gas temperatures <400 °C. Taking production capacity into consideration the two categories become more or less equal.

Economics

Investment costs: Cost of AMI unit: EUR 2.1 Million. Because of the experience gained with the AMI unit it is expected to be able to reduce the investment cost for future units for this nitric acid plant capacity to around EUR 1.7 Million by making savings in parts of the equipment.
Operating costs: Approximately zero additional energy costs, because the higher pressure drop (approx. +50 mbar) is compensated by the increased tail gas temperature (approx. +4 K; decomposition of N_2O is an exothermic reaction).
Specific catalyst costs and lifetime of catalyst are not available, therefore total operating costs and specific cost calculations are not known.

Conclusions:

- Combined catalytic abatement of NO_X and N_2O in nitric acid plants with tail gas temperatures >400 °C realised at commercial scale
- Consistently high N_2O and NO_X reduction rates achieved since start-up (~3 months of operation)
- Open questions for lifetime of the catalyst.

Example plant

Agrolinz Melamine International GmbH (AMI, formerly Agrolinz Melamin GmbH) operates two nitric acid plants referred to as Line E (M/H-dual-pressure plant) and Line F (N/M-dual-pressure plant). Using the process concept of UHDE GmbH, AMI installed the world's first combined catalytic $DeN_2O/DeNO_X$ reactor in Line E. Figure 2.8 shows a simplified flowsheet of the plant, into which the combined N_2O and NO_X abatement reactor has been integrated. The reactor was installed in September 2003 after a 2 year test phase in a miniplant (side stream of the tail gas of Line E).

Characteristic features of the process:

- dual (M/H) pressure NHO_3 plant with a production capacity of 1000 t HNO_3/d; tail gas flowrate: 120000 Nm_3/h
- working temperature: 425 °C; Working pressure: 7 bar gauge
- untreated gas concentration: 1000 ppm N_2O and 500 ppm NOX
- N_2O abatement efficiency: over first three months (status mid-January 2004) consistently ~99 %.

From miniplant results >80 % N_2O expected after two years; An average removal rate of more than 90 % over 2 years is expected in commercial scale unit.

- NO_X clean gas concentration: currently adjusted to ~30 ppm – higher reduction rates possible down to ~0 ppm NO_X, – no ammonia slip occurring. (Due to limitations from ammonia slip the former SCR achieved about 100 ppm NO_X);

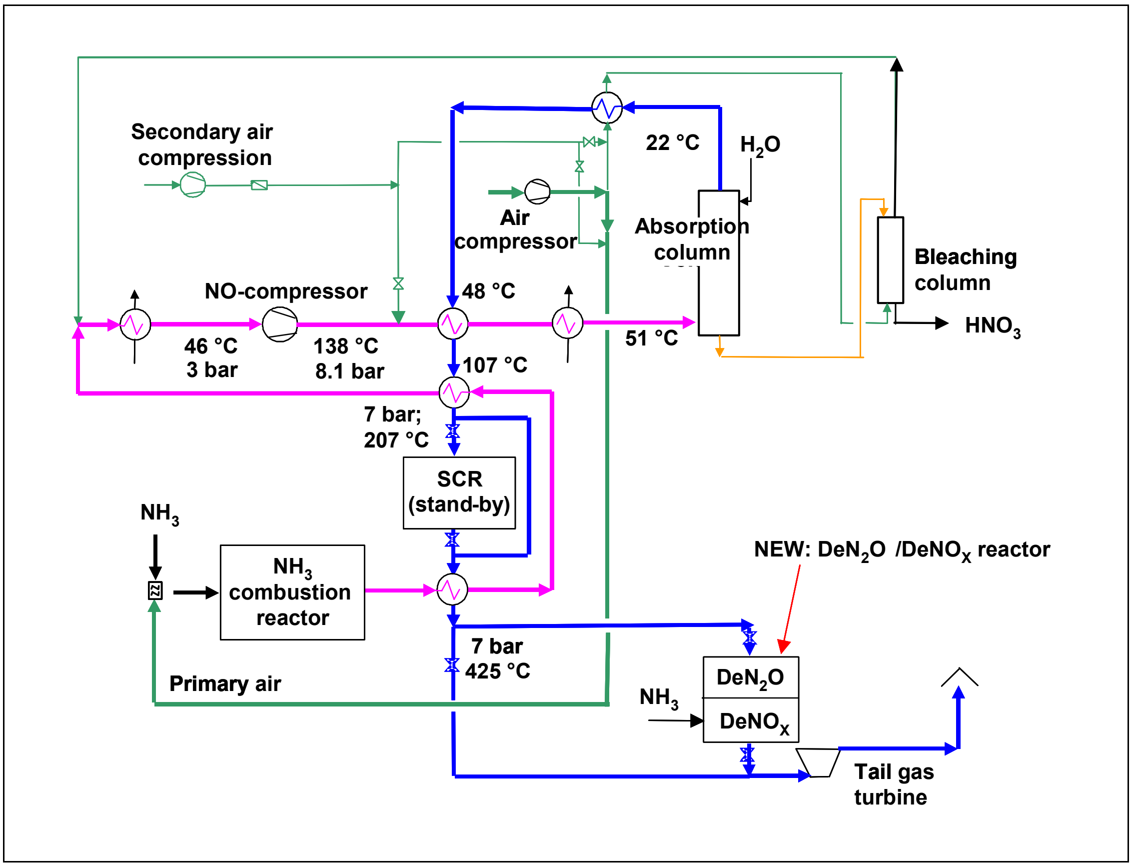


Figure 2.8: Simplified scheme of combined N_2O/NO_X abatement UHDE concept at Agrolinz Melamine

References

2.2.2.4 Final stage

The technologies described in Section 2.2.3.3 can also be applied downstream of the expander, at atmospheric pressure. The main advantage of this application for existing plants is that the measure will hardly influence the existing nitric acid process. In Figure 2.9, a flowchart of a downstream SCR is presented Figure 2.10 presents a flowchart of a downstream catalytic decomposition reactor Two disadvantages are the relatively high investment costs and the need for additional energy. However, feasibility studies show that the costs per tonne CO_2-equivalent or per tonne HNO_3 will be comparable or even lower than when installing the catalyst upstream the expander [35, InfoMil/novem, 2001].

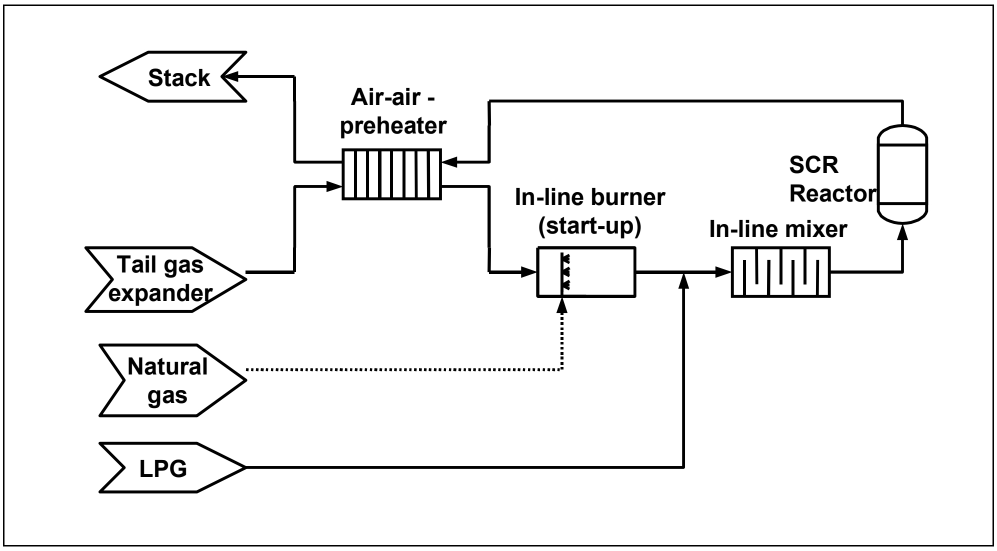


Figure 2.9: SCR reactor downstream tail gas expander

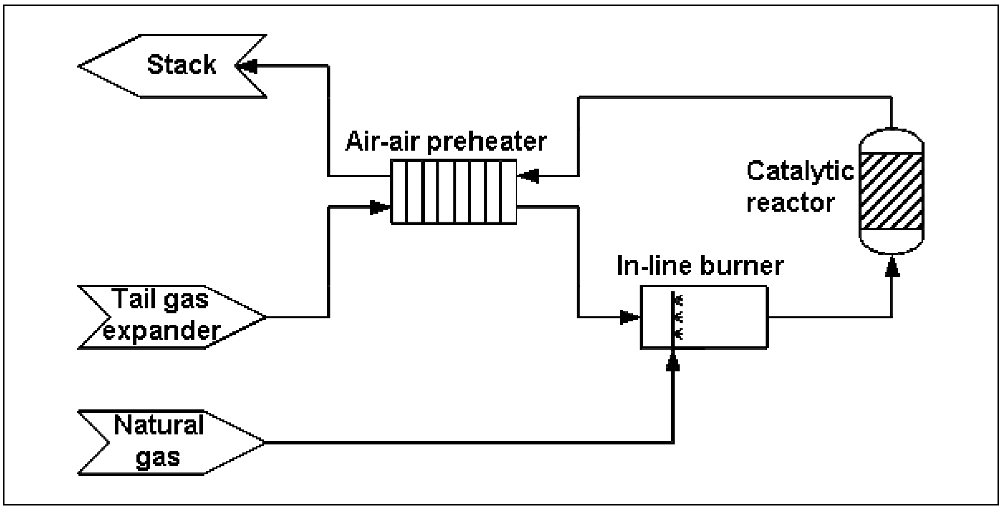


Figure 2.10: Catalytic decomposition downstream tail gas expander

2.2.3 Catalyst recovery

Description

Platinum and rhodium in catalysts vaporise at high combustion temperatures, i.e. 700 – 950 °C. The catalyst then has to be replaced regularly, i.e 1.5 - 4 times a year, to maintain a high NO yield [11, InfoMil, 1999]. Table 2.7 gives some typical loss rates.

Pressure (bar)	**Number of catalyst gauzes**	**Gas velocity (m/s)**	**Reaction temperature (°C)**	**Gross catalyst Loss (g/tonne HNO_3)**
1 - 2	3 – 5	0.4 – 1.0	840 – 850	0.05 – 0.10
3 – 7	6 – 10	1 – 3	880 – 900	0.15 – 0.20
8 – 12	20 – 50	2 – 4	900 – 950	0.25 – 0.50

Table 2.7: Typical design data for ammonia burners
[11, InfoMil, 1999]

Both platinum and rhodium are expensive materials; most nitric acid plants therefore have systems installed to recover these precious metals. Two of these systems are described; the so-called "getter" and the mechanical filter.

"Getter":
Most nitric acid plants have a recovery gauze installed immediately downstream of the catalyst gauzes. This system is known as a "getter" or catchment. Early recovery system consisted of a gold-palladium alloy (20 % gold -80 % palladium). Nowadays, most getters are gold-free but have a low nickel content of up to 5 % to improve the strength. The trapped platinum diffuses into the palladium gauze and forms an alloy. The uppermost gauze is often designed to reach saturation in one campaign (usually 90 – 180 days) [11, InfoMil, 1999].

Mechanical filters:
Mechanical filters are made of glass, mineral wool, or ceramic fibres. They are normally installed where the gas temperature is <400 °C. These filters have the advantage of low capital costs, but the disadvantage of high operating costs, as a result of the large pressure drop build up across the filter (up to 0.25 bar between filter changes). For economic reasons, these are only used in mono pressure/high pressure plants [11, InfoMil, 1999].

Some catalyst material settles on plant equipment, such as on the heat-exchangers or the waste heat boiler, even when recovery systems are in use. During shutdown, this 'dust', often containing high concentrations of platinum and rhodium, is collected. Catalyst manufacturers can recover precious metals from this ‘dust’. Part of the precious metals can also alloy with the plant equipment metal surfaces, but specialised companies can also recover these precious metals, by using non-corrosive leaching chemicals [35, InfoMil/novem, 2001]. After plant demolition, the scrap metal is melted down and the precious metals recovered. [11, InfoMil, 1999]

Small amounts of the catalyst can also end up in the product. Techniques are available to recover the catalyst materials from the nitric acid. Typically this is uneconomical, so, for instance, none of the Dutch plants uses this technique.

Achieved environmental effects
"Getter" systems can recover more than 80 % of the platinum lost from the catalyst. Up to 30 % of the rhodium from the catalyst is captured by a getter. Mechanical filters recover 40 – 50 % platinum, but recovery rates of 50 – 75 % have been reported [11, InfoMil, 1999].

Cross-media effects
No significant cross-media effects occur.

Operational data

Applicability
Mechanical filters can only be used in mono pressure-high pressure plants. "Getters" can be used in both new and existing plants, at any pressure (although their application at high pressure is less feasible due to a high pressure drop) [11, InfoMil, 1999].

Economics
Not available

Driving force for implementation

Example plants
Recovery systems are installed in most nitric acid plants to improve process economics.

Reference literature
[11, InfoMil, 1999]

2.2.4 Optimisation of the absorption step

Description

Optimising the absorption step not only results in an efficient formation of the nitric acid, but in addition it prevents emissions of NO and NO_2 to air. In this section, the oxidation of nitrogen monoxide (NO) to nitrogen dioxide (NO_2), the absorption of NO_2 in water as N_2O_4 and the reaction of N_2O_4 to HNO_3 are considered as one step (i.e. the "absorption step"). These reactions are favoured by the same parameters:

High pressure:

The absorption stage in nitric acid production is favoured by high pressure. The benefit of high pressure is the efficient formation of nitric acid and the minimisation of NO_X emissions. The absorption step is carried out at pressures above atmospheric, and at least medium pressure (1.7 – 6.5 bar) is preferred in modern nitric acid plants, and is considered optimal [11, InfoMil, 1999].

Low temperature:

The absorption stage in particular nitric acid formation takes place in the lower third of the absorption column and is exothermic, so cooling is needed for heat removal. This is achieved by applying cooling before the absorption column to optimise absorption.

Optimal contact between NO_X, O_2 and water:

Optimal contact is mainly dependent on the absorption tower design. Several parameters contribute to an optimal design, e.g. the volume, the number and kind of trays used, the distance between the trays and the number of columns. In addition, a long residence time will ensure a high recovery of NO_X to form HNO_3, and also minimise NO_X emissions. Most nitric acid plants have a single absorption tower with sieve or bubble cap trays. The tray spacing progressively increases up to the top of the absorber.

Optimising these parameters for nitric acid production minimises the emission of non-oxidised NO and non-absorbed NO_2. Various systems are available, optimising one or more of the specified parameters.

High-pressure systems:

Absorption reactions are improved by optimising HNO_3 formation and reducing NO_X emissions. In mono-pressure processes, ammonia oxidation and NO_2 absorption take place at the same pressure. In general, 3 types of mono-pressure plants are possible: low pressure ($p < 1.7$ bar), medium pressure ($p = 1.7 - 6.5$ bar) and high pressure ($p = 6.5 – 13$). Dual-pressure plants, on the other hand, use a higher pressure for the absorption step than for the oxidation step. Most dual-pressure plants use a combination of low and medium pressure or a combination of medium and high-pressure. [11, InfoMil, 1999]

Extended absorption:

Extended absorption reduces NO_X emissions by increasing absorption efficiency. This is accomplished by either installing a single large tower, extending the height of an existing absorption tower, or by adding a second tower in series. Increasing the volume and the number of trays in the absorber results in more NO_X being recovered as nitric acid and in reduced emission levels. [11, InfoMil, 1999]

Extended absorption is sometimes combined with variable cooling. The lower 40 – 50 % of the absorber is cooled by normal cooling water. The balance of trays (50 – 60 %) in the absorber use chilled water or coolant at approx. 2 – 7 °C. This is accomplished by either a closed-loop refrigeration system using a proprietary refrigerant or by refrigeration from the ammonia evaporation system. [11, InfoMil, 1999]

High Efficiency Absorption:
During NO_2 absorption, some nitrous acid (HNO_2) is also formed. Nitrous acid may be formed as follows:

$$2\ HNO_2 + O_2 \leftrightarrow 2\ HNO_3$$
$$3\ HNO_2 \leftrightarrow HNO_3 + H_2O + 2NO$$

The 'High Efficiency Absorption' (HEA) process enables HNO_3 to be made without the formation of NO. The gas-liquid contacts in the absorption column are designed to increase the oxygen loading in the circulating acid. As a result, the oxidation of HNO_2 in the liquid phase is enhanced, thereby favouring the first reaction above rather than the second.

Achieved environmental benefits
A very low NO_X in the tail gas of up to 40 - 50 ppm NO_X (82 - 103 mg NO_X/m^3) is technically feasible if the absorption columns are completely optimised. However this will lead to economic penalties such as reduced steam export. The combination of technical and economic viability of a new absorption column, combined with the high absorption pressure, can result in values of up to 100 - 150 ppm (210 - 308 mg NO_X/m^3). The existing absorber column design limits the achievability of these figures, as absorption columns need to be retrofitted or replaced by a more modern design.

Cross-media effects
Extended absorption with an adjusted form of cooling can be expected to use more energy. Cooling systems are necessary to reach the lower temperatures.

Mono-pressure, high-pressure systems give a lower NO-yield at the oxidation stage compared to dual-pressure systems at the same absorption pressure. As a result, the production of nitric acid is less efficient and N_2O emissions are likely to be higher. [11, InfoMil, 1999]

Operational data

Applicability
High-pressure systems:
In existing plants, the pressure in the absorption unit can be raised within certain technical limits. In new plants, the absorption section can be designed to perform at high pressure, i.e. >6.5 bar. Using a mono-pressure, high-pressure plant will result in a lower NO yield, a bigger loss of catalyst and a higher energy usage compared to a dual-pressure, medium-high pressure plant. Some extra energy can be recovered as a result of the higher pressure, compensating in part for the extra energy input. Capital costs of a mono-pressure plant are lower, as an expensive compression unit is unnecessary [11, InfoMil, 1999].

Mono pressure operation has been shown in the past to give special economical advantages when feedstock and energy prices are low: low investment costs ensure a quick payback. If feedstock and energy prices are high, yield and energy efficiency must be maximised, so higher investment costs are more acceptable Plant size also plays an important role For a large production capacity (>1000 tonne 100 % HNO_3/day) it is more realistic to build a dual-pressure plant, [11, InfoMil, 1999]

Extended absorption abatement:
Extended absorption can be applied to existing and new plants. In existing plants, retrofit applications involve adding a second absorption column in series with an existing column, or replacing the old column(s) by a new design absorption column. New plants are generally designed with a single large column that is an integral component of the new plant design. Optimum design of the new absorption column, combined with a high pressure, can result in very low NO_X content in the flue-gas. [11, InfoMil, 1999]

The extended absorption abatement using a different form of cooling is only practical in nitric acid plants operating with an absorber pressure above 9 bar [11, InfoMil, 1999]. Also refrigeration equipment and associated pipe-work will need additional expenditure [11, InfoMil, 1999]

High Efficiency Absorption:
The HEA column can be applied both in existing and new nitric acid plants. In existing plants, the HEA column can be placed in series with an existing absorption tower [11, InfoMil, 1999].

Economics
In a dual-pressure system, stainless steel compressor units are necessary to compress NO_X. As a result, dual-pressure plants need investments that are $1^1/_2$ - 2 times higher than the investment for a mono-pressure plant [11, InfoMil, 1999]. On the other hand, a dual-pressure plant optimises the NO-yield and energy recovery, thereby recovering the higher investment costs. As stated above, a dual-pressure plant is more feasible if a large production capacity is desired (>1000 tonne 100 % HNO_3/day).

Total costs for NO_X removal using the HEA system are USD_{1998} 0.6/tonne HNO_3 produced ~EUR_{1998} 0.55/tonne HNO_3 produced; figures based on a 365 tonne 100 % HNO_3/day plant) [11, InfoMil, 1999]

Driving force for implementation

Example plants
A Nitrogen works in Tarnow (Poland) decided to replace its existing 8 production lines by one dual-pressure line (5 + 15 bar) of 700 tonne HNO_3/day. The Instytut Nawozow Sztucznych (INS) developed a computer programme to optimise the design of this new absorption column. This program could also simulate the performance of the absorption column. As a result of the high absorption pressure and the optimum design (structure of the sieve plates, distance between the sieve plates, size of the column), very low NO_X values were achievable.

Absorption pressure (bar)	HNO_3-conc. (%)	NO_X emission		Remarks
		ppm	mg/m^3	
15	65	100	205	Design values, low steam export
15	56	40	82	Low HNO_3-concentration, low steam export
12	60	130 - 170	267 - 349	Most economic option, high steam export

Table 2.8: Achievements of the nitric acid plant in Tarnow, Poland
[11, InfoMil, 1999]

The platinum/rhodium catalyst (catalyst used to oxidise NH_3) has gross losses of 0.1 g/tonne HNO_3: net losses are 0.02 g/tonne HNO_3 [11, InfoMil, 1999].

The nitric acid plant of Hydro Agri in Porsgrunn (Norway) was built in 1992 and has a capacity of 2000 tonne HNO_3/day. The ammonia oxidation takes place at 5 bar and the absorption at 11 bar. Due to the design of the absorption column and the temperature of the cooling water (as a result of the climate in Porsgrunn, the temperature of the water is 4 – 6 C without cooling), NO_X emissions at 80 - 90 ppm (164 - 185 mg NO_X/m^3) were achievable without using end-of-pipe measures. [11, InfoMil, 1999]

Reference literature
[11, InfoMil, 1999]

2.2.5 Optimisation of the start-up/shutdown

Description
The process of nitric acid production is unstable during start-up and shutdown. At start-up, NO_X emissions are higher (varying from 600 - 2000 ppm/1230 - 4100 mg NO_X/m^3) for the first 10 - 45 minutes, resulting in an extra emission of 100 - 1000 kg NO_X/year. Shutdown results in the same range of NO_X concentrations (600 - 2000 ppm/1230 - 4100 mg NO_X/m^3) during a shorter period (10 - 30 minutes), resulting in a maximum extra emission of 500 kg NO_X/year.

The application of installed end-of-pipe technologies is less possible, or even impossible, due to the unstable circumstances. [11, InfoMil, 1999]

During normal operations, the percentage of NO_2 in the NO_X varies between 50 and 75 %. Especially during start-up, the NO_2 emission is larger than the NO emission (70 % NO_2, 30 % NO), colouring the stack gas reddish-brown or yellow. The visual appearance of the stack gas is often a source of complaint from people living in the locality. [11, InfoMil, 1999]

Various techniques are available to reduce NO_X emissions during start-up and shutdown, but investments are often high compared to the amount of NO_X reduced. Extra NO_X emissions due to start-up and shutdown are less than 1 % of the overall NO_X emissions during the whole year. The measures could be specifically considered in order to reduce the visual nuisance of the colour of the plume. Possible end-of-pipe measures are described later, while possible process-integrated measures during start-up are described below:

- enlarging the absorption capacity: enlarging the absorption capacity (by adjusting the absorption column, see previous) will reduce NO_X emissions in general, and during start-up in particular
- steam injection in the stack: utilising steam injection in the stack will initiate a reaction between the steam (water) and nitrous oxides, forming nitric acid. [11, InfoMil, 1999]

Excess NO_X emissions can be prevented by stopping the ammonia feed and continuing the air compression, so maintaining process conditions. No vaporised ammonia is fed and the residual NO_X is absorbed. Sometimes during an unscheduled stoppage, this method can be used, thereby avoiding the need for a complete new start-up. Only the ammonia supply has to be restored. [11, InfoMil, 1999]

Achieved environmental benefits
Using the technologies described can significantly reduce NOx emissions during start-up. Figures to corroborate the reductions are unavailable.

The air pressure unit can be used in a dual-pressure plant to prevent additional emissions during complete shutdown.

Cross-media effects
Not available.

Operational data

Applicability

- enlarging the absorption capacity: in a new plant, the absorption section is designed to reduce NO_X emissions to a minimum during normal operating (see previous). It is expected that the NO_X emissions during start-up will also be reduced. The achievable values of existing plants are mainly limited by the absorber tower design [11, InfoMil, 1999]
- steam injection in the stack: Nitric acid formed in the stack is corrosive to normal stack construction materials. Stainless steel is used in most stacks to provide the necessary corrosion resistance [11, InfoMil, 1999].

Any dual-pressure plant can use the air compression unit to prevent elevated emissions during shutdown. The use of this technique in a mono-pressure plant is very dependent on the characteristics of the compressor unit [11, InfoMil, 1999].

Economics

- enlarging the absorption capacity: cost figures are unavailable, but these are dependent on the parameter being modified and the methodology used
- steam injection in the stack: installation of a steam injector and replacing the existing stack with one made of stainless steel, costs approximately EUR 204000.

No extra costs are incurred by using the air compressor unit to prevent additional emissions during shutdown in a dual-pressure plant.

Driving force for implementation

Example plants

The SZF5 plant of DSM Geleen (Netherlands) has a dual-pressure system, operating at 5 and 11 bar. By using the air pressure unit to maintain pressure during shutdown, additional emissions are completely prevented.

Reference literature

[11, InfoMil, 1999]

2.2.6 End-of-pipe measures

End-of-pipe measures are described in some detail compared to process integrated measure. This is simply because more information about end-of-pipe technology is available, but it is not a preference.

Many different end-of pipe technologies are described in literature, but no reliable reference plants are available. The technologies nevertheless are pertinent.

2.2.6.1 Selective catalytic reduction (SCR)

Description

The selective catalytic reduction of NO_X utilises the reaction of ammonia with nitrogen oxides, producing nitrogen and water vapour according to the following equations [11, InfoMil, 1999]

$$6NO+4NH_3 \leftrightarrow 5N_2 +6H_2O$$
$$6NO_2+8NH_3 \leftrightarrow 7N_2 +12H_2O$$
$$NO+NO_2+2NH_3 \leftrightarrow 2N_2 +3H_2O$$
$$4NO+O_2+4NH_3 \leftrightarrow 5N_2 +6H_2O$$

Ammonia or (evaporated) ammonia solution is injected, in the required stoichiometric amounts, into the waste gas stream. The ammonia reacts preferentially with the nitrogen oxides in the tail gas using a catalyst to initiate the reaction. [11, InfoMil, 1999]

Only certain catalysts can be used in nitric acid plants, although many different catalysts have been tested on a laboratory scale. Many companies can provide slightly different SCR systems, but the basic principle is always the same Table 2.9.

	BASF (Germany)		**Rhone-Poulenc (France)**	**CRI catalysts (Netherlands)**	**Institute of Catalysis and Petroleum Chemistry (Spain)**	**GIAP (Russia)**
Active component	V_2O_5		V_2O_5	Ti/V	CuO/NiO and Pt*	V_2O_5
Carrier material	Al_2O_3**	TiO_2**	Al_2O_3	Wire mesh type reactor housing	Al (all 4 beds)	--
Carrier structure	Honeycomb**	Honeycomb**	Spheres	Particles	CuO/NiO: cylinders Pt: spheres	--
Size components carrier	∅ pores=15nm**	∅ pores =4nm**	∅=3 mm	∅=1mm	CuO/NiO: 4 x 4 mm Pt: ∅ =3 mm	--
Operating range	--		170 – 400 °C	120 – 350 °C	--	--
Optimum temperature range	180 – 350 °C		240 – 300 °C	--	± 200 °C	250 – 300 °C
Pressure drop	0.04 - 0.1 bar		0.01 bar	<0.015 bar	--	--
Catalyst lifetime	>10 years		>10 years	***	--	--
Ammonia consumption	--		1.3 kg/tonne HNO_3	--	--	--
NO_X conversion	>90 %		90 – 98 %	>85 %	92 – 95 %	93 – 95 %
Formation of N_2O	negligible		negligible	0	not detected	not measured
NH_3 slip	<5 ppm (<3.8 mg/m^3)		<2 ppm (<1.5 mg/m^3)	<10 ppm (<7.6 mg/m^3)	0 - 1 ppm (0 - 0.8 mg/m^3)	<50 ppm (<38 mg/m^3)
Costs	--		--	EUR 0.36/kg NO_X removed	--	--
First application on industrial scale	1975		1981	1995	1982	end of the 1960s
Number of nitric acid plants	>35		>50	3	10	>10
References	[11, InfoMil, 1999]					

* This multibed system is based on 4 beds (2 of each kind)
** BASF started using a TiO_2 carrier instead of an A1203 carrier (approx. 1993)
***First SCR facility installed in a nitric acid plant in 1995 ∅=cross-sectional diameter

Table 2.9: Variations between some suppliers of SCR catalysts (based on suppliers information)

Achieved environmental benefits

Advantages:

- high NO_X conversion of 80 – 95 % can be obtained. As a result, low NO_X contents can be achieved. In most cases, a NO_X emission of 100 ppm is possible. Lower values (75 ppm/154 mg/m^3) have been achieved [11, InfoMil, 1999]
- low optimum operating temperature varying from 200 to 350 °C [11, InfoMil, 1999]
- low pressure drop before the expander unit of 0.01 - 0.1 bar [11, InfoMil, 1999]
- ammonia reacts preferentially with nitrogen oxides so less reducing agent is needed compared to NSCR [11, InfoMil, 1999]
- the tail gas temperature after reduction of 200 – 360 °C is significantly lower than in non selective processes of 650 – 800 °C, allowing the use of simpler, cheaper construction materials [11, InfoMil, 1999]
- ammonia is readily available in a nitric acid plant. [11, InfoMil, 1999]

Disadvantages:

- at higher temperatures, i.e. >350 °C, some side reactions take place. A possible side reaction is the formation of nitrous oxide (N_2O), according to the equations: [11, InfoMil, 1999]

$$4NO+4NH_3 +3O_2 \leftrightarrow 4\ N_2O+6H_2O$$
$$8NO+2NH_3 \leftrightarrow 5\ N_2O+3H_2O$$
$$8NO_2+6NH_3 \leftrightarrow 7N_2O+9H_2O$$
$$2NH_3 + 2O_2 \leftrightarrow N_2O + 3\ H_2O$$

Older catalysts in particular can produce some N_2O. Another possible side reaction at higher temperatures is the oxidation of ammonia, according to the equation [11, InfoMil, 1999]:

$$4NH_3+3O_2 \leftrightarrow 2\ N_2+6H_2O$$

These side reactions have a detrimental effect on the ammonia usage and produce unwanted components (nitrous oxide). At 400 °C, about 5 – 10 % of the NH_3 can be taken up by side reactions. [11, InfoMil, 1999]

At lower temperatures <200 °C and during start-up, the formation of ammonium nitrate (NH_4NO_3) and/or ammonium nitrite (NH_4NO_2) is possible. The formation of these salts could damage the expansion turbine blades or even cause explosions. Some SCR facilities operate at temperatures below or close to 200 °C, increasing the risk of salts formation [11, InfoMil, 1999]

All SCR facilities have some ammonia slip. Most SCR facilities are designed for an ammonia slip less than 10 ppm (7.6 mg/m^3), but this improves during normal operating. The chance of ammonia slip is reduced by utilising a good mixing of ammonia with the tail gas. [11, InfoMil, 1999]

The SCR catalyst has to be replaced when it starts to lose efficiency. The lifetime of the catalyst varies between suppliers, but a lifetime of at least 10 years has been proven. Normally, all spent catalysts are recycled by the catalyst manufacturer. [11, InfoMil, 1999]

The production of ammonia has an environmental effect. This effect is small compared to the achieved NO_X reduction. If a stoichiometric NH_3: NO_X molar ratio of 1:1 is assumed, the reduction of one tonne of NO_X at a nitric acid plant would require 0.37 tonnes of ammonia. The production of ammonia (according to the most common "conventional steam reforming process") has the following main environmental issues:

- NO_X emission of 450 - 1300 g/tonne ammonia
- energy consumption (feedstock and fossil fuel) of 29 - 31 GJ/tonne ammonia.

It can be calculated from these figures, that NO_X generation resulting from ammonia production is only 0.02 to 0.05 % of the amount of NO_X reduced by the use of ammonia in a SCR. Likewise, the energy consumption needed to reduce one tonne of NO_X is around 10 GJ. [11, InfoMil, 1999]

Cross-media effects
Ammonia is used as a reducing agent. The environmental effects of NH_3 production are small compared to the reduction obtained, as previously stated. Ammonia slippage is unavoidable, but most SCR facilities are designed to have an ammonia slip of less than 10 ppm (7.6 mg/m^3). Older catalysts in particular could produce some N_2O at higher temperatures (>350 °C), but no figures are available.

Operational data

Applicability
In principle, SCR facilities can be applied in both new and existing nitric plants and can operate at all pressures. The tail gas needs heating to the operational temperature depending on the catalyst being used i.e. between 120 °C and 400 °C. This is normally carried out by passing the tail gas through a heat-exchanger using heat recovered from the ammonia oxidation unit. An SCR facility can be used both before and after the expander.

NO_X removal from nitric acid plants using SCR presents significant differences in comparison to removal of this contaminant from e.g. power plants, mainly due to the differing compositions of the untreated gases. The high NO_2 concentration in the tail gases of a nitric acid plant i.e. the percentage of NO_X in the NO, varies between 50 – 75 %, and this significantly affects the catalyst behaviour [11, InfoMil, 1999]. As a result of this some catalysts used in power plants cannot be used in nitric acid plants.

Several factors can influence the performance of the SCR facility:

NH_3/NO_X mole ratio:
Equi-molar quantities of NH_3 need be added to ensure the maximum NO_X reduction. Ammonia injected in excess of stoichiometric requirements leads to ammonia slippage [11, InfoMil, 1999]

Gas stream temperature:
The gas temperature in the SCR reactor chamber must be within the operating range (and preferably the optimum temperature range) of the catalyst to achieve an efficient operation. The operating range varies from 120 to 400 °C [11, InfoMil, 1999]

Gas residence time:
Gas residence time is primarily a function of the flue-gas flow and the catalyst volume. As the flue-gas flow increases, the residence time of the gas within the catalytic reactor decreases, along with the NO_X removal efficiency. [11, InfoMil, 1999].

Economics
In 1998, the Dutch Ministry of Housing, Spatial Planning and the Environment (in Dutch: VROM for short) had an inventory made of NO_X sources in the Netherlands, including possible measures and matching costs. Research was split in two: large sources (>250 tonne NO_X/year) and remaining sources. In most cases, the best technical results were obtained with SCR [11, InfoMil, 1999]. A simulated nitric acid plant is described in the following Table 2.10.

Flue-gas flow	40000 m^3/h
Flue-gas temperature	250 °C
Flue-gas pressure	9 bar
NO_X concentration (before DeNox)	12000 mg/m^3 (= 975 ppm/2000 mg/m^3)
Chosen SCR-type	Low temperature (T=200 ºC)
Pressure drop SCR	<8 mbar
Installation SCR	Before the expander_unit
NO_X reduction	85 % (→ = 145 ppm/300 mg/m^3)

Table 2.10: Design of a simulated acid plant

In this simulated situation, the total costs for NO_X removal (assuming 85 % reduction) was 1.7/kg NO_X removed (≈ EUR_{1999} 0.77/kg NO_X removed). The average accuracy of these estimations is ± 40 %. Catalyst costs can influence the total costs strongly, varying from 2 to 36 % [11, InfoMil, 1999].

According to [11, InfoMil, 1999], the capital costs of an SCR facility are EUR 2000000 (based on a medium/high dual-pressure plant, production of 1000 tonne 100 % HNO_3/d (≈ 365 kt/d) and an operating time of 8400 h/yr). The annual costs (under the same conditions) are EUR 300000. According to [11, InfoMil, 1999], the total costs of tail gas cleaning using the DCN system are c. 1.3 US $1998/tonne HNO_3 produced (≈ 1.16 EUR_{1998}/tonne HNO_3 produced).

According to [11, InfoMil, 1999], the price of an SCR catalyst varies between 35000 and 53000 (≈ EUR/m^3 32000 - 49000). Technical and maintenance costs are excluded. A catalyst volume of 3.75 m^3 is required to treat a flowrate of 48235 d/h. In this example, 77 kg NH_3/hr are necessary to reduce the NO_X concentration from 2000 ppm to 150 ppm (from 4100 mg/m to 308 mg/m^3). As a result, fuel operating costs are USD 15.40/h (≈ EUR 14.20/h)[1] or USD 1.03/tonne 100 % HNO_3 produced (≈ EUR 0.95)[2]. Note, this only includes catalyst and ammonia costs. Installation, maintenance and depreciation are excluded.

[1] Based on a price of USD 200/MT NH_3 (= EUR 185/Mtonne NH_3)
[2] Assuming an average flow of 3230 m^3/tonne 100 % HNO_3 (derived from [11, InfoMil, 1999] and 8640 operating hours/year, a flow of 48235 m^3/hr = 129 ktonne 100 % HNO_3/year).

Driving force for implementation

Example plants

DSM Agro Geleen (the Netherlands) has 2 nitric acid plants, referred to as SZF4 and SZF5. Both plants produce 60 % HNO_3. SZF4 has a capacity of 575 t/d and operates at a pressure of 5 bar (mono pressure). In 1989, an SCR facility was installed in SZF4, operating at a temperature of c. 285 °C. The NO_X inlet is ± 2200 ppm; the NO_X outlet is 75 ppm. Ammonia slippage has not been detected. According to [11, InfoMil, 1999] a possible contribution of the SCR facility to the overall N_2O emission cannot be detected. [11, InfoMil, 1999]

A SCR facility has been installed in SZF5 in 1999. This plant has a dual pressure system (5 bar at the oxidation step and 11 bar at the absorption step) and has a capacity of 1600 t/d. The NO_X inlet is 170 ppm (350 mg/m^3). The licensed concentration is 170 ppm (348 mg/m^3). The average yearly value in 2002 was 68 mg/Nm^3. [11, InfoMil, 1999]

Kemira Agro Denmark has 3 nitric acid plants, producing respectively 200, 450 and 650 tonnes of 100 % HNO_3/day. All three plants produce 62 % nitric acid. Kemira Agro Denmark used to have 4 plants. The SCR facility previously installed on one of the redundant units has been re-installed on the 200 t/day plant (= 73 ktonne 100 % HNO_3/year). This plant is operating at dual-pressure: the burning chamber is at atmospheric pressure, whilst absorption takes place at a pressure of 3.5 bar. [11, InfoMil, 1999]

The SCR is installed before the expander unit. The tail gas entering the SCR has a temperature of 210 °C and a NO_X content of 500 ppm (1025 mg/m^3). The tail gas leaving the stack has a NO_X content of 100 ppm (205 mg/m^3). No ammonia is detected in the tail gas. Nitrous oxide is not measured, but expectations are that the SCR facility will have no influence on the N_2O level. Despite the relatively low temperatures in the SCR facility, Kemira Agro Denmark has no problems with the formation of ammonium nitrate and ammonium nitrite. Due to moving the SCR to a different plant, the capital and annual costs cannot be determined yet [11, InfoMil, 1999].

BASF Antwerpen (Belgium) has 4 nitric acid plants, 3 of which have an SCR facility. These 3 plants are all dual-pressure plants: the oxidation stage is around 5 bar, while the absorption stage is around 10 bar. The throughputs are 650, 945 and 945 tonnes of 100 % HNO_3/day. [11, InfoMil, 1999].

All 3 SCR facilities operate at a temperature of about 350 °C. The 650 t/day plant has a NO_X inlet of 200 - 300 ppm (410 - 610 mg/m^3); the NO_X outlet is <100 ppm (<205 mg/m^3). Both 945 t/day plants have a NO_X inlet of 400 - 500 ppm (820 - 1025 mg/m^3); the NO_X outlet is <120 ppm (<245 mg/m^3). The ammonia slip is always below 10 ppm (7.6 mg/m). Most of the time, the ammonia slip is less than 5 ppm ammonia (3.8 mg/m). The SCR facility does not contribute to the overall N_2O level of BASF Antwerpen. [11, InfoMil, 1999]

The nitric acid plant of Sasol Mining Explosives (SMX) in Sasolburg (South Africa) has a capacity of 115 t/day (= 65 ktonne 100 % HNO_3/year), producing 56 % nitric acid. It has a working pressure of 4.5 bar (mono-pressure) [11, InfoMil, 1999].

The SCR is sited after the expander unit. The tail gas entering the SCR has a temperature of 230 °C and a NO_X content of 1200 ppm (2460 mg/m^3). The tail gas leaving the stack has a NO_X content of 200 ppm (410 mg/m^3). The ammonia slip and the nitrous oxide emission are not measured.

The Institute for Nitrogen Industry (GIAP) in Moscow (Russia) has developed 2 types of nitric acid plants. The UKL-7 is a mono-pressure plant operating at 7 bar, producing 120 ktonne 100 % HNO_3/year. The AK-72 operates on dual-pressure (4+10 bar) and produces 380 ktonnes of 100 % HNO_3/year. About 90 UKL-7 plants and about 16 AK-72 plants are installed, mainly in Russia and CIS-countries. [11, InfoMil, 1999]

Approx. 10 plants (both UKL-7 and AK-72) have an SCR facility to reduce NO_X in the tail gas. The SCR facility in an UKL-7 plant works at a temperature of 250 – 280 °C and reduces the NO_X concentration from around 1000 ppm (2050 mg/m^3) to 50 ppm (103 mg/m^3). In an AK-72 plant, the SCR facility operates at 280 – 300 °C reducing the NO_X concentration from ± 700 ppm (1435 mg/m^3) to 50 ppm (103 mg/m^3). In both systems, the ammonia slip is approx. 50 ppm (38 mg/m^3). [11, InfoMil, 1999]

AGROLINZ GmbH operates two nitric acid plants, referred to as line E and line F, for the production of weak nitric acid with a concentration of 59.6 % HNO_3.

- line E is a dual-pressure plant (M/H process) and has a capacity of 300000 t/yr. Working pressures are 3.3 bar for ammonia oxidation and 8 bar for the absorption (pressures above atmospheric). In 1994, a supplementary SCR reactor was installed in line E. The NO_X concentration of the waste gas leaving the absorption column is <500 ppm (<1000 mg NO_X/Nm^3 as NO_2). The NO_X concentration of waste gas leaving the SCR reactor is about 180 – 190 mg/Nm^3. Ammonia slip is between 0.26 and 2.6 mg/Nm^3
- line F is a dual-pressure plant (N/M process) and has a capacity of 180000 t/yr. Working pressures are -0.08 bar (slight negative pressure) for ammonia oxidation and 3.8 bar for the absorption (pressures above atmospheric). As part of an adaptation project (1992), an SCR reactor was installed in line F. The NO_X concentration of the waste gas before the SCR reactor is 2000 – 3000 ppm (4000 – 6000 mg NO_X/Nm^3 as NO_2). The NO_X concentration of waste gas leaving the SCR reactor is about 320 – 330 mg/Nm^3. Ammonia slip is between 0.05 mg/Nm^3 and 0.10 mg/Nm^3.

Reference literature
[11, InfoMil, 1999]

2.2.6.2 Non Selective Catalytic Reduction (NSCR)

Description
The non-selective catalytic reduction of NO_X enables the reaction of a reducing agent (fuel) with nitrogen oxides, to produce nitrogen and water. This process is termed non-selective because the fuel first depletes all the free oxygen present in the tail gas and then removes the NO_X. The fuels used are natural gas or methane (CH_4), hydrogen (H_2) or ammonia plant purge gas (mainly H_2) and naphtha. An excess of the reducing agent is required to reduce nitrogen oxides to nitrogen. [11, InfoMil, 1999]

When an excess of methane (natural gas) is present, the following reactions take place:

$$CH_4 + 2O_2 \leftrightarrow CO_2 + 2H_2O$$
$$CH_4 + 4NO_2 \leftrightarrow CO_2 + 2H_2O + 4NO$$
$$CH_4 + 4NO \leftrightarrow CO_2 + 2H_2O + 2N_2$$
$$CH_4 + 4N_2O \leftrightarrow CO_2 + 2H_2O + 4N_2$$

When an excess of hydrogen or purge gas is present, the following reactions take place:

$$2H_2 + O_2 \leftrightarrow 2\ H_2O$$
$$H_2 + NO_2 \leftrightarrow 2H_2O + NO$$
$$2H_2 + 2NO \leftrightarrow 2H_2O + N_2$$
$$H_2 + N_2O \leftrightarrow H_2O + N_2$$

NSCR catalysts are usually platinum, vanadium pentoxide, iron oxide or titanium based; catalyst supports are typically made of aluminia pellets or a ceramic honeycomb substrate. The fuel requirement is determined by the stoichiometric amount needed to reduce all the oxygen present, i.e free oxygen and that in nitrogen oxides, plus an excess around 0.5 % CH_4. The amount of fuel can be increased to maintain the same NO_X value in the tail gas as the catalyst ages and degenerates. [11, InfoMil, 1999]

The tail gas must be preheated before the catalyst initiates the reaction. The preheat temperature is directly related to the fuel selected, varying from 200 – 300 °C (H_2) to 450 - 575 °C (natural gas). The tail gas temperature can increase in excess of >800 °C due to the exothermic reactions in the NSCR facility, which is greater than the maximum temperature permissible for the unit. In this case with these high temperatures, two methods of NSCR have been developed: single-stage and two-stage reduction [11, InfoMil, 1999].

Single stage units can only be used when the oxygen content of the absorber tail gas is <2.8 %. An oxygen content of 2.8 % will result in a tail gas temperature of about 800 °C after the NSCR unit. The effluent gas from these units must be cooled by a heat-exchanger or quenched to meet the temperature limitation of the gas expander unit. [11, InfoMil, 1999]

Two stage units with an internal quench section are used when the oxygen content is >3 %. Two systems of two-stage reduction are used. One system uses two reactor stages with interstage heat removal. The second system involves a preheating of 70 % of the tail gas to about 480 °C, mixing it with more fuel, and then passing it over the first stage catalyst bed. The amount of fuel added to the first stage is adjusted to obtain the required outlet temperature. The remaining 30 % of the tail gas, preheated to about 120 °C, is combined with the first stage exit gas. The two streams and fuel to complete the reduction are together passed over the second stage catalyst bed. The tail gas after the second stage then passes to the tail gas expansion turbine. [11, InfoMil, 1999]

Achieved environmental benefits

Advantages:

- NO_X conversions of >90 % can be obtained, resulting in a low NO_X content (100 - 150 ppm/205 - 308 mg/m^3)
- CH_4 or H_2 can be used as the reducing agent if they are frequently available at a relatively low cost from an adjacent ammonia plant
- non selective oxidation is exothermic, raising the temperature by 130 °C when 1 % oxygen with natural gas as fuel is used, whilst the temperature is raised 150 °C when 1 % oxygen is used with hydrogen as the fuel. This gas temperature rise gives the opportunity to generate power using a gas turbine
- an NSCR facility reduces the NO_X as well as reducing the N_2O emission, in accordance with the reactions:

$$CH_4 + 4\ N_2O \leftrightarrow CO_2 + 2\ H_2O + 4N_2$$

$$H_2 + N_2O \leftrightarrow H_2O + N_2$$

- A reduction of N_2O of at least 95 %, results lowering emissions well below 50 ppm NO (<100 mg NO/m^3) [11, InfoMil, 1999]

Disadvantages:

- using hydrocarbon fuels leads to emissions of carbon monoxide (CO), carbon dioxide (CO_2) and hydrocarbons (C_XH_y). Normally, carbon monoxide emission will be less than 1000 ppm (1250 mg/m^3), but emissions of hydrocarbons can be up to 4000 ppm. Emissions of CO_2 can be over 6300 ppm (12348 mg/m^3) [11, InfoMil, 1999]
- the tail gas needs a high preheat temperature, especially when hydrocarbon fuels are used. The tail gas needs heating from 50 °C to between 250 – 300 °C for H_2 or to 450 – 550 °C for natural gas. This abatement technique can use the excess heat from the process, but this reduces the potential amount of exportable steam [11, InfoMil, 1999]
- the high tail gas temperature after the NSCR facility, necessitates the use of more expensive construction materials [11, InfoMil, 1999]
- the NSCR facility cannot be started until the oxygen content has stabilised. The oxygen content must be monitored and controlled to prevent temperatures that could lead to catalyst deactivation (T<800 °C). In a one stage NSCR, problems could occur when the oxygen content is >2.8 % [11, InfoMil, 1999]
- when hydrocarbon fuels are used, the expected lifetime of the catalyst is reduced to 3 - 5 years. When e.g. hydrogen is used as a fuel, the lifetime of the catalyst will be much longer. [11, InfoMil, 1999]

Cross-media effects

When hydrogen is used as a fuel, no cross-media effects occur. When using hydrocarbons (C_XH_y) as a fuel, emissions of carbon monoxide (CO), carbon dioxide (CO_2) and hydrocarbons (C_xH_y) occur. [11, InfoMil, 1999]

Operational data

Applicability

In principle, NSCR facilities can be applied to both new and existing nitric acid plants operating at any pressure. As stated above, the tail gas must be preheated to initiate the reaction. Energy is needed to heat the tail gas. Furthermore, high temperature equipment (e.g. a gas expansion turbine) is needed to handle the exit gases from the NSCR. Major modifications are needed for retrofitting an existing plant, which makes the installation of an NSCR unattractive. [11, InfoMil, 1999]

Several factors can influence the performance of the NSCR facility [11, InfoMil, 1999]:

- oxygen content of the absorber tail gas: it is essential that the oxygen content of the inlet gas to the catalytic converter is controlled. An excessive O_2 content can result in high tail gas temperatures. The exit temperature increases by about 130 °C for every one per cent of oxygen consumed when using hydrocarbon fuels. Using hydrogen as fuel increases the temperature by 150 °C for each per cent oxygen consumed. The final reduction reaction must be limited to approx. 800 °C. due to the thermal limitations of the catalyst. This tail gas oxygen limit is equivalent to about 2.8 O_2 %, which limits catalyst deactivation in a single stage unit [11, InfoMil, 1999]
- fuel type: the type of fuel selected is based mainly on availability and cost (e.g. natural gas and hydrogen are readily available in some ammonia plants). The fuel must be compatible with the thermal constraints of the NSCR facility as mentioned above
- concentration/flow distribution: The fuel requirement is the stoichiometric amount needed to reduce all the oxygen present (i.e. free oxygen and that present in nitrogen oxides) with an excess. Less surplus fuel is needed when hydrogen is used, in comparison to hydrocarbon fuel. Poor control of the fuel/oxygen ratio can lead to carbon deposition on the catalyst, which reduces its effectiveness. Excessive fuel consumption can be minimised by employing a close control of the fuel/tail gas mixing and the flow gas distribution through the catalyst bed [11, InfoMil, 1999]
- catalyst support type: Different types of catalyst support can affect the system performance. Honeycomb supports give a relatively low-pressure drop. The available surface area of the honeycomb structure allows greater exposure of the tail gas to the embedded catalyst. Honeycomb supports however are more susceptible to damage by overheating. Pellet beds on the other hand have proven more durable but offer less gas space velocity. In addition, there is evidence that catalyst fines from pellet beds can lead to gas turbine blade erosion. [11, InfoMil, 1999]

Economics

According to [11, InfoMil, 1999] the price of an NSCR catalyst varies between 106000 and USD 143000/m^3 (≈ EUR 98000 - 131000/m^3). Technical and maintenance costs are excluded. A catalyst volume of 1.20 m^3 is required to treat a flowrate of 48235 d/h. In this example, 290 m^3 natural gas/h are necessary to reduce the NO_X concentration from 2000 ppm to 150 ppm (from 4100 to 308 mg/m^3). As a result, fuel operating costs are USD 29.0/hr (≈EUR 26.8 h/r) or USD 1.95/tonne 100 % HNO_3 produced (≈ EUR 1.80). Note that this only includes the catalyst and ammonia costs. Installation, maintenance and depreciation are excluded. Some of the cost of the natural gas will be credited to increased power recovery. On the other hand, the high temperatures (T>800 °C) reduce the lifetime of the catalyst to 3 - 5 years.

The capital costs for the NSCR unit as supplied by GIAP (Russia) is 5 – 10 % of the total plant cost (including the catalyst). [11, InfoMil, 1999]

Driving force for implementation

Example plants
Kemira Agro Rozenburg (the Netherlands) has a capacity of 400 ktonne of 100 % HNO_3/year and operates at 9 bar (mono-pressure). This plant of Kemira Agro Rozenburg is designed to be combined with a NSCR [11, InfoMil, 1999].

The NO_X concentration before abatement is about 2000 ppm/4100 mg/m^3 (estimation); the NO_X emission after the NSCR is about 100 ppm/205 mg/m^3 (estimation). This system of Kemira Agro Rozenburg considerably reduces the emission of N_2O to about 27 ppm/53 mg/m^3 (measurement). Kemira Agro Rozenburg uses natural gas as a fuel, resulting in emissions of CH_4 of 0.4 tonne/yr, CO of 0.7 tonne/yr, CO_2 of 6216 tonne/yr and VOC of 0.3 tonne/yr.

The Institute for Nitrogen Industry GIAP in Moscow (Russia) has developed 2 types of nitric acid plants. The UKL-7 is a mono-pressure plant operating at 7 bar, producing 120 ktonne of 100 % HNO_3/year. The AK72 operates on dual-pressure (4+10 bar) and produces 380 ktonne of 100 % HNO_3/year. About 90 UKL-7 plants and about 16 AK-72 plants are in operation, mainly in Russia and CIS-countries [11, InfoMil, 1999].

About 90 plants (both UKL-7 and AK-72) have an NSCR facility to reduce NO_X in the tail gas. The catalyst in the NSCR facility consists of two beds: the first bed is made of $A1_2O_3$ and 2 % lead (Pb), while the second bed is made of $A1_2O_3$. The catalyst has a lifetime of up to 5 years. Natural gas (CH_4) is used as a fuel, so the tail gas needs to be preheated to 450 – 500 °C. The NSCR facility in an UKL-7 plant reduces the NO_X concentration from ± 1000 ppm to 50 ppm (from 2050 mg/m^3 to 103 mg/m^3); in an AK-72 plant, the NO_X concentration is reduced from ± 700 ppm to 50 ppm (from ± 1435 mg/m^3 to 103 mg/m^3). In both systems, the tail gas contains up to 1200 ppm CO (1500 mg/m^3) and up to 200 ppm CH_4 (142 mg/m^3). [11, InfoMil, 1999]

After NO_X reduction, the hot tail gas (680 – 800 °C) vents through the high temperature tail gas expansion turbine and waste heat boiler. The steam export is about 1.0 Gcal/tonne HNO_3 (= 4.18 GJ/tonne HNO_3). [11, InfoMil, 1999]

Reference literature
[11, InfoMil, 1999]

2.2.6.3 NO_X reduction during start-up/shutdown

Description
The process for producing nitric acid is unstable at start-up and shutdown. At start-up, NO_X emissions are higher (varying from 600 - 2000 ppm/1230 - 4100 mg NO_X /m^3) for the first 10 - 45 minutes, giving an extra emission of 100 - 1000 kg NO_X/year. Shutdown results are in the same range as NO_X concentrations (600 - 2000 ppm/1230 - 4100 mg NO_X/m^3) for 10 - 30 minutes, giving a maximum extra emission of 500 kg NO_X/year. It is impossible to install end-of-pipe technologies in these unstable conditions. [11, InfoMil, 1999]

During normal operation, the percentage NO_2 in the NO_X varies between 50 – 75 %. Especially during start-up, the NO_2 emission is larger than the NO emission (70 % NO_2, 30 % NO), colouring the stack gas reddish-brown or yellow. The visual appearance of this stack gas often results in complaints from people in the locality. This is a local problem and therefore will not be described in detail. [11, InfoMil, 1999]

Various techniques are available to reduce NO_X emissions during start-up and shutdown, but investments are often high compared to the amount of NO_X reduction achievable. Extra NO_X emissions due to start-up and shutdown are less than 1 % of the overall NO_X emissions during a year. The measures could be considered to reduce the visual appearance of a fume. Possible process-integrated measures have been described previously whilst potential end-of-pipe measures during start-up are described below:

Heating the tail gas:
A furnace, steam heater or separate burner could be used to heat the tail gas. Operated between 180 and 450 °C, at the optimum for SCR/NSCR this measure will reduce NO_X at an earlier stage and minimise the start-up period.

Installing a low temperature SCR:
Installing an SCR facility with a large temperature range will allow NO_X reduction at lower temperatures (from 180 °C and higher) and as a result shorten are down-time for the SCR. [11, InfoMil, 1999]

Installing a scrubber:
Excessive emissions at start-up can be minimised by the use of caustic, sodium carbonate or ammonia alkali scrubber [11, InfoMil, 1999].

Installation of a tower with a dry adsorbent material:
NO_X reduction at start-up can be achieved by using a dry adsorbent e.g. silica gel or molecular sieves [11, InfoMil, 1999].

The above procedures are less suitable during shutdowns, as pressure and temperature quickly reduce [11, InfoMil, 1999].

Achieved environmental benefits
Heating the tail gas:
Exact figures are not known, but a NO_X reduction of at least 70 % during part of the start-up can be expected.

Installing a low temperature SCR:
Exact figures are not known. Despite the lower temperature (from 180 °C and higher), some extra emissions during start-up will take place, but for a shorter period of time. During the period that the SCR facility operates, a NO_X reduction of 80 – 95 % can be obtained.

Installing a scrubber:
Exact figures are not known, but NO_X reduction of at least 70 % during start-up can be expected.

Installation of a tower with a dry absorbent material:
Figures, not known but a NO_X reduction of at least 70 % during start-up can be expected.

Cross-media effects
Heating the tail gas:
Energy is required to raise the temperature to the optimum needed for the SCR- or NSCR facility. [11, InfoMil, 1999]

Installing a low temperature SCR:
The NH_3 added to the SCR and the nitrous gases in the tail gas could react to form ammonium nitrate or ammonium nitrite when the tail gas passes through an SCR as a result of these unstable process conditions and low temperatures during start-up. Deposits of these salts could potentially cause an explosion. The temperature of the tail gas must be 180 °C or higher when the SCR is started to minimise the risk. [11, InfoMil, 1999]

Installing a scrubber:
A large amount of water vapour will escape from the scrubber liquid due to the high tail gas temperature when an SCR is used at between 200 and 350 °C. As a result, water consumption is high. The used scrubber fluid cannot be re-used, and is has to be disposed of waste [11, InfoMil, 1999]

Installation of a tower with a dry adsorbent material:
The spent adsorbent material is a waste for disposal. [11, InfoMil, 1999]

Operational data

Applicability
Heating the tail gas:
A tail gas heating unit needs lots of space, particularly when enclosed, but can be applied in new and existing nitric acid plants with an SCR or an NSCR. Energy is needed to raise the temperature to the optimum needed for the SCR or NSCR facility, i.e. 180 °C to 450 °C [11, InfoMil, 1999].

Installing a low temperature SCR:
Enough space should be available to install this facility. When the old catalyst is replaced, the new one should fit into the facility.

Installing a scrubber:
There must be enough room to place the rather large scrubber facility.

Installation of a tower with a dry adsorbent material:
Free space must be available and sufficient to install an adsorber facility. The high temperatures that are necessary before the SCR can be started i.e. 200 – 350 °C, could damage the adsorbent [11, InfoMil, 1999].

Economics
Generally, most end-of-pipe technologies to reduce start-up and shutdown emissions are quite expensive in comparison to the NO_X reduction. These measures do however reduce the visual appearance from the reddish-brown or yellow stack gas.

Heating the tail gas:
Equipment costs for a burner are about FRF 200000 (≈EUR 91000). Installing a furnace (equipment and engineering) will cost at least FRF 1000000 (EUR 450000). Other economics are not known. [11, InfoMil, 1999]

Installing a low temperature SCR:
Capital costs of a complete SCR-facility are at least FRF 1000000 (≈EUR 450000). To reduce only the start-up emissions, the costs of an SCR are unacceptable in most cases. Other economics are not known. [11, InfoMil, 1999]

Installing a scrubber:
Since water cannot be used as a scrubber fluid (the NO_X turns the tail gas acid, so an alkaline scrubber liquid is required), the annual costs of the scrubber are expected to be considerable, although the exact figures are not known. [11, InfoMil, 1999]

Installation of a tower with a dry absorbent material:
Annual costs are expected to be considerable, since the saturated absorbent material has to be replaced regularly. Exact figures are not known [11, InfoMil, 1999].

Driving force for implementation

Example plants
No reference plants were found.

Reference literature
[11, InfoMil, 1999]

2.2.6.4 Other measures mentioned in literature

As mentioned already many end-of-pipe technologies are described in literature. Unfortunately, no reliable references were found for these following technologies.

Chemical scrubbing or absorption
Scrubbing the tail gas with a scrub liquid to reduce NO_X emissions is often mentioned in literature. Various methods are described, but all of them seem to encounter the same problems related to the scrub liquid: high costs, few possibilities for regeneration of the used liquid, large quantities of liquid and an adverse environmental impact of the used liquid. Some methods are described below:

Ammonia scrubbing
In 1973, Goodpasture Texas, US, developed a process that uses ammonia as a scrubbing liquor. Here the NO_X in the tail gas reacts with ammonia, forming a solution of ammonium nitrate (NH_4NO_3) and ammonium nitrite (NH_4NO_2) according to the reactions:

$$2NO_2 + 2\ NH_3 \leftrightarrow N_2 + H_2O + NH_4NO_3$$
$$2NO_2 + 2NH_3 + H_2O \leftrightarrow NH_4NO_3 + NH_4NO_2$$

The formation of NH_4NO_2 is surpressed by aeration and the presence of free acid. The scrubbing product is a 30 – 50 % ammonium nitrate solution, while the NO_X emissions are reduced to 200 ppm. Installation in both new and existing plants of any pressure is possible as the system has a low-pressure drop of 0.07 - 0.13 bar. [11, InfoMil, 1999]

Special precautions must be taken to prevent the deposition of mainly NH_4NO_3 on the gas turbine, as this may cause serious damage to the turbine. Ammonia has to be used within strict safety limits. Furthermore, additional equipment (evaporators) is necessary to concentrate the ammonium nitrate solution to 85 %, essential for usage in the fertiliser industry. [11, InfoMil, 1999]

Urea scrubbing
In this process, an aqueous solution of urea ($CO(NH_2)_2$) is used as a scrub liquid. The overall reaction is:

$$HNO_2 + CO(NH_2)_2 + HNO_3 \leftrightarrow N_2 + CO_2 + NH_4NO_3 + H_2O$$

Recirculation of the scrubbing solution causes the concentration of nitric acid and ammonium nitrate to rise. A bleed stream is thus needed to keep the system in balance. In addition, the scrubbing solution needs cooling to maintain temperature control. Urea is readily available in most fertiliser plants and is relatively cheap. This process has been reported to reduce NO_X emissions from 4000 to 100 ppm. Both MASAR and Norsk Hydro developed urea scrubbing systems: MASAR developed the system described above. [11, InfoMil, 1999]

Hydrogen peroxide scrubbing
Several Japanese firms have developed systems with hydrogen peroxide (H_2O_2) scrubbing based on the following overall reactions:

$$NO + NO_2 + 2H_2O_2 \rightarrow 2HNO_3 + H_2O$$
$$2NO_2 + H_2O_2 \rightarrow 2HNO_3$$

Scrubbing with hydrogen peroxide has some advantages. The hydrogen peroxide scrubbing gives a NO_X conversion of 90 % and higher, resulting in nitric acid but without the need to add impurities. Furthermore, the process is fast at moderate temperatures of 30 – 80 °C. However hydrogen peroxide is very expensive. Based on a NO_X concentration of 2000 ppm (4100/1230 - 4100 mg NO_X/m) and a gas flow of 48235 d/h, hydrogen peroxide costs are around USD 22.75/tonne 100 % HNO_3 (≈EUR 21.0/tonne 100 % HNO_3). Selling the formed nitric acid repays some of the costs.

About 10 years ago, the German company Degussa performed a pilot test in a waste incinerator to reduce NO_X with H_2O_2 in the presence of a catalyst. The NO_X reduction was not as high as expected. Exact figures are not known, but the reduction obtained was low compared to other end-of-pipe technologies such as SCR or NSCR. Furthermore, the H_2O_2 also reacted with SO_2 in the tail gas, increasing the H_2O_2 use. Degussa stopped research after this pilot-test. [11, InfoMil, 1999].

Sodium hydroxide scrubbing or caustic scrubbing
A more old-fashioned method to reduce NO_X in the tail gas is by scrubbing the tail gas with caustic (NaOH). The high absorption rate results from the simultaneous absorption of NO and NO_2, according to the overall equations:

$$NO + NO_2 + 2NaOH \rightarrow 2NaNO_2 + H_2O$$
$$3NO_2 + 2NaOH \rightarrow 2NaNO_3 + H_2O$$

This process cannot handle concentrations higher than 600 ppm NO_X (1230 mg NO_X/m^3). When concentrations are lower than 600 ppm (mg NO_X/m^3), emissions of NO_X of 200 ppm (410 mg NO_X/m^3) can be achieved. The by-product of this process is a low concentration of sodium nitrite ($NaNO_2$) and sodium nitrate ($NaNO_3$) that requires safe disposal (e.g. waste water plant) or further use. The capital cost of this process is 4.3 % of the total investment cost of a dual-pressure nitric acid plant. Annual costs are considerable, since sodium hydroxide is relatively expensive. According to [11, InfoMil, 1999] an improved version of this system is installed in a plant in Kedzierzyn Poland [11, InfoMil, 1999]

Adsorption
Adsorption of NO_X to a suitable solid substance is technically possible, but high capital costs prevent the adoption of this tecnique. Furthermore, the NO_X reduction is discontinuous, since the adsorption substance has to be regenerated. Some systems are described below:

Molecular sieves
After cooling the tail gas to 7 – 10 °C, the tail gas is passed through a mist eliminator to remove entrained water droplets and acid mist. The weak nitric acid collected is recycled to the absorption tower, while the partially dried tail gas is passed through a sieve bed. The remaining moisture is removed from the gas stream, NO is converted to NO_2, which is selectively adsorbed. Both absorption and regeneration of the sieve bed take approx. 4 hours. NO_X emissions can be reduced to 20 – 50 ppm (41 – 103 mg NO_X/m^3). Some disadvantages of the system are the high capital and energy costs, the problem of coupling a cyclic system to a continuous acid plant operation, and bed fouling. [11, InfoMil, 1999]

Silica gel
Union Carbide developed the Pura-Siv-N process: the exact process is not mentioned in literature, but values of 50 ppm NO_X (103 mg NO_X/m^3) in the tail gas are claimed. High investment costs and 'other' problems not described further have prevented its adoption. [11, InfoMil, 1999]

2.3 Sulphuric acid

The basic route for the production of sulphuric acid is to convert sources of SO_2 to SO_3 in a catalytic process either by the single or double contact processes. The following section looks at the various sources of SO_2 and what is needed to convert them to sulphuric acid.

Unless otherwise stated the data used is [37, UBA, 2002].

2.3.1 Routes for sulphuric acid production

Description

Starting Materials

Raw materials used for sulphuric acid production are elemental sulphur and pyrite. Sulphuric acid is also formed by processes which are used to control waste gas emissions and by processing wastes and residual materials arising from various industrial processes. The following processes are relevant for sulphuric acid production:

- burning of elemental sulphur with air
- burning of pyrite (FeS_2)
- processing of pyritiferous ores for the production of non-ferrous metals (metallurgical off-gases)
- decomposition of gypsum, metal sulphates ($FeSO_4$) and waste sulphuric acids
- burning or catalytic conversion of waste gases containing hydrogen sulphides; Waste gases containing H_2S arise e.g. from the production of viscose gases (rich gases with high levels of H_2S and CS_2) and from purifying coke oven gas
- exhaust gases arising from the burning of fossil fuel.

The raw gases usually contain 0.3-12 vol. % of SO_2. Raw gases with higher SO_2 contents (20 vol. %) arise from processing pyritiferous ores with oxygen enriched air. The hot SO_2 gases are usually cooled in a waste heat boiler and may be diluted to obtain an O_2/SO_2 ratio leaner than stoichiometric.

Raw gases produced by pyrite burning, by the processing of pyritiferous ores and by waste acid regeneration processes contain pollutants which are detrimental for sulphuric acid production. These raw gases need to be cleaned before the contact process. The following steps are applied for the cleaning the SO_2 raw gases:

- dry separation of grit and fine dust
- wet gas scrubbing (separation of volatile and gaseous substances such as AsO_3, Se, HCl)
- cooling and drying of the SO_2 crude gas
- wet separation of fine dust with a wet electrostatic filter.

Contact process: The exothermic reaction of SO_2 into SO_3 takes place on V_2O_5 based catalysts at temperatures between 420 and 620 °C. The conversion takes place in a contact tower, which usually has 4 or 5 catalyst layers. Gases leaving one of the catalyst layers are cooled by heat-exchangers to the inlet temperature of the next catalyst layer.

Dry contact processes: are used for processing raw gases from the burning of sulphur and pyrite, for processing metallurgical off-gases and for processing raw gases from waste acid regeneration processes. SO_3, which is formed by the catalytic process, is cooled and absorbed outside the contact tower in concentrated sulphuric acid. Process technologies differ with regard to the number of absorption steps and with regard to the temperature of the SO_2 inlet gases.

SO_3 is absorbed in a final absorber installed after the last catalyst layer in a **single** contact process. SO_3 is absorbed in an intermediate absorber installed after the second or third catalyst layer in **double** contact processes. Gases supplied to the intermediate absorber are cooled by reverse current with the gases leaving the intermediate absorber, thereby SO_2 gases leave the intermediate absorber being heated. The gases are conducted to the final catalyst layer(s). SO_3 formed in these catalyst layers is absorbed in a final absorber.

Raw gases without contamination (e.g. from sulphur burning) are directly supplied into the contact tower at a temperature of about 400 °C (dry hot gas processes). In the case of gas cleaning (e.g. metallurgical off-gases), the SO_2 raw gases are reheated to the inlet temperature of the contact tower by using the waste heat of the contact tower (dry cold gas processes).

Wet contact processes: Wet SO_2 gases (e.g. from the burning of H_2S gases or from the catalytic conversion of H_2S gases) are directly fed to the contact tower with no pre drying. SO_3 formed by the catalytic conversion immediately reacts with the wet gases, thereby forming sulphuric acid. The sulphuric acid is condensed in a condenser installed after the contact tower. Process variants (e.g. WSA process, Concat process) enable an improved condensation and the production of concentrated acid.

Combined wet/dry contact processes are used in particular for processing gases containing H_2S. If the H_2S content is low, H_2S gases are co-burned with elemental sulphur. The wet combustion gases are directly fed to the contact tower after the temperature has been lowered to about 400 °C. SO_3 formed by the catalytic conversion immediately reacts with the wet gases producing sulphuric acid. The sulphuric acid is absorbed in an intermediate absorber installed after the second or third catalyst layer. The remaining SO_2 is converted in the following catalyst layer(s) in a dry contact process.

Regenerative processes for waste gas cleaning directly produce sulphuric acid (Desonox process, SNO_X) or deliver concentrated SO_2, which has been separated from the waste gas (Wellman Lord, Bergbau Forschungs process).

Starting material	SO_2 in raw gas (vol.%)	SO_2 before contact process (vol.%)	Variation of SO_2-content with time	Characteristic features	Production of sulphuric acid
Sulphur	9 - 12	9 - 12	Very low	Cleaning of raw gases is not required	Double contact process
Pyrite	<15	8 - 10	Low	Cleaning of raw gases is required; high amounts of burning residues, which are usually not utilised	Double contact process
Non-ferrous metal prod			Rather high, due to discontinuous processes	Cleaning of raw gases is required; SO_2 conversion is lower at high fluctuations of SO_2 contents or of waste gas volume; increasing of SO_2 content by application of air enriched with O_2	Double contact process, at SO_2 contents <4 % single contact process with emission control of SO_2
Copper (primary)	1 - 20	1 - 12			
Lead (sinter)	2 - 6	2 - 6			
Lead (other processes)	7 - 20	7 - 12			
Zinc	6 - 10	6 - 10	Rather low		
Gypsum	7 - 10	7 - 10	Medium	Simultaneous production of cement, high energy input	Double contact process
Fe-II-sulphate	6 - 7	6 - 7	Medium	$FeSO_4$ is processed together with diluted acid from the production of pigments	Double contact process
Waste acid with org. contamination; acid sludge	5 - 10	5 - 10	Depending on waste acid, usually high	Cleaning of raw gas is required; waste gas might contain unburned hydrocarbons → therm. post-combustion	Double contact process
H_2S gases (coke oven gas, spinning bath waste gas, gases from processing of natural gas and crude oil)	0.3 - 10; Higher SO_2 contents with burning of sulphur	Depending on process	Medium, with additional combustion of sulphur low	Wet crude gases are formed from combustion of H_2S; Coke oven gas: H_2S gas is separated by scrubbing processes	Low SO_2 contents: wet or dry contact process/single contact plant with emission control of SO_2, Concat, WSA; higher SO_2 contents or simultaneous combustion of sulphur: combined wet/dry contact process
Exhaust gases of sulphurous fossil fuel	0.1 - 6	Depending on process	Low to high	Low SO_2 content, high waste gas volumes	Regenerative processes for waste gas cleaning (Bergbau Forschung, Wellmann Lord, SNOX and DESONOX)

Table 2.11: Sulphuric acid processes depending on raw gas composition

Achieved environmental benefits

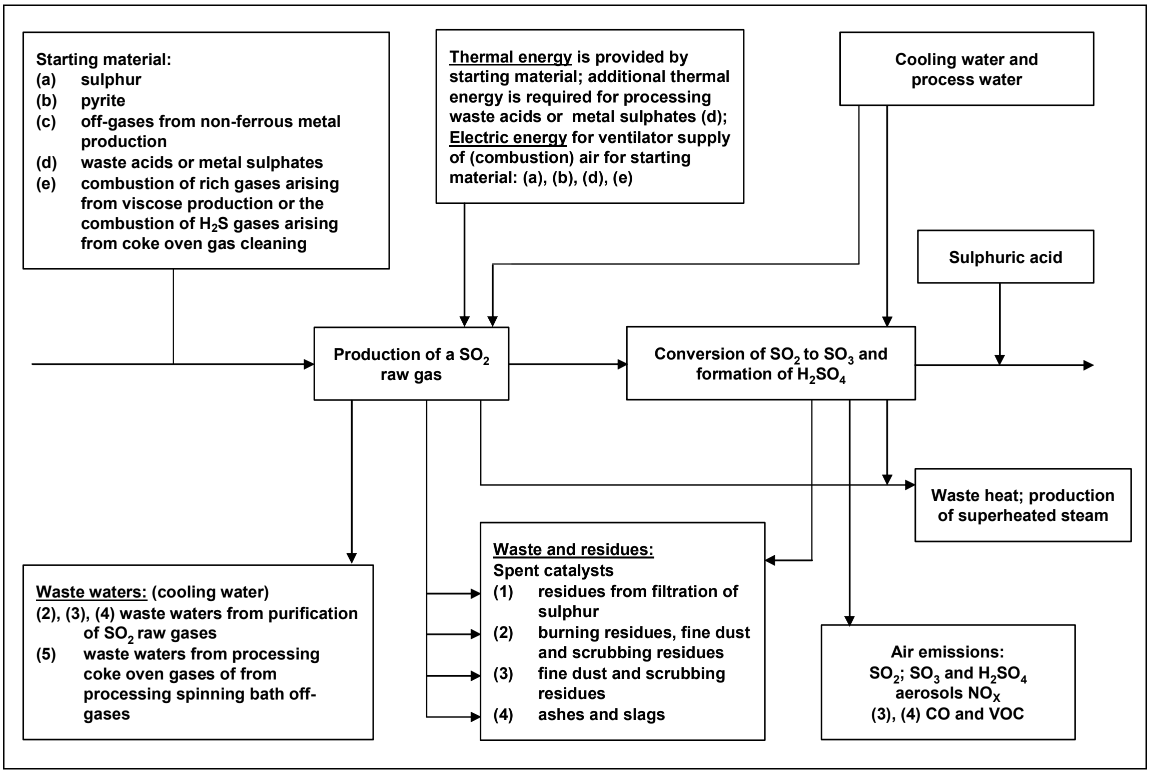


Figure 2.11: summary of essential environmental parameters of H_2SO_4 production

Energy

Energy is provided for the production of sulphuric acid from the input of the starting materials. An essential feature of the double contact process is the autothermic operation of the plant, which is possible with a minimum SO_2 content of 4 % volume.

Up to 67 % of the process waste heat, which is released from a double contact plant on the basis of sulphur burning, is recovered as high-pressure steam from the gaseous combustion and reaction heat of the contact process. Waste heat released from acid cooling is about 30 - 40 % of the process waste heat. A thermal efficiency of 85 - 90 % can be obtained by using waste heat released from the cooling of acid for drying processes and for the production of low-pressure steam.

If gas cleaning processes are needed (e.g. metallurgical off-gases), the cold raw gases are reheated to the reaction temperature of the catalyst by using waste heat from the contact tower. Low-level energy is released from acid cooling, which can be used for drying processes or for the production of low-pressure steam.

Waste acid regeneration processes and the decomposition of metal sulphates are characterised by relatively high energy consumptions. By concentrating, preheating and predrying the starting materials the energy consumption can be reduced.

Wastes and residues

High ash sulphur is filtered before burning. Residues from the filtering are used in pyrite burning processes. The roasting residues which arise from pyrite burning are contaminated with heavy metals such as lead, cadmium and arsenic. Reprocessing of the roasting residues for utilisation in the steel in-dustry is hardly done and roasting residues are usually disposed of. Arsenic and thallium are concentrated in the fine dusts. Separated fine dusts are disposed of. Fine dusts separated from metallurgical off-gases are processed in the non-ferrous metal industry or are internally recycled to the respective smelting plants. Compounds containing mercury are separated by reactive filters or by scrubbing processes. Scrubbing residues arising from gas purification are re-used in the non-ferrous metal industry or disposed of.

The formation of coke, ash and slag takes place in waste acid regeneration processes. Coke is recycled in the process. Depending on the composition of the waste acid, ashes and slag could be contaminated with heavy metals. Ashes and slag are disposed of.

Spent catalysts and residues from catalyst cleaning are re-used in the non-ferrous metal industry. When using a regenerative exhaust gas cleaning for the production of SO_2 and H_2SO_4, fine dusts and scrubbing residues are produced, which are disposed of. From the Wellman Lord process Na_2SO_4 is produced, which can be used in the chemical industry.

Air emissions

SO_2 and SO_3 (H_2SO_4 aerosols) are the major air emissions of the contact process. NO_X, CO, CO_2 and VOC emissions can be released during the production of the SO_2 raw gases.

Gases of pyrite burning, metallurgical off-gases and gases of waste acid regeneration processes contain pollutants such as dust, volatile substances (As, Se, Cd and Hg) and gaseous substances (HCl, HF, AsO_3), which are separated before the contact process. These substances are released via roasting residues, fine dusts, scrubbing residues and sewage.

SO_2 emissions

The formation of SO_2 emissions is due to an incomplete reaction of SO_2 into SO_3 on the catalyst. SO_2, which is not converted into SO_3, is only partially absorbed in water. SO_2 emissions are dependent on the SO_2 content of the raw gases and on the conversion rate of the contact process. The conversion rate of the contact process depends on the process (e.g. single contact process or double contact process) and on the design of the plant (e.g. number of catalyst layers, kind of catalyst and quantity of catalyst). Operating characteristics such as the working temperature, the O_2/SO_2 ratio, and the time rate of change of the SO_2 content in the reaction gas are also relevant for the conversion rate. Table 2.12 presents achievable conversion rates and SO_2 emissions for sulphuric acid production with typical SO_2 contents in the raw gas. The conversion rates and SO_2 emissions can be achieved under normal operating conditions.

Emissions of SO_3 and H_2SO_4 mists

The formation of SO_3 emissions and H_2SO_4 mists occur due to an incomplete absorption (dry contact processes) and due to ineffective condensation (wet contact processes). Adequate designs of the absorption tower and of the condenser, and the use of candle mist eliminators can limit SO_3 emissions to 20 - 30 mg/Nm^3.

In order to minimise SO_3 (H_2SO_4) emissions, dry contact processes require the use of sulphur with low impurity contents and an adequate drying of the combustion air (processes based on sulphur burning) and an adequate drying of the SO_2 gases (other processes for the production of SO_2 gases). Wet catalytic processes especially may give rise to high SO_3 (H_2SO_4) loads, which can be separated by electrostatic filters.

VOCs, CO and CO_2

Emissions of CO, CO_2 and VOCs arise from metallurgical processes (metallurgical off-gases) and from waste acid regeneration processes. Metallurgical processes may involve the emissions of dioxins due to the charging of secondary raw materials. The reduction of VOCs and CO emissions by using an afterburner is state-of-the-art.

Nitrogen oxides (NO_X)

NO_X emissions have to be considered when elemental sulphur or gases containing sulphur are burnt at higher temperatures and when a thermal decomposition of waste acids or waste gypsum takes place. By using two-stage burners for sulphur burning, NO_X emission levels of 20 mg/Nm^3 can be achieved.

Cross media effects

Operational data

	Typical SO_2 gas content (vol. %)	Assumed SO_2 content (vol. %)	Achievable conversion rate (%)	Achievable SO_2 emissions (mg/Nm^3)
Double contact process with 4 catalyst layers; (burning of elemental sulphur; constant SO_2 content)	9 - 11.5	9.5 11.5 11.5	99.7 - 99.8 99.7 - 99.8 99.9	600 – 700 810 250
- metallurgical off-gas (fluctuating SO_2 content)	4 - 12	5 - 8.4	99.6 - 99.8 99.7 - 99.8	400 - 1200 700 – 800
Double contact process with 5 catalyst layers; (constant and fluctuating SO_2 content)	4 - 11.5	5 - 8.4	99.9	300
Wet/dry contact process	8 - 10	8	99.8	500
Single contact process				
- before emission control	<4	2	97.5 – 98	1200 - 1500
- after emission control		2	99.5	<500
Wet contact process	<4	c. 0.3	99.0	120

Table 2.12: Achievable rates and SO_2 emissions

Economics

Driving force for implementation

Example plants

Reference literature

2.3.2 Measures for the reduction of SO_2 emissions

Description

Process-integrated measures for the reduction of SO_2 emissions

A reduction of SO_2 emissions can be achieved by replacing conventional catalysts with catalysts of a higher activity, which enable SO_2 conversion rates of 99.8 % to be achieved (without using catalysts dozed with Cs). Reduction rates of up to 50 % are possible. Table 2.13 presents some estimates of the main costs.

		EUR/unit	EUR/yr
Waste gas volume (Nm^3/h)	36000		
Operating time (h/yr)	8400		
SO_2 concentration of waste gas before emission reduction (mg/Nm^3)	1200		
SO_2 concentration of waste gas after emission reduction (mg/Nm^3)	700		
Reduction of SO_2 emissions (kg/h)	18		
Extra investment costs	-		
Extra costs for catalyst (incl. 6 % interest rate)			**17800**
Catalyst volume (m^3)	120		
Lifetime of catalyst (yr)	10		
Specific extra costs of catalyst		EUR 1090/m^3	
Recovered sulphuric acid (kg/h)	28	EUR 0.051/kg	**-11800**
Estimated annual extra costs (EUR/yr)			**6000**
Specific costs related to reduction of SO_2 emissions (EUR/t SO_2)			**40**
Specific extra costs related to the production of H_2SO_4 (EUR/t H_2SO_4)			**0.041**

Table 2.13: Main extra costs for replacing conventional catalysts

Increasing the O_2/SO_2 ratio of the inlet gas

Higher O_2/SO_2 ratios thermodynamically favour the conversion of SO_2 into SO_3 due to the lower temperature level. An application of higher O_2/SO_2 ratios can be considered, if production is lower than the output capacity. A reduction of SO_2 emissions of about 30 % can be achieved. However, the energy output of a sulphuric acid plant decreases due to the dilution of the inlet gases, as less energy can be recovered and more energy is required for gas transport. Table 2.14 presents, some estimates of the main costs.

		EUR/unit	**EUR/yr**
Waste gas volume (Nm^3/h) at a SO_2 content in the reaction gas of 10.5 vol. %	36000		
SO_2 waste gas concentration (mg/Nm^3) at a SO_2 content in the reaction gas of 10.5 vol. %	1200		
Waste gas volume (Nm^3/h) at a SO_2 content in the reaction gas of 9.5 vol. %	40000		
SO_2 waste gas concentration (mg/Nm^3) at a SO_2 content in the reaction gas of 9.5 vol.	700		
Operating time (h/yr)	8400		
reduction of SO_2 emissions (kg/h)	15		
Extra investment costs	-		
Extra energy consumption/energy losses	-		
Extra energy consumption for ventilator at an SO_2 concentration of 9.5 vol. % (kWh/h)	68	EUR 0.044/kWh	**24900**
Loss of steam production (40 bar) due to an SO_2 concentration of 9.5 vol. % (t/h)	1.1		
Loss of electric energy corresponding to the loss of steam production (9.5 vol.% SO_2) (kWh/h)	40	EUR 0.044/kWh	**14650**
Recovered sulphuric acid (kg/h)	23	EUR 0.051/kg	**-9950**
Estimated annual extra costs (EUR/yr)			**29600**
Specific costs related to reduction of SO_2 emissions (EUR/t SO_2)			**232**
Specific extra costs related to the production of H_2SO_4 (EUR/t H_2SO_4)			**0.204**

Table 2.14: Main extra costs for reducing SO_2 emissions at a double contact plant

By application of Cs-dosed catalyst

The conversion of SO_2 into SO_3 takes place at lower temperatures, thereby achieving higher conversion rates and lower SO_2 emission levels. An emission reduction of 50 - 70 % is possible. Cross-media effects do not take place. Table 2.15presents the estimated costs for retrofitting a single contact plant for the use of Cs-dosed catalysts. Table 2.16 presents estimates of the main costs for the use of Cs-dosed catalysts in a double contact plant.

		EUR/unit	EUR/yr
Waste gas volume (Nm^3/h)	10000		
Operating time (h/yr)	8400		
SO_2 concentration of waste gas before emission reduction (mg/Nm^3)	1500		
SO_2 concentration of waste gas after emission reduction (mg/Nm^3)	500		
Reduction of SO_2 emissions (kg/h)	10		
Extra investment costs (EUR)	**580000**		
Repayment on investment including interest (EUR/yr)	**59900**		**59900**
Period of depreciation (yr)	15		
Interest rate (%)	6		
Extra costs of maintenance and wear (EUR/yr)	11650		**11600**
Maintenance and wear (% of investment costs)	2		
Extra costs for catalyst (incl. 6 % interest rate)			**13450**
Extra amount of catalyst (m^3)	16		
Lifetime of catalyst (yr)	10		
Specific costs of catalyst		EUR 6200/m^3	
Recovered sulphuric acid (kg/h)	15	EUR 0.051/kg	**-6550**
Estimated annual costs (EUR/yr)			**78400**
Specific costs related to reduction of SO_2 emissions (EUR/t SO_2)			**930**

Table 2.15: Main extra costs for retrofitting single contact plant

		EUR/unit	EUR/yr
Waste gas volume (Nm^3/h)	36000		
Operating time (h/yr)	8400		
SO_2 concentration of waste gas before emission reduction (mg/Nm^3)	1200		
SO_2 concentration of waste gas after emission reduction (mg/Nm^3)	400		
Reduction of SO_2 emissions (kg/h)	29		
Extra investment costs	-		
Extra costs for catalyst (incl. 6 % interest rate)			**21700**
Extra amount of catalyst for fifth catalyst layer (m^3)	40		
Lifetime of catalyst (yr)	10		
Specific costs of catalyst		EUR 4000/m^3	
Recovered sulphuric acid (kg/h)	44	EUR 0.051/kg	**-18800**
Estimated annual extra costs (EUR/yr)			**2900**
Specific costs related to reduction of SO_2 emissions (EUR/t SO_2)			**12**
Specific extra costs related to the production of H_2SO_4 (EUR/t H_2SO_4)			**0.020**

Table 2.16: Main extra costs for application of Cs-dosed catalyst in the 4th layer

If the raw gas of a single contact plant contains more than 4 vol. % SO_2, the plant can be retrofitted into a double contact plant by the installation of an intermediate absorber. A reduction of SO_2 emissions of about 75 % can be achieved. Cross-media effects do not take place.

Retrofitting a double contact plant with a fifth catalyst layer

A conversion rate of 99.9 % can be achieved and fluctuations of the inlet SO_2 concentration can be compensated. The retrofitting of an existing contact plant with a fifth layer is possible provided there is sufficient room. Table 2.17 presents some estimates of the main costs.

		EUR/unit	EUR/yr
Waste gas volume (Nm^3/h)	36000		
Operating time (h/yr)	8400		
SO_2 concentration of waste gas before emission reduction (mg/Nm^3)	1200		
SO_2 concentration of waste gas after emission reduction (mg/Nm^3)	300		
Reduction of SO_2 emissions (kg/h)	32		
Extra investment costs (EUR)	**1090000**		
Repayment on investment incl. interest (EUR/yr)			**112300**
Period of depreciation (yr)	15		
Interest rate (%)	6		
Extra costs of maintenance and wear (EUR/a)			**21800**
Maintenance and wear (% of investment costs)	2		
Energy consumption extra pressure drop for 5. catalyst layer (mbar)	60		
Extra energy consumption of ventilator (kWh/h)	92	EUR 0.044/kWh	**33700**
Extra energy consumption of circulating pumps and additional energy consumers (kWh/h) extra catalyst costs (incl. 6 % interest rate)	42	EUR 0.044/kWh	**15500** **8900**
Extra amount of catalyst for 5. catalyst layer (m^3)	30		
Lifetime of catalyst (yr)	10		
Specific costs of catalyst		EUR 2180/m^3	
Recovered sulphuric acid (kg/h)	50	EUR 0.051/kg	**-21200**
Estimated annual extra costs (EUR/yr)			**171000**
Specific costs related to reduction of SO_2 emissions (EUR/t SO_2)			**629**
Specific extra costs related to the production of H_2SO_4 (EUR/t H_2SO_4)			**1.18**

Table 2.17: Main extra costs for retrofitting a fifth catyst layer at a double contact plant

2.3.3 End-of-pipe measures for the reduction of SO_2 emissions

Description

Waste gas scrubbing with calcium hydroxide is used in particular for the reduction of SO_2 emissions at power plants, waste incineration plants and industrial plants. Thereby SO_2 emission reduction rates of about 90 – 95 % are achievable. The use of this process for emission reduction at sulphuric acid plants is possible. Contrary to other scrubbing techniques, an insoluble residue (gypsum) is directly formed which can be re-used or disposed of. Estimates of the main costs of this method are given Table 2.18for emission reduction at a double contact plant and Table 2.19 for emission reduction at a single contact plant.

		EUR/unit	**EUR/yr**
Waste gas volume (Nm^3/h)	36000		
Operating time (h/yr)	8400		
SO_2 concentration in crude gas (mg/Nm^3)	1200		
SO_2 concentration in clean gas (mg/Nm3)	100		
Reduction of SO_2 emissions (kg/h)	40		
Investment costs (EUR)	1465000		
Repayment on investment incl. interest (EUR/yr)			150600
Period of depreciation (yr)	15		
Interest rate (%)	6		
Costs of maintenance and wear (EUR/yr)			29250
Maintenance and wear (% of investment costs)	2		
Energy consumption			
Pressure drop (mbar)	25		
Extra energy consumption of ventilator (kWh/h)	49	EUR 0.044/kWh	**17900**
Additional energy consumers (kWh/h)	100	EUR 0.044/kWh	**36600**
Consumption of resources			
Consumption of CaO (kg/h)	35	EUR 0.073/kg	**21150**
Disposal of residues (kg/h)	118	EUR 0.015/kg	**14450**
Consumption of water (m^3/h)	2.7	EUR 0.145/m^3	**3250**
Estimated annual costs (EURO/a)			**273200**
Specific costs related to reduction of SO_2 emissions (EUR/t SO_2)			**865**
Specific extra costs related to the production of H_2SO_4 (EUR/t H_2SO_4)			**1.82**

Table 2.18: Main costs for waste scrubbing with CaOH)$_2$ in double contact process

		EUR/unit	**EUR/yr**
Waste gas volume (Nm^3/h)	10000		
operating time (h/yr)	8400		
SO_2 concentration in crude gas (mg/Nm^3)	1500		
SO_2 concentration in clean gas (mg/Nm^3)	100		
Reduction of SO_2 emissions (kg/h)	14		
Investment costs (EUR)	**770800**		
Repayment on investment incl. interest (EUR/yr)			**79400**
Period of depreciation (yr)	15		
Interest rate (%)	6		
Costs of maintenance and wear (EUR/yr)			**15400**
Maintenance and wear (% of investment costs)	2		
Energy consumption			
Pressure drop (mbar)	25		
Extra energy consumption of ventilator (kWh/h)	14	EUR 0.044/kWh	**5000**
Additional energy consumers (kWh/h)	26	EUR 0.044/kWh	**10200**
Consumption of resources			
Consumption of CaO (kg/h)	12.3	EUR 0.073/kg	**7500**
Disposal of residues (kg/h)	41.8	EUR 0.015/kg	**5100**
Consumption of water (m^3/h)	0.7	EUR 0.145/m^3	**900**
Estimated annual costs (EUR/yr)			**123400**
Specific costs related to reduction of SO_2 emissions (EUR/t SO_2)			**1100**

Table 2.19: Main costs for Ca(OH)$_2$ scrubbing in single contact process

Waste gas scrubbing with ammonia

SO_2 is scrubbed with an aqueous NH_3 solution and converted into ammonium sulphate. When using ammonia scrubbing at a sulphuric acid plant, the utilisation of the residual ammonia sulphate has to be considered (e.g. for the production of fertilisers). A reduction of SO_2 emission of >88 % is achievable.

Waste gas scrubbing with NaOH or Na_2CO_3

SO_2 is scrubbed with an aqueous alkaline solution and converted into Na_2SO_4. Na_2SO_4 is reprocessed with lime into NaOH and gypsum. Reduction rates of 85 – 95 % are achievable.

Sulfacid process

Waste gases are humidified with steam and absorbed on activated carbon, with the SO_2 thereby being converted into H_2SO_4. Activated carbon is regenerated with water, which is re-used for the production of H_2SO_4. Reduction rates of 90 % are achievable.

Waste gas scrubbing with H_2O_2

This is applied for the conversion of SO_2 in the waste gas into SO_3, which reacts with water to form sulphuric acid. Instead of hydrogen peroxide, H_2SO_5 formed by electrochemical processes and can be used for scrubbing. Reduction rates of 98 % are achievable.

Measures for the reduction of SO_2 emissions	Reduction of SO_2	Clean gas concentration (examples of plants)		Cross media effects
		Without emission reduction	With emission reduction	
Replacing conventional catalysts with catalysts with higher activity in double contact plant	Up to 50 %	1500 mg/Nm^3	700 mg/Nm^3	No cross media effects
Increasing the O_2/SO_2 ratio of the inlet gas	ca. 35 %	2.5 kg SO_2/t H_2SO_4	1.6 kg SO_2/t H_2SO_4	Extra energy consumption and loss of energy
Catalyst doped with Cs in double contact plant	50 – 70 %	700 mg	250 mg	No cross media effects
Catalyst doped with Cs in single contact plant	50 – 70 %	1500 mg/Nm^3	>500 mg/Nm^3	No cross media effects
Retrofitting of a single contact plant into a double contact plant	75 %	Not available	Not available	No cross media effects
Additional fifth catalyst layer in double contact plant	50 – 70 %	Not available	300 mg/Nm^3	No cross media effects
Waste gas scrubbing with calcium hydroxide	90 – 95 %	Not available	Not available	Consumption of resources; SO_2 is transformed into $CaSO_4$
Waste gas scrubbing with ammonium hydroxide	>88 %	Not available	210 mg/Nm^3	Consumption of resources; SO_2 is transformed into NH_4SO_3/SO_4
Waste gas scrubbing with sodium hydroxide	85 – 95 %	Not available	Not available	Consumption of resources; SO_2 is transformed into Na_2SO_4, ($CaSO_4$)
Waste gas scrubbing with hydrogen peroxide	98 %	1100 mg/Nm^3	100 mg/Nm^3	Consumption of energy or resources
Sulfacid process	90 %	Not available	Not available	No cross media effects

Table 2.20; Sunmmary of measures for reduction of SO_2 emissions

Waste water

Waste water emissions arise from gas scrubbing processes and in particular from cleaning metallurgical off-gases, from cleaning pyrite roasting gases and from cleaning gases from waste acid regeneration processes. Waste waters also arise from the separation of H_2S gases from coke-oven gases. Due to leakage, diffuse emissions can be released, which are collected in collection basins.

Example plants

In Austria five sulphuric acid plants are in operation. Two double contact plants produce H_2SO_4 on the basis of sulphur burning. At another plant H_2SO_4 is produced by using a combined wet/dry catalytic process; where the rich gas from viscose production is burned together with sulphur. At a single contact plant (with a modified 4th catalyst layer for the application of Cs-dosed catalyst) H_2SO_4 is produced from H_2S gas, which is obtained from coke oven gas. At a wet catalytic contact plant, the rich gases arising from the viscose production are used for H_2SO_4 production. Table 2.21 gives a summary of sulphuric acid plants in Austria.

	Donau Chemie	**VOEST Linz**	**Lenzing AG**	**Lenzing AG**	**Glanzstoff Austria GmbH**
Capacity related to H_2SO_4 (100 %)	690 t/d	20 t/d	270 t/d	66 t/d	5000 t/yr
SO_2 source	Elemental sulphur	H_2S in coke oven gas	Elemental sulphur	Elemental sulphur and rich gases arising from viscose prod.	Catalytic conversion of rich gases arising from viscose production
Process	Double contact process with 4 catalyst layers	Single contact process with modified 4th catalyst layer	Double contact process with 4 catalyst layers	Combined wet/dry double contact process with 4 catalyst layers	Wet catalytical process (single catalyst layer)
Inlet SO_2 concentration	9.5 vol. %	appr. 2 vol. %	11 - 11.5 vol. %	8 vol. %	8400 mg/Nm^3
Conversion rate (%)	99.7-99.8	99.5	99.8	99.8	99
SO_2 emissions (mg/Nm^3) (kg/t H_2SO_4)	600 – 700 2.1	<500 appr. 4.5	810 appr. 1.4	500 1.18	120 appr. 9
SO_3 emissions (mg/Nm^3) (kglt H_2SO_4)	10 – 15 0.01 -0.02	30 appr. 0.3	<50 <0.08	appr. 30 appr. 0.07	Not detectable
Emission reduction	Higher SO_2 conversion rate due to reduced SO_2 content before contact tower	Higher SO_2 conversion rate by using catalyst doped with Cs at the 4th catalyst layer	Higher SO_2 conversion rate due to change of catalyst and use of catalyst with higher activity	Combined wet/dry contact process	Wet electrostatic filter for reduction of SO_3 emissions

Table 2.21: Sulphuric acid plants according to Austrian producers

Conclusions

The operative ranges of double contact processes and single contact processes or wet contact processes depend on the SO_2 raw gas concentrations. According to state-of-the-art technology, single contact or wet catalytic processes are only operated if a double contact process (dry or combined wet/dry process) cannot be used, typically due to a low SO_2 content in the raw gas. With a minimum SO_2 content of 4 vol. %, the autothermic operation of a double contact plant is state-of-the-art technology.

Double contact plant with 4 catalyst layers: Conversion rates of 99.8 % can be achieved under constant SO_2 raw gas conditions (dry and combined wet/dry process) by application of catalysts without Cs. Conversion rates of 99.7-99.8 % can be achieved under variable raw gas conditions. Conversion rates of 99.9 % are achievable by the application of Cs-dosed catalysts or, under adequate spatial conditions, by retrofitting a fifth catalyst layer. The application of Cs-dosed catalysts is possible at new and existing plants and is more cost-effective than the retrofitting of a fifth catalyst layer.

Double contact plant with 5 catalyst layers: Conversion rates of 99.9 % can be achieved under constant and variable raw gas conditions (new and existing plants).

The operation of **single contact processes** without additional SO_2 emission control techniques is not state-of-the-art technology. Process integrated emission control measures enable a conversion rate of 99.5 % to be achieved. Assuming a raw gas with 2 vol. % SO_2, an SO_2 emission level of 500 mg/Nm^3 can be achieved.

Wet catalytic processes without additional SO_2 emission control measures are state-of-the-art only if the raw gases have low SO_2 contents (<0.5 vol. %). A conversion rate of 99 % and, assuming a raw gas with 0.3 vol. % SO_2, an SO_2 emission level of 120 mg/Nm^3 can be achieved.

SO_2 emission levels of 100 – 200 mg/Nm^3 can be achieved with **end-of-pipe** measures (e.g. waste gas scrubbing with calcium hydroxide). The application of end-of-pipe measures is possible for both single catalytic processes and for double catalytic processes. End-of-pipe measures are more cost-intensive than process-integrated measures (e.g. they need the application of Cs dosed catalysts or retrofitting of a fifth layer at a double contact plant).

SO_3 (H_2SO_4) emissions levels of 20 - 30 mg/Nm^3 (as SO_3) can be achieved.

An **efficient recovery of waste heat** should be considered for the operation of a sulphuric acid plant.

2.4 Phosphoric acid

2.4.1 General preventive measures

2.4.1.1 Application of high-grade phosphate rock

Description
Ideally, the best possible phosphate source rock would consist entirely of tricalcium phosphate $Ca_3(PO_4)_2$. The impurities in phosphate rock are mostly undesirable for an assortment of reasons - economic, technical and environmental.

The most basic objection to anionic impurities is that by taking the place of phosphate, they increase the CaO/P_2O_5 ratio of the phosphate rock. An increase in this ratio means an increase in the amount of acidulating agent required per tonne of P_2O_5 processed, and this impairs the economics of the process. Per tonne of P_2O_5, it also means an increase in the mass of calcium sulphate produced requiring disposal. For producers in some areas, such as in the Netherlands, calcium sulphate disposal is the most serious problem that they have to face. Apart from these problems, most of the individual impurities cause problems arising out of their chemical properties. They can give rise to environmental and toxic hazards as previously discussed. Furthermore, they can interfere in the phosphoric acid reaction system (scaling, corrosion) or influence the filtration (crystal size and shape, slurry viscosity), thereby affecting the efficiency of the phosphoric acid production process. In addition, they may impair the quality of the product(s), particularly for use in downstream processes. If dealing with the gypsum disposal problem requires finding a useful application for the gypsum, this latter aspect does not only hold for the acid product but also for the gypsum by-product; clean, pure gypsum offers more and better opportunities for useful application than highly contaminated gypsum. Therefore, for an assortment of reasons it is preferable to use phosphate rocks with a high P_2O_5 content and a low level of impurities.

Achieved environmental benefits
A clean gypsum by-product will limit the spread of contaminants. Clean gypsum is a more saleable product into the market.

Cross media effects

Applicability
This is limited by the availability of good quality phosphate rock.

Economics

Driving force for implementation

Example plants
No information available.

Reference literature

2.4.1.2 Application of an high efficiency phosphoric acid process

Description
The P_2O_5 recovery efficiency of a phosphoric acid plant is an important environmental parameter. The consumption of a particular phosphate rock per tonne of P_2O_5 produced will decrease with increasing efficiency, thus reducing the amount of impurities that will enter and then will have to leave the process. An increase in efficiency means that per tonne of P_2O_5 less sulphuric acid is required and less gypsum is produced. Additionally, cleaner gypsum will be produced, especially with respect to its P-content, thus enhancing the possibility of finding a useful application for the gypsum.

Achieved environmental benefits

Cross media effects

Applicability
With respect to the P_2O_5 recovery efficiency, the data shows that the recrystallisation processes (HDH-1, HDH-2 and DHH) are preferred over the more straightforward dihydrate and hemihydrate processes.

P_2O_5 which leaves the process with the gypsum, consists both of small undissolved phosphate rock particles and phosphoric acid still adhering to the gypsum after filtration. With respect to the latter type of loss, a further optimisation can be obtained by applying an end-of-pipe repulp filter By re-slurrying and washing the gypsum, followed by an extra filtration step, most of the free acid which is not removed in a previous filtration step, can be removed in this filter, resulting in a higher P_2O_5 efficiency and a higher grade gypsum.

Economics

Driving force for implementation

Example plants

Reference literature

2.4.2 Specific techniques and measures to minimise emissions and waste

2.4.2.1 Measures to prevent fluoride emissions to air

Description
Fluoride in the form of HF and SiF_4, which is released during the digestion of phosphate rock and during the concentration of phosphoric acid to 54 % P_2O_5, can be removed by a number of different scrubbing systems. The fluorine scrubber is normally an unpacked spray tower made of rubber-lined steel, which is operated at atmospheric pressure. Other types such as packed bed, cross-flow venturi and cyclonic column scrubbers are also used extensively.

Vapours from vacuum flash coolers and vacuum evaporators are usually first led through a separator for the removal of phosphoric acid droplets that are entrained with the vapours to minimise fluosilicic acid contamination with P_2O_5, or something just to minimise contamination of the scrubber effluent.

Achieved environmental benefits
If the fluorine is not recovered the scrubber effluent will be discharged. The effluent can be neutralised with lime or limestone to precipitate fluorine as solid calcium fluoride before discharge. Seawater can be used as a scrubbing liquid as an alternative. Also in seawater, fluoride reacts to give the harmless substance CaF_2.

Cross media effects

Applicability
Many companies recover the fluorine as fluosilicic acid (H_2SiF_6), which can be used for the production of aluminium fluoride, and other fluorine compounds such as sodium and/or potassium fluosilicates. In this case, a dilute solution of fluosilicic acid is used as the scrubbing liquid. The reaction to fluosilicic acid results in the formation of free silica. By carefully controlling the fluosilicic acid strength, silica deposition is controlled. The silica is the removed by filtration. Usually, a product containing 20 - 25 % fluosilicic acid is recovered in the fluoride recovery system. With two or more absorbers a recovery efficiency of 99 % or more can be achieved. According to [8, EFMA, 2000] achievable fluoride emission levels for new plants are 5 mg/Nm^3 (40 g/t P_2O_5).

Economics

Driving force for implementation

Example plants
In The Netherlands, emission levels in the order of 1 – 5 mg/Nm^3 are achieved in the existing plants.

Reference literature

2.4.2.2 Measures to prevent dust emissions to air

Description
The spread of phosphate rock dust from the unloading of ships and transportation is commonly prevented by using covered conveyor belts and indoor storage.

Achieved environmental benefits
Dust originating from phosphate rock grinding can be recovered by passing the dust containing air through fabric filters. In general, dust emission levels of 10 mg/Nm^3 can be achieved by using fabric filters. However, rock particles are rather adherent and therefore easily blind the

filter cloth. This has a negative effect on the recovery efficiency of a fabric filter. According to EFMA the achievable dust emission level of fabric filters in new phosphoric acid plants is: 50 mg/Nm^3.

Cross media effects
Localised effects.

Applicability
A further dispersion of phosphate rock dust (by wind or rain) can be prevented by good housekeeping measures such as frequently cleaning/sweeping the plant grounds and the quay.

Economics

Driving force for implementation

Example plants
By using of fabric filters, in The Netherlands, dust emission levels of less than 30 mg/Nm^3 are achieved in the existing plants.

Reference literature

2.4.2.3 Measures to prevent emissions to water

Description
Emissions to water are mainly formed by the effluents from the fluorine scrubbers and the direct contact condensors. In phosphoric acid plants in the systems operating under vacuum, direct contact condensors are normally used to condense the vapours from the the flash cooler or the evaporator, so as to maintain a vacuum (vacuum pumps are used to remove the non-condensable gases). The vapours are led through the condensor either directly, or after treatment in a fluorine scrubber.

Achieved environmental benefits
Before discharge the effluent can be neutralised with lime or limestone to precipitate fluoride as solid calcium fluoride. As an alternative seawater can be used as a scrubbing liquid. Also in seawater, fluoride reacts to give the harmless substance CaF_2.

Cross media effects

Applicability
Fluorine emissions
As described above, many companies recover the fluorine as fluosilicic acid (H_2SiF_6). If the fluorine is not recovered, or cannot be recoverd for technical reasons e.g. due to the (excessive silica formation plugging the scrubber), the scrubber effluent will be discharged.
To prevent fluoride emissions with condenser water, the application of an indirect condensation system may be considered instead of a direct contact condenser, thus avoiding that condensor water becoming contaminated with fluoride.

Phosphate emissions
To minimise contamination of the scrubber effluent with P_2O_5, vapours from vacuum flash coolers and vacuum evaporators are usually first led through a separator for the removal of phosphoric acid droplets that are entrained with the vapours.

Despite the use of a separator, gas scrubber and condensor effluents may contain low levels of phosphoric acid. Phosphate removal can be achieved by applying magnesium ammonium phosphate (struvite) or by calcium phosphate precipitation. Although several phosphorus recovery plants have been implemented, phosphate removal has not been practiced yet in phosphoric acid plants.

Economics

Driving force for implementation

Example plants

Reference literature

2.4.3 Useful application of phosphogypsum

Description
There are two basic disposal options for phosphogypsum depending on local conditions; disposal to sea or disposal on land. Gypsum often contains a wide range of impurities, some of which are considered a potential hazard to the environment and public health. Because of this, there is a large pressure to end the practice of gypsum diposal in the sea. In Europe, where most phosphoric acid plants used to discharge waste gypsum to the sea, much of the industry chose the option of closing down, because the alternative option of land disposal was in most cases impracticable, mainly as a result of agricultural policy changes and bad economies of scale.

Locally, the disposal on land, however, also presents potential hazards for the environment and public health. Many of the important considerations in the design and construction of gypsum disposal areas are therefore based on the necessity to keep both the gypsum and the acidic stack effluent within a closed system. To avoid pollution of the subsoil and groundwater pollution by acidic and contaminated phosphogypsum leachate and run-off (process water and rainwater), severe preventive measures are necessary, such as seepage collection ditches, intercept wells, natural barriers and lining systems. Furthermore, to prevent or minimise pollution of the surrounding area and water systems, it is necessary to make provisions for any effluent overflow. The effluent requires appropriate treatment, such as immobilisation of soluble P_2O_5 and trace elements by neutralisation, before it can be released from the system. Besides applying control during the build-up of a gypsum stack, the run-off from gypsum stacks will require treatment for many years after the acid plant has ceased production.

A third and interesting way of dealing with the phosphogypsum disposal problem is to improve the quality of the gypsum, so that it can be used as a resource like natural gypsum and flue-gas desulphurisation gypsum. Many examples of phosphogypsum usage exist. Table 11 gives an overview of phosphogypsum applications. It should be noted that different commercial applications require different types of gypsum.

In the past, not all efforts to use the gypsum have been succesful, mainly because of quality considerations. In most cases, the radioactivity aspects of the gypsum have presented a particular problem. Also the residual acidity or P_2O_5 content of the gypsum is an important factor. Application of phosphogypsum requires the production of a clean pure gypsum. Measures that contribute to achieve this goal are outlined below.

Achieved environmental benefits

Applicability

Application	Anhydrite, AH ($CaSO_4$)	Dihydrate, DH ($CaSO_4.2H_2O$)	Hemihydrate, HH ($CaSO_4.½H_2O$)
Construction	Floor screed cement (as setting regulator)	Cement(as setting regulator)	Plaster(stucco) plasterboard ceiling tiles gypsum blocks floor screed
Agriculture	Soil conditioner as a source of calcium and sulpher carrier and filler in insecticides as filler in the production of fertiliser	Soil conditioner carrier and filler in insecticides as filler in the production of fertiliser	As a source of calcium and sulphur
Industrial uses/other	Filler/pigment in variety of applications	Filler/pigment in variety of applications production of ammonium sulphate and sulphuric acid	Filler/pigment in variety of applications

Table 2.22: Overview of phosphogypsum applications

Cross media effects
Water contamination

Economics

Driving force for implementation

Example plants
In Europe, at this moment, only phosphogypsum produced by Prayon Rupel (Belgium) is used on a commercial scale (20-25 % of the total production), where the gypsum is used as plaster. In Finland (Kemira), some phosphogypsum is applied in the paper industry. In the Netherlands, the application of phosphogypsum (Kemira) in a variety of gypsum building products (plaster, building blocks, plasterboard) has been demonstrated on a pilot scale with positive results.

Reference literature

2.4.3.1 Phosphate rock

Description
The production of clean gypsum requires the use of phosphate rock with low levels of impurities. Regarding size and economy, construction materials, in particular in-door building products, are an important area of application for the by-product gypsum. To enable use in this market, it is important that the gypsum contains only low levels of radioactive components, especially radium.

Achieved environmental benefits
Less potential contamination for dispersal into the environment.

Cross media effects

Applicability
The possibilities for useful application of phosphogypsum will largely be enhanced if phosphate rock with low levels of radionuclides are used.

Economics

Driving force for implementation

Example plants
No information.

Reference literature

2.4.3.2 Phosphoric acid production process

Description
In the DH- and HH processes 4 - 10 % of the P_2O_5 is retained in the filter cake. If the calcium sulphate is made to recrystallise into its other hydrate, some of this loss will again pass into solution and can be recovered when the recrystallised calcium sulphate is finally separated. Besides P_2O_5, also part of the impurities will again pass into solution.

Achieved environmental benefits
The levels of impurities in gypsum from two-stage filtration processes are generally lower than in gypsum from single-stage filtration processes.

Applicability
In recrystallisation processes with two-stage filtration, phosphoric acid is separated from the gypsum before recrystallisation. Thus a substantial part of the impurities is removed from the system before recrystallisation takes place. This is not the case in recrystallisation processes with single-stage filtration.

Economics

Driving force for implementation

Example plants
No information.

Cross media effects

Reference literature

2.4.3.3 Repulp unit

Description
With respect to P_2O_5 removal from the gypsum, a further optimisation of single-stage filtration processes can be obtained by extending the process with an extra filtration step, or repulp filter unit.

Achieved environmental benefits

Cross media effects

Applicability
In this unit, the gypsum is re-slurried, washed and filtered, thus removing most of the free acid which is not removed in the previous filtration step.

Economics

Driving force for implementation

Example plants
No information.

Reference literature

2.4.3.4 Reduction of cadmium levels in waste gypsum by chloride dosing

Description
If the cadmium content of phosphogypsum is a problem, the addition of chloride in the acidulation stage may be considered. Chloride forms complexes with cadmium which are not incorporated in the gypsum crystals, but which stay in the acid.

Achieved environmental benefits
The phosphogypsum produced contains less cadmium.

Cross media effects

Applicability
The addition of chloride may put a strain on the choice of construction materials because of the risk of an increase in corrosion.

Economics

Driving force for implementation

Example plants
No information.

Reference literature

2.4.3.5 Upgrading of phosphogypsum

Description
It appears that many of the impurities present in phosphogypsum are enriched in the smallest gypsum particles. Among these impurities are mercury, the common heavy metals, the radionuclides and the lanthanides. By separating the particle size fraction with the smallest particles, the quality of the remaining gypsum can, therefore, be improved substantially. Separation can be achieved by passing the gypsum through a hydrocyclone, as has been demonstrated on a pilot scale by Kemira and Hydro Agri in the Netherlands. In this case, only 4 % of the total amount of gypsum was separated as fines. Production on a commercial scale should be no problem as this only requires more hydrocyclones to be applied but not a larger one.

An additional advantage of the separation of the smallest particles from the gypsum slurry can be an improvement in the washing and filtering characteristics of the gypsum. Pilot plant tests at Kemira and Hydro Agri in the Netherlands showed that upon washing and filtration of the remaining slurry after particle size separation by means of a hydrocyclone, a substantial amount of P_2O_5 was still removed from the gypsum despite the fact that Kemira employs a repulp filter in its regular process.

Achieved environmental benefits
Cleaner phosphogypsum for disposal.

Cross media effects

Applicability
It should be technically possible to return these P_2O_5-values to the process, thus increasing the overall P_2O_5 efficiency. After vacuum filtration, a gypsum cake remains with a moisture content of less than 10 %. Such a value is required by the gypsum industry for the further processing of the gypsum to products.

The fines that are separated in the hydrocyclone are released as a dilute slurry (0.5-1 wt %). It is difficult to find a useful application for this fraction because of the relatively high impurity content of the fines What remains then are the two basic options for disposal discussed above, namely discharge to sea or storage on land. In the latter case, the fines will first have to be recovered from the slurry, e.g. by filtration.

Economics

Driving force for implementation

Example plants
No information.

Reference literature

2.4.4 The nitrophosphate route: an alternative phosphoric acid production process

Description
The sulphuric route has become established as the industry standard for the production of phosphoric acid, principally for economic reasons and also because it provides a high flexibility in the range of (fertiliser) products that can be made of the acid. The main alternative to the sulphuric route is the nitrophosphate route, in which nitric acid rather than sulphuric acid is used for the digestion of phosphate rock. Around 10-15 % of world phosphate fertiliser production uses the nitrophosphate route. The main advantage of the nitrophosphate route is that no gypsum is produced, thus avoiding later waste gypsum disposal problems. A diagram with the principal process steps of a nitrophosphoric acid process is shown in Figure 2.12.

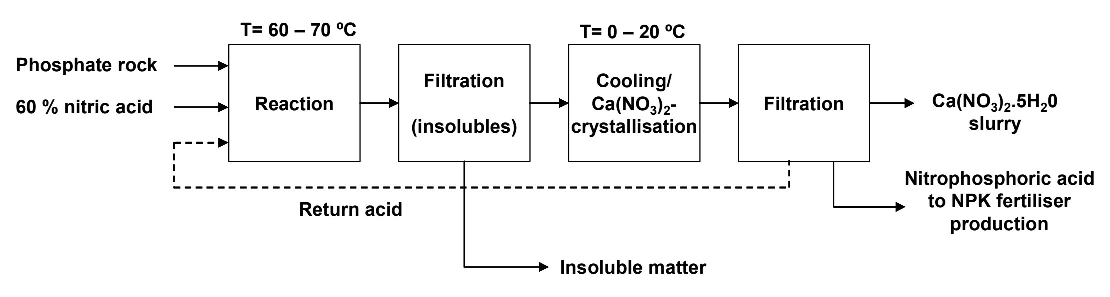


Figure 2.12: Diagram of nitrophosphoric acid process

One disadvantage of the nitro-route is that the acid will always contain calcium and nitrate ions, thereby resulting in limitations in the water-soluble P_2O_5 (due to a possible recombination with phosphate to water-insoluble dicalciumphosphate during the fertiliser manufacture), and the N/P_2O_5 ratio of the products that can be made of the acid. Under the reaction conditions, calcium nitrate is soluble. To remove calcium nitrate, generally, the reaction liquor is cooled so that calcium nitrate partially crystallises. About 60 % of the calcium nitrate comes out of solution at 20 ºC. At -5 ºC this is about 85-90 %.

Furthermore, the nitrophosphoric acid is more dilute, so that more energy is required to remove the water. One specific environmental disadvantage is the release of NO_X from the digestion unit. With respect to environmental impact it is further noticed that in the nitro-route all phosphate rock impurities end up in the acid, and will finally end up in the environment diffusively through the use of end product fertilisers.

Achieved environmental benefits
The main advantage of the nitrophosphate route is that no gypsum is produced, thus avoiding waste gypsum disposal problems.

Cross media effects

Applicability
Using nitric acid leads to the formation of calcium nitrate tetrahydrate as a by-product. This can be upgraded to a calcium nitrate fertiliser or converted to ammonium nitrate and calcium carbonate. When using nitric acid, however, it is not economically possible to remove the calcium, nitrate and certain dissolved impurities to the standard required for making phosphoric acid as a commercial product. Therefore after first removing the calcium, nitrophosphoric acid is then always turned into fertilisers on the spot.

Economics

Driving force for implementation

Example plants
No information.

Reference literature

2.5 Hydrofluoric acid

The currently commercially available techniques for the prevention or the reduction of the emissions and wastes and for the reduction of energy and raw materials consumption related to hydrofluoric acid production are described in this chapter. They can be divided in three types:

- in-process measures
- valorisation of co-products
- end-of-pipe treatments (the so-called "abatement techniques").

2.5.1 In-process measures

2.5.1.1 Heat transfer design

Description
One of the main heat transfer problems in HF manufacturing comes from the limitation to supply enough energy for the main reaction:

$$CaF_2 + H_2SO_4 \rightarrow 2HF + CaSO_4$$

$$\Delta H_o = 59 \text{ kJ/mole } CaF_2$$

This limitation is due to:

- the properties of the powder products, namely that they become viscous and adherent, and the corrosive products, thereby limiting the choice of the materials
- the large surface area of the equipment, leading to significant heat losses, along with wall temperatures limitations resulting from the corrosion and mechanical resistance of the equipment.

Achieved environmental benefits

All the possible options described above are technical solutions giving a balance between the total investment cost, the total maintenance cost, and the expected HF productivity. They are not critical for BAT selection regarding the energy consumption (which is globally the same) nor the environmental aspects: they are only relevant for the investment optimisation.

Cross media effects

Applicability

Several designs have been developed to improve heat transfer to the reaction products. The following is a list of advantages and drawbacks, from the simplest to the most complicated design.

The total energy to be transferred is proportional to the HF production flow, disregarding energy losses, as the temperature of kiln outputs and the reaction rates are similar for all kilns. A correction can arise from heat losses to the environment, which differs depending on the kiln design, but this factor is only secondary. The heat transfer system is basically designed to minimise the investment requirement.

a) in the basic process, dried fluorspar and feed sulphuric acid are fed at a given ratio directly to a rotary kiln. All the energy needed for the endothermic reaction is supplied by heating the kiln shell. This indirect heating leads to the following points:

- a higher heating gas temperature resulting from the production levels needed expressed as tonnes of HF/m^2 of kiln surface area
- Consequently, in some cases, higher kiln corrosion levels, poorer anhydrite and crude HF qualities may occur.

b) the first improvement of this basic process involves of the installation of several double jackets around the rotary kiln and feeding the heating gases in at decreasing temperature from the inlet to the outlet of the kiln, thereby allowing a better control of the temperature profile inside the kiln along with an improvement in energy usage.

This improvement is only cost effective in new plants as the investment needed to modify the jacket and associated piping of an existing unit is cost prohibitive.

c) The second improvement is achieved by preheating the reactants of sulphuric acid and/or fluorspar before they are fed into the kiln.

Preheating the sulphuric acid feed is generally easier but special materials of construction are needed if it contains some HF.

More complex equipment is needed for indirect preheating of the powdery fluorspar. Dust entrainment (either from the preheater itself or from the kiln) significantly increases when the fluorspar temperature increases, due to the higher reactivity of the hot reactants, which in turn leads to a limited maximum temperature.

Direct preheating can be achieved for calcining fluorspar by heating directly with oxygen containing gases to about 400 – 450 °C. This option has the advantage of removing most of the flotation chemicals, giving a product that mixes more easily with the sulphuric acid feed and increasing the reaction rate. Consequently the kiln workload is considerably reduced.

The disadvantage is that the fluorspar calcining equipment involves a substantial investment. The profitability of such an investment needs careful evaluation.

d) a third improvement involves feeding the raw materials into a prereactor before feeding them to the kiln. This rotary equipment, which is is designed to mix and heat the reactants to give a conversion rate of CaF2 of around 50 %, is expensive as it is complex and made of special corrosion resistant alloys. In fact, as it must handle sticky, corrosive and hot reactants it is subjected to severe corrosion.

The substantial conversion of CaF_2 in the prereactor has two important beneficial consequences.

1) it lowers the kiln workload
2) it suppresses the pasty and sticky state in the kiln almost completely, which gives better heat transfer and avoids many scaling problems.

Using a prereactor leads to lower heating gas temperatures, and consequently to lower corrosion risks in the kiln itself, and to a more stable reaction.

Applying a prereactor requires a significant investment, and involves high maintenance costs. The profitability of such an installation needs to be carefully considered.

Economics

Driving force for implementation

Example plants
No information.

Reference literature

2.5.1.2 Energy recovery

Description
The kiln shell exit gas temperature goes up to temperatures around 400 °C, depending on the HF production rate (expressed as tonne HF/m^2 of shell). Several heat recovery systems remove the excess heat to reduce the gas temperature down to 200/250 °C. This recovered heat is either used to pre-heat reactant feeds, the combustion air, or by other fluids in the production unit.

The recovered energy for the whole installation is estimated to be around 20 % of the total energy used.

Achieved environmental benefits
Energy savings.

Cross media effects

Applicability
The installation of a recovery system for an existing plant is sometimes impossible for that particular design. When it is possible to install a recovery system, the associated cost and modifications is usually disproportionate compared with the actual energy savings.

Economics

Driving force for implementation

Example plants
No information.

Reference literature

2.5.1.3 Spar calcinations

Description
25 % of the total fuel is used in a separate burner for the the fluorspar feed calcination process. The spar is heated to about 400 °C by countercurrent contact with flue-gases at a temperature of about 900 ºC. The gases exit the calcinator at about 110 °C so energy efficiency is very good in that part of the plant. Relatively small kiln dimensions are needed because of the high energy input into the feed to the rotary kiln. The downside of this process is the emission of about 2 to 5 % of the flotation chemicals as organic carbon in the form of cracked products.

Achieved environmental benefits
No SO_2 is produced by the reaction of the flotation chemicals with sulphuric acid.

Cross media effects

Applicability
Due to the high reactivity of the very hot spar, the reactants must be sent to the kiln directly without going to a pre-reactor. The advantages of a pre-reactor are consequently missing, for instance, the process is quite sensitive to feed ratio variations and acid concentration, which may in turn cause heavy kiln scaling.

Economics
The investment cost for spar calcination is about 50 % to 100 % higher than for the pre-reactor. This may be compensated for by a lower fuel consumption and lower maintenance costs in comparison to the pre-reactor.

Driving force for implementation

Example plants
No information.

Reference literature

2.5.1.4 Process gases purification

Description
The quality of HF produced for most users can be met without any additional distillation beeing needed to separate the high boilers, H_2O and H_2SO_4 in a comparitively high energy consuming column, using also an effective sulphuric acid scrubber and HF scrubber along with an HF condensation fractionator.

However some customers need higher grade HF. This means that a distillation column will be needed to remove the high-boilers along with a significant amount of energy, estimated at 350 kg steam per tonne of HF which equates to 0.6×10^9 Joules/t HF. The corresponding amount of refrigeration energy required to condense the HF also needs to be taken into account.

Achieved environmental benefits
Comparatively low amounts of energy used.

Cross media effects

Applicability
A column integrated in the process line or added at the end of one or more lines can be used to remove the low boiling impurities: SO_2, SiF_4 and others.

Economics

Driving force for implementation

Example plants
No information.

Reference literature

2.5.2 Valorisation of co-products

2.5.2.1 Hexafluorosilic acid

Description
The absorption of SiF_4 in hydrofluoric acid solutions yields a 25 % to 35 % hexafluorosilicic acid technical grade solution.

The possible uses of this product are:

- direct use in the fluorination of potable water
- production of the hexafluorosilicates of sodium, potassium, magnesium, lead, copper, zinc, ammonium
- production of sodium fluoride
- production of kryolith (sodium hexafluoroaluminate), potassium hexafluoroaluminate, and aluminum fluoride, for aluminum production.

Achieved environmental benefits
Disposal of bi-product into environment avoided.

Cross media effects

Applicability
As this production is in competition with the by-products originating from glass etching with HF and phosphoric acid production, and as the demand is limited, excess production has to be neutralised with lime to CaF_2 and SiO_2, before landfilling.

Attempts have been made to recover HF and SiO_2 from H_2SiF_6 as an alternative to landfilling. This is only possible when connected with a phosphoric acid production unit that can enable a re-use of the associated diluted H_2SO_4 production, but this implies modifications in the HF unit.

Economics
This option has been developed on a pilot scale and tested once on an industrial scale, but it has not proved to be economically feasible at present.

Driving force for implementation

Example plants
No information.

Reference literature

2.5.2.2 Anhydrite

Description
A substantial amount of calcium sulphate is co-produced with hydrogen fluoride in the anhydrite form ($CaSO_4$ without crystallisation water).

The preferential use of this product is as a raw material. The potential uses for synthetic anhydrite are numerous: plaster, binder for floor screed, cement industry additives, agriculture, fillers of plastics, porous bricks.

Anhydrite is the preferred material in some of these applications but for many reasons such as other raw material competition, fear of change, and quality reasons, the quantities of anhydrite produced are always in excess of demand.

For the excess quantities, two options remain:

- landfilling
- dispersion in surface waters or into the sea.

Achieved environmental benefits
Use of anhydrite as a raw material reduces the need for disposal to the environment.

Cross media effects

Applicability
The following are the main limiting factors for excess anhydrite sales:

Competition with other materials
These calcium sulphate co-products have to compete in open markets with natural and synthetic anhydrite and cement, e.g.:

- with natural anhydrite, extracted cheaply in some countries, less abundant in some others
- with synthetic anhydrite, produced by the calcination of natural gypsum or gypsum from waste gas desulphurisation, titanium dioxide and phosphoric acid production or others
- cement as a binder for floor screed
- in cement industry, it event might have to compete with gypsum.

Quality
Anhydrite is sometimes not of an equivalent quality to other products (for its use as a binder for floor screed according to European norm prEN13454 – 1 and 2, existing in the draft form). Conditions for its re-use as a raw material depend on its physical properties and on the pattern of its impurity concentrations. In many cases anhydrite quality upgrading is necessary. The cost of upgrading the co-product, and of performing the necessary analytical determinations, demonstration tests, etc, may be dissuasive.

Fear of change
Anhydrite has to compete with natural material. For example, even though anhydrite as a binder for floor screed has proven advantages over the commonly used cement, to develop a market is difficult because of local ways and customs, leading to market resilience.

All these reasons explain the slow increase in the recovery rate of by-produced calcium sulphate. Recovery is of course eased in countries in which natural anhydrite or gypsum availability is limited.

Economics

Driving force for implementation

Example plants
No information.

Reference literature

2.5.3 Abatement techniques

2.5.3.1 Absorption of gas containing HF

2.5.3.1.1 Principle of absorption

Description
Gaseous HF is readily absorbed in water or alkaline solutions. The absorption is exothermic. With pure water, an acidic solution is produced which may be re-used on the site.

The scrubbing of an HF containing vent gas can be carried out by a once-through water countercurrent contact absorber. HF is completely absorbed by water, and by an alkaline solution.

Typically the vent gas will be variable in concentration and flow so the absorption equipment (frequently a packed tower) has to be designed for maximum gas flow conditions with a minimum liquid flow, to ensure efficient wetting of the packing.
As a consequence, large liquid effluent flows with no possible valorisation of absorbed HF are obtained.

Alternatively the liquid flow can be increased by recirculation of a part of the sprayed liquid, which allows for a higher HF concentration in the liquid and some recovery of the yield.
In this case, the HF concentration in the gas at the outlet of the equipment is not zero, with the HF concentration in the exiting gas being driven by a thermodynamic equilibrium, which depends on the liquid composition and the temperature.

In addition to the HF concentration corresponding to the thermodynamic equilibrium, other sources of acidic emissions can result from:

- gas channelling in the equipment with non absorbed gas leaving the absorption unit
- entrainment of liquid acidic droplets with the gas flow.

The later problems normally do not occur if an alkaline solution is used for absorption but the recovery of the absorbed gas is feasible. A demister can also be used after the scrubber.

Whenever HF solutions need to be recovered and a very low gas emission needs to be ensured, a two steps absorption system is recommended.

Achieved environmental benefits
Release to air minimised.

Applicability,

Absorption techniques

Water absorption

- Single stage, once through absorption with copious amounts of water make up

The absorption may be implemented countercurrent in a column sprayed with water. Raw water is frequently used. Acid concentrations in the effluent water remain low or are even absent due to the usual alkaline buffer effect of raw water.

An equivalent effect can be obtained by using multistep water sprayers. A combination of sprayers with an absorption column is also possible.

The equipment is very simple (no recirculation needed nor temperature control). Investment costs are also limited.

The water consumption is large, as is the flow of waste water. HF concentrations in the range 5 – 10 mg/m^3 can be achieved in stable conditions, depending on the pH of the raw water and the equipment performance. Even lower values have been reported by scrubbing with slightly alkaline raw water, especially seawater. An eductor can also be used for absorption and gas suction. In using only one eductor, the efficiency is reduced. (reduced contact time).

- Single stage, closed loop with HF solution production

The absorption is implemented the same way as in the open loop option, but with the difference that the acidic solution is recirculated loopwise at the head of the absorber. The make-up is made of a limited pure water flow. The resulting acid is purged and may be re-used for other purposes, with concentrations up to 20 %. It may be necessary to control the temperature by cooling the recirculated solution. The HF concentration in the exiting gas depends on the acid concentration in the loop, so a second scrubber to clean the off gas is usually necessary.

- Double stage water absorption

In this option, the first stage is a operated in closed loop with acid recovery and the second stage is operated with a once through water flow, thereby achieving low emissions values.

The environmental situation is similar to the one described in the once through option.

Liquid phase alkaline absorption (single stage)

Caustic soda is frequently used as alkali. Sodium carbonate, lime or ammonia are valid alternatives. The absorption efficiency is high: typical values of 1 - 5 mg/m^3 are met in stable conditions in the exhaust gas. Single stage alkaline absorption is sufficient for limited or intermitent HF flows. As neither HF nor alkali are recovered in this option, and as large quantities of NaF in the waste water can be a problem, this solution is not recommended for large continuous amounts of HF. In this case, the solution developed in the combination of water and alkalin absorption is preferred.

Combination of water and alkaline absorption

Usually the first stage is made up of a closed loop with water make-up and hydrofluoric acid solution recovery (identical to water absorption).

The second stage is designed for the total elimination of non absorbed pollutants in an alkaline solution as described in liquid phase alkaline absorption (single stage**).** HF recovery is maximised, and the alkali consumption is minimised. Absorption efficiency is very high (typical HF concentration less than 1 – 5 mg/m^3 for stable conditions in the exiting gas). Investment is high (more than twice as in water absorption. due to necessary control instrumentation).

Solid alkaline absorption

For small effluent streams of moist HF containing gases, absorption with $Ca(OH)_2/CaCO_3$ - granulate in fixed bed is an economic possibility to prevent HF emissions. The off-gas usually contains less than 5 mg HF/m^3.

Cross media effects

Economics

The equipment necessary for HF absorption is typically made of rubber lined steel or massive PVC, polypropylene or polyethylene (optionally it may be fibre glass reinforced).

The process control equipment is not sophisticated, but nevertheless difficulties may occur with the continuous measuring of low HF concentrations in the exhaust gas.
The investment for a 100 m^3/h gas flow in a single stage, once-through absorption is in the range EUR 50 – 80000 (data valid for new plants).

For a double stage gas treatment the investment cost is in the range of EUR 150 – 200000 (new plants).

A significant additional investment cost may arise if no alkaline solution is available on-site. In such a case, the installation of a tank, a transfer line and an unfilling station may be necessary.

Operating costs mainly involve alkali consumption (if any), energy consumption, liquid effluent neutralisation and maintenance costs.

For HF solutions recovery, the alkali consumption is very low (disregarding the SO_2 absorption). When HF is not recovered, an equivalent alkali flow is consumed, either at the absorption step or at the effluent neutralisation step.

This is not true if an alkaline effluent is yielded by another production unit, with a mixing of the two flows in a common effluent treatment. There the energy consumption basically corresponds to water pumping and is usually not critical.

Maintenance costs are usually around 5 % of the investment costs per year of operation.

Driving force for implementation

Example plants
No information.

Reference literature

2.5.3.2 Effluents containing HF along with SO_2 and CO_2

Description
<u>Absorption conditions</u>
HF is readily absorbed in water as previously described.

SO_2 absorption in water is limited, and at the low pHs resulting from the absorption of HF, SO_2 absorption is virtually zero. Nevertheless the absorption efficiency can be enhanced if a copious amount of alkaline buffered water is used in a once-through process. This is especially valid when seawater is used for scrubbing.

CO_2 is not absorbed at pH values of 8 or less.

In some circumstances, an oxidative treatment of the waste water may be necessary to oxidise SO_2 into sulphates.

Achieved environmental benefits
SO_2 is converted to sulphites and then oxidised naturally into sulphates after absorption. Any problems of excess COD levels in surface waters from the releases are avoided by this conversion to neutral sulphates.

Cross media effects

Applicability
Absorption techniques

- Water absorption (single stage)
- once through absorption with copious amounts of water make up
- same principle and operation applies as for HF alone applies
- HF but also SO_2 absorption can be high thanks to the alkaline buffer effect of water used.
- same advantages/drawbacks as with HF are met

HF concentration in the exhaust gas is in the range 1 – 10 mg/m^3.

SO_2 abatement rates are in the range of 20 to near 100 %, depending on the amount and alkalinity of the water used.

- Closed loop absorption with weak acid purge

Same principle and operation applies as for HF alone.
HF absorption efficiency is high, SO_2 is not absorbed (low pH value).
The weak acid purge can be re-used in another process.

Alkaline absorption

Single stage absorption
Alkali is usually caustic soda. Lime is also possible.

Design and operation are identical to HF alone
pH value has to be above 7 to allow SO_2 absorption and below 9 to limit CO_2 absorption.

The HF concentration in the exhaust gas is in the range 1 – 10 mg/m^3.

SO_2 concentration is typically in the range 5 –100 mg/m^3.

Double stage absorption
First stage is usually fed with water, and allows HF recovery. Second stage absorbs SO_2 in an alkaline solution. pH value at the second stage has to be in the range 7 to 9.
An HF concentration in the range 1 to 5 mg/m^3 can be expected whereas SO_2 concentration in the range 1 – 100 mg/m^3 (depends on the pH and the design) result

Economics
Investments are identical as for the HF alone case, for the same exhaust gas flow and the same combination of absorption steps.

The same applies to the operating cost after the addition of the alkali consumption corresponding to SO_2 absorption.

Driving force for implementation

Example plants
No information.

Reference literature

2.6 NPK/MN and superphosphates fertilisers

These techniques are included in the common abatement Section 2.9.2

2.7 Urea

The information for this chapter has been taken from the Dutch notes on BAT for the production of fertilisers.

2.7.1 Pool reactor and pool condenser

Description

The stripper off-gases are condensed in a horizontal submerged condenser, which is an intrinsic part of the urea reactor. In this way, two complete process steps, i.e. condensation and dehydration can be combined in one vessel. The CO_2 stripper is left unchanged. However, the stripper off-gases along with the recycle carbamate solution and the ammonia feed are introduced into the pool reactor. The liquid phase is thoroughly agitated by the gases from the stripper. The heat of condensation is used for aiding the dehydration reaction and for generating steam in the tube bundle. The pressure of the generated steam controls the rate of condensation. The part of the pool reactor that is equipped with the tube bundle is the condensing part of the reactor, while the other section can be called the reaction part. The pressure at the shell side of the reactor is 140 bar, the temperature at the reactor outlet is 185 °C. [10, InfoMil, 2001]

It is also possible to install only a pool condenser. Basically, the pool condenser is a horizontal vessel with a submerged U-tube bundle. It is fabricated from carbon steel with internals and lining in stainless steel. Strip-gases are condensed in a pool of liquid on the shell side, with a low-pressure steam being generated on the tube side. Applying an adequate residence time allows the reaction of ammonium carbamate to urea and water to proceed for up to 60 % of equilibrium. The condensation temperature on the shell side is high as a result of the formation of high boiling components of urea and water, resulting in a higher temperature differential for the exchanger. The formation of gas bubbles ensures a high degree of turbulence and provides a large area for mass and heat transfer. Both phenomena contribute to a higher heat transfer [10, InfoMil, 2001].

Achieved environmental benefits

When a pool reactor is used, an ammonia emission in the synthesis phase of 2.5 gram/tonne product (<700 mg/m^3) is achievable.

Advantages:

The technical advantages of the pool reactor are:

- the heat transfer in the reactor condenser bundle is much better than in falling film condensers
- the baffles in the reactor prevent back-mixing
- the inverse response of the synthesis loop is eliminated
- the synthesis is much less sensitive to deviations in the N/C ratio.

Technical advantages of the pool condenser are:

- the urea reactor volume is reduced by some 40 %
- 45 % less heat-exchange area
- structure height is reduced by some 10 metres
- less stress corrosion, because of the absence of crevices between the tube and tubesheet
- higher operational flexibility.

Environmental advantages:

- reduction in NH_3 emission
- less heavy equipment
- savings can be achieved in energy consumption and raw materials in the heavy equipment industries.

Cross-media effects
Reduction in energy consumption.

Operational data

Applicability
The pool reactor can be used for new and existing urea plants. The installation of this type of reactor in an existing urea plant could be economically prohibitive. The pool condenser can also be used in new and existing urea plants.

Economics
Installation of a pool reactor in existing urea plants may be cost prohibitive. Energy and process efficiencies are economically advantageous.

Driving force for implementation

Example plant
In 1998, Stamicarbon introduced the pool reactor at the urea plant of DSM Geleen (the Netherlands). This plant had a capacity of 425 ktonne of urea a year. However, due to optimising the production process and installing an intermediate pressure recirculation system, the capacity of this plant has been recently upgraded to 525 ktonne/year. The NH_3 emission to the atmosphere from process vents is <700 mg/m^3 (2.5 g/tonne product). DSM Geleen use the urea produced as a liquid raw material in melamine production. Therefore solidification is not necessary and there is no NH_3 emission to the atmosphere due to a solidification process.

The pool condenser is used in the urea plant of Karnaphulli Fertilisers Company in Chittagong, Bangladesh.

Reference literature
[10, InfoMil, 2001]

2.7.2 Granulation as a finishing technique

Description
Several finishing processes have been used to solidify fertiliser melts, including graining, flaking, granulation, crystallisation, and prilling. Currently, the most common finishing techniques are prilling and granulation. The suitability of these granulation and prilling processes is dependent on the required product qualities.

The disadvantage of prilling for limited product-size and strength has brought about the development of several granulation techniques. Various types of granulation equipment are now available, such as pugmills, drum granulators, pan granulators and fluidised-bed granulators. In order to improve conditions or product quality, binding agents and other additives (e.g. pigments) can be added to the granulation feed stock. [10, InfoMil, 2001]

After the formation of the granules, it may be necessary to dry and/or to cool the product. Various pieces of equipment are available for this, but mixing drums, drying drums and fluidised bed systems are widely used. Additionally, the granules are often coated to improve anticaking properties. Pigments may also be added to to urea based fertilisers as a marketing tool. e.g. based on their N-percentage.

Achieved environmental benefits
Dust emissions from product finishing in the range of 90 - 150 g/tonne product are achievable.

Advantage:
Urea granulation plants using a reduced airflow give a higher but coarser urea dust content than prilling plants. The coarser dust particles can be easily removed from the exit gas stream, e.g. by means of a scrubber. Ammonia releases from granulation in urea plants are reported to be 0.2 - 0.7 kg/tonne product and dust emissions as 0.1 - 0.5 kg/tonne product.

Cross-media effects

An addition of acid to the scrubber enhances scrubbing efficiency, however the suitability of this technique will depend upon the local site specific situation related to recovery potential of the scrubber effluent (such as eg. for UAN production).

Operational data

Applicability

In principle, granulation can be applied to all fertiliser plants that solidify their product. However, when technical grade urea is produced the client may require certain properties of the final product that makes granulation technically impossible, e.g. a relatively small average diameter or a relatively low biuret content (1 % w/w).

The quality of the granules e.g. the size, roundness, strength, moisture content, caking tendencies, and hygroscopicity, is influenced by the following factors:

- type and fineness of the feedstock
- moisture content of the granules
- surface tension of the wetting liquid
- wettability of the particles
- mode of motion in the granulator
- inclination and speed of the granulator
- type and properties of the binding agents
- humidity
- temperature
- amount and particle size of the recycle.

Economics

Driving force for implementation

Example plants

In the EU, both prilling and granulation plants are in operation. Most of the Dutch fertiliser plants apply granulation as a finishing technique. However, one company has a granulation section as well as a prilling section. The prilling section is used to produce technical urea.

Reference literature

[10, InfoMil, 2001]

2.7.3 Plate bank product cooler

Description

In the urea solidification process, the product is normally directly air-cooled, which leads to a urea dust emission. Dust emissions in the cooling section can be avoided by using a plate bank product cooler. In this “closed” cooling system there is no direct contact with the water-cooled plates. Hot material is fed to the top hopper where it is distributed to the plate bank. The product is cooled while it moves under true mass flow conditions between the water-cooled stainless steel plates. A gate valve in the discharge hopper regulates the flowrate.

Achieved environmental benefits

Advantages:

- no dust emission, so extra emission control techniques are not necessary
- the heat can be recovered in other processes.

Disadvantage:

- regular cleaning of the installation is needed.

Cross-media effects

A small reduction in the energy demand of the cooling process is achieved. For example: the energy demand of the plate bank cooler is approximately 80 – 100 kWh less than a cooling drum.

Operational data

Applicability

In principle, a plate bank production cooler can be used for the production of all fertilisers.

Typical performance per unit:

- throughput: 5 – 60 t/h
- heat capacity approximately: 209300 – 3140000 kJ/h
- cooling water: 280 – 4200 l/min
- instrument air: 10 l/m.

Economics

Investment is approximately EUR 136000 (for an installation with a capacity of 15 tonne/hour).

Driving force for implementation

Example plants

Grande Paroisse (France) produced prilled urea. The prilling tower in the urea plant had a production rate of 1020 Mt per day and had an airflow of 376500 Nm^3/h. Due to capacity problems with the conventional cooler in the summer, Grande Paroisse installed a plate bank product cooler in their urea plant in Toulouse in July 1997. The product cooler was used to cool the urea prills and had a capacity of 900 tonne/day. The temperature of the product at the inlet of the cooler was 105 °C and the product was cooled to a temperature of 65 °C. Water with a temperature of 40 °C was used as cooling medium; the cooling water had a temperature of 45 °C at the outlet of the cooler.

When the cooler was installed there were some problems with urea sticking on the plates of the cooler when stopping the production process. This problem occurred as a result of the hydroscopic nature of urea. However, this had been overcome by using a small proportion of hot air when the process was stopped. No problems occurred when starting the production process. Grande Paroisse was studying the possibility of installing a plate bank product cooler in the production process of NPK.

The Toulouse plant is now shut-down.

Fosfertil (Brazil) uses a plate bank cooler for the production of prilled urea. SKW has 3 plate bank coolers for granulated urea production.

Reference literature

[10, InfoMil, 2001]

2.7.4 Redirecting dust into a concentrated solution

Description

When granulation is used as a finishing technique, oversized (after crushing) and undersized products are recycled to the granulator and form the nuclei for the granules. Dust is often separated after the granulator and also redirected to the installation. These particulates are transported along with the fluidisation air to the scrubber, ending up as a diluted solution that is concentrated by evaporation. But, it is also possible to re-route the particulates to a concentrated solution instead of to the granulator**.**

Achieved environmental benefits

Advantages:

Particulate emissions are reduced and a less dilute solution is produced, which also means that less energy is needed for evaporation.

Cross-media effects

Operational data

Applicability

In principle, diverting the particulates to the concentrated solution can be carried out in any urea fertiliser plant where a solidification process is used.

Economics

The project costs at HAS were approximately EUR 143300.

Driving force for implementation

Example plants

Hydro Agri Sluiskil (HAS) introduced this technique in the Netherlands in 1999. HAS has two urea plants (urea 5 and urea 6). The finishing section of urea 5 consist of a granulation installation for the production of urea granules or ureas granulates; the installation has a capacity of 1050 t/day for urea and 1360 t/day for ureas. The finishing section of urea 6 consists of a prilling installation with a capacity of 1300 t/day. By applying this technique the company saves about 32000 tonnes of steam a year. The reduction of dust emission is not clear as yet.

Reference literature

[10, InfoMil, 2001]

2.7.5 Process water and process condensate purification

Description

A 1000 t/day urea plant generates approximately 500 m^3process water/day. The principal source of this water is the synthesis reaction, where 0.3 tonnes of water is formed per tonne of urea produced. The other sources of water are ejector steam, flush and seal water and the steam used in the waste water treatment plant.

Three techniques are described to purify the process water/process condensate of a urea plant:

1. Hydrolysis system

Heated process water is fed to the top of the first desorber (desorber 1) where NH_3 and CO_2 are removed by the gas flow from the second desorber (desorber 2) and the hydrolyser. The liquid leaving desorber 1 bottom is preheated to 190 °C and fed at 17 bar pressure to the top of the hydrolyser. Steam at 25 bar pressure is fed into the base of the hydrolyser. Under these conditions urea is decomposed and the gases are stripped countercurrently. The vapours go to desorber 1. The urea free liquid stream leaving the desorber is used to heat the hydrolyser feed stream and is fed, after expansion, to desorber 2 where LP steam countercurrently strips the remaining NH_3 and CO_2 and the off-gases pass to desorber 1.

The off-gases from desorber 1 are condensed in a cooled reflux condenser/separator. Part of the separated liquid is pumped back to desorber 1 and the remainder is returned to the LP recirculation section of the urea plant. Residual NH_3 in the separator off-gas is recovered in an atmospheric absorber and returned to the LP recirculation section also.

The treated gas from desorber 2 is cooled and concentrations of 5 mg/l free NH_3 and 1mg/litre urea are possible.

2. Distillation-hydrolysis system

Heated process water is fed to the top section of a distillation tower for NH_3 and CO_2 removal. The effluent liquid is preheated before feeding to the hydrolyser where urea is decomposed to NH_3 and CO_2. The hydrolyser and distillation tower vapours are mixed with off-gases from the LP decomposer separator, cooled and recycled to the process. After effluent treatment, water suitable for boiler feed is possible. Treated water containing 5 mg/l free NH_3 and 1mg/liter urea can be achieved.

3. Stripping-hydrolysis system

Heated process water containing NH_3, CO_2 and urea is fed to the top of a steam stripper operated at 1.5 – 3 bar to separate the NH_3 and CO_2. The water is then fed from the middle section to the hydrolyser operating at 16 – 30 bar. The gaseous overheads are then sent through the LP decomposer/absorber to the synthesis for recovery of NH_3 and CO_2.

Free NH_3 and urea concentrations of 3 – 5mg/l ^{1} for each component are expected in the treated water.

The process water, as well as the process condensate/turbine condensate, can be re-used as boiler feed after treatment. The treatment could consist of: ion exchange, distillation or membrane separation techniques

The LP steam produced in the carbamate condenser is used for heating purposes in the downstream section of the plant. The excess may be sent to the CO_2 booster or exported for use in other site activities.

Achieved environmental benefits

Advantages:

- reduction of the emissions to the surface water, which also has an economic advantage due to the decreasing of the applied levy
- possible re-use of recovered urea and ammonia
- reduction of the amount of fresh-water used.

Cross-media effects

Energy is consumed from the hydrolysis and stripping operations.

Operational data

Applicability

In principle, all the technologies described above can be applied to all types of urea plants. Before re-use as a boiler feed, the process water/condensate needs treatment. The re-use of process steam is preferable to condensation, when energy savings are considered.

Economics

Driving force for implementation

Example plants

Quite a number of urea plants in the EU and all urea plants in the Netherlands treat their process water/process condensate and partly re-use the purified water (as e.g. boiler feed or scrubbing water).

Reference literature

2.7.5.1 Ammonia emission control in fluidised beds

Description

The liquid urea feedstock to the solidification section, either as a melt or as a concentrated solution, contains some dissolved ammonia. This arises from residual traces of ammonium carbonates, urea decomposition products and the dimerisation to biuret. This residual ammonia is stripped/flashed during the solidification process and is released along with cooling air to atmosphere.

Hydro Agri Sluiskil has studied a chemical scrubbing process based on the same organic formaldehyde-based additives already used in the granulation process for product quality improvement (shape, crushing strength, anticaking). Gaseous formaldehyde, vaporised from a fine liquid mist injected into the hot air stream at the granulator vent, reacts preferentially with the stripped ammonia to form HMTA (hexamethylenetetramine). In this hot dry atmosphere, this is the preferential reaction rather than the standard urea-formaldehyde reaction. The urea-formaldehyde reaction would be prevalent in the dilute urea solution stage of the scrubbing operation downstream. The unstable HMTA compound is dissolved in the dilute scrubbing liquor and is recycled to the vacuum concentration section, where HMTA decomposes to ammonia and formaldehyde. The formaldehyde is kept in solution, where it reacts with the large excess of urea and finally becomes a part of the granulation additive.

The ammonia is absorbed in the process water condensate and is recycled to the urea synthesis section.

Achieved environmental benefits

Application of this technique can lead to a 50 % reduction of the ammonia emission**.** This ammonia abatement system has comparatively low operational costs. The ammonia that reacts with formaldehyde to hexamethylene tetramine is recycled to the pre-evaporator, where it decomposes to formaldehyde and ammonia. The formaldehyde is then used as a standard urea additive.

Disadvantage:

The system is sensitive to the type of urea-formaldehyde (UF) present. Free formaldehyde is the active component. If not readily available due to being in a very stable molecular structure, the efficiency will be less. The recycling of urea-formaldehyde containing compounds to the urea evaporation section can have a negative influence on the quality of the waste water produced in the desorption/hydrolyses stage of the urea plant.

Cross-media effects

None.

Operational data

Applicability

It is important to have sufficient free formaldehyde for the ammonia abatement. This is the reactive component which combines with the ammonia. The instability of urea-formaldehyde (UF) would lead to it reacting with and depleting free formaldehyde. Formaldehyde-based additives instantaneously react with the wide excess of urea to form polymers, leaving no free formaldehyde. The additive does not affect the final product safety**.** The product can be used in all fertiliser applications, as an animal feed component and in most formulations with other compounds, particularly with urea-formaldehyde glues where the additive already replaces a part of the reactants. A part of the granulation additive can still be injected, via the standard route, at this stage for flexibility of operation.

Economics

The ammonia abatement system has relatively low operational costs; formaldehyde is already available at the production site.

Driving force for implementation

Example plants
Hydro Agri Sluiskil has two urea production plants: urea 5 and urea 6. The finishing section of urea 5 consist of a granulation installation for the production of urea granules or ureas granules; the installation has a capacity of 1050 t/day for urea and 1360 t/day for ureas. The finishing section of urea 6 consists of a prilling installation with a capacity of 1300 t/day. By applying this process Hydro Agri has been able to reduce its average ammonia emission to 0.2 – 0.3 kg ammonia/tonne. i.e. half the unabated level of c. 0.4 – 0.6 kg ammonia/tonne, without any significant emission of the formaldehyde reactant.

Incitec (Brisbane, Australia) operates a urea synthesis plant with the Vulcan process, with a capacity of 750 t/day. This product was traditionally prilled. However under market and environmental pressure, it was decided to switch from prill to granulation technology.

Reference literature
[10, InfoMil, 2001]

2.7.5.2 Waste water purification

The purification of contaminated water as an end-of-pipe technology can be achieved through several techniques: reverse osmosis, ion exchange, distillation, stripping, biologically, and by coagulation/sedimentation. However, reverse osmosis, ion exchange, distillation and stripping are commonly used as integrated measures to anable a re-use of the process water.

2.7.5.2.1 Biological waste water treatment

Description
Biological treatment involves the treatment of nitrogen contaminated waters using activated sludge or aerated systems to promote nitrification, converting ammonia to nitrate. Further biological treatment using anaerobic processes can transform the nitrate to gaseous nitrogen and oxygen, depending on the level of nitrate.

Achieved environmental benefits
Advantage:
This technology is capable of treating 20 – 60 mg/l of ammonia-contaminated waste water at less than 10 mg/l, assuming a 90 % treatment efficiency.

Cross-media effects
None.

Operational data

Applicability
The optimum temperature for nitrification is between 20 and 32 °C, and ceases when the temperature drops below 5 °C. Fortunately, process effluents are normally warm and this ensures that the reaction is sustained. Process waste water is normally low in organic matter that could limit the biological oxidation. A source of alkali is also needed to control acidity levels. Most integrated sites have ready supplies of organic matter and neutralising agents. In principle, a biological waste water treatment can be applied to all types of urea plants, but, it is probably only economically feasible if several plants can utilise a common purification facility.

Economics
This technique is only economical feasible when several plants make use of a common purification facility.

Driving force for implementation

Example plants

Reference literature
[10, InfoMil, 2001]

2.7.5.2.2 Physical-chemical waste water treatment

Description
Chemical precipitation is a technique used for forming particulates that can be separated by a secondary process, such as sedimentation, air flotation or filtration, backed up if necessary by micro-filtration and ultra-filtration. Fine separation by membrane techniques may be needed to protect downstream facilities or to prevent the discharge of hazardous particulates. It could also be a useful technique for the removal of colloidal precipitates, such as heavy metal sulphides. A precipitation facility usually consists of one or two stirred mixing tanks, where the reagent and other chemicals are added along with a sedimentation tank and storage tank for the chemical reagents. Further treatment equipment may be added if needed. The sedimentation tank may be replaced further downstream by other sludge collecting systems. Typical reagents used are milk of lime along with the necessary mixing systems, dolomite, ferrous/ferric salts, sodium sulphide, aluminium sulphate, polymers and polyorganosulphides. In the fertiliser industry, lime is usually used as the precipitation chemical.

Application limits and restrictions:
The optimum pH range for heavy metals, phosphate, and fluorides is pH 9 - 12. Precipitation of heavy metals, such as copper and nickel may be limited by the presence of complex forming substances.

Achieved environmental benefits (with lime as reagent)
Prevention of an increasing salt content in the waste water, improvement in sludge sedimentation, sludge thickening, improvement of mechanical dewatering of the sludge, reduction of chemical dewatering cycle time. Achieved emission levels using lime as agent (in general): Cadmium: 0.09 mg/l; Copper 0.07 mg/l; Fluoride <3 mg/l, phosphate 0.5 – 1.0 mg/l.

Disadvantages:
Operating problems associated with the handling, storage and feeding of lime, as well as maintenance problems.

Applicability
Chemical coagulation-sedimentation techniques using lime and with a polyelectrolyte have proven to be a successful techniques for purifying waste water produced from the scrubbing towers. However, for more dilute effluents, electrodialysis, reverse osmosis, ion exchange, or evaporation and distillation concentration processes are potentially more suitable. In principle, precipitation can be applied in all SSP/TSP plants. However, it is only economically feasible when several plants can make use of the same purification facility.

Cross-media effects

Operational data

Applicability

Economics

Driving force for implementation

Example plants
DSM Geleen in the Netherlands uses a physico-chemical waste water treatment as well as a biological waste water treatment system that collects all plant waste water at the DSM-site (urea, synthetic rubber, plastics, melamine, ammonia etc). For Kj-N the treatment system has an efficiency of about 93 – 95 %; for NO_3-N the efficiency is about 70 – 85 % [10, InfoMil, 2001].

BASF Ludwigshafen (Germany). Waste water from the off-gas scrubbing, the sand washer and the washing and rinsing processes arises from the raw phosphate decomposition in NPK-fertiliser production. The effluents from the sand washer and the off-gas scrubber are treated in the biological waste water plant. The principal waste water parameters are fluoride, nitrate and phosphate. The content of phosphate has a positive impact on the nutrient ratio in the waste water treatment. The measurements of 23 March and 6 April 1998 revealed an average waste water volume of 3026 m^3/day, the single measurements fluctuating between 2400 and 4000 m^3/day [10, InfoMil, 2001].

	Load per day	**Specific load in relation to phosphate volume**
P	237 kg/d	1.12 kg/tonne P_2O_5
F	282 kg/d	1.33 kg/tonne P_2O_5
NO_3 N = total N	901 kg/d	4.26 kg/tonne P_2O_5

Table 2.23: The average loads of the waste water parameters as well as the specific loads in relation to the phosphate volume

The values stated in the table can significantly fluctuate, depending on the phosphate quality.

Reference literature
[10, InfoMil, 2001]

2.8 Ammonium nitrate

The description which follows is for a typical plant. Plant configuration will vary from plant to plant. Operating parameters such as temperatures, pressures, compositions will also vary considerably from the quoted values.

2.8.1 Process integrated measures for AN (derivatives) production

2.8.1.1 Optimisation neutralisation section

Description
The neutralisation section has a significant effect on the environmental performance of the system. As previously described, many different neutralisation processes are used. Several parameters can affect the neutralisation section environmental performance:

Preheating:
AN formation is an exothermic reaction. The heat produced is frequently used to preheat the nitric acid or to concentrate the AN solution. Preheating of the nitric acid is used to increase the reactivity.

pH:
Lowering the pH during neutralisation, reduces the nitrogen losses will be. On the other hand, many acid solutions have the tendency to heat themselves. When the reaction temperatures are below 170 °C, the pH level is generally kept between 2.4 and 4. Higher pressure neutralisers tend to operate at higher pH than atmospheric neutralisers. The pH should be strictly controlled and kept stable, particularly to prevent the decomposition of ammonium nitrate. At higher

temperatures, other, more hazardous reactions start taking place. Several factors influence the decomposition of AN:

- **pH**: AN solutions containing >0.01 % free NH_3 (pH >4.5) normally do not decompose below 169 °C. A more acid solution might heat itself, depending on the temperature of the environment
- **contaminations**: all contaminations are potentially hazardous, but especially organic materials (<100 ppm total carbon compared to 100 % AN), chloride (<300 ppm), heavy metals (Cu, Zn, Mn, Fe, Cr <50 ppm) and nitrite (<200 ppm) should be avoided
- **pressure**: building pressure might cause physical explosions, however in all cases. it should be possible to relieve pressure
- **temperature and water content**: the decomposition of AN **proceeds** faster at higher temperatures and slower at higher water contents. [10, InfoMil, 2001]

Temperature:
Higher temperatures leads to the decomposition of AN. The higher the temperature in the neutraliser, the more important it is to control the pH value and the level of impurities [10, InfoMil, 2001]

Pressure:
Neutralisation at an increased pressure increases the steam temperature and the concentration of AN in the solution. Although energy is needed to pressurise the neutraliser, modern processes at elevated pressures are net producers of energy (excluding product finishing). Older plants working at atmospheric pressure need to import steam [10, InfoMil, 2001]. Atmospheric neutralisers have relatively low capital costs and are relatively simple to operate, so atmospheric neutralisers are often preferred when sufficient steam is readily available from the by-product or from other low-cost sources [10, InfoMil, 2001].

Impurities:
Many substances have a significant catalytic effect on AN decomposition. Organic materials, chloride, heavy metals and nitrite will give particularly hazardous mixtures, and in fact it can be assumed that all impurities are potentially hazardous. Some manufacturers do not recycle screenings to the neutraliser for this reason. If the screenings are potentially contaminated by organic anticaking additives, recycling is not advisable.

A two-stage neutraliser operates with a low pH in the first stage and a neutral pH in the second. Due to this change in pH value, most of the steam is produced in the first stage and most of the ammonia emission in the second. A two-stage neutraliser reduces the overall ammonia emission compared to a single stage neutraliser, but it is more expensive [10, InfoMil, 2001].

AN formation is exothermic and this excess energy converts water from the nitric acid solution to steam at approximately 2 bar. A balanced design of the neutraliser reduces the concentration of NH_3 and AN in the steam to a few hundred ppm instead of a few thousand ppm [10, InfoMil, 2001].

In some plants, part of this steam is recycled to the process (e.g. in the evaporation section or for preheating the feedstock) or used in co-located plants. The remainder of this steam is often condensed to prevent releases to atmosphere. This process condensate can be recycled in the process or used in other plants, but this recycling is often combined with the water emission from the evaporation section.

Achieved environmental benefits
A balanced design of the neutraliser reduces the concentration of NH_3 and AN in the steam to a few hundred ppm instead of a few thousand ppm. Neutralisation at an elevated pressure will produce steam at a higher temperature and AN of a higher concentration [10, InfoMil, 2001].

Cross-media effects
No cross-media effects occur.

Operational data

Applicability

The issues listed above are not only relevant to prevent environmental effects, and hazardous conditions, but also ensure a high quality of product and a more efficient process. The balance between these parameters is very sensitive. It can be assumed that these parameters will have been optimised for the technical specification of the existing plant. Neutralisers working under pressure or over two stages to improve environmental performance are technically feasible for backfitting to existing plant but may be economically non-viable

Economics

The optimisation of the neutralisation section is not only relevant from an environmental point of view, it also optimises the process. Higher investments for e.g. two stage neutralisers are likely to repay themselves. Single stage neutralisers are cheaper and simpler [10, InfoMil, 2001].

Driving force for implementation

Example plants

As above, the parameters should be optimised from an economic and environmental point of view, as well as for safety reasons. All plants across the world could be expected to operate at an optimum within the technical limitations of the plant. In principal, better performances are obtained using neutralisers working at low pH and/or at high pressure.

DSM Agro IJmuiden (the Netherlands) uses two stage neutralisers. The first stage takes place in an acid environment, pressurised to 2 bar. The AN solution is depressurised before sending it to the second stage, where the solution is neutralised. [10, InfoMil, 2001]

Kemira Agro Rozenburg (the Netherlands) (now shut-down) used a two-stage neutraliser. The first step of the neutralisation takes place at a pH value of 2 to prevent ammonia losses. In the second step, the solution is neutralised to pH=6.

Reference literature

[10, InfoMil, 2001]

2.8.1.2 Re-use of process steam and process water

Description

Ammonium nitrate plants might be integrated with other plants on site to use common steam or liquid effluent streams. For example, the integration of these plants with nitric acid production leads to reductions in the ammonium effluent from the ammonium nitrate production. Process condensate from ammonium nitrate production contaminated with ammonium nitrate and ammonia can be used as process water in the nitric acid plant.

Process steam can also be used to vaporise and heat ammonia or to heat nitric acid. The heat of reaction of AN evaporates part of the water from the nitric acid solution (normally 45 – 60 % nitric acid). The approximately 2 bar steam raised is contaminated with NH_3, HNO_3 and AN. This unclean steam can be used to vaporise and heat ammonia or nitric acid. The condensed steam can be further used as scrubber water. The effluent could be further used as boiler water feed (possibly after further purification) or for control/analysis purposes.

Process steam and process water may be directly re-used or purified before use in other processes. The process steam may also be condensed before direct re-use or purification. Several purification techniques for process steam or process water are described as follows:

<u>Steam purification techniques in the neutralisation stage:</u>

These techniques can be divided into droplet separation techniques (e.g. knitted mash de-mister pads, wave plate separator and fibre pad separation) and scrubbing devices (e.g. packed columns, venturi scrubbers and irrigated sieve plates).

Scrubbing devices usually use nitric acid to neutralise any free ammonia and help in the removal of fine ammonium nitrate particles. An alternative use is scrubbing with ammonium nitrate solution followed by a suitable de-misting.

<u>Steam purification techniques in the evaporation stage:</u>
Steam can be purified through droplet separators similar to those used for the neutralisers or through scrubbers used for fine dust and fume. These scrubbers are similar to those used in the production of solid product. Candle, venturi and cyclonic devices are frequently used in combination with scrubbers.

<u>Condensate purification techniques:</u>
For the purification of steam after condensation, techniques include: membrane separation processes, ion exchange, distillation, and stripping with air or steam with the addition of alkali to liberate ionised ammonia if required.

Achieved environmental benefits
<u>Advantages:</u>

- fresh water usage minimised
- releases to surface water minimised. This also has an economic benefit by decreasing the levy cost
- process energy balance optimised
- releases of NH_3, HNO_3 and AN mist minimised
- recovered ammonia can be re-used in the main ammonium nitrate process.

Cross-media effects

- a stream of contaminated waste water is produced when process steam is condensed
- the relatively high-energy consumption is a cross-media effect if reverse osmosis is used.

Operational data

Applicability
In principle, the re-use of process steam and process condensate may be applicable in all types of fertiliser plants. It may be more economically viable to release waste water to the environment, if acceptable, although a partial re-use is possible in almost all AN plants.

The choice of purification technique depends on the local situation and if nitrogen removal is needed, for the receiving water. A combination of several purification techniques can be applied if needed. The re-use of process steam is preferred to condensation when considering process economics.

Economics
The re-use of process steam offers an economic advantage due to the energy saving achieved through the reduced need for steam generation. Re-use of process water also offers economic advantages due to a reduction in the generation of waste water, which has on an effect on the waste water.

The total project costs (including research etc.) of the reverse osmosis installation at the BASF side was approximately EUR 2.1 million.
Operational data

Driving force for implementation

Example plants
The AN plant of DSM Geleen (the Netherlands) produces about 25 m^3 process condensate/hour. The unclean steam is cleaned by means of a venturi scrubber and a candle filter and then used to vaporise and heat ammonia to 90 °C and to heat nitric acid to 60 °C. Used steam is condensed, with 20 – 25 % then being recycled as scrubber water, and the remainder being sent to the DSM waste water treatment.

At DSM IJmuiden (the Netherlands), the unclean 2 bar steam is used to vaporise and heat ammonia, as well as to heat nitric acid and to produce 1.5 bar clean steam. The remainder of the unclean steam is condensed and partly re-used, with the rest being released to surface water. Water vapour from the concentration section is condensed, cleaned by scrubbing with a circulating, impure AN-solution, and then released to the surface water.

Kemira Rozenburg (the Netherlands) (now closed) condensed the unclean steam and combined this with the condensate from the evaporation section. Half of this water was re-used as absorption water in the nitric acid plant, while 3 % was re-used as dilution water in the UAN-plant. The remainder was released to the surface water.

Reference literature
[10, InfoMil, 2001]

2.8.1.3 Integral re-use of low thermal contaminated vapours using a coolant cycle

Large volumes of contaminated low-temperature (125 – 130°C) steam are generated in the manufacture of AN. Some of this steam is discharged into the atmosphere.
It is possible to use the energy from the residual low-temperature vapours by means of an air conditioning unit, namely to cool the air, which in turn cools the final product. The process steam can be partially used as a heat source in a lithium bromide absorption-cooling unit to provide the cooling necessary for the fluidised bed in a granulation plant.

Description of the AN liquor unit
Gaseous ammonia at 8 bar pressure is reacted with hot nitric acid in a venturi type reactor where the temperature is raised to about 200 °C. The reactor product is fed to a packed column where it is concentrated as steam evolves. The pressure drops to about 1.2 bar. The steam flashes off the liquor in the column but as equilibrium conditions are not achievable there is a resultant imbalance with the steam temperature and liquor, that results in a loss of energy efficiency. As the reaction is incomplete, an alkaline vapour and acid liquor remain.

This liquor/steam mixture is discharged through a cyclone separator. The separated liquor is pumped to the storage tank and steam which remains uncondensed after heating the raw materials is discharged to atmosphere.

Process steam can be used for: heating demineralised water to the de-aerator, providing the energy supply to the lithium bromide absorption cooler, in steam supply to the granulation units, and in consumption by the AN plant.

The process steam from the pre-concentrator is partly condensed by heating the raw materials. The balance of the steam is discharged to the atmosphere.

Description of the LiBr absorption cooling system
Cooling by using this type of absorption processes is not unique and has been widely used in industry. The advantage of the process, which is based on an aqueous solution of LiBr, is that the product is relatively harmless and its properties make it suitable for reaching temperatures for chilled water of 4 °C.

The refrigeration cycle can be divided into 5 steps:

1. **Concentrator (also called generator):** An external heat source of hot water, flue-gas, or steam is used to heat a dilute solution of LiBr and water at 0.1 bar. In this case, the process steam from the AN reaction is used. The resulting concentrated LiBr solution passes to the absorber and the water vapour is drawn into the condenser
2. **Condenser**: Water evaporated from the LiBr solution is condensed by cooling water flowing through the condenser tubes, and passes to the evaporator
3. **Evaporator**: Water designated as the refrigerant is sprayed across a tube bundle where it is evaporated at a much lower pressure, about 0.01 bar, by "hot" chilled water, which in turn is cooled. The absorption which occurs lowers the pressure
4. **Absorber**: The refrigerant vapour is drawn into this section by the vacuum effect created by the absorption of the refrigerant in the concentrated LiBr solution (absorbent) from the absorber. As the LiBr has a high affinity for water, the water refrigerant vapour is absorbed by the concentrated solution, which becomes more diluted. The absorbent uptake of refrigerant vapour is a function of the absorbent solution concentration and temperature. The more concentrated and cooler the solution, the greater the uptake of refrigerant vapour. Cooling water flowing through this bundle takes up the heat of absorption. The cycle is completed by the dilute solution returning to the concentrator
5. **Heat-exchanger:** The dilute solution from the absorber is heated by cooling the concentrated solution from the concentrator, reducing both the amount of heat to be supplied to the generator and the amount of heat to be removed from the absorber.

The chilled water from the refrigeration unit cools the air to the fluidised bed in a finned bank heat-exchanger before returning to the refrigeration unit closed circuit.

Achieved environmental benefits
Energy optimisation (reduction of steam and electricity consumption), nitrogen recovery and a reduction in pollutants of approximately 50 %.

Cross-media effects

Operational data

Applicability
The evaporation pressure of the ammonia must be as low as possible in order to utilise the cooling effect for the water cooling in the closed circuit. These conditions are achieved by modifying the process so that ammonia is evaporated at 5 bar absolute pressure and the process steam is produced at 3 bar absolute. At this pressure, the low temperature of ammonia can be used as cooling water and for chilling the process condensate.

Economics
Approximately EUR 900000.

Driving force for implementation

Example plants
Fertiberia S.A. in Cartagena (Spain) has two granulation units for the production of AN/CAN and NPK fertilisers, with a capacity of up to 900 t/day each unit.

The units have been in operation since 1969. The production is based on a AN liquor supplied by the neutralisation plant built at the same time and revamped in 1975 when a second nitric acid unit was built. The P_2O_5 is supplied as TSP and MAP. Another product of the plant is ASN, which is based on the AS supplied from the factory.

The factory originally had problems with the concentration of AN liquor, energy consumption, pollution, quality and its production capacity.

To overcome these problems the site decided to install the described system in the AN plant with the following equipment data:

• heat source:	process steam
• process steam pressure:	180 kPa
• process steam flow:	2.76643 kg/kWh
• concentrator n° passes:	1
• cooling power:	2019.05 kW
• power consumption:	
- system pumps:	11.19 kW
- chilled water pump:	88 kW
- condensate pump:	14 kW
- cooling water pump:	57 kW.

	Evaporator	Absorber	Condenser
Fluid	Chilled water	Cooling water	Cooling water
Inlet Temperature, ºC	8	32	*
Outlet Temperature, ºC	4.5	*	42.5
Flow, l/s	137.32	124.15	124.15
Pressure drop, kPa	104.55	-	34.69
Tube material	95/05 Cu Ni	316 SS	316 SS
* Tube bundles in series			

Table 2.24: Equipment performance

Reference literature
[10, InfoMil, 2001]

2.9 Common tecnniques

2.9.1 Environmental management tools

Description
The best environmental performance is usually achieved by the installation of the best technology and its operation in the most effective and efficient manner. This is recognised by the IPPC Directive definition of 'techniques' as *"both the technology used and the way in which the installation is designed, built, maintained, operated and decommissioned"*.

For IPPC installations an Environmental Management System (EMS) is a tool that operators can use to address these design, construction, maintenance, operation and decommissioning issues in a systematic, demonstrable way. An EMS includes the organisational structure, responsibilities, practices, procedures, processes and resources for developing, implementing, maintaining, reviewing and monitoring the environmental policy. Environmental Management Systems are most effective and efficient where they form an inherent part of the overall management and operation of an installation.

Within the European Union, many organisations have decided on a voluntary basis to implement environmental management systems based on EN ISO 14001:1996 or the EU Eco-management and audit scheme EMAS. EMAS includes the management system requirements of EN ISO 14001, but places additional emphasis on legal compliance, environmental performance and employee involvement; it also requires external verification of the management system and validation of a public environmental statement (in EN ISO 14001 self-declaration is an alternative to external verification). There are also many organisations that have decided to put in place non-standardised EMSs.

While both standardised systems (EN ISO 14001:1996 and EMAS) and non-standardised ("customised") systems in principle take the *organisation* as the entity, this document takes a more narrow approach, not including all activities of the organisation e.g. with regard to their products and services, due to the fact that the regulated entity under the IPPC Directive is the *installation* (as defined in Article 2).

An environmental management system (EMS) for an IPPC installation can contain the following components:

(a) definition of an environmental policy
(b) planning and establishing objectives and targets
(c) implementation and operation of procedures
(d) checking and corrective action
(e) management review
(f) preparation of a regular environmental statement
(g) validation by certification body or external EMS verifier
(h) design considerations for end-of-life plant decommissioning
(i) development of cleaner technologies
(j) benchmarking.

These features are explained in somewhat greater detail below. For detailed information on components (a) to (g), which are all included in EMAS, the reader is referred to the reference literature indicated below.

a) Definition of an environmental policy

Top management are responsible for defining an environmental policy for an installation and ensuring that it:

- is appropriate to the nature, scale and environmental impacts of the activities
- includes a commitment to pollution prevention and control
- includes a commitment to comply with all relevant applicable environmental legislation and regulations, and with other requirements to which the organisation subscribes
- provides the framework for setting and reviewing environmental objectives and targets
- is documented and communicated to all employees
- is available to the public and all interested parties.

b) Planning

- procedures to identify the environmental aspects of the installation, in order to determine those activities which have or can have significant impacts on the environment, and to keep this information up-to-date
- procedures to identify and have access to legal and other requirements to which the organisation subscribes and that are applicable to the environmental aspects of its activities
- establishing and reviewing documented environmental objectives and targets, taking into consideration the legal and other requirements and the views of interested parties
- establishing and regularly updating an environmental management programme, including designation of responsibility for achieving objectives and targets at each relevant function and level as well as the means and timeframe by which they are to be achieved.

c) Implementation and operation of procedures

It is important to have systems in place to ensure that procedures are known, understood and complied with, therefore effective environmental management includes:

(i) Structure and responsibility

- defining, documenting and communicating roles, responsibilities and authorities, which includes appointing one specific management representative
- providing resources essential to the implementation and control of the environmental management system, including human resources and specialised skills, technology and financial resources.

(ii) Training, awareness and competence

- identifying training needs to ensure that all personnel whose work may significantly affect the environmental impacts of the activity have received appropriate training.

(iii) Communication

- establishing and maintaining procedures for internal communication between the various levels and functions of the installation, as well as procedures that foster a dialogue with external interested parties and procedures for receiving, documenting and, where reasonable, responding to relevant communication from external interested parties.

(iv) Employee involvement

- involving employees in the process aimed at achieving a high level of environmental performance by applying appropriate forms of participation such as the suggestion-book system or project-based group works or environmental committees.

(v) Documentation

- establishing and maintaining up-to-date information, in paper or electronic form, to describe the core elements of the management system and their interaction and to provide direction to related documentation.

(vi) Efficient process control

- adequate control of processes under all modes of operation, i.e. preparation, start-up, routine operation, shutdown and abnormal conditions
- Identifying the key performance indicators and methods for measuring and controlling these parameters (e.g. flow, pressure, temperature, composition and quantity)
- documenting and analysing abnormal operating conditions to identify the root causes and then addressing these to ensure that events do not recur (this can be facilitated by a ‘no-blame’ culture where the identification of causes is more important than apportioning blame to individuals).

(vii) Maintenance programme

- establishing a structured programme for maintenance based on technical descriptions of the equipment, norms etc. as well as any equipment failures and consequences
- supporting the maintenance programme by appropriate record keeping systems and diagnostic testing
- clearly allocating responsibility for the planning and execution of maintenance.

(viii) Emergency preparedness and response

- establishing and maintaining procedures to identify the potential for and response to accidents and emergency situations, and for preventing and mitigating the environmental impacts that may be associated with them.

D) Checking and corrective action

(i) Monitoring and measurement

- establishing and maintaining documented procedures to monitor and measure, on a regular basis, the key characteristics of operations and activities that can have a significant impact on the environment, including the recording of information for tracking performance, relevant operational controls and conformance with the installation's environmental objectives and targets *(see also the Reference document on general Monitoring of Emissions)*
- establishing and maintaining a documented procedure for periodically evaluating compliance with relevant environmental legislation and regulations.

(ii) Corrective and preventive action

- establishing and maintaining procedures for defining responsibility and authority for handling and investigating non-conformance with permit conditions, other legal requirements as well as objectives and targets, taking action to mitigate any impacts caused and for initiating and completing corrective and preventive action that are appropriate to the magnitude of the problem and commensurate with the environmental impact encountered.

(iii) Records

- establishing and maintaining procedures for the identification, maintenance and disposition of legible, identifiable and traceable environmental records, including training records and the results of audits and reviews.

(iv) Audit

- establishing and maintaining (a) programme(s) and procedures for periodic environmental management system audits that include discussions with personnel, inspection of operating conditions and equipment and reviewing of records and documentation and that results in a written report, to be carried out impartially and objectively by employees (internal audits) or external parties (external audits), covering the audit scope, frequency and methodologies, as well as the responsibilities and requirements for conducting audits and reporting results, in order to determine whether or not the environmental management system conforms to planned arrangements and has been properly implemented and maintained
- completing the audit or audit cycle, as appropriate, at intervals of no longer than three years, depending on the nature, scale and complexity of the activities, the significance of associated environmental impacts, the importance and urgency of the problems detected by previous audits and the history of environmental problems – more complex activities with a more significant environmental impact are audited more frequently
- having appropriate mechanisms in place to ensure that the audit results are followed up.

(v) Periodic evaluation of legal compliance

- reviewing compliance with the applicable environmental legislation and the conditions of the environmental permit(s) held by the installation
- documentation of the evaluation.

e) Management review

- reviewing, by top management, at intervals that it determines, the environmental management system, to ensure its continuing suitability, adequacy and effectiveness
- ensuring that the necessary information is collected to allow management to carry out this evaluation
- documentation of the review.

f) Preparation of a regular environmental statement

- preparing an environmental statement that pays particular attention to the results achieved by the installation against its environmental objectives and targets. It is regularly produced – from once a year to less frequently depending on the significance of emissions, waste generation etc. It considers the information needs of relevant interested parties and it is publicly available (e.g. in electronic publications, libraries etc.).

When producing a statement, the operator may use relevant existing environmental performance indicators, making sure that the indicators chosen:

i. give an accurate appraisal of the installation's performance
ii. are understandable and unambiguous
iii. allow for year on year comparison to assess the development of the environmental performance of the installation
iv. allow for comparison with sector, national or regional benchmarks as appropriate
v. allow for comparison with regulatory requirements as appropriate.

g) Validation by certification body or external EMS verifier:

- having the management system, audit procedure and environmental statement examined and validated by an accredited certification body or an external EMS verifier can, if carried out properly, enhance the credibility of the system.

h) Design considerations for end-of-life plant decommissioning

- giving consideration to the environmental impact from the eventual decommissioning of the unit at the stage of designing a new plant, as forethought makes decommissioning easier, cleaner and cheaper
- decommissioning poses environmental risks for the contamination of land (and groundwater) and generates large quantities of solid waste. Preventive techniques are process-specific but general considerations may include:
  i. avoiding underground structures
  ii. incorporating features that facilitate dismantling
  iii. choosing surface finishes that are easily decontaminated
  iv. using an equipment configuration that minimises trapped chemicals and facilitates drain-down or washing
  v. designing flexible, self-contained units that enable phased closure
  vi. using biodegradable and recyclable materials where possible.

i) Development of cleaner technologies

- environmental protection should be an inherent feature of any process design activities carried out by the operator, since techniques incorporated at the earliest possible design stage are both more effective and cheaper. Giving consideration to the development of cleaner technologies can for instance occur through R&D activities or studies. As an alternative to internal activities, arrangements can be made to keep abreast with – and where appropriate – commission work by other operators or research institutes active in the relevant field.

j) Benchmarking

- carrying out systematic and regular comparisons with sector, national or regional benchmarks, including for energy efficiency and energy conservation activities, choice of input materials, emissions to air and discharges to water (using for example the European Pollutant Emission Register, EPER), consumption of water and generation of waste.

Standardised and non-standardised EMSs

An EMS can take the form of a standardised or non-standardised ("customised") system. Implementation and adherence to an internationally accepted standardised system such as EN ISO 14001:1996 can give higher credibility to the EMS, especially when subject to a properly performed external verification. EMAS provides additional credibility due to the interaction with the public through the environmental statement and the mechanism to ensure compliance with the applicable environmental legislation. However, non-standardised systems can in principle be equally effective provided that they are properly designed and implemented.

Main achieved environmental benefits

Implementation of and adherence to an EMS focuses the attention of the operator on the environmental performance of the installation. In particular, the maintenance of and compliance with clear operating procedures for both normal and abnormal situations and the associated lines of responsibility should ensure that the installation's permit conditions and other environmental targets and objectives are met at all times.

Environmental management systems typically ensure the continuous improvement of the environmental performance of the installation. The poorer the starting point is, the more significant short-term improvements can be expected. If the installation already has a good overall environmental performance, the system helps the operator to maintain the high performance level.

Cross-media effects

Environmental management techniques are designed to address the overall environmental impact, which is consistent with the integrated approach of the IPPC Directive.

Operational data

No specific information reported.

Applicability

The components described above can typically be applied to all IPPC installations. The scope (e.g. level of detail) and nature of the EMS (e.g. standardised or non-standardised) will generally be related to the nature, scale and complexity of the installation, and the range of environmental impacts it may have.

Economics

It is difficult to accurately determine the costs and economic benefits of introducing and maintaining a good EMS. A number of studies are presented below. However, these are just examples and their results are not entirely coherent. They might not be representative for all sectors across the EU and should thus be treated with caution.

A Swedish study carried out in 1999 surveyed all 360 ISO-certified and EMAS-registered companies in Sweden. With a response rate of 50 %, it concluded among other things that:

- the expenses for introducing and operating EMS are high but not unreasonably so, save in the case of very small companies. Expenses are expected to decrease in the future
- a higher degree of co-ordination and integration of EMS with other management systems is seen as a possible way to decrease costs
- half of all the environmental objectives and targets give payback within one year through cost savings and/or increased revenue
- the largest cost savings were made through decreased expenditure on energy, waste treatment and raw materials
- most of the companies think that their position on the market has been strengthened through the EMS. One-third of the companies report increasing revenue due to EMS.

In some Member States reduced supervision fees are charged if the installation has a certification.

A number of studies[1] show that there is an inverse relationship between company size and the cost of implementing an EMS. A similar inverse relationship exists for the payback period of invested capital. Both elements imply a less favourable cost-benefit relationship for implementing an EMS in SMEs compared to larger companies.

According to a Swiss study, the average cost for building and operating ISO 14001 can vary:

- for a company with between 1 and 49 employees: CHF 64000 (EUR 44000) for building the EMS and CHF 16000 (EUR 11000) per year for operating it
- for an industrial site with more than 250 employees: CHF 367000 (EUR 252000) for building the EMS and CHF 155000 (EUR 106000) per year for operating it.

These average figures do not necessarily represent the actual cost for a given industrial site because this cost is also highly dependent on the number of significant items (pollutants, energy consumption,...) and on the complexity of the problems to be studied.

A recent German study (Schaltegger, Stefan and Wagner, Marcus, *Umweltmanagement in deutschen Unternehmen - der aktuelle Stand der Praxis*, February 2002, p. 106) shows the following costs for EMAS for different branches. It can be noted that these figures are much lower than those of the Swiss study quoted above. This is a confirmation of the difficulty to determine the costs of an EMS.

Costs for building (EUR):
minimum - 18750
maximum - 75000
average - 50000

Costs for validation (EUR):
minimum - 5000
maximum - 12500
average - 6000

A study by the German Institute of Entrepreneurs (Unternehmerinstitut/Arbeitsgemeinschaft Selbständiger Unternehmer UNI/ASU, 1997, *Umweltmanagementbefragung - Öko-Audit in der mittelständischen Praxis - Evaluierung und Ansätze für eine Effizienzsteigerung von Umweltmanagementsystemen in der Praxis*, Bonn.) gives information about the average savings

---

[1] E.g. Dyllick and Hamschmidt (2000, 73) quoted in Klemisch H. and R. Holger, *Umweltmanagementsysteme in kleinen und mittleren Unternehmen – Befunde bisheriger Umsetzung,* KNI Papers 01/02, January 2002, p 15; Clausen J., M. Keil and M. Jungwirth, *The State of EMAS in the EU.Eco-Management as a Tool for Sustainable Development – Literature Study,* Institute for Ecological Economy Research (Berlin) and Ecologic – Institute for International and European Environmental Policy (Berlin), 2002, p 15.

achieved for EMAS per year and the average payback time. For example, for implementation costs of EUR 80000 they found average savings of EUR 50000 per year, corresponding to a payback time of about one and a half years.

External costs relating to verification of the system can be estimated from guidance issued by the International Accreditation Forum (http://www.iaf.nu).

Driving forces for implementation
Environmental management systems can provide a number of advantages, for example:

- improved insight into the environmental aspects of the company
- improved basis for decision-making
- improved motivation of personnel
- additional opportunities for operational cost reduction and product quality improvement
- improved environmental performance
- improved company image
- reduced liability, insurance and non-compliance costs
- increased attractiveness for employees, customers and investors
- increased trust of regulators, which could lead to reduced regulatory oversight
- improved relationship with environmental groups.

Example plants
The features described under (a) to (e) above are elements of EN ISO 14001:1996 and the European Community Eco-Management and Audit Scheme (EMAS), whereas the features (f) and (g) are specific to EMAS. These two standardised systems are applied in a number of IPPC installations. As an example, 357 organisations within the EU chemical and chemical products industry (NACE code 24) were EMAS registered in July 2002, most of which operate IPPC installations.

In the UK, the Environment Agency of England and Wales carried out a survey among IPC (the precursor to IPPC) regulated installations in 2001. It showed that 32 % of respondents were certified to ISO 14001 (corresponding to 21 % of all IPC installations) and 7 % were EMAS registered. All cement works in the UK (around 20) are certified to ISO 14001 and the majority are EMAS registered. In Ireland, where the establishment of an EMS (not necessarily of a standardised nature) is required in IPC licenses, an estimated 100 out of approximately 500 licensed installations have established an EMS according to ISO 14001, with the other 400 installations having opted for a non-standardised EMS.

Reference literature
(Regulation (EC) No 761/2001 of the European parliament and of the council allowing voluntary participation by organisations in a Community eco-management and audit scheme (EMAS), OJ L 114, 24/4/2001, http://europa.eu.int/comm/environment/emas/index_en.htm)

(EN ISO 14001:1996, http://www.iso.ch/iso/en/iso9000-14000/iso14000/iso14000index.html; http://www.tc207.org)

2.9.2 Abatement systems

I have retained this part as it does cover techniques that are common to the various sections in the BREF. I would like to add other common sytems such as water and/or waste treatment treatment systems that are common to all the sections and request thw TWG to suggest commonalities.

This section has been added to bring together the common abatement systems that have been identified from each one of the production processes covered. They are as follows:

2.9.2.1 End-of-pipe measures for urea production

Scrubbers are widely used as an end-of-pipe technique to reduce dust emissions. Fabric filters are unsuitable, as urea particulates are hygroscopic combining with moisture from the gas streams blinding the bags. Dry cyclones offer lower collection efficiencies than scrubbers in urea particulate emissions.

Scrubbers

Description
Gas scrubbing is an absorption technique in which contaminants from the gas are absorbed in liquid (usually water) by intimate contact between the gas and the liquid. Essentially a gas scrubber consists of three parts: an absorption section for dust exchange on irrigated packing, a demister, and a recirculation tank. The efficiency of the gas scrubber is an interaction between the residence time of the gas in the absorption section, the type of packing, the gas-liquid ratio (L/G) and the replacement level and temperature of the water.

Acid scrubbers are also used in the fertiliser industry. The acid scrubber is characterised by the fact that the scrubbing water has a low pH. This enables the basic components in the gas to be better separated. As a result of neutralisation a concentrated salt solution is formed (up to 15 %) which is discharged or recycled into the process (see also example plants).

Doyle scrubber:
For many years the fertiliser industry has used the Doyle impingement, scrubber in which the contaminated gases are passed through an annular section formed by the insertion of a cone in the bottom of the down-comer duct. This allows the dusty gas to impinge at high velocity on to the surface of a bath of liquid. The scrubber liquor contains up to 40 % of dissolved solids. Such a unit results in a pressure drop of 1471 – 1960 Pa. The disadvantage (for the granulator gas cleaning duty) is that the gas has to pass through two units in series to ensure satisfactory dust removal. Furthermore, the Doyle scrubber cannot be regarded as an effective absorption device. It has been found that when the Doyle scrubber are operated under acidic conditions, e.g. with the addition of phosphoric acid, there was a 'steamy' plume and emissions of hydrogen fluoride. There was also a tendency for blockages to occur.

Airmix scrubber**:**
The Airmix scrubber has been widely used in the industry. This is a self-induced spray-type device in which the gas and scrubbing liquid enter the bottom of the unit at high velocity. They are then slowed down in the diffuser section so that the liquid droplets tend to fall out of the gas stream and form a curtain of spray through which the gas stream passes and is scrubbed accordingly.

Granivore:
The cyclonic spray unit, in which liquid is fed tangentially through the sides of the scrubber, also relies on a vigorous scrubbing action in a dense spray for effective separation. The Granivore uses this principle. The location of spray nozzles across the gas stream should be avoided because of the risk of plugging, erosion and corrosion.

Turbulent contact absorber:
Gas scrubbing with entrained solids in static packed towers is inadvisable, as blockages are likely to occur. Contact absorbers may be used under turbulent conditions, and consist of several beds of hollow propylene spheres that are 'fluidised' by an upward flow of dusty gas.

Applicability
In principle, scrubbers can be applied at all types of fertiliser plants.

Achieved environmental benefits

New ammonia plants:

Ammonia emission (in the syntheses phase) level of 2g/tonne product (syntheses by means of pool reactor).
Ammonia emission (due to product finishing) levels in therangeof 250 – 400 g/tonne product.
Dust emission (due to product finishing) level in the range of 90 - 150 g/tonne product.

Existing urea plants:

Ammonia emission (in the syntheses phase) in the range of 4.3 – 8 g/tonnefinished product.
Dust emission level (due to product finishing) in the range of 90 – 250 g/tonne finished product

Advantage:

Very high efficiencies possible, also at relatively high temperatures (50 – 80°C) and concentrations (>1000 mg/m^3). The installation is quite compact.

Disadvantage:

Waste water from spent scrubber liquors. Civil engineering work will be needed for roof fitting support structure, or if outside applying frost protection. If an acid scrubber is used the acid consumption and salt by-products are may be issues.

Example plants

The urea plant of DSM in Geleen uses water scrubbers in the synthesis section. The actual NH_3 emission from the urea plant is less than 700 mg/m^3 (2.5 g/tonne product). In the dissociation stage of the urea plant the unconverted carbamate (after the CO_2 stripper) is neutralised with sulphuric acid as AN (87 %), which is used in the production of urea. The off-gases from the dissociation stage consist of H_2O, CO_2 and AN vapour. The off-gases are scrubbed by an acid scrubber and condensed. The final release goes through a high efficiency filter before discharge. The maximum emission level as stated in the licence of DSM is 10 mg/m^3 AN vapour (c. 0.08 kg/h). A part of the acid condensate, which is produced due to gas cleaning, is used in the sulphuric acid and caprolactam plant. The remainder is released to sewer [10, infoMil, 2001]

Hydro Agri Sluiskil use gas scrubbers at their Urea 5 plant. When urea is being produced a water scrubber is used. After the urea is produced an acid scrubbers is used. One scrubber has a flowrate of 150000 Nm^3/hour and a NH_3 emission of <165 mg/Nm^3 when urea is produced and <65 mg/Nm^3 with the production of urea. The scrubber has a dust emission of <100 mg/m^3. The second scrubber has a flowrate of 12000 Nm^3/hour and a NH_3 emission of <100 mg/Nm^3 (urea) and <30 mg/Nm^3 (urea). This scrubber has a dust emission of <30 mg/Nm^3 [10, infoMil, 2001].

Cross-media effects

Economics

Scrubber: (EUR/1000 Nm^3/hr): 2000 - 4000 (recirculating scrubber with pump, excluding control).
Acid scrubber: (EUR/1000 Nm^3/hr): 5000 - 20000 (recirculating scrubber with pump, excluding control).

Reference literature

[10, infoMil, 2001]

2.9.2.2 End-of-pipe measures for AN production

Fabric filters

Description

Fabric filters have been used for decades in a wide range of industrial gas cleaning applications. Their use has become more widespread across the world as emission control legislation becomes more stringent. The ability of fabric filters, to collect dust efficiently for extremely fine dusts or fumes has made it the preferred abatement technique.

Fabric filters consist of a metal casing which accommodates the filter bags. For the actual filter fabric, a broad range of materials is available.

Typically, needle-felts made of synthetic fibres with or without reinforcement by a woven insert are used as a filter fabric. The individual types of synthetic fibre vary considerably in their properties, a fact that has to be taken into account when choosing the fabric material for a given service.

The following list shows working temperature ranges for different types of fabric:

- up to about 130 °C, e.g. polyacrylonitrile, polyester, Dralon T, may be silicone sprayed for better filter cake release
- up to about. 160 °C, e.g. Nomex Ryton and similar
- up to about. 180 °C, e.g. Nomex, Ryton and similar, the fibres being felted on Rastex woven fabric
- up to about 220 °C, e.g. PTFE fibres if necessary, with admixtures, felted on Rastex woven fabric.

Additionally, the humidity and presence of aggressive compounds in the flue gases influence the choice of filter material.

Applicability

Fabric filters are less suitable for urea plants because of the hygroscopic nature of urea particles as well as due to problems with the gas streams moisture content causing bag blinding. In principle fabric filters can be used in all other fertiliser plants.

Achieved environmental benefits

Advantages:

Particle emissions can be reduced to >99 %. Achieved emission reduction concentrations can be well <10 mg/Nm^3.

Disadvantages:

Fabric filtration creates a solid waste. It also needs energy to overcome the pressure drop of the system. Energy consumption varies from 0.2 to 2.0 kWh/1000 Nm^3 treated and is directly proportional to the pressure drop.

Example plants

Many fertiliser plants in the world and all fertiliser plants in the Netherlands are equipped with fabric filter systems.

Cross-media effects

Economics

Investments of a combined dry scrubbing and fabric filtration system, treating 65000 Nm^3/hr, were reported as EUR 2.9 million 1998. Operational costs for this system are about EUR 1 million/year.

Reference literature

[10, infoMil, 2001]

Cyclones

Description

Cyclones are generally used as the main particulate abatement technique in the manufacture of chemical fertilisers. They can be made from a wide range of materials and designed for high - temperature and high-pressure operation. Cyclones are suitable for removing particles down to about 5 µm, which makes them suitable for exhaust air from granulators, coolers and dryers. Smaller particles down to about 0.5µm can be separated where agglomeration occurs. High-efficiency cyclones are capable of removal efficiencies in the order of 90 % for particles down to 20 µm.

Waste gases are fed tangentially into a cylindrical body. Centrifugal forces cause a movement of the dust to the wall of the body. The solid material separates by gravity and the clean gas exits the separation vessel at the top. In the case of a wet cyclone, water is added to the waste gases, thereby increasing the weight of the solid material and aiding separation. Fine material <0.02 mm can be removed with this technique and the efficiency can be increased. A multiple cyclone is a unit, which contains several cyclones, in parallel.

Applicability

In principle, cyclones can be used in all AN plants. Cyclones are usually combined with fabric filters.

Achieved environmental benefits

Advantage:

A dust emission reduction up to 95 % is possible depending on particle size.

Cross-media effects

Economics

Capital costs (≈EUR900 /1000Nm^3).

Reference literature

[10, infoMil, 2001]

Plate bank product cooler

Description

In the AN solidification process the product is normally directly air-cooled which leads to dust emission. Dust emissions in the cooling section can be avoided by using a plate bank product cooler. In this “closed” cooling system there is no direct contact with the water-cooled plates. Hot material is fed to the top hopper where it is distributed to the plate bank. The product is cooled while it moves under true mass flow conditions between the water-cooled stainless steel plates. A gate valve in the discharge hopper regulates the flowrate.

Applicability

The AN granule can become lumpy due to the water vapour pressure of AN at high temperatures and a change of phase of AN at 32 °C, which could result in a blockage in the product cooler. This technique can be considered more suitable as an end cooling technique from 50 °C to 30 °C in AN production.

Example plants

DSM AGRO IJmuiden introduced this technique in the fertiliser industry in the Netherlands in 1994, when it installed two plate bank product coolers. DSM Agro IJmuiden produces AN, CAN and multi nutrient fertilisers. In the production process, the end-products must be cooled from above 100 °C to approximately 30 °C. However, DSM Agro IJmuiden encountered problems within this temperature range (see applicability).

The supply system for the above consists of the following mechanical equipment:

- bucket chain, transports the product from the drying drum to the plate bank coolers
- scalper, to protect the coolers from the too large granules
- distribution valve, which divides the input over the two coolers.
- a level controller is installed on the upper side of the cooler, which regulates the gate in the discharge hopper.

The product cooler at DSM AGRO consists of the following elements:

- two cooling units per cooler
- a level controller
- a high level detector on the upper side
- a gate valve in the discharge hopper which regulates the flowrate.

The product is transported by two small conveyor belts (one for each cooler) and one central conveyor belt, to the end section. The cooling-water circuit consists of:

- a small cooling system
- a circulation system with two pumps (one is used as a spare)
- temperature control, which regulates a by-pass valve of the small cooling system
- a conditioning system, which prevents bacterial contamination.

Demineralised water is used as a cooling medium. The cooling system has a capacity of approximately 1744 kW. By using the plate bank cooler instead of a conventional system, DSM Agro has reduced their dust emission by approximately 30 t/year. By applying the plate bank cooler, DSM Agro do save energy compared with conventional cooling.

Simplot (Branbon, Canada) use a plate bank product cooler in the production of ammonium nitrate [10, infoMil, 2001]

Economics
Investment approximately EUR 136000 – EUR 227000 (installation with a capacity of 15 tonne/hours) The cost of the pilot project at DSM Agro IJmuiden was approximately EUR 1400000 (including research, engineering and construction costs).

Reference literature

2.9.2.3 End-of-pipe measures for SSP and TSP and MN fertiliser production

Fabric filters
Description
As before

Cyclones
Description
As before

Ceramic filter
Description
The use of ceramic filters during the grinding of phosphate rock results in a significant reduction of dust emission. Particulates in the gas stream collect on the ceramic filters forming a layer that builds up and provides a surface to filter more particles. The particles are captured either by direct impingement sieving or attraction to the filter surface.

Pulse jets/mechanical vibration dislodge the particulates from the filter surfaces. The particulates drop to the bottom of the vessel and are removed.

Applicability

These filters are not applicable for hygroscopic particles. The use of a pre-separation technique, such as a cyclone, may be necessary.

Achieved environmental benefits

Advantages:

- the emission of phosphoric dust to the atmosphere can be reduced to <4 mg/Nm^3.
- in comparison to fabric filters ceramic filters do not need a lot of maintenance.
- the dust can be recycled to the process.

Disadvantage:

The amount of energy needed for a ceramic filter is slightly higher compared to the fabric filters.

Example plants

Zuid-Chemie in the Netherlands has installed 3 ceramic filters at their phosphate rock grinding facility of the superphosphate plant. When the filters were installed the dust emission was reduced to about <2 mg/Nm^3. After two years the dust emission was about 2.5 – 3.8 mg/m^3 with flowrates of 3600 (one filter) and 4900 Nm^3/h (two filters) [10, infoMil, 2001].

Cross-media effects

Economics

- investment (EUR/1000 Nm^3/hr): 30000 - 55000 (approximately linear with the gas volume, as the filter material largely determines investment).
- operational costs (EUR/1000 Nm^3/hr): approximately >650*flow/1000 per year [10, infoMil, 2001].

Reference literature

[10, infoMil, 2001]

3 BEST AVAILABLE TECHNIQUES

In understanding this chapter and its contents, the attention of the reader is drawn back to the preface of this document and in particular the fifth section of the preface: “How to understand and use this document”. The techniques and associated emission and/or consumption levels, or ranges of levels, presented in this chapter have been assessed through an iterative process involving the following steps:

- identification of the key environmental issues for the Large Volume Inoganic Chemicals-Ammonia, Acids and Fertilisers sector
- examination of the techniques most relevant to address those key issues
- identification of the best environmental performance levels, on the basis of the available data in the European Union and world-wide
- examination of the conditions under which these performance levels were achieved; such as costs, cross-media effects, main driving forces involved in implementation of these techniques
- selection of the best available techniques (BAT) and the associated emission and/or consumption levels for this sector in a general sense all according to Article 2(11) and Annex IV of the Directive.

Expert judgement by the European IPPC Bureau and the relevant Technical Working Group (TWG) has played a key role in each of these steps and in the way in which the information is presented here.

On the basis of this assessment, techniques, and as far as possible emission and consumption levels associated with the use of BAT, are presented in this chapter that are considered to be appropriate to the sector as a whole and in many cases reflect current performance of some installations within the sector. Where emission or consumption levels “associated with best available techniques” are presented, this is to be understood as meaning that those levels represent the environmental performance that could be anticipated as a result of the application, in this sector, of the techniques described, bearing in mind the balance of costs and advantages inherent within the definition of BAT. However, they are neither emission nor consumption limit values and should not be understood as such. In some cases it may be technically possible to achieve better emission or consumption levels but due to the costs involved or cross-media considerations, they are not considered to be appropriate as BAT for the sector as a whole. However, such levels may be considered to be justified in more specific cases where there are special driving forces.

The emission and consumption levels associated with the use of BAT have to be seen together with any specified reference conditions (e.g. averaging periods).

The concept of “levels associated with BAT” described above is to be distinguished from the term “achievable level” used elsewhere in this document. Where a level is described as “achievable” using a particular technique or combination of techniques, this should be understood to mean that the level may be expected to be achieved over a substantial period of time in a well maintained and operated installation or process using those techniques.

Where available, data concerning costs have been given together with the description of the techniques presented in the previous chapters. These give a rough indication about the magnitude of costs involved. However, the actual cost of applying a technique will depend strongly on the specific situation regarding, for example, taxes, fees, and the technical characteristics of the installation concerned. It is not possible to evaluate such site-specific factors fully in this document. In the absence of data concerning costs, conclusions on economic viability of techniques are drawn from observations on existing installations.

It is intended that the general BAT in this chapter are a reference point against which to judge the current performance of an existing installation or to judge a proposal for a new installation.

In this way they will assist in the determination of appropriate "BAT-based" conditions for the installation or in the establishment of general binding rules under Article 9(8). It is foreseen that new installations can be designed to perform at or even better than the general BAT levels presented here. It is also considered that existing installations could move towards the general BAT levels or do better, subject to the technical and economic applicability of the techniques in each case.

While the BREFs do not set legally binding standards, they are meant to give information for the guidance of industry, Member States and the public on achievable emission and consumption levels when using specified techniques. The appropriate limit values for any specific case will need to be determined taking into account the objectives of the IPPC Directive and the local considerations.

Some aids to understanding the remainder of this chapter

In subsequent sections of this chapter, the BAT conclusions for the LVIC-AAF sector are set out on two levels. Section 3.1 deals with generic BAT conclusions that are generally applicable to all sectors as a whole and Section 3.2 contains the more specific BAT conclusions for the various processes and activities under analysis. So, BAT for any specific LVIC-AAF installation is the combination of the non-unit-specific elements applicable to the LVIC-AAF sector as a whole (generic BAT) and the unit-specific-BAT applicable to the particular case. Both these approaches are complementary rather than contradictory in practical situations.

3.1 Generic (integrated installation) BAT

A LVIC-AAF installation can consist of a number of interrelated plants. The way these single units are built up into an integrated installation can have a considerable effect on the emissions. A well-integrated installation will be characterised by a comparatively low overall level of emissions of pollutants. In determining BAT, the environmental effects of the various plants of the whole installation have to be considered. This section provides the elements for BAT determined for the installation as a whole. It includes the BAT determined to be applicable to an LVIC-AAF for environmental management and the reduction, in a general sense, of emissions to air, water and solid waste. This chapter reflects the fact that emissions to air are the most important environmental concern of integrated installations.

It is recognised that certain plants (e.g. sulphuric acid plants) can and do operate as separate entities and do not form a part of the integrated complex. This section looks at the situation for an integrated complex only. Ideally as the majority of the plants in the LVIC-AAF portfolio are co-located it is however appropriate to consider the whole installation.

Environmental management

A number of environmental management techniques are determined as BAT. The scope (e.g. level of detail) and nature of the EMS (e.g. standardised or non-standardised) will generally be related to the nature, scale and complexity of the installation, and the range of environmental impacts it may have.

BAT is to implement and adhere to an Environmental Management System (EMS) that incorporates, as appropriate to individual circumstances, the following features: (see Chapter 2.9)

- definition of an environmental policy for the installation by top management (commitment of the top management is regarded as a precondition for a successful application of other features of the EMS)
- planning and establishing the necessary procedures
- implementation of the procedures, paying particular attention to
  - structure and responsibility
  - training, awareness and competence
  - communication
  - employee involvement
  - documentation
  - efficient process control
  - maintenance programme
  - emergency preparedness and response
  - safeguarding compliance with environmental legislation.
- checking performance and taking corrective action, paying particular attention to
  - monitoring and measurement (see also the Reference document on Monitoring of Emissions)
  - corrective and preventive action
  - maintenance of records
  - independent (where practicable) internal auditing in order to determine whether or not the environmental management system conforms to planned arrangements and has been properly implemented and maintained
- review by top management.

Three further features, which can complement the above stepwise, are considered as supporting measures. However, their absence is generally not inconsistent with BAT. These three additional steps are:

- having the management system and audit procedure examined and validated by an accredited certification body or an external EMS verifier
- preparation and publication (and possibly external validation) of a regular environmental statement describing all the significant environmental aspects of the installation, allowing for year-by-year comparison against environmental objectives and targets as well as with sector benchmarks as appropriate
- implementation and adherence to an internationally accepted voluntary system such as EMAS and EN ISO 14001:1996. This voluntary step could give higher credibility to the EMS. In particular EMAS, which embodies all the above-mentioned features, gives higher credibility. However, non-standardised systems can in principle be equally effective provided that they are properly designed and implemented.

Specifically for this industry sector, it is also important to consider the following potential features of the EMS:

- the environmental impact from the eventual decommissioning of the unit at the stage of designing a new plant
- where practicable, the application of sectoral benchmarking on a regular basis, including energy efficiency and energy conservation activities, choice of input materials, emissions to air, discharges to water, consumption of water and generation of waste.

Reduction of emissions to air

The overall reduction of emissions to air is typically achieved in practice by a combined effort on the performance of the 'processes/activities' (e.g. improved particulate removal efficiency, application of low NO_X techniques) and on the performance of the 'integrated/whole' installation (e.g. energy efficiency, fuel management, catalyst use). The energy efficiencies of the various processes have been included in the current emissions and consumptions sections for each plant and provide a typical examples of overall efficiencies l. The use of this data serves as a benchmark to compare the efficiencies of comparable units throughout the EU+. Local circumstances and location for the use of low grade heat is important to consider where this heat can be externally exchanged. It is recognised that the standardisation of calculating energy efficiency is important in order to compare energy performance in the sector. The competiveness of the industry overall is dependent on the efficient use of energy. For instance nitric acid can be produced remote from the ammonia production facility but the energy balance and the cost of transporting the ammonia have to be considered.

Generally to reduce emissions to air BAT is to:

- improve the energy efficiency (resulting in a reduction of all the air pollutants generated by combustion and the various processes) by enhancing heat integration and recovery options throughout the integrated installation, applying energy conservation techniques and by optimising the energy production/consumption. The energy usages of all the processes are presented in the section on energy efficiency and provide the base information and indicate where improvements can be made
- reduce sulphur dioxide emissions by
  - using low sulphur feedstock in all combustion processes particularly in ammonia partial oxidation plants
  - optimising the conversion in all types of sulphuric acid plant according to the sulphur dioxide feedstock
- reduce nitrogen oxides emissions by
  - identifying the main sources of emitters and quantifying the amounts
  - Nitric acid production is identified as a substantive potential source of nitrogen oxides and will be covered in the specific process BAT
  - optimising the use of low NOX burners, shifting primary reforming duty to secondary reformer and the use of heat exchanger reformer in ammonia production
- reduce particulate emission by:
  - quantifying the particulate emission sources in order to identify the main emitters in each specific case.
  - minimising the particulate emissions from solids handling situations (potash, fertiliser handling, catalyst loading/unloading, drying) by applying good housekeeping and control techniques.
  - using suitable abatement equipment (cyclones, scrubbers, bag filters) where appropriate.

The achievable emission levels are included in the various sections where particulates/dust occur.

Reduction of discharges to water

Generally to reduce emissions to water BAT, is to:

- apply a water management scheme (as part of the EMS) aimed at reducing releases
- implement good housekeeping activities by:
  - minimising the volume of water used in the integrated installation
  - using as much as possible the cleaned waste water
  - applying techniques to reduce the level of waste water generated within each specific process/activity
- minimise the contamination of water by:
  - applying good housekeeping in operation and regular maintenance of existing facilities (as part of the EMS)
  - applying spill prevention and control
  - applying techniques to reduce the contamination of waste water within each specific process/activity.

For solid waste management BAT is to

- implement a solid waste management system. This includes:
  - annual reporting of waste quantities
  - implementing a plan with measures for waste reduction, including recycling and/or recovery
  - implementing good housekeeping activities
  - applying BAT determined on forthcoming waste BREF
- apply techniques to reduce the amount of solid waste generated within each specific process/activity. Special attention should be given to the management and storage of waste/reject fertilisers, implementing the recommendations arising from the Toulouse accident in 2001.

3.2 Specific process/activity related BAT

This section presents BAT elements for each process/activity covered in this document. Numbers in the headings of the following BAT sections correspond with the numbers used in previous chapters.

The analysis of production techniques from an environmental perspective is a task that is required for this BREF as well as comparisons between alternative production techniques, where they exist. The latter has only been possible to a limited extent because of a lack of the information.

Ammonia Production (2.1)

Applied operational practices in ammonia plants, described in this chapter, have a significant effect on the released emissions and generally on the achieved operating efficiency. The techno economic evaluation of BAT is carried out in the relevant section of the present BREF. BAT relevant input output levels are specified for new ammonia plants; these can only be met if appropriate operational practices, as presented below are applied.

Management practices

BAT is to implement aspects such as staff training with focus on safe handling of non constant operations (as start-up, shut-down and abnormal conditions), good housekeeping practices, reporting to authorities on accidental releases, spares management, maintenance, repair planning and appropriate application of automatic control and computerisation in the production process.

BAT requires a general introduction about the known operational practices related to releases to air, water and land including also measures for minimising energy consumption. Specific operational practices related to pressure relief systems, start up, shut down, abnormal operations, flaring systems, handling of ammonia releases, and fugitive emissions are presented in the relevant sections.

Releases into air:

Focus on the control of prescribed substances such as NO_X, NH_3, SO_X, particulates and odorous releases. They include among others measures to minimise venting, minimise flaring, vaporisation from collection and open treatment of waste water, equipment decoking, catalyst handling and regeneration. Vented releases from such operations are returned to the process or treated.

Releases into water:

Implement site specific spillage contingency plans to prevent the accidental release of raw materials, products and waste materials into water. General rules of segregating the streams of process water, storm-water and indirect cooling water apply also to ammonia plants. Spillages are most likely to occur in storage tanks and sampling points. In the normal case such spillages drain to sumps which are discharged to effluent treatment plants following checking of the composition of the contents. Fouling and corrosion problems in cooling water systems are usually avoided by the use of appropriate additives, corrosion inhibitors and good maintenance of cooling towers, pumps, etc. Treatment chemicals are stored in sealable bunded areas, or equivalent. Absorbents used to mop up minor leaks and spills are disposed off in leak proof containers for further treatment. Bunded areas are sheltered to prevent transfer of pollutants to storm-water.

Releases to land:
Implement the reclamation of raw materials and products from residues and mainly from spent catalysts prior to their disposal as common practices for modern ammonia plants.

Operational practices:
Meet lowest energy consumption standards in ammonia production including daily balances and accounting checks of energy use. Monthly or quarterly inventory checks are also to be applied according to local conditions and needs. Steam systems, heat transfer points on main coolers, condensers, heaters, etc. are to be monitored continuously for losses, including insulation, flange tightness and steam traps. Regular reviews of the steam availability and demands at various pressure and temperature levels contribute to further optimising the utilisation of the steam system. Repair and maintenance of existing insulation play also an important role in energy balance. Insulation is to be upgraded to improve the performance over the original design basis. The use of infrared photography for locating hot or cold points is a particularly effective tool for locating areas that require attention.

Pressure relief systems:
Identify the potential abnormal events activating emergency pressure relief devices, that could lead to release of pollutants to the environment, including the likely frequency of the event, quantities released, chemical species involved, their concentrations and discharge rates. Plant relief systems are to be designed to minimise the frequency with which such systems are required to operate, for example by design of control and protection systems, use of adequate margins between operating and relief pressure and provision of adequate facilities for maintenance of relief valves.

Use two relief devices in parallel set at different relief pressures where appropriate. The relief device at the lower set pressure may be of a smaller capacity which can relieve small excursions such that the maximum capacity of the relief device is capable of being scrubbed in emergency equipment. The relief device at the higher set pressure will be sized for the low probability high flow rate event that cannot be abated and must be released at a sufficient height to promote dispersion, prevent hazardous concentrations at ground level, in buildings or plant structures and protect the process system integrity.

Start up, shut down and abnormal operating conditions:
Start up or shut down in a controlled sequence, which results in reformer and synthesis gases being vented through various vents of the plant. It may also be necessary to vent natural gas during the start up of the desulphurisation section. The normal vent points are the desulphuriser outlet, high temperature shift converter outlet, CO_2 absorber inlet, methanator inlet and outlet, the ammonia converter outlet, and the purge from the synloop and refrigeration system.

Minimise emissions as follows:
- minimisation of the start up and shut-down time by using interlocks and a logical operational sequence.
- use recycled inert gases for preheating.
- apply maximum allowed pre-heat rates for equipment and catalysts.
- use pre reduced ammonia synthesis catalyst to reduce activation time.
- reduce the low temperature shift catalyst with inert gas carrier.
- switch on recycle in the synloop as soon as possible.
- recover vent gases and use as fuel (after scrubbing to recover ammonia and possibly hydrogen in the case of synloop purge gas)
- flare untreatable vent gases.

Carry out a proper risk analysis which provides the necessary preventive or control sequence in case of emergency. This includes:

- instrument interlocks
- emergency backup equipment such as batteries
- equipment spares
- instrument voting systems
- adequate system inventory
- computer control
- scrubbers to be used to reduce emissions during, an emergency
- establish proper shut down procedures to prevent formation of the toxic nickel carbonyl from gases containing carbon monoxide.

Flaring systems and handling of ammonia releases
Only apply flaring systems to ammonia plants when there is no suitable alternative solution for dealing with emergency releases. Continuous flaring of process vents is not BAT.

Have smokeless flares under all conditions designed to accommodate varying flow rates.

Instal knock-out pots/drums as close as practicable to the flare to catch liquids/condensable material where feasible.

Prevent the release of liquid ammonia by suitable high integrity design such as adequately sized vent gas/liquid separators and warning systems.

Consider the disposal of ammonia vapour from vent stacks on an individual basis taking account of the inherent hazards.

Managing fugitive releases:
Implement regular inspection and maintenance programmes.

Analyse material flow routinely.

Improve equipment design.

Apply ventilation, and liquid containment.

Use diaphragm, seal less pumps and welded pipework.

Specially consider sample points and drain points that are normally blanked or capped.

Storage tanks:
Fit level alarms or similar devices, with suitable bunds or containment facilities.

Install high level interlocks to shut off feed wherever practicable.

Prevent damage to tanks by providing suitable barriers, from drums and process equipment and from the movement of vehicles.

The "whole plant concept"
An inventory of 23 single techniques that can reduce emissions waste and energy consumptions possible environmental measures has been tabled for consideration as BAT. These techniques cannot be considered in isolation only as part of the basic plant design. These associated techniques have been collected together and are referred to as "whole- plant concepts". For the steam reforming route, 3 concepts were identified:

1. Advanced convential process(SR-A)
2. Reduced primary reformer process(SR-B)
3. Heat exchange primary reformer process(SR-C)

The partial oxidation process has only one basic design and consequently has only one whole-plant concept.

Whole-plant concept		**Environmental Performance**					**New Inst.**	**Existing Inst.**
		Energy GJ/t	**NO_X**		**Waste kg/t**	**Water gNH_3/t**		
			mg/m^3	**g/t**				
Steam Reforming (SR)	**A**	29.2	160	320	0.2	0	+	+
	B	28.9	90	270	0.2	0	+	+
	C	29.5	a) 80 b) 20	175	0.2	0	+	+
Partial Oxidation		38.7	a) 560 b) 185 c) 350	1100	n.i	130		+/-

a) Process air heater
b) Auxiliary boiler
c) Thermal post-combustion
n.i. No information

Figure 3.1: Summary table environmental performance

Hence, the BAT environmental performance levels are as given below:

energy consumption	29.5	GJ/tonne ammonia
atmospheric NOx emission	320	g/tonne ammonia
waste generation	0.2	kg/tonne ammonia
ammonia discharge	0	g/tonne ammonia

Existing steam reforming installations:
Use the whole-plant concepts summarised in the table above. It is acknowledged, however, that all figures in practice will show variability. Arguably, the performance of the three concepts may largely fall within the boundaries of such variability. Furthermore, reconstruction of "concept A" installations (conventional process), which represent over 90 % of the EU "stock", would seem to render limited benefits (15 – 45 %, only for NO_X emissions). The implementation of the whole plant concepts to existing plants will most likely not involve the application of all individual techniques within these concepts. More data will be required for a more comprehensive analysis.

New installations, BAT is to:
Use both concepts B and C. Where concept C consumes 2 % more energy, concept B emits (at most) one third more NO_X. Arguably energy consumption by this sector is relatively more important than NO_X thus making it impossible to assess the trade-off. This line of reasoning implies the inclusion of concept A as a reference as well, as its environmental performance does not deviate substantially from concept B: only 1 % more energy consumption, and 15 % more NO_X emission. Such differences are likely to fall within the boundaries of normal variability.

Partial Oxidation
Partial oxidation processes inherently give rise to higher emissions and energy consumption than steam reforming processes, even with a comprehensive set of techniques attached to it. This route can therefore not be given as BAT for new plants. Whereas such new plants are not expected in the near future, less wide availability of natural gas may lead to increased interest for this route. By that time, a renewed assessment will be necessary.

For existing plants, the environmental benefits to be gained by reconstruction to steam reforming, are far from negligible. More information will be required in order to make a better evaluation. Although it could be recommended that this option should be thoroughly investigated, as an alternative to the dedicated "wholeplant concept" package of measures, for any partial oxidation plant where environmental measures need to be taken, it would seem imprudent not to include the "whole plant concept" as a reference.

Nitric acid production (2.2)

For both new and existing nitric acid plants, BAT is to:
Reduce fugitive emissions and breathing loses of e.g. NO_X, NH_3 and HNO_3 to a minimum by good maintenance and installation of appropriate equipment (most of the relevant aspects will be handled in the forthcoming horizontal document "Emissions from Storage").

Optimise the use of cooling water. Minimising the use of cooling water e.g. by using a recirculation system is preferred (most of the relevant aspects are covered in the horizontal document "Vacuum and cooling"). On the other hand, insufficient cooling will result in NO_X emissions to air, so cross-media effects have to be prevented.

Prevent emissions to water. Emissions to water are to be prevented completely in nitric acid plants by:

- cooling and neutralising the boiler blow-down
- reprocessing and/or correct disposal of the ammonia vaporiser blow-down
- reprocessing and or correct disposal of occasional emissions from purging and sampling.

Recycle catalyst materials by regular replacement of the platinum catalyst in the oxidation chamber (approx. 1.5 – 4 times a year). The old catalyst materials will be returned to the catalyst manufacturer. If present, the SCR catalyst of the NSCR catalyst will be returned to the manufacturer.

Install. a catcher to recover platinum and, if present, rhodium of the catalyst

Re-use filter cartridges. The filter cartridges can be cleaned and re-used

Dispose in a proper way whenever these cartridges lose their effect

Recover solid deposits with significant catalyst content.

Optimise the energy balance. The production of nitric acid is exothermic and heat recovery needs to be as high as possible. Energy consumption is to be minimised by using high efficiency equipment and insulation.

New nitric acid plants
In addition to the measures mentioned above BAT is to:

Optimise the oxidation step (N_2O reduction).

In a new nitric acid plant, the oxidation step is to be optimised by design and operation by using:

-an optimum ammonia-air ratio (depending on pressure, but c. 10 % ammonia and 90 % air)

-a good air-ammonia mixing and a good distribution of this mixture across the catalyst

-a relatively low oxidation pressure pressure of 4-5 bar and temperature of 850-950°C.

Optimise the platinum catalyst performance which prevents reduction of NO yield and formation of nitrous oxide (N_2O), by regularly replacement (c. 1.5 - 4 times a year). As a result, NO yield will be as close to 98 % as possible.

Install an extended reaction chamber reducing emissions of N_2O with c. 85 % compared to a nitric acid plant with a "standard" oxidation chamber. Installation of such an oxidation chamber will result in an N_2O emission of about 200 ppm (392 mg N_2O/m^3).

Optimise the absorption step (NO_X reduction)/additional NO_X reduction by operating at dual pressure. A new nitric acid plant operates preferably with a relatively low oxidation pressure (see above) and an optimum absorption pressure (approx. 11 bar). The design of the absorption tower is to be optimised as much as possible by adjustment of the control parameters.

Combine a close to optimum absorption tower design (a new but relatively short absorption tower) with an end-of-pipe technology from an economical and environmental point of view. The result of this optimum balance between absorption tower design and an end-of-pipe technology, is that NO_X emissions are limited to 50-75 ppm (102-153 mg NO_X/m^3). The end of pipe technology in this instance, is an SCR (or any other end-of pipe technology that is very effective in achieving a high general level of protection of the environment as a whole. If an SCR facility is installed, an ammonia slip of less than 10 ppm is achievable. Furthermore, the catalyst must be in a good condition, to minimise the formation of nitrous oxide (N_2O).

Prevent an extra emission during a planned shut-down/start-up in a new dual-pressure plant, using the air compressor and the large absorption capacity. This will give relatively small NO_X emissions

Existing nitric acid plants
In addition to the measures mentioned above for existing nitric acid plants BAT is to:

Optimise the oxidation step. In existing nitric acid plants, possibilities to improve the oxidation step are limited. Replacing the oxidation chamber is limited because of technical and economical limitations. The other possibilities are:
- optimise the ammonia-air ratio (depending on pressure, but c. 10 % ammonia);
- a good air-ammonia mixing and a good distribution of this mixture across the catalyst
- the platinum catalyst must perform at an optimum. To prevent reduction of NO yield and formation of nitrous oxide (N_2O), the catalyst will be be replaced regularly (2 - 4 times a year). Depending on design and age of the plant, it is expected that the NO-yield will be between 93 % and 98 %

Optimise the absorption step. The best way to optimise the absorption step is by adjusting the absorption tower. The parameters contributing to the performance of the tower are to be optimised, obtaining more product and reducing NO_X emissions. The remaining design features will limit the the adjustments made to NO_X reduction. along with technical or economical factors.

The installation of a new absorption tower in series with the existing tower or replacing the old one by a new one, will reduce NO_X emissions to 100 - 150 ppm. but the addition of a new tower or replacing the old one may lead to technical and economical limitations.

Where applicable install a Selective Catalytic Reduction (SCR) or Non-Selective Catalytic (NSCR) to reduce NO_X. If an SCR facility is installed in an existing nitric acid plant, reducing NO_X emissions to 100 ppm with an ammonia slip of less than 10 ppm is possible. Furthermore, the catalyst must be in a good condition, preventing the formation of nitrous oxide (N_2O). In the case of an NSCR, hydrogen or purge gas is preferred as a fuel. A reduction of the NO_X emissions to 100 ppm is possible, while the slip of natural gas (CH_4) is less than 0.5 %. The catalyst must be in good condition and the process must be optimised, preventing the formation of carbon monoxide (CO).
In a dual-pressure plant, use the air compressor to prevent an extra emission during a planned shut-down.

Sulphuric Acid production (2.3)
The following BAT are presented for new plants due to the fact that it is generally not possible to change the source of SO_2 or to change or modify the conversion process. For existing plants, only tail gas scrubbing is BAT taking into account that addition of a tail gas scrubbing to a

double absorption is considered as unnecessary and can only be justified by severe local considerations.

Sulphur burning
BAT is to use the double contact process because of the high concentration of SO_2 and stability over time.

To achieve the highest possible conversion efficiency in this process BAT is to:

- select a caesium-promoted catalyst with a lower working temperature in one or several layers, usually in the last layer. Four layers are normally sufficient. A Cs-promoted catalyst is about three times more expensive than normal catalyst
- alternatively increase the catalyst-volume with a cheaper normal catalyst in four layers. The preferred method is to add a fifth layer. In both alternatives a conversion efficiency of 99.6 % (daily average except start-up and shut down conditions) is achievable in new plants.

Metal Sulphide Roasting/Smelting
Pyrite Roasting:
BAT is to use the double contact process with a conversion efficiency of about 99.5 to 99.6 depending on the quality of the pyrite (daily average excluding start up and shut-down conditions) although the stability over time is slightly variable:

To get the highest possible conversion efficiency BAT is the same two options as for sulphur burning.

Zinc Roasting:
BAT is to use the double contact process as the range of SO_2 content after possible dilution is about 6 to 13 % and the variability over time is low, Á conversion efficiency of about 99.6 % (daily average except start up and shut down conditions) when using gases with SO_2 content >8 % is achievable.

Copper Smelting:
When the SO_2 content in gases is high (6 - 13 % after possible dilution) and the variability over time is low, BAT is the double contact process with a conversion efficiency of about 99.6 % (daily average except start up and shutdown conditions).

When the SO_2 content in gases is low (1 - 6 %) and the variability over time is high, (daily average except start up and shut down conditions), BAT is to use the single contact process with a conversion efficiency of about 98.5 %

When the SO_2 content is 5 - 10 % and the variability over time is high. BAT is the double contact process with a conversion efficiency of about 99.5 % (daily average except start up and shut down conditions)

When a plant experiences the full range of variability, the efficiency will vary between 98 and 99.5 %. Similar circumstances will permit an achievable SO_2 level, in terms of converter throughput based on 100 % H2SO4 acid of between 3 - 6 kg SO2t/H2SO4 due to fluctuating absorption conditions.

Off-Gas Specific Process Composition
The key to a correct purification of metallurgical gases lies in continuous, stable operation of the purification process, normally in an acid plant. The gas flows, which are susceptible to wide fluctuations in volume and concentration, are to some extent incompatible with this criterion.

BAT is to to minimise the fluctuations is to carry out the conversion process in various converters, or by mixing the gases with the more concentrated flow coming from the smelting stage. This produces gas flows with a concentration range that is adequate to maintain the autothermal process. This is the procedure followed in modern copper smelters that use Outokumpu flash smelting furnaces and Pierce Smith converters.

Lead Smelting:
BAT is to use the single contact process in the case of sintering lead ores when the variability is relatively high and SO_2 content is very low but also the wet process and the process based on NO_X with a conversion efficiency of about 98.5 - 98 and 100 % respectively. This low or variable SO_2 content is due to a down-draught sintering which limits SO_2 emissions.

In other cases (lead smelters), the SO_2 can be much higher and less variable over time. In this case BAT is to use the double contact process with a conversion efficiency of about 99.5 % (daily average except start up and shutdown conditions).

Sulphuric Acid Regeneration
The ratio O_2/SO_2 is important to get a conversion rate of SO_2 to SO_3 as high as possible. Upsteam the converter the gases are reheated to the ignition temperature through gas/gas heat exchangers with the conversion heat.
BAT is to use a double absorption process only if the SO_2 content of the gases is high enough (about 8 %) at the converter inlet. The conversion rates for different SO_2-concentrations are given below:

Single absorption
- SO_2 content at the converter inlet 8 % with O_2/SO_2 ratio of 1.1 : 98 %
- SO_2 content at the converter inlet from 5 to 8 % with O_2/SO_2 ratio of 1.1 : 97 to 98 %
- SO_2 content at the converter inlet below 5 % with O_2/SO_2 ratio of 1.1 : 96 to 97 %

Double absorption
When achievable, leads to conversion rates from 99 to 99.6 %. Double absorption is BAT for existing plants, a single absorption can be advantageously combined with an ammonia scrubber, the by product obtained being either sold on the market or recycled in the furnace.

Metal Sulphate Roasting
The conclusions are exactly the same as those for sulphuric acid regeneration.

Combustion of H_2S and Other S Containing Gases
The conclusions are the same as those for sulphuric acid regeneration.

Contact processes

Process type for manufacturing sulphuric acid	**Range for SO_2 conc.** Vd. %	**Single adsorption kg SO_2/**	**Double adsorption* kg SO_2/**	**Double adsorption + Bed 5 or Bed 4 Caesium***	**Single adsorption + tailgas scrubbing with usage byprod.**
	SO_2	tH_2SO_4	tH_2SO_4	kg SO_2/tH_2SO_4	kg SO_2/tH_2SO_4
Sulphur burring	6 – 12	6.7 – 13.3	1.5 – 3.9	1.0 – 2.6	<2
Pyrite roasting	8 -10		2.6 – 3.9	1.5 – 3	<2
Zirc/lead ores roasting	4 – 9	7 – 12	1.7 – 3.3	1.5 – 2.5	<2
		(4 – 6 % SO_2)	(6 – 12 % SO_2)		
Copper smelting	3 – 13	6.5 – 20	1.2 – 3.3	1.2 – 2.5	<2
Lead/copper smelting	2.7	6 – 10			<2
Organic spent acid regeneration	2 – 10	10 – 27	2.6 – 6.6	1.5 – 4.5	<2
Metal sulphate roasting	8 - 12		1.6 – 3.3	1.3 – 2.6	–
*Not achievable for low SO_2 Gas content					

Figure 3.2: BAT associated values for SO_2 emissions dependent from process type and absorption type

Process type for manufacturing sulphuric acid	**Range for SO_2 conc.**	**Single adsorption**	**Double adsorption**	**Double adsorption + Bed 5 or Bed 4 Caesium**	**Single adsorption + tailgas scrubbing with usage byprod.**
	Vd. % SO_2	$kgH_2SO_4^*/tH_2SO_4$	kg $H_2SO_4^*/tH_2SO_4$	kg $H_2SO_4^*/tH_2SO_4$	kg $H_2SO_4^*/tH_2SO_4$
Sulphur burring	6 – 12	<0.1	<0.1	<0.1	<0.1
Pyrite roasting	8 - 10	0.2	0.2		
Zirc/lead ores roasting	4 – 9	0.15 – 0.3	0.1 – 0.16		
		(4 – 6 % SO_2)	(6 – 12 % SO_2)		
Copper smelting	3 – 13	0.06 – 0.35	0.05 – 0.2		
Lead/copper smelting	2.7	0.15			
Organic spent acid regeneration	2 – 10	0.05 – 0.2	0.05 – 0.2		0.01 – 0.03
Metal sulphate roasting	8 - 12		0.065 – 0.13	0.065 – 0.13	
* $H_2SO_4=SO_3+H_2SO_4$					

Figure 3.3: BAT associated values for energy outputs dependent from process type and absorption type

Process type for manufacturing sulphuric acid	Range for SO_2 conc.	Single adsorption	Double adsorption
	Vd. % SO_2	MJ/tH_2SO_4	MJ/tH_2SO_4
Sulphur burring	6 – 12		2500
Pyrite roasting	8 - 10		4500
Zirc/lead ores roasting	4 – 9		600
		(4 – 6 % SO_2)	(6 – 12 % SO_2)
Copper smelting	3 – 13	2000 – 2900	2000 – 2900
Lead/copper smelting	2.7	900	
Organic spent acid regeneration	2 – 10	2500	2500

Figure 3.4: BAT associated values for energy outputs dependent from process type and absorption type

BAT for tail gas scrubbing produces sulphites and sulphates, which possibly entail problems of reasonable disposal of wastes. They are applicable if par example Sodium bisulphite, ammonium sulphate or gypsum is produced as marketable by products near the sulphuric acid plant.

Phosphoric acid production (2.4)

BAT is to:
Use the best possible phosphate rock that contains ideally tricalcium phosphate. The impurities in phosphate rock leads to an assortment of economic, technical and environmental difficulties. Igneous rock is lower in impurities but not as abundant. Consequently the main source is from sedimentary rock which includes all the various contaminants. So, for an assortment of reasons it is preferable to use phosphate rock with a high P_2O_5 content and low impurity content.

Extract in the most efficient way the P_2O_5 contained in the rock. An increased efficiency means a reduced consumption of rock, sulphuric acid and production of bi-product gypsum. This will also result in cleaner gypsum with a lower P-content, and less impurities which means that there is more chance of finding a useful outlet for the gypsum. The recrystallization processes (HDH-1, HDH-2 and DHH) are preferablen over the more straightforward dihydrate and hemihydrate processes as the P_2O_5 recovery is the most efficient in comparison to the dehydrate and hemihydrate processes.

Minimise emissions and waste as follows:
- the measures to minimise fluoride emissions to air which are formed in the process as HF and SiF_4 is by absorbing in a suitable scrubbing system such as a spray tower packed bed, cross-flow venturi and cyclonic column. The fluorine is recovered as fluosilic acid (H_2SiF_6) which can be used for the production of aluminium fluoride, and other fluorine compounds such as sodium and/or potassium fluosilicates. In this case a dilute solution of fluosilicic acid is used as the scrubbing liquid
- dust emissions from the handling and transportation of the phosphate rock are minimised by the use of covered conveyor belts and contained storage. Good housekeeping and regular cleaning/sweeping of the roads and surrounding areas including the quayside during the unloading of ships. Installed extraction systems that are vented through fabric filters for new plants are capable of achieving levels of less than 50 mg/Nm^3

- emissions to water arise as effluents from the fluorine scrubber and direct contact condensers in the vacuum system used for the flash cooler or evaporator. Fluoride emissions from condenser water are prevented by the use of an indirect condensation system instead of a direct contact condenser. Where fluorine is not recovered as fluosilic acid then the effluent is neutralised with lime or limestone to precipitate fluorine as solid inert calcium fluoride.

Remove low levels of phosphate arising from the separator, gas scrubber and condenser by the use of magnesium ammonium phosphate (struvite) or by calcium phosphate precipitation

Disposal/use of phosphogypsum
Phosphogypsum can be used in of the following applications.

Application	**Anhydrite, AH($CaSO_4$)**	**Dihydrate, DH($CaSO_4.2H_2O$)**	**Hemihydrate, HH($CaSO_4.½H_2O$)**
Construction	Floorscreed cement (as setting regulator)	Cement (as setting regulator)	Plaster(stucco)plaster board ceiling tiles gypsum blocks floor screed
Construction	Floor screed cement (as setting regulator)	Cement (as setting regulator)	Plaster(stucco) plasterboard ceiling tiles gypsum blocks floor screed
Industrial uses/Other	Filler/pigment in variety of applications	Filler/pigment in variety of applications production of ammonium sulphate and sulphuric acid	Filler/pigment in variety of applications

Table 3.1: Overview of phosphogypsum applications

Unfortunately these outlets only account for no more than 5 % of the overall production of phosphogypsum and cannot be regarded as BAT. Gypsum as a bi-product of other industrial processes and/or extracted from naturally occurring deposits dominate this market. However it must also be recognised that about 5 tonne phosphogypsum is produced for every tonne of fertiliser as P_2O_5 produced. In Europe at the present time it is estimated that 5 - 6 million tonne of gypsum is produced each year.

Disposal of the majority of phosphogypsum BAT is to:

Transport to a separate land storage area and dry stack the wet cake with up 20 - 25 % water where it will be managed and maintained to contain the contaminants in the phosphogypsum or the preferred route is wet stacking which involves pulping the gypsum cake as it comes off the filter with either fresh or seawater and pumping the slurry through a pipeline to a gypsum disposal where the solids are allowed to settle out. Clarified excess water is decanted, and in the case of a fresh water system, pumped back to the plant for re-slurrying gypsum and re-use in the process. When sea-water is used to slurry the gypsum, the clarified seawater is not returned to the plant for re-use, but discharged back to the sea. Direct discharge of the phosphogypsum is not BAT. The management of these waste disposal areas is covered in the BAT for the Management of Tailings and Waste-Rock in Mining Activities.

Hydrofluoric Acid production (2.5)

BAT is to:

In-process measures
Take account of the limitations of heat supply for the main reaction in the heat transfer design which needs to include the physical characteristics of the feed and product material, and the bulk size of the equipment which inhibits the input of heat.

Keep the design needs simple and uncomplicated as the highly corrosive nature of the reactants and products does limit the materials of construction particularly at the elevated temperatures. Install for new kilns several double jackets around the rotary kiln and feed the heated gas in a temperature profile along the length of the kiln which will optimise the energy requirement and help to control the product quality.

Preheat. either/or of the sulphuric acid or the fluorspar to provide some of the heat input necessary for the reaction. The preferred technique is to heat the sulphuric acid instead of the fluorspar. Heating the fluorspar does result in a higher dust entrainment at the elevated temperatures with the consequent difficulties in the abatement equipment. Direct heating with oxygen enriched gas does have the benefit of destroying any flotation chemicals that may be contained in the fluorspar. The pre-heating of the fluorspar does need a significant capital investment for the necessary equipment.

Install in where practicable a pre-reactor which reduces the workload and required temperatures in the main kiln reducing corrosion and subsequent maintenance. However the implementation of this technique is costly and has to be judged on the subsequent environmental and product quality benefits.

Recover up to 20 % heat in new installations. The recovered heat is utilised for preheating the reactants or the combustion air whichever is appropriate.

Remove low boiling impurities when higher grade HF is required with a low energy column integrated in or at the end of the process line in preference to installing a separate distillation column that has a high energy consumption.

Valorisation of co-products
Use the hexafluorsilic acid co-product in the fluorination of potable water, production of sodium, potassium, magnesium, lead, copper, zinc, ammonium, sodium fluoride, kryolith (sodium hexafluoroaluminate), potassium hexafluoroaluminate, aluminum fluoride, for aluminum production or recover HF and SiO_2 from H_2SiF_6.

Use the anhydrite co-product as a raw material e.g. a plaster, binder for floor screed, additives for cement industry, agriculture, fillers for plastics, porous bricks. It is recognised that there are market constraints as anhydrite from this route may be unacceptable due to the availability of suitable anhydrite from alternative sources. The disposal of the solid anhydrite to landfill and water courses is not considered BAT.

Abatement Techniques
Absorb the HF from off-gases where HF releases have to be minimised in a two-stage absorption using water and alkali. It is dependent on the availability of suitable alkali for scrubbing, materials of construction and process control. The investment and maintenance costs will need to be taken into account when capital investment for this type of abatement is used.

Absorb off gases containing HF, SO_2 and CO_2 in a similar way to HF alone but the alkali stage needs to be controlled between pH 7-9 to maximise the absorption of SO_2 and CO_2. An alternative is to use a once through technique with copious amounts of water with an alkaline buffer or sea-water.

NPK/MN and superphosphates production (2.6, 2.7)

BAT is to
Use phosphate rock with a low content of impurities. For a variety of reasons it is preferable to use phosphate rock with a high P_2O_5 content and low impurity content. However, one should consider that rock with a lower heavy metal content has the disadvantage that it has a higher fluorine content.

Minimise dust emissions from the cooling section. Low dust levels are achieved by using a plate bank product cooler or redirecting the airflow from the cooling drum to the reaction vessel thus reducing dust emissions to a minimum. A zero dust emission is considered achievable in case of the plate bank product cooler when the appropriate cooling range (from >100 °C to approximately 30 °C). However, a maximum dust emission of 10 g/tonne finished product due to non-standard situations is acceptable. Dust emissions in the range of 0 – 10 g/tonne finished product are acheivable.

Reduce fugitive emissions and breathing losses of e.g. NH_3 to a maximum by good maintenance and installation of appropriate equipment (most of the relevant aspects are handled in the horizontal document "Emissions from storage of bulk or dangerous materials

Use granulation as a finishing technique in the production of SSP, TSP and MN.

Minimise dust emission in the grinding section by using fabric filters. The emission can be reduced to <10 mg/m^3 or by using ceramic filters the dust emission can even be lower (<4 mg/m^3).

Use scrubbers (or any other end-of-pipe technology that is very effective in achieving the emission level of protection of the environment as a whole), that result in a total fluoride emission level of <5 mg/m^3

Use scrubbers (or any other end-of-pipe technology that are effective in achieving the emission level of protection of the environment as a whole), that result in a Cl emission of <30 mg/m^3.

Optimise of the re-use of process water (such as the re-use of scrubbing water)

Purifiy waste water or process water

Urea production (2.7)

For both new and existing urea plants, BAT is to:

- reduce fugitive emissions and breathing losses of e.g. NH_3 and HNO_3 to a minimum by good maintenance and installation of appropriate equipment (most of the relevant aspects are handled in the horizontal document "Emissions from storage of bulk or dangerous materials")
- granulate the urea. In almost all cases, granulation is possible without affecting the quality of the product. End-of-pipe technology might be necessary to meet acceptable NH_3 and dust emissions. Using a scrubber (or any other end-of-pipe technology that is very effective in achieving a high general level of protection of the environment as a whole) makes it possible to achieve dust emissions of 100 - 150 g/tonne product to the atmosphere due to product finishing (granulation). In this emission value it is considered that there is no dust emission from the cooling section. The ammonia emission might differ between new and existing plants. When using a scrubber, special attention is to be paid to the scrubber water. Emissions of scrubber water are to be prevented or at least minimised by means of recycling or re-using the scrubber water
- minimise dust emissions from the cooling section. Dust emissions in the cooling section are avoided by using a plate bank product cooler. A zero dust emission is achievable when cooling (from >100 °C to approximately 30 °C) using the plate bank cooler. However, a maximum dust emission of 10 g/tonne product due to non-standard situations is acceptable. Dust emission from the cooling section in the range of 0 - 10 g/tonne product is achievable.
- redirect urea dust after the granulator to the concentrated solution. This can be achieved e.g. by installing a classifier
- prevent emissions of process water or at least minimise by means of recycling or re-use. Process water can be re-used as e.g. boiler feed or scrubbing water; re-use of process water/steam in other site activities should also be taken in account
- use a biological waste water treatment, but only when several site plants make use of one installation for economical viablity.

Use in other cases, a physical-chemical waste water treatment.

For new urea plants, BAT is to:

- Optimise the synthesis phase, the relevant parameters being:
  - temperature (180 – 200 °C)
  - pressure (140 - 250 bar/14 - 25 MPa)
  - molar ratios (NH3/CO2: 3:1 to 4:1)

Install a pool reactor. A regular ammonia emission to the atmosphere from process vents in the range of 2.5 - 3.5 g/tonne product is achievable.

Neutralise the unconverted carbamate (after the CO_2 stripper) with nitric acid as ammonium nitrate to reduce the NH_3 emission.

Use stripping systems for new urea plants Once-through processes, partial recycle processes and total-recycle processes other than stripping systems are not be regarded as BAT.

Apply options such as gas scrubbers and injection of formaldehyde for ammonia emission due to product finishing. Achievable release levels of 250 g/tonne product are possible.

For existing urea plants, BAT is to:

- Optimise the synthesis phase. Relevant parameters are:
  - temperature (180 - 200 °C)
  - pressure (140 - 250 bar/14 - 25 MPa)
  - molar ratios (NH3/CO2: 3:1 to 4:1)

- Install a pool condenser is the process optimisation for existing urea plants. The achievable limit of ammonia emission to atmosphere from process vents is in the range of 4.3 – 8 g/tonne product.

- Use stripping systems.

- Reduce ammonia emission due to product finishing. By applying scrubbers (or any other end of pipe technology that is very effective in achieving a high general level of protection of the environment as a whole), NH_3 emission levels to the atmosphere due to product finishing in the range of <400 g/tonne product are achievable.

Ammonium Nitrate production (2.8)

BAT for AN and AN derivatives plants is to:

- optimise the neutralisation section. The optimisation of the neutralisation section in the production of AN (derivatives) consists of:
  - pre-heating of raw material
  - pH control; pH 2.4 - 4 (T <170 °C)
  - pH 4.6 - 5.4 (pressurised neutraliser)
  - temperature control; 175 - 180 °C (evaluated pressure)
  - pressure control; 4 - 5 bar
  - contamination control
  - the possible use of a two-stage neutraliser (in first stage pH 3-4)

- reduce fugitive emissions and breathing losses of e.g. NH_3 and HNO_3 to a minimum by good maintenance and installation of appropriate equipment (most of the relevant aspects are handled in the horizontal document "Emissions from Storage"
- reduce the total NH_3 emission of the AN(derivatives) plant by means of scrubbers (or any other end of pipe technology that is very effective in achieving a high general level of protection of the environment as a whole) which result in an emission value between 85 - 100 g/tonne
- reduce the total dust emission of the AN(derivatives) plant with scrubbers, fabric filters and/or a plate bank product cooler (or any other end-of-pipe technology that is effective in achieving a high general level of protecting the environment as a whole), which result in an emission value <100g/tonne product. However, these emission values are more easily obtained in a new AN plant due to combination with process integrated measures. The application of a plate bank product cooler in an AN (derivatives) plant might in some cases (especially in existing plants) be limited to end cooling (from 50 °C to 30 °C)
- use granulation as the finishing technique in the production of AN and AN derivatives
- re-use process water and process steam. "Dirty" steam can be used to vaporise and heat ammonia or to heat nitric acid. Other possibilities for re-use of the effluent are as boiler water feed (possibly after further purification) or for control/analysis purposes. The final possibility for re-use is the integral re-use of low thermal contaminated vapours for cooling purposes and to purify liquid effluent.

4 EMERGING TECHNIQUES

Emerging technique is understood in this document as a novel technique that has not yet been applied in any industrial sector on a commercial basis. This chapter contains those techniques that may appear in the near future and that may be applicable to the LVIC-AAF sector:

LVIC-AAF activities overview
Throughout its history the LVIC-AAF industry has continuously developed new and improved processes in response to changes in feed availabity/quality, product specifications, product ranges, new product outlets and economic and environmental requirements. These developments have slowed down in recent years for the following reasons:

- rationalisation of the sector as a whole has resulted in closures of installations that are unable to maintain profitability in the sector and/or are surplus to requirements. The demand for fertilisers in Europe continues to reduce
- the disposal of phosphogypsum continues to be an unsurmountable problem with only 3 production plants remaining in Europe supplying the fertiliser industry. The whole environmental issue of phosphogypsum and containment of the contaminants inherent in the by-product has hastened the closure of phosphoric acid plants
- technological developments are concentrating on optimising current systems for higher yields (e.g. more selective catalysts), higher energy efficiency (e.g. improved reactor design and better heat integration) and shorter downtimes (e.g. improved materials of construction, more efficient maintenance programmes) rather than on novel processes.

The revamping of existing facilities continues to be the applied way to improve the performance of the various units but it is recognised that the capital expenditure is often a limiting factor and low margins will inevitably lead to the search for cost savings.

Phosphate removal from waste water effluents
Waste water from a phosphoric acid plant may contain significant concentrations of phosphates, particularly from gas scrubber effluents. The addition of flocculating agents can be utilised to precipitate phosphates in solution, such as iron and aluminium salts. However, this method will limit recycling of the phosphate as the resulting iron or aluminium compounds are not compatible with the technologies currently used in the phosphate industry. A better option for recycling phosphates from waste water is with processes that precipitate crystalline products of a reasonable purity, and which could be utilised as a raw material substitute in standard phosphate fertiliser production technology or directly as fertiliser material. Several processes of this nature have been developed. The primary products are usually either (insoluble) hydroxy-apatite or soluble magnesium ammonium phosphate (struvite). In most of these processes, phosphate recovery is carried out in fluidised, agitated or fixed bed crystallisation columns, with sand or phosphate rock particles usually being used as seed material. Hydroxy, calcium and magnesium ions are usually added to the process to facilitate precipitation (see section on application of recycled phosphate).

No examples are available for phosphate recovery from the waste waters of phosphoric acid plants. Kemira Agro Pernis (the Netherlands) did investigate the fluidised bed process of DHV (Crystalactor process) for phosphate removal from the effluents of the gas scrubber systems. In this process, phosphate and fluoride were precipitated and crystallised on seed material (phosphate rock) under the controlled addition of lime (CaO). The process produced a slurry which could have been recycled to the phosphoric acid process (solids roughly consisted of 45 % calcium phosphate, 45 % calcium fluoride and 10 % phosphate rock). The treated effluent could be recycled to the gas scrubber system, thus creating a closed loop system. Unfortunately, the installation was not cosiderd as economically feasible at the time (1991).

In-process phosphoric acid purification
At the Technical University of Delft (the Netherlands) a process is currently being developed for the removal of heavy metal ions from process streams under conditions typically

encountered in wet phosphoric acid processes, especially during the conversion of gypsum from hemihydrate to dihydrate in recrystallisation processes. The in-process removal of impurities will yield a cleaner phosphoric acid as well as purer gypsum thereby enhancing the chances 0f finding a useful application of the gypsum, and can also be used when phosphate rocks with relatively high levels of impurities are used. The process is based on the liquid membrane or liquid-liquid extraction technique. An experimental transverse flow hollow fibre module has been designed and built. Lab-scale tests have shown positive recovery results for lead, mercury, copper, cadmium and cerium from actual plant acid (1 % gypsum, 70 °C). Further research is aimed at optimisation and scale-up of the test module, the finding of better extraction liquids and the specific removal of radium (by combining with other techniques, e.g. specific precipitation of radium with barium salts), as this is regarded to be the most limiting factor for the useful application of phosphogypsum.

End-of-pipe technology to reduce nitrous oxide (N_2O)

Nitric acid production is a significant source of nitrous oxide (N_2O). In new nitric acid plants, the use of an extended oxidation reactor can prevent at least 85 % of the N_2O emission. In existing nitric acid plants on the other hand, the installation of an extended oxidation chamber might encounter technical and economical limits.

The possibilities of catalytic N_2O reduction have been researched by two different Dutch project-teams. One team was developing a catalyst without a reducing agent, while the other team was developing a catalyst with a reducing agent. The initial results were expected in 2 - 4 years time. Most information about these investigations is classified

Production of nitric acid using oxygen

In the past, much research has been carried out to investigate the possibilities of oxidising ammonia with pure oxygen (O_2) instead of air. Low NO_X emissions can be obtained, using oxygen mixed with the tail gas, forming so-called circulating gas

The values given in table are obtained in a nitric acid plant of the type AK-72, as developed by GIAP.

O_2 concentration in circulating gas (v %)	**Concentration (m^3/t HNO_3)**				**NO_X concentration**	
	N_2	**Ar**	**H_2O(vapour)**	**O_2**	**ppm**	**mg NO_X/m^3**
2.5	1979.3	848.7	17.5	70.0	390	800
10.0	1803.0	756.5	11.4	284.4	108	221
30.0	1358.8	583.0	10.8	832.2	43	88
50.0	935.7	405.5	10.8	1341.2	30	62

Table 4.1: Composition of gas at the outlet of the absorber

The production of oxygen involves a high consumption of electricity: making the use of oxygen expensive. The capital costs increase with c. 35 %, while annual costs increase with 27 - 31 %.

Ion-changing membranes to purify waste water from the fertiliser industry

Research carried out by TNO and the University of Groningen in the Netherlands, has demonstrated that the re-use of acids and bases can be achieved by purifying industrial waste water/process water using ion-exchange membranes. This technique is a variation on the conventional electrodialysis technique, which separates ions by means of selective ion membrane technology.

By applying this new technology the salt-ions are extracted as concentrated acids and bases and can be re-used in the production process. The research has shown that the principle of electrodialysis as a purification technique with re-use of salt ions is technical possible and has been tested on pilot scale at several small companies. However, due to the fact that the fertiliser plants in the Netherlands alredy comply with their regulations regarding effluent-discharge on the surface water, it is not yet economically viable to introduce this technique.

Reference literature
[10, infoMil, 2001]

Membrane reactor in urea production
Research has been carried out by a research centre and an engineering firm, on the feasibility of using a ceramic membrane in the urea synthesis section to remove water under extreme conditions. It is intende that by applying this membrane the second equilibrium reaction of the urea synthesis should be modified to a non-equilibrium reaction. In this way all the raw material should react to urea. This would have the following environmental advantages: a lower energy demand, a reduction of ammonia and urea emission, a reduction in the process cooling water requirement, and better waste water quality.
A technical advantage is the significant reduction of the volume of the process installations.

Reference literature
[10, infoMil, 2001]

Purifying of waste water by means of reverse osmosis
Description
A membrane process is the permeation of a liquid through a membrane, with the segregation of the liqid into permeate that passes the membrane and concentrate that is retained. The driving force of this process is the pressure differential across the membrane. Reverse osmosis (RO) membranes can hold back all particles down to the size of organic molecules and even ions. Provided that the feed is particle-free, these membranes are mainly used when the complete recycling of permeate and/or concentrate is needed.

The typical characteristics of RO membranes are: pore diameter (µm) <0.001, operating pressure (Mpa) 2 - 20, cut-off size (nm) <1000 g/mol, permeate flow (l – 2 m^3/h) 10-35, cross flow speed (m/s) <2, membrane type: polymeric asymmetric or composite, membrane configuration; spiral-wound/tubular.

Membranes are available in several materials and configurations. The optimum modification for a particular application will depend on the nature of the waste water, since the different materials have varying resistance to dissolved substances. Membrane materials for RO are organic polymers. Polyamide-based membranes are normally superior to cellulose acetate-based membranes for the removal of trace organic molecules.

RO processes are usually operated cross-flow, i.e. the permeate flow is directed perpendicular to the flow. The impurities remain in the feed which, reduces volumetrically, and exits the membrane system as a concentrated waste stream. Even under the best pre-treatment regimes and programmes, membranes will foul and deteriorate in performance if cleaning is not ensured. Consequently membrane systems should be designed in such a way that the modules can be taken offline and cleaned mechanically or chemically.

An industrial membrane plant usually consists of three separate sections:
1. the pre-treatment section, where the feed is treated by chemicals clarification (precipitation, coagulation/flocculation or flotation) and subsequent filtration, or by filtration and subsequent UF
2. the membrane section, where high pressure is applied and the waste water cross-flows across the membrane
3. the post treatment section where permeate is prepared for re-use or discharge, and the concentrated brine collected for further work-up or disposal.

Membrane units are arranged as modules either in parallel- to provide the necessary hydraulic capacity, or in series, to increase the degree of efficiency.

Applicability: RO is a process to separate water and to dissolve constituents down to their ionic species. It is applied when a high grade of purity is required. The segregated water phase is recycled and re-used. Examples are desalination, the final removal of e.g. degradable components if biological treatment is not available, the removal of heavy metals, toxic components.
Segregation of pollutants with the aim of concentrating or further processing them.

RO is often used in combination with permeate post-treatment techniques, e.g. ion exchange or GAC adsorption.

The application limits of RO are:

- concentration, in particular concentrated solutions with an osmotic pressure so high that it either exceeds available operating pressure or is not economically viable
- salt solubility, salt solutions with low solubility tend to precipitate and thus cause fouling
- Polymerisation monomers: contaminants tending to polymerisation cause fouling
- Membrane material: low thermal and chemical resistance properties of membrane materials limits their application to a restricted pH and temperature range (18 – 30 °C).

Achieved environmental benefits

- high separation efficiency
- modular system, i.e. flexible in usage, recycling of permeate and concentrate is possible
- low operating temperatures, possible of fully automatic operations.

Disadvantages:
Clogging, plugging and fouling processes are possible, compaction in the presence of softening agents, high pressure required, low permeate fluxes.

Achievable emission levels:
There were no achieved emission levels found for the fertiliser industry. However, it is assumed that the emission levels mentioned in are also achievable in the fertiliser industry.

Cross media effects
Membrane treatment produces a waste stream (concentrate) of approximately 10 % of the original feed volume, in which the target substances are present at levels approximately 10 times their concentration in the waste water. AN assessment needs to be made as to whether this residue can be disposed of or whether it needs further treatment, e.g. wet oxidation.

Consumables: membrane material, chemicals for cleaning and energy (kWh/m^3). The energy consumption is directly related to the flow rate and pressure requirements. It is mainly associated with the maintaining a minimum velocity of about 2 m/s across the membrane surface.

Economics
Capital costs: GBP 350-1100 per m^2 membrane (for spiral and tubular membranes) (EUR 10 - 12 million per 1000 m^3/h], replacement costs: GBP 60 - 140 per m^2 membrane.

The capital costs, including automated cleaning facilities, can be broken down approximately as follows: pumps 30 %, replacement membrane components 20 % membrane modules (housings) 10 %, pipework/valves/frame work 20 %, control system 15 % and other 5 %.

The operational costs can be broken down approximately as follows: replaceable membrane components: 35 - 50 %, cleaning 12 - 35 %, energy 15 - 20 % and labour 15 - 18 %.

Example plant
In 1994, BASF Antwerp (Belgium) started a project to purify their process water of the single nitrogen fertiliser production process through reversed osmosis. About 40 m^3/h condensate was produced, which was loaded with ammonium nitrate in concentrations of about 100 kg/h. This

condensate could not be directly used in other processes and had to be treated to remove the ammonium nitrate. Tests on a pilot scale resulted in an elimination of ammonium as well as nitrate of 95 % to 98 %, and a proportion of volume concentrate in relation to permeate of less than 0.1. The strongly varying pH (2 - 10) had no influence on the efficiency. The reverse osmosis installation has also been used on full-scale bases. However, due to economical reasons the installation is no longer in use.

Reference literatures
[10, infoMil, 2001]

Application of recycled phosphate
The recycling of phosphate can be a sustainable process for the SSP and TSP industry. Nowadays it is possible to extract phosphate from waste. Phosphorus can be removed with comparatively little difficulty in two potentially recyclable inorganic forms:

- magnesium ammonium phosphate ($MgNH_4PO_4$): struvite or potassium ammonium phosphate (KNH_4PO_4): K-struvite
- calcium phosphate $Ca_x(PO_4)_y$.

The difficulty for the phosphate industry is that struvite can not be processed using any of the industry's established process technologies. The problem lies in the magnesium, which cannot be processed by the wet route, and the ammonia, which would pose major problems in the thermal route. Literature on the use of struvite in the fertiliser industry is limited.

However, research into the applicability has been done and has concluded that it might be possible to use 15-20 % recycled phosphate in a SSP/TSP plant. It must be stressed that the use of recycled phosphate is only possible when no AN is used (as a starting material or as an additive), due to the high detonation risk resulting from the catalytic nature of the impurities in the recycled phosphate on AN.

Calcium phosphate of a suitable physical form can be extracted from sewage. The best known example of this is the Geestmerambacht sewage treatment plant in the Netherlands, which runs a fluidised bed to recover calcium phosphate as a pellet, formed around a seed particle of silica sand. Because the sand acts as a seed crystal, the phosphorus content will never reach that of high-grade phosphate rock, but the trace metal analyses of the product and the phosphoric acid derived form it, show the material may be considerably purer then its natural counter parts.

Several pilot and full-scale processes already operate in different countries, recovering phosphates from waste water streams through calcium phosphate formation, e.g.

- DHV Crystalactor process at the waste water plants of Westerbork (12000 t demonstration plant), Heemstede (35000 t) and Geestmerambacht (230000 t) in The Netherlands
- pilot plant developed by DHV and Essex and Suffolk Water at Chelmsford sewage works, UK
- pilot plant developed by Karlsruhe University at Darmstadt Süd sewage works in Germany;
- demonstration plant (5000 t) developed by Sydney Water Board at Warriewood, Australia;
- three plants constructed by Kurita, Japan
- a fixed bed precipitation installation (160 m^3/hr) is operational at the Mercedes motor car factory at Gagenau, Germany.

Full scale processes which recover phosphates as struvite are already operational or being built in Japan and in The Netherlands:

- the DHV Crystalactor fluid bed process is used in a full scale struvite recovery installation at the AVEBE potato processing plant in The Netherlands (150 m^3/hr), now dismantled due to closure of the potato processing factory
- the Unitika Ltd (Osaka) struvite precipitation process (Phosnix process) is already in application at the Ube Industries Sakai plant (industrial waste water) and at the Shimane Prefecture sewage works in Japan.

Samples of struvite are currently being evaluated by the European fertiliser industry (EFMA). Struvite's low solubility may limit its attraction as a fertiliser but it might be possible to boost its value with one or two simple process steps.

Other examples of fertiliser sites that apply recycled phosphate were not found.

Reference literatures
[10, infoMil, 2001]

5 CONCLUDING REMARKS

REFERENCES

1 UBA (2001). "Nitric acid production", Umweltbundesamt, 3-85457-612-9.

2 EFMA (2000). "Production of Ammonia", EFMA.

3 ESA (2000). "Production of sulphuric acid", EFMA.

4 EFMA (2000). "Production of NPK fertilisers by the mixed acid route", EFMA.

5 EFMA (2000). "Production of Urea and Urea Ammonium Nitrate", EFMA.

6 EFMA (2000). "Production of Ammonium Nitrate and Calcium Ammonium Nitrate", EFMA.

7 EFMA (2000). "Production of NPK Fertilizers", EFMA.

8 EFMA (2000). "Production of Phosphoric acid", EFMA.

9 EFMA (2000). "Production of NPK Fertilizers by the Nitrophosphate Route", EFMA.

10 infoMil (2001). "Dutch Notes on BAT for the production of Fertilisers", Ministry of Housing,Spatial Planning and the Environment Directorate for Climate Change and Industry, 90-76323-05-4.

11 infoMIL (1999). "Dutch Notes on BAT for the Production of Nitric Acid", Ministry of Housing,Spatial Planning and the Environment Directorate for Climate Change and Industry.

12 EIPPCB, E. C. (2000). "Preliminary Document Inorganic Chemical Sector", European Commision.

13 EC (1997). "Pilot Document for Ammonia Production", European Commision.

14 EA (1999). "IPC Guidance Note Series 2 (S2) Chemical Industry Sector S2 4.04 Inorganic Chemicals", The Stationery Office, 011 310140 6.

16 RIZA/Tebodin (2000). "Dutch Notes on BAT for the Phosphoric Acid Industry", Ministry of Transport,Public Works and Water Management Directorate-General for Public Works and Water Managememnt Institute for Inland Water Management and Waste Water Management and Waste Water Treatment-RIZA.

19 CEFIC (2000). "Best Available Techniques for Producing Hydrogen Fluoride", CTEF, Issue 1.

29 EIPPCB (Draft). "BREF Large Combustion Plants".

32 EFMA (2000). "Production of Nitric Acid", EFMA.

33 Ullmann`s (2000). "Encyclopedia of industrial chemistry".

34 IFA (2001). "Survey of urea capacities", International Fertilisers Association, A/01/89.

35 infomil/novem (2001). "Reduction of nitrous oxide in the nitric acid industry".

36 (EFMA), I. F. I. A. I. a. E. F. M. A. (1992). "Handbook for Safe Storage of Ammonium Nitrate Fertilisers".

37 UBA (2002). "State of the art for Production of sulphuric acid with regard to the IPPC directive".

GLOSSARY

ABS	Acrylo-Butadiene Styrene
ACES	Advanced Cost and Energy Saving
AMDEA	Activated Methy1diethanolamine
AN	Ammonium Nitrate
BAT	Best Available Technique
BOD	Biological Oxygen Demand
BREF	BAT Reference Document
C.A.S.	Chemical Abstract Service
CAN	Calcium Ammonia Nitrate
CIS	Commonwealth of Independent States Azerbaidzhan, Armenia, Belarus', Gruziia, Kazakhstan, Kyrgyzstan, Tadzhikistan, Turkmenistan, Uzbekistan, Ukraina
C/H	Carbon/Hydrogen Ratio
COD	Chemical Oxygen Demand
CN	Calcium Nitrate
CNTH	Calcium Nitrate Tetrahydrate
DH	Dihydrate
EA	Environment Agency
EC	European Commission
ESP	Electro Static Precipatator
EFMA	European Fertilisers Manufacturers Association
EIPPCB	European Integrated Pollution Prevention and Control Bureau
EU	European Union
HDH	Hemi-Dihydrate
HF	Hydrofluoric Acid
HH	Hemihydrate
HHV	High Heating Value
HP	High Pressure
HRC	Hemihydrate Recrystallisation
HMTA	Hexamethylenetetramine
HMIP	Her Majesty's Inspectorate of Pollution, UK
HTS	High Temperature Shift
IEF	IPPC Information Exchange Forum
IPPC	Integrated Pollution Prevention and Control
IPTS	Institute for Prospective Technological Studies
ISO	International Standards Organisation
IUCLID	International Uniform Chemicals Information Database
LHV	Low Heating Value (does not include heat of condensation of water vapour)
LP	Low Pressure
LPG	Liquefied Petroleum Gas
LTS	Low Temperature Shift
MEA	Monoethanolamine
MID	Medium-pressure
NGOs	Non-Governmental Organisations
NMP	N-methyl-2-pyrrolidone
NP	Nitrophosphate
NPK	Compound fertiliser containing nitrogen, phosphate and potash
PAPR	Partially Acidulated Phosphate Rock
PSA	Pressure Swing Adsorption
PUR	Polyurethane
S/C	Steam/Carbon ratio
SAN	Styrene Acrylo Nitril
SCR	Selective Catalytic Reduction
SNCR	Selective Non Catalytic Reduction
SSP	Single Super Phosphate

STEL	Short Time Exposure Limit
TEA	Triethanolamine
TLV	Threshold Limit Values
TWA	Time Weighted Average
TWG	Technical Working Group
UAN	Urea Ammonia Nitrate
UBA	Umweltbundesamt (German Federal Agency for the Environment)
VOC	Volatile Organic Compounds
VROM	Dutch Ministry of Housing, Spatial Planning and Environment
ΔHo	Standard enthalpy of formation (at 25 °C)
ISBL	In Site Battery Limits

CHEMICAL SYMBOLS

As	Arsenic
C	Carbon
Cd	Cadmium
CFC	Chloro-fluorocarbons
CH_X	Hydrocarbons
CH_3OH	Methanol
CH_4	Methane
CO	Carbon monoxide
Co	Cobalt
CO_2	Carbon dioxide
COS	Carbonyl sulphide
Cr	Chromium
CrO	Chromium oxide
CuO	Copper oxide
Fe	Iron
FeO	Iron oxide
H_2	Hydrogen
H_2O	Water
H_2S	Hydrogen sulphide
N_2	Nitrogen
NH_3	Ammonia
NH_4^+	Ammonium
Ni	Nickel
NO	Nitrogen monoxide
NO_2	Nitrogen dioxide
NO_3^-	Nitrate
NO_X	Nitrogen oxides
O_2	Oxygen
Pb	Lead
SO_2	Sulphur dioxide
SOx	Sulphur oxides
ZnO	Zinc oxide
ZnS	Zinc sulphide

UNITS

°C	Degree Celsius
A	Ampére
bar	Unit of pressure (appr. equivalent to one atmosphere)
GJ	Giga Joule (10 9 joule)
h	Hour
kg	Kilogram
kJ	Kilo Joule (1000 joule)
kPa	Kilo Pascal (1 x 10^{-2} bar)
kWh	Kilowatt-hour (3.6 x 10^{6} joule electricity)
m	Metre
m^3	Cubic metre
mg	Milligram
MJ	Mega Joule (10^{6} joule)
MWh	Megawatt-hour (3.6 x 10^{9} joule electricity)
MWth	Megawatt thermal
Nm 3	Cubic metre at standard conditions (gas volume), (0 °C, 101.3 kPa)
ppmv	Parts per million by volume
t	Metric tonne (10^{3} kilogram)
tonne	Metric tonne
tpd or mtpd	Metric tonne per day
$	Dollar
DFL	Dutch florins or guilders
€	EURO

6 ANNEXES

6.1 Annex 1

IRMA and Grande Paroisse develop a new catalytic process for combined treatment of nitrous oxide (N_2O) and nitrogen oxides (NO and NO_2) for nitric acid workshops

6.1.1 Reminder of the general context concerning the combating of global warming

Nitrous oxide (N_2O) is a powerful greenhouse effect gas with a global warming power (GWP) over 100 years, which is 310 times higher than an equivalent mass of carbon dioxide (CO_2).

For this reason, the Kyoto protocol has drawn up within the framework of the Rio agreement (1992) at the third conference of the parties in 1997 indicating that it is a matter of priority to reduce emissions of this compound in the same way as it to reduce emissions of CO_2, CH_4, HFC, PFC and SF_6.

This protocol for the first time also defined a global objective of a 5.2 % reduction compared to 1990 for the 2008 - 2012 period concerning the countries in Appendix 1, and the sharing of efforts between these countries.

The European Union, for its part, has committed itself to an 8 % reduction over the same reference periods.

It was also decided in the course of a meeting of European Union environment ministers on the 17th of June 1998 that France will have to return on average for the 2008 - 2010 period to its level of emissions in 1990.

6.1.1.1 The global stakes for France

For the six gases cited by the Kyoto protocol, France emitted 131 Mt of carbon equivalent (MtCe) in 1990.

The measures already adopted bring the 2010 projections to a figure of 144 MtCe.

With the implementation of these steps already taken before the adoption of the Kyoto protocol, a further reduction of 13 MtCe will need to be achieved to meet the national objective resulting from the Kyoto protocol.

N_2O emissions from industrial sources

Three main industrial sources of N_2O have been identified.
These are workshops producing adipic acid, glyoxal and glyoxylic acid, and nitric acid.

A summary of the emissions from these various sources, together with their relative shares with respect to greenhouse effect gases as a whole, is presented in table 1 for a 2010 reference scenario.

This 2010 summary obviously takes into account the reductions already made or in progress for categories 2 and 3 presented in the table below.

Nitric acid workshops therefore constitute a considerable factor at national level, accounting from just a few sources for approximately 1.2 % of the national emissions of carbon equivalent in the 2010 reference scenario.

Categories		Annual emissions of N_2O (in tonnes)		Share of current emissions of N_2O in industrial emissions of CO_2 equivalent for 2010 (France – reference scenario – 23.18 % of the total of 144 MtCe)
		Gross before treatment	After possible treatment	
1	Nitric acid workshops	21000	21000 (no treatment)	5.3 %
2	Glyoxal and glyoxylic acid workshops	8 to 10000	400 to 500	0.023 to 0.029 %
3	Adipic acid workshops	58000 (1)	8000 (1)	2.01 %
(1): 1997 project base				Share of current emissions of N_2O in total emissions of CO_2 equivalent for 2010 (France – reference scenario – 144 MtCe)
All of these sources		88000	29450	1.72 %
Nitric acid workshops		21000	21000	1.2 %

Table 6.1: Main French sources of nitrous oxide and contribution to national emmissions of greenhouse effect gases

Today, N_2O emissions from these main sources represent nearly 29450 tonne and increases in the capacity of certain units seem to be in the offing.

It should also be noted that in addition to these main sources there are also a number of sources of emission, which are still not taken into account sufficiently.
These include fluidised bed combustion or low temperature combustion, processes using precious metal based catalysts or nitric acid, etc.

6.2 The problem posed by nitric acid workshops

Nitric acid workshops do account for notable sources of nitrous oxide, and therefore more generally of greenhouse effect gases. The levels of emission depend on the technology used. However, an emission level of 6 to 8 kg of N_2O per tonne of 100 % nitric acid is representative of the European situation. The emissions for all French workshops of around twenty on this basis are estimated at approximately 21000 t/year. Given a coefficient of 310 this corresponds to 6510000 tonne of CO_2 equivalent, or 1.35 % of all French greenhouse effect gases (1990 base). This is respectively 1.2 % and 5.3 % of the French emissions and of the industrial emissions in the 2010 projections, evaluated at 144 MtCe on the basis of the measures already adopted.

6.2.1 Nitric acid manufacturing principle

Nitric synthesis comprises three main phases:

Oxidation of ammonia

An air-ammonia mixture passes through platinum grids arranged in a burner.
On contact with the platinum, the gaseous ammonia combines with the oxygen in the air to give mainly nitrogen monoxide.
However, a secondary reaction also leads to the formation of nitrous oxide.
The oxidation of the ammonia is exothermic, which raises the gases to approximately 850 °C.

Transformation of nitrogen oxide

In the course of cooling in various exchangers, the nitrogen monoxide turns into nitrogen dioxide.
Nitrous oxide, however, which is stable and of low solubility, passes through the installations.

Absorption of nitrogen oxides

The compressed gaseous flow is driven back into an absorption column.
On contact with water, the nitrogen dioxide is converted into nitric acid.
However, the reaction: $3 NO_2 + H_2O \prod 2 HNO_3 + NO$ leads to the forming of NO which needs to be re-oxidised for a new conversion into nitric acid.
The exhaustion of the gases cannot be total, which is what leads to NO_X emissions from nitric acid workshops, in addition to nitrous oxide emissions.

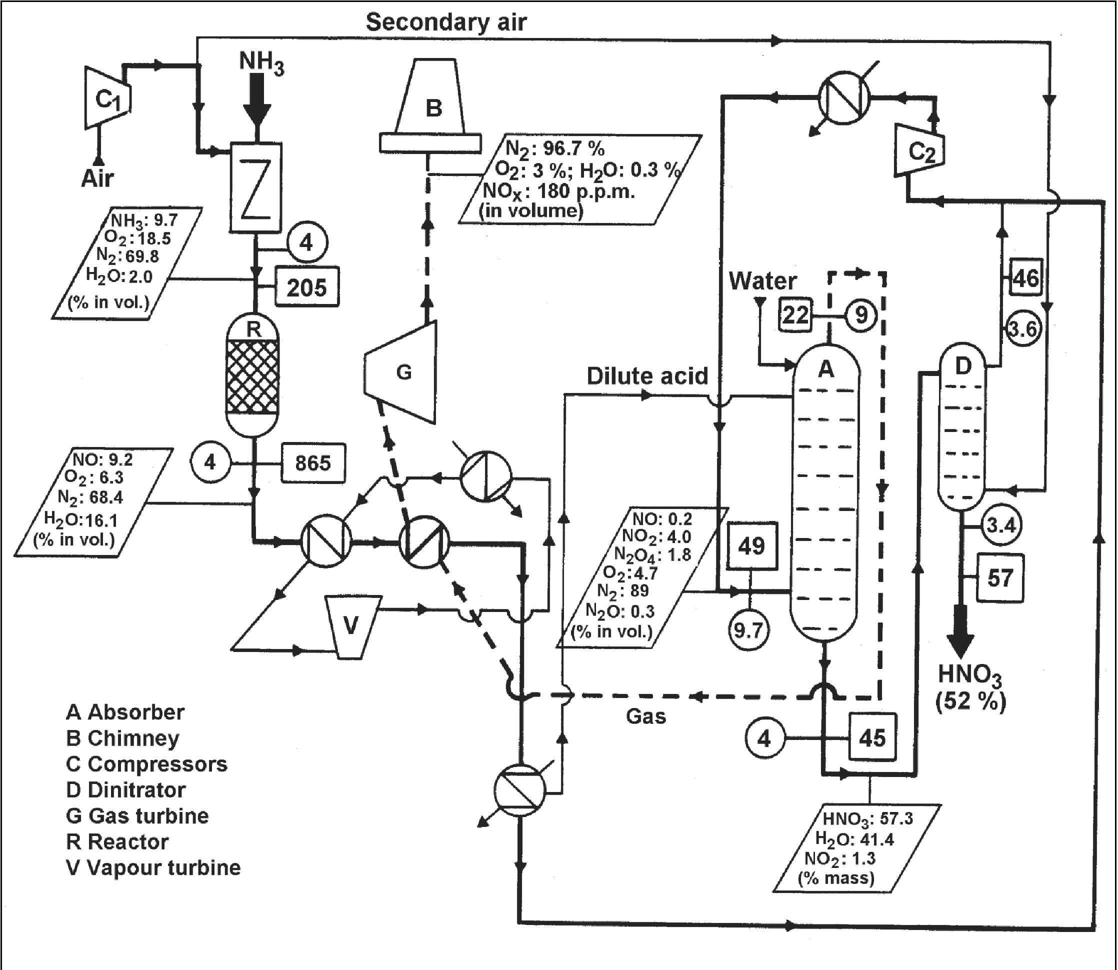


Figure 6.1: Principle of a twin-pressure nitric acid workshop

6.2.2 Possibilities for reducing the nitrous oxide emissions of nitric acid workshops

5 methods can be envisaged

Homogeneous decomposition

This solution requires the use of an ammonia oxidation reactor of sufficient dimensions so that the process gas remains at high temperature over a period enabling spontaneous decomposition of the N_2O into N_2 to be obtained.

This method was patented by the Norwegian group HYDRO and was installed in the most recent workshop built in Porsgrunn (Norway) in 1991.

This method can be applied to new units through an increase in investment deemed acceptable, which does not mean that it will be negligible. For an existing unit, its cost (approximately 20 MFRF) is judged to be too high by the operators.

The efficiency of this method can also present certain limitations.

Modification of platinum grids

Research work is in progress to modify the composition of the grids and avoid the formation of N_2O at source. The potentials for reduction of emissions by this method nevertheless appear limited and consequences for the efficiency of the workshop cannot be totally ruled out.

Catalytic decomposition in the process gas

This solution consists in implanting behind the platinum grids a catalyst, which carries out the decomposition of the N_2O at approximately 850 °C.

This process can be envisaged for existing workshops at an investment cost considered to be moderate, provided that a catalyst with a reasonable service life and cost is available. This method can lead to a loss of efficiency concerning the oxidation of NH_3 to NO.

The Norwegian company HYDRO has started work based on the development of a catalyst of this type capable of reducing N_2O emissions by approximately 90 %, with an acceptable loss of efficiency on the NO.

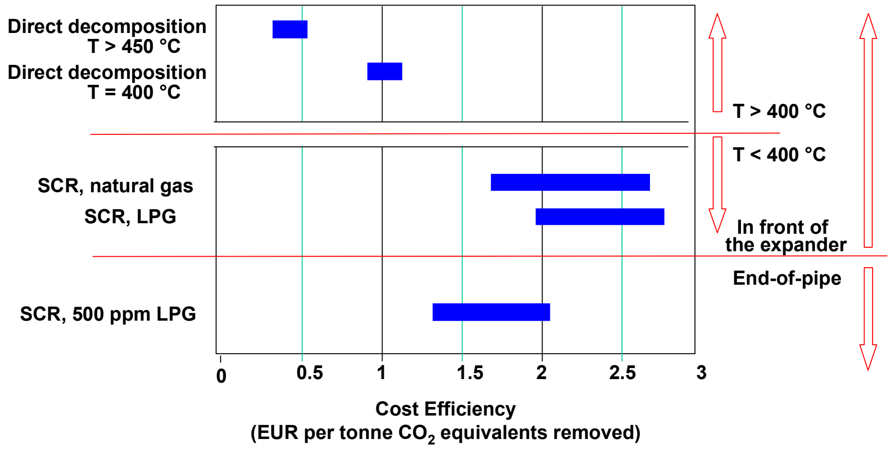


Figure 6.2: Comparison of costs of different options for treatment of N_2O in a nitric acid workshop

BASF has been testing a catalyst operating under these conditions for approximately two years on three of its units.

It should be noted that this solution could be adapted to all nitric acid workshops.

Catalytic decomposition in the tail gas

This method is used after the absorption of the nitric acid. It requires a temperature of approximately 400 °C.

The Hydro group, which has also carried out research work along these lines in partnership with Dutch laboratories, does not seem however to give priority to it in spite of its own rather effective formulations (approximately 70 % reduction of N_2O emissions).

The problem posed by this method lies in the operating temperature of the catalyst.

In direct decomposition, the required temperature of 400 °C is not available on all the nitric acid workshops before the expansion turbine xx. Only the most recent workshops lend themselves to an integration of the catalytic process without heating of the gases.

The addition of heating of the gases (gas/gas exchanger) reduces the benefits of the process.
A reduction of the operating temperature of the catalyst can be obtained by adding a reducing agent (methane/GPL), which nevertheless also has an effect on the operating costs and can lead to the formation of other pollutants depending on the type of reducing agent used.

The economic evaluations made by ECN (Netherlands) give the following treatment costs according to the configurations:

These costs are greater in particular for selective catalytic reduction SCR) with a hydrocarbon than those envisaged for decomposition at high temperature.
It should be noted however that certain catalysts, in particular if the reducing agent is ammonia, have the faculty of carrying out combined treatment of NO_X (nearly all) and N_2O (approximately 80 %).

The taking into account of simultaneous processing of NO_X in the economic evaluation is therefore likely to modify these results quite markedly, although they depend on the type of workshop.

This option must indeed therefore be compared with a treatment combining a catalytic decomposition of the N_2O at high temperature and a treatment of the nitrogen oxides (by SCR with ammonia, for example) at low temperature.

Non-selective reduction in the tail gas

This solution, which combines treatment of the NO_X and the N_2O, requires a considerable temperature and the consumption of all the oxygen present. It therefore requires a quite large consumption of make-up fuel, which limits its benefits with respect to the greenhouse effect problem. This method presents some long-established applications in the United States, the aim of which was to reduce emissions of NO and NO_2.

Possible levels of elimination of N_2O in nitric acid workshop:

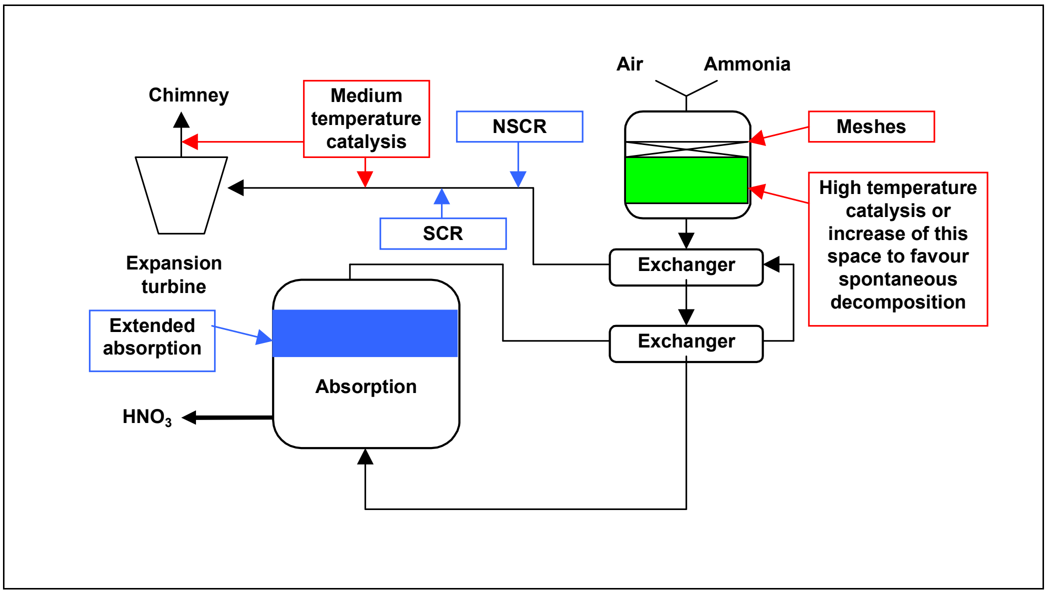


Figure 6.3: Possible levels of elimination of N_2O in nitric acid worshop

6.2.3 French regulation arrangements

New or modified nitric acid workshops are subject to the following stipulations of the ministerial decree of the 2nd of February 1998:

	Limit value
NO_X (in HNO_3)	1.3 kg/tonne of 100 % acid produced
N_2O	7 kg/tonne of 100 % acid produced

Table 6.2: French regulation requirements

6.3 IRMA/Grande Paroisse pilot operation

Following promising results obtained at laboratory level, Grande Paroisse decided to undertake in 1998 a pilot operation on the effluents of a nitric acid workshop concerning selective catalytic reduction (SCR) of nitrous oxide (N_2O) by ammonia (NH_3) on iron-exchanged zeolite type catalysts at medium temperatures (MT).

This operation with a provisional budget of FRF 4 M was 40 % financed by ADEME, within the framework of an agreement linking ADEME, Elf Aquitaine (now Total Fina Elf) which also provided 28 % of the funding for the project, the IRMA (Institut Régional des Matériaux Avancés – a supplier of certain catalytic formulations) and Grande Paroisse.

The catalytic tests were carried out on six loads (4 loads of ferrierite type iron zeolite prepared by IRMA and two loads of Beta type iron zeolite prepared by Grande Paroisse). The DeN_2O pilot was installed on a bypass from a nitric acid workshop in Grand Quevilly (Grande Paroisse).

6.3.1 Characteristics of the Grand Quevilly nitric acid workshop

The technical characteristics of the nitric acid workshop located in Grand Quevilly are presented in Table 6.3. The DeN_2O pilot, which enabled the MT study to be carried out, was installed on a bypass from this workshop. This workshop is equipped with SCR type NO_X treatment with ammonia. The flow of gas to be treated is 130000 Nm^3/h, for a volumic velocity per hour of use of the catalyst of 20000/h.

Capacity (t/day of acid 100 %)	1000
Acid concentration (%)	62
Oxidation pressure (bar abs.)	4.9
Grids % Pt/% Rh	95/5
NO_X content (kg of HNO_3/t of 100 % HNO_3)	0.9
N_2O content (kg/t of 100 % HNO_3)	9.5
Type of $DeNO_X$/commissioning	SCR/89/91
$DeNO_X$ catalyst	zeolite-based GP
$DeNO_X$ temperature (°C)	230

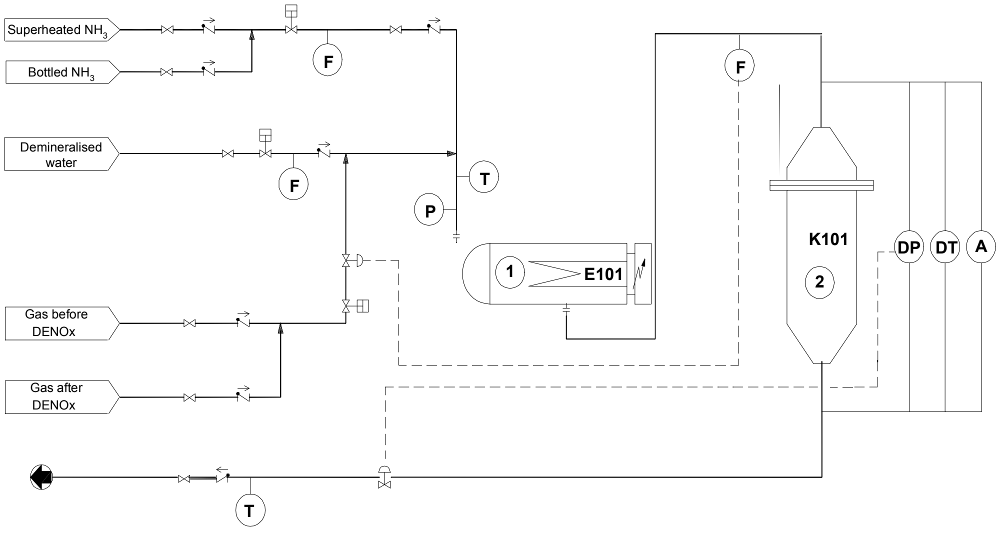
Table 6.3: Main technical characteristics of the Grand Quevilly nitric acid workshop

The purpose of the DeN_2O pilot reactor was to test N_2O destruction catalysts, which can be active at temperatures between 200 and 550 °C.

The pilot reactor was supplied by effluents (NO_X + N_2O) from the nitric acid workshop located in Grand Quevilly.

The pressure of the pilot reactor could be adjusted between 3.8 and 2 bar abs. The temperature of the effluent at the entry of the reactor could reach a maximum of 550 °C. An injection of ammonia made it possible to obtain NH_3 contents in the neighbourhood of 2000 ppm. The volume of catalysts to be tested could vary between 15 and 30 litres and the flow could be adjusted between 180 and 500 Nm^3/h to cover a range of volumic velocity per hour (VVH) of 10000 to 40000/h.

A diagram of the pilot is presented in Figure 6.4



(F): Flow measurement **(T): Temperature measurement** **(1): Gas heater**
(P): Pressure measurement **(A): Analyser** **(2): Catalytic reactor**

Figure 6.4: Diagram of the DeN_2O pilot installed on a bypass from the Grand Quevilly plant

6.3.2 Analytical means

The performances of the catalysts were verified by an on-line Fourier transform infra-red (FTIR) analysis of the NO, NO_2, N_2O and NH_3 contents of the effluents before and after the catalytic reactor. The composition of the gases passing through the catalytic reactor was validated at certain points by calibration of the FTIR analyser with standard gases.

The measurement ranges considered were the following:

- NO: 0 to 2000 ppm
- NO_2: 0 to 2000 ppm
- N_2O: 0 to 4000 ppm
- NH_3: 0 to 100 ppm

For the majority of the measurements made after the catalytic reactor, the NO_X and N_2O contents were measured at the ammonia leak.

6.3.3 Nature of catalysts tested

The work, concerning SCR of N_2O by NH_3 at medium temperatures, was carried out on zeolite-based catalysts. Two types of zeolitic structures (ferrierite and beta) exchanged with iron were considered. The active sites of the reaction are the iron atoms.

6.3.3.1 Ferrierite type zeolite

The ferrierite (FER) type zeolitic structure has the general formula $Na_xK_yAl_6Si_{30}O_{72}$, $8H_2O$ (x+y=6), or Na_xK_y-FER. It is comparable to the mordenite (MOR) zeolite in its network of channels (4.3 * 5.5 Å and 3.4 * 4.8 Å), but has elementary units with 10 oxygens (Figure 6.5).

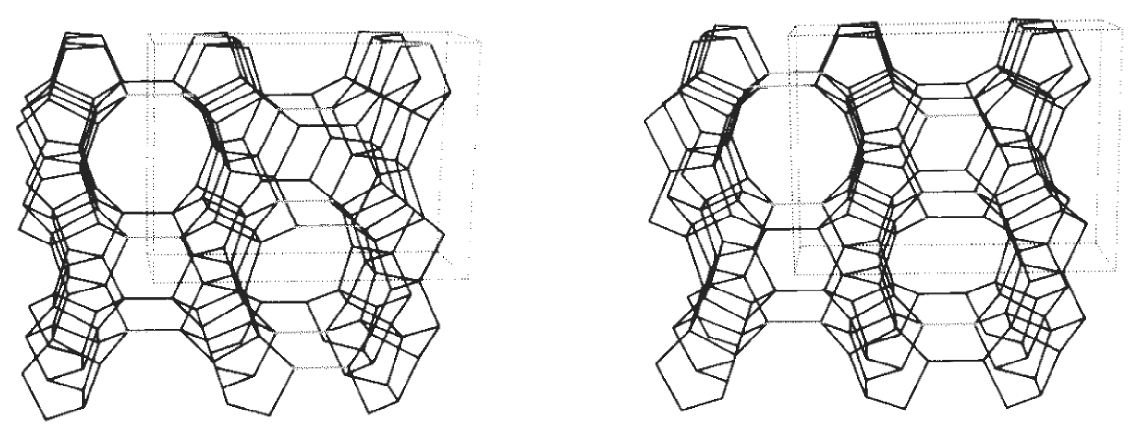


Figure 6.5: Representation of the structure of the zeolite Na_xK_y-FER

To obtain the desired catalysts, the sodium (Na^+) and potassium (K^+) cations were replaced by Iron (Fe^{3+}) cations.

The simplified production stages of Fe-FER catalysts are as follows:

- on-line extrusion ferrierite zeolite (an average diameter of 3 or 1.8 mm is obtained), and calcination at 500 °C.
- exchange of the extruded elements in aqueous phase with an ammonium salt to obtain a zeolite free of the sodium cations and of a majority of the potassium cations
- exchange of the zeolite $(NH_4)_6Al_6Si_{30}O_{72}$ in aqueous phase with a solution of iron sulphate ($FeSO_4$, $7H_2O$), drying at 150 °C.

The drying stage fixes and positions the load compensating cations (Fe^{3+}) in the structure of the zeolite. The active sites of this catalyst are the iron atoms, or more precisely the Fe^{2+}/Fe^{3+} redox pair.

Four catalytic loads of Fe-FER, prepared by IRMA and referenced as being batches A 7033, A 7465, A 7615 and A 7976 were tested in selective catalytic reduction of N_2O by NH_3.

6.3.3.2 Beta type zeolite

The beta type zeolitic structure (BEA) has the general formula $Na_zAl_7Si_{57}O_{128}$, or Na-BEA. Its channel system (5.5 * 5.5 Å and 7.6 * 6.4 Å), Figure 6.6, is comparable to that of the ferrierite zeolite (FER).

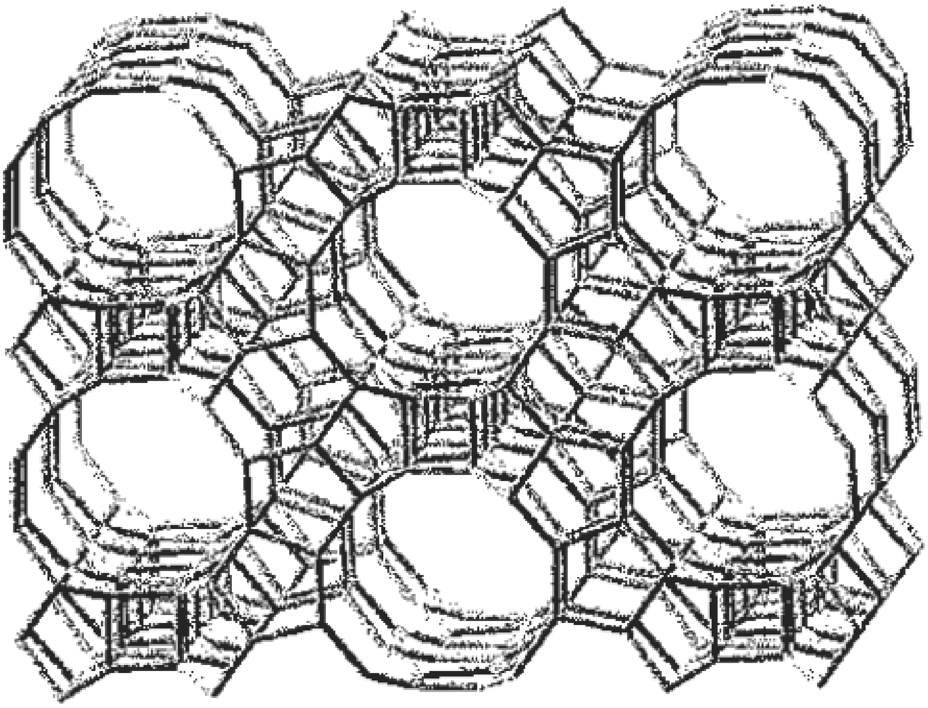


Figure 6.6: Representation of the structure of the zeolite Na-BEA

As for the Fe-FER catalyst, the sodium ions were exchanged with iron. The simplified production stages of Fe-BEA catalysts are as follows:

- exchange in aqueous phase of Na-BEA powder with iron nitrate to obtain the Fe-BEA structure
- addition of 5 % binder
- granulation (steam fertilising type) of the Fe-BEA gel to obtain grains of approximately 3.3 mm.

Two catalytic loads of Fe-BEA, manufactured by Grande Paroisse, referenced as being batches GP 1 and GP 2, were tested in selective catalytic reduction of N_2O by NH_3.

Batch	**A 7033**	**A 7465**	**A 7615**	**A 7976**	**GP1**	**GP2**
Type	Fe-FER	Fe-FER	Fe-FER	Fe-FER	Fe-BEA	Fe-BEA
Shape	Extruded 3 mm	Extruded 3 mm	Extruded 1.8 mm	Extruded 1.8 mm	Granulated 3.3 mm	Granulated 3.3 mm
Density	-	0.51	0.46	0.52	-	-

Table 6.4: Recapitulative data concerning the characteristics of the catalytic loads tested

6.3.4 Conducting of tests and experimental procedure

The six catalysts prepared (four Fe-FERs and two Fe-BEAs) were tested in decomposition of N_2O and in SCR of N_2O by NH_3. Certain operating parameters (temperature, volumic velocity per hour, pressure and variation of NO content) were the subject of more extensive studies. In addition, the evaluation of the catalytic loads after several months' ageing was studied.

6.3.4.1 Direct decomposition of N_2O

The N_2O decomposition on the Fe-FER and Fe-BEA catalysts is a first step towards understanding of the reactions brought into play. This reaction results in equation 1.

$$2N_2O \rightarrow 2N_2 + O_2 \qquad \text{eqn. 1}$$

This reaction brings into play the active sites (*) as described in equations 2 to 4.

$$N_2O + * \rightarrow N_2O^* \qquad \text{eqn. 2}$$
$$N_2O^* \rightarrow N_2 + O^* \qquad \text{eqn. 3}$$
$$2O^* \rightarrow O_2 + 2^* \qquad \text{eqn. 4}$$

These reactions take place easily at high temperatures on different types of catalysts. However, at the lowest temperatures (<500 °C), the N_2O decomposition reaction is limited by the desorption of the excessively adsorbed oxygen (eqn. 4). The challenge then consists in finding a catalyst which can lower the desorption energy of the oxygen. Compared to other zeolites (MFI, FAU, etc.) exchanged by metals (Cu^{2+}, Ni^{2+}, Zn^{2+}, etc.), the Fe-FER and Fe-BEA catalysts would allow the strong adsorption of the oxygen to be counteracted.

Figure 6.7 shows the N_2O conversion profiles according to temperature for the two most efficient batches of catalysts (A7976 and GP 2). A VVH of 20000/h is characteristic of the operation of the existing $DeNO_X$ reactors for selective catalytic reduction of NO_X by NH_3 (SCR).

The N_2O catalytic conversion activity of Fe-BEA is lower than that obtained with the Fe-FER load: 50 and 70 % conversion respectively at 450 °C. The other catalytic loads of Fe-FER and Fe-BEA have catalytic activities comparable to these two loads.

In direct decomposition of N_2O, a 70 % conversion of N_2O can therefore be obtained at 450 °C.

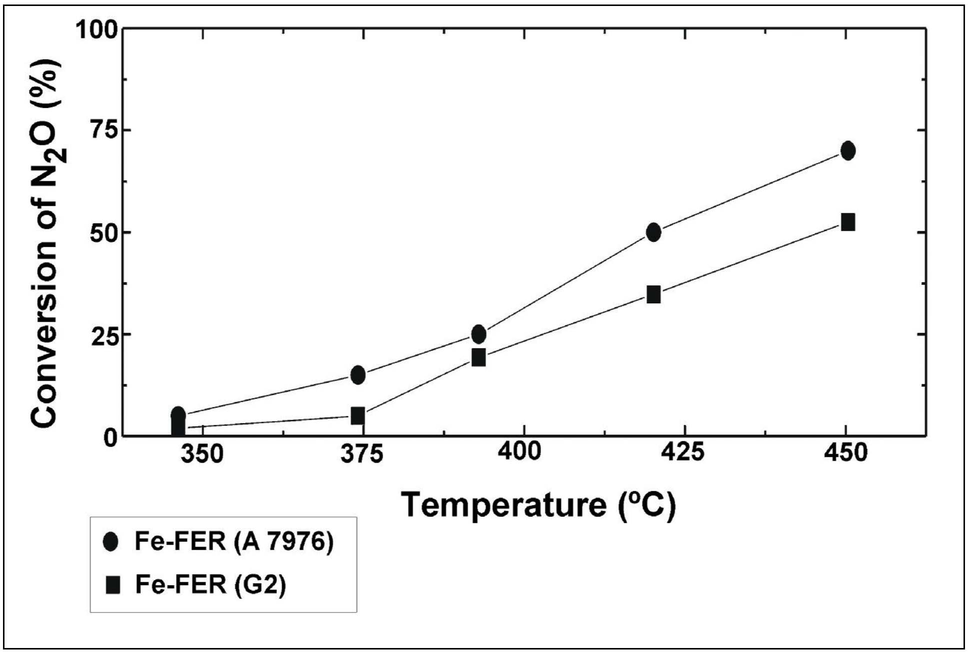


Figure 6.7: Decomposition of N_2O on Fe-FER

(A 7976, ●) and Fe-BEA(G2, ■) according to temperature. $N_2O \approx 1700$ ppm, 700 ppm, O_2 =2.5 %, $H_2O \approx 1$ %, VVH =2000/h and 3.2 abs.

6.3.4.2 Selective catalytic reduction of N_2O by NH_3

In a second stage, the addition of ammonia (NH_3) to the reactional medium (NO_X, N_2O, O_2 and H_2O) was envisaged. The reaction between NH_3 and N_2O is called selective catalytic reduction (SCR) because there is no formation of sub-products (equation 5).

$$4N_2O + 4NH_3 + O_2 \rightarrow 6N_2 + 6H_2O \text{ eqn.} \qquad 5 \text{ (supposed reaction)}$$

Figure 6.8 shows the curves for conversion of N_2O and NO_X at 418 °C according to the ammonia content in the medium.

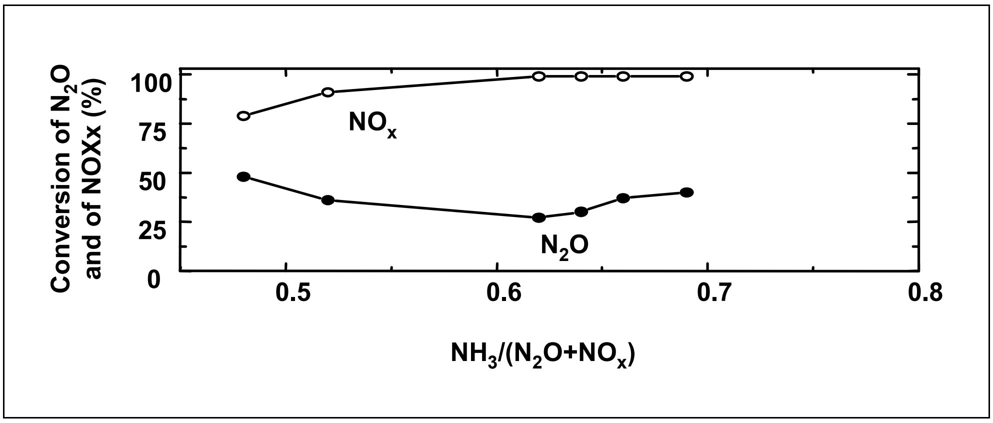


Figure 6.8: SCR of N_2O by NH_3 on Fe-FER (batch A 7033) at 418 °C

Conversion of N_2O in solid symbols and conversion of NO in unfilled symbols.
VVH ≈ 20000/h, Pressure = 3.2 bar abs., $N_2O \approx 1700$ ppm, NO ≈ 700 ppm, $NO_2 \approx 700$ ppm, $O_2 = 2.5$ % and $H_2O \approx 1$ %.

The presence of NH_3 allows a reduction of the NO_X as soon as it is added to the medium. The shapes of the NO_X and N_2O reduction curves have already been explained in the literature for an Fe-MOR type catalyst (mordenite exchanged with iron)

Different zones are defined:

$NH_3/(N_2O+ NO_X) <0.5$: improved decomposition of N_2O in the presence of NO, but decreasing because in competition with SCR of NO_X by NH_3 on the same active sites as SCR of N_2O by NH_3, and by lowering of the NO_X content consumed in its SCR
$NH_3/(N_2O+ NO_X) >0.5$: increase in the conversion of N_2O accompanied by SCR of NO_X by stable NH_3

A ratio of 0.5 probably corresponds to the consumption of NH_3 necessary to the reduction of NO_X. The stoichiometry $NH_3/(NO_X +N_2O) = 1$ is not attained for this catalyst at this temperature. However, for the most active catalysts (A 7976 and GP 2), the stoichiometry of the reaction is quite close to the value 1.

Figure 6.9 and Figure 6.10 give all the results obtained from conversion of N_2O in the presence of NH_3 at the different temperatures for the Fe-FER and Fe-BEA catalysts. Each point of the curves was noted before the ammonia leak.

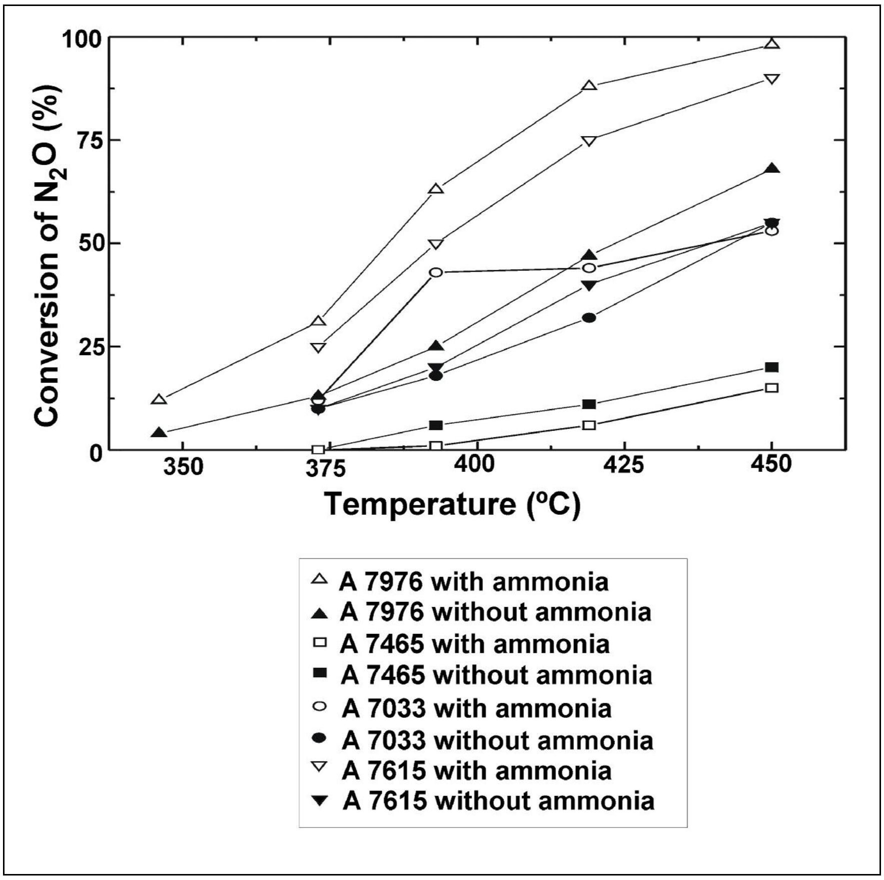


Figure 6.9: SCR of N_2O by NH_3 on Fe-FER in presence or absence of ammonia

Conversion of N_2O in of ammonia in solid symbols and conversion of N_2O in presence of ammonia (before the leak) in unfilled symbols. VVH = 20000/h, Pressure = 3.2 bar abs, $N_2O \approx 1700$ ppm, $NO \approx 700$ ppm, $NO_2 \approx 700$ ppm, $O_2 = 2.5$ % and $H_2O \approx 1$ %.

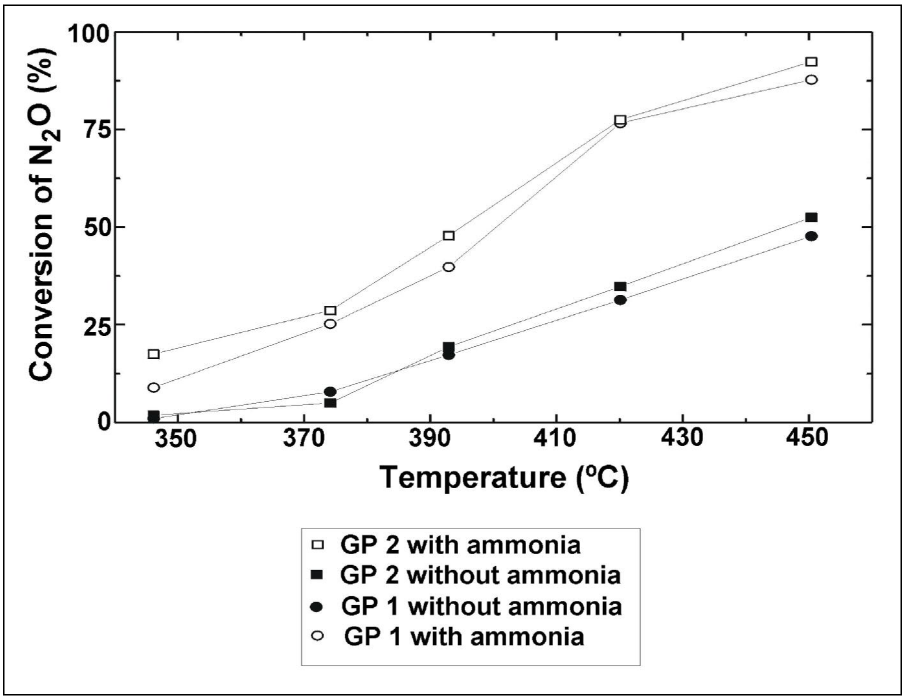


Figure 6.10: SCR of N_2O by NH_3 on Fe-BEA in presence or absence of ammonia

Conversion of N_2O in the absence of ammonia of ammonia in solid symbols and conversion of N_2O in presence of ammonia (before the leak) in unfilled symbols. VVH = 20000/h, Pressure = 3.2 bars abs, $N_2O \approx 1700$ ppm, NO ≈ 700 ppm, $NO_2 \approx 700$ ppm, $O_2 = 2.5$ % and $H_2O \approx 1$ %.

The conversion of NO_X is almost total (approximately 99 %) for all the temperatures and VVH studied. This reaction is very exothermic, which means that the temperature is maintained in the whole of the reactor: the difference in temperature between the exit and entry of the reactor is low, approximately ± 5 °C.

Compared to the curves for conversion of N_2O by decomposition, we observe a notable conversion gain after addition of the NH_3 reducing agent for all the catalytic loads, except for batch A 7465. This difference in behaviour may possibly be linked to the volumic velocity per hour which was selected for these tests. In addition, in view of all the results obtained, Grande Paroisse thinks that for batch A 7033 the measured conversions of N_2O at 425 and 450 °C are not correct. The deviation probably results from a compacting of the catalytic load which led to preferential paths in the bed of the catalyst (it was the most brittle catalytic load).

In SCR of N_2O by NH_3, a conversion of 70 % of N_2O can be obtained at 390 °C with the Fe-FER catalytic load. It reaches approximately 90 % at 425 °C. The conversion of the NO_X, moreover, is almost total.

6.3.4.3 Influence of NO content and temperature

To broaden the field of study, Grande Paroisse considered higher temperatures and a gas flow comprising less NO_X. These new conditions are related to those encountered in certain workshops. A temperature of 515 °C was envisaged for a gas flow consisting of 1300 ppm of N_2O and 200 ppm of NO_X. These catalytic conditions can be simulated on the DeN_2O pilot by taking into account the exit gas flow from the $DeNO_X$ reactor of the nitric acid workshop.

Table 6.5 summarises the results obtained in decomposition of N_2O and in SCR of N_2O by NH_3 with the catalytic load A 7615.

Conditions: Pressure = 3.0 bar abs, $N_2O \approx 1700$ ppm, NO ≈ $NO_2 \approx 50$ ppm, $O_2 = 2.5$ % and $H_2O \approx 1$ %.

		N_2O = 1700 ppm NO_X = 2500 ppm	N_2O = 1700 ppm NOx = 100 ppm
Decomposition	N_2O	80 %	60 %
	NO_x	0 %	0 %
SCR	N_2O	93 %	96 %
	NO_x	80 %	40 %

Table 6.5: Decomposition of nitrous oxide and SCR of nitrous oxide by ammonia for different NOx contents at 515 °C

In decomposition of N_2O, the presence of a small quantity of NO_x in the gases to be treated leads to a lowering of the catalytic activity (60 % conversion of N_2O at 100 ppm into NOx instead of 80 % at 2500 ppm). This difference may be the consequence of a lower decomposition of N_2O by coupling with NO (equation 6).

$$N_2O + NO \rightarrow 2N_2 + NO_2 \qquad \text{eqn. 6}$$

With the introduction of the reducing agent (ammonia) in the gases, a 96 % N_2O conversion is finally obtained. However, the conversion of the NO_X at 515 °C is not complete with ammonia; approximately 60 ppm of NO_X appears. It is probable that at this temperature the ammonia can be re-oxidised into NO.

Too high a reaction temperature leads to the oxidation of the ammonia, and the absence of NO in the flow to be treated is unfavourable at the same temperature to SCR of N_2O by NH_3.

6.3.4.4 Influence of volumic velocity per hour (VVH)

Figure 6.11 and Figure 6.12 group together all the results obtained from conversion of N_2O in the presence of NH_3 at the different temperatures and volumic velocities per hour envisaged for two batches of catalysts (A 7033 and A 7615).

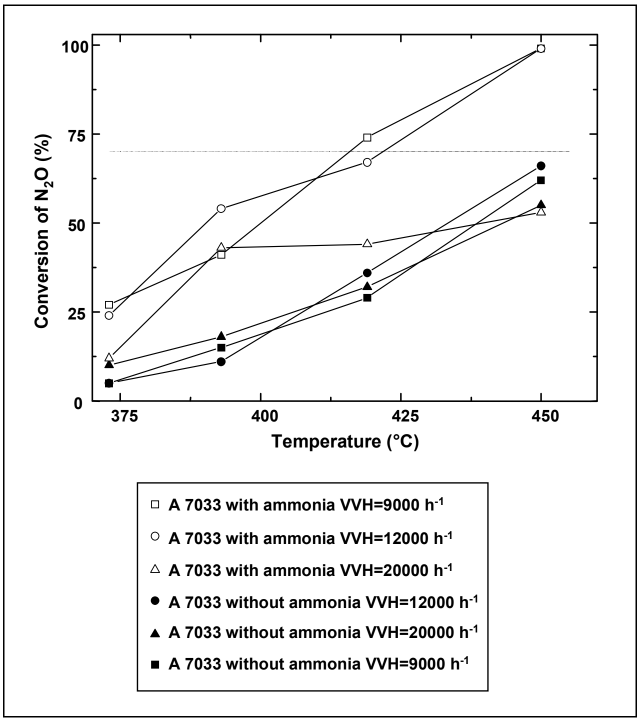


Figure 6.11: Influence of volumetric velocity per hour (VVH) on SCR of N_2O by NH_3

On Fe-FER in presence or absence of ammonia for batch A 7033.
Conversion of N_2O in the absence of ammonia in solid symbols and conversion of N_2O in absence of ammonia (before the leak) in unfilled symbols.
Pressure = 3.2 bars abs, $N_2O \approx 1700$ ppm, $NO \approx 700$ ppm, $NO_2 \approx 700$ ppm, $O_2 = 2.5$ % and $H_2O \approx 1$ %.

For the three VVHs chosen (VVH = flow of gases in m^3/h/volume of catalyst m^3), the conversions of N_2O by decomposition are very close at the different temperatures, see Figure 6.11.

This observation does not comply with expectations. Indeed, we ought to observe, in theory, an increase in the conversion of N_2O inversely proportional to the VVH.
One explanation for this phenomenon could be the diffusion of the reagents (NO_X, N_2O, O_2 and H_2O) through the catalyst in a non-adiabatic reactor. Indeed, the temperature gradient in the reactor, resulting in a calorific loss, is not compensated by the N_2O decomposition reaction which is not very exothermic for the different temperatures studied. This means that the results obtained on the pilot are probably reduced.

As stated previously, the addition of the reducing agent NH_3 allows an increase in conversion to be obtained. Moreover, it should be recalled that for batch A 7033 the measured conversions of N_2O at 425 and 450 °C are not exact. As for the decomposition, we do not note any major differences when the VVH values are varied: it is certain that the non-adiabatic nature of the reactor markedly reduces the conversion gains which could be reached by lowering the volumic velocity per hour. This hypothesis is also confirmed in the case of load A 7615, which is more active Figure 6.12.

In the final analysis, under the conditions of this pilot, a conversion of approximately 70 % is obtained at 420 °C for this catalytic load.

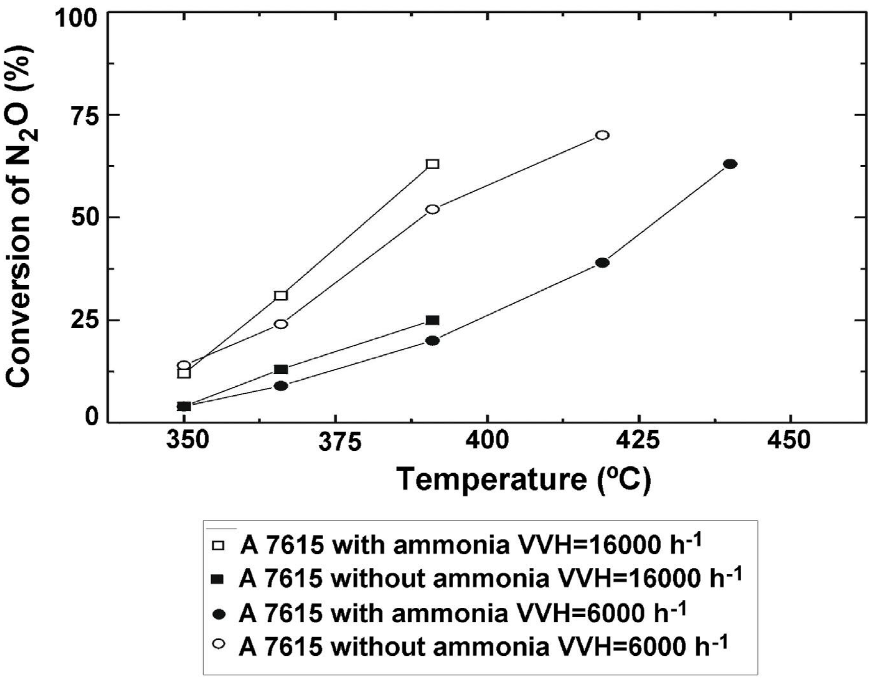


Figure 6.12: Influence of volumic velocity per hour (VVH) on SCR of N_2O by NH_3

On Fe-FER in presence or absence of ammonia for batch A 7615. VVH = 6000/h (λ,μ) and 16000/h (ν,o).

Conversion of N_2O in absence of ammonia in solid symbols and conversion of N_2O in presence of ammonia (before the leak) in unfilled symbols.
Pressure = 3.2 bar abs, $N_2O \approx 1700$ ppm, NO ≈ 700 ppm, $NO_2 \approx 700$ ppm, $O_2 = 2.5$ % and $H_2O \approx 1$ %.

Because of the non-adiabatic natures of the DeN_2O pilot, the variations of the VVH affected the conversion profiles only very slightly.

6.3.4.5 Influence of pressure on decomposition of N_2O and on SCR of N_2O by NH_3

The influence of the pressure was considered on the reactions of decomposition of N_2O and SCR of N_2O by NH_3, figure 13.

In N_2O decomposition, according to equation 1, an increase in the pressure affects only very slightly the conversion of N_2O: only a gain of around 5 % is obtained.

However, in N_2O SCR by NH_3, nearly 20 % is obtained by going from 2 to 4 bar in the range of temperatures studied.

The total pressure increase in the reactor has an influence on the ammonia content in the medium: the content increases with the pressure. If we suppose that the order of reaction of the ammonia (**a**) in equation 7 is positive (non-limiting adsorption of NH_3), a conversion gain proportional to the speed of reaction can be envisaged.

Speed of reaction = k (constant) * $(NH_3)^a$ * $(N_2O)^b$ * $(O_2)^c$ eqn. 7

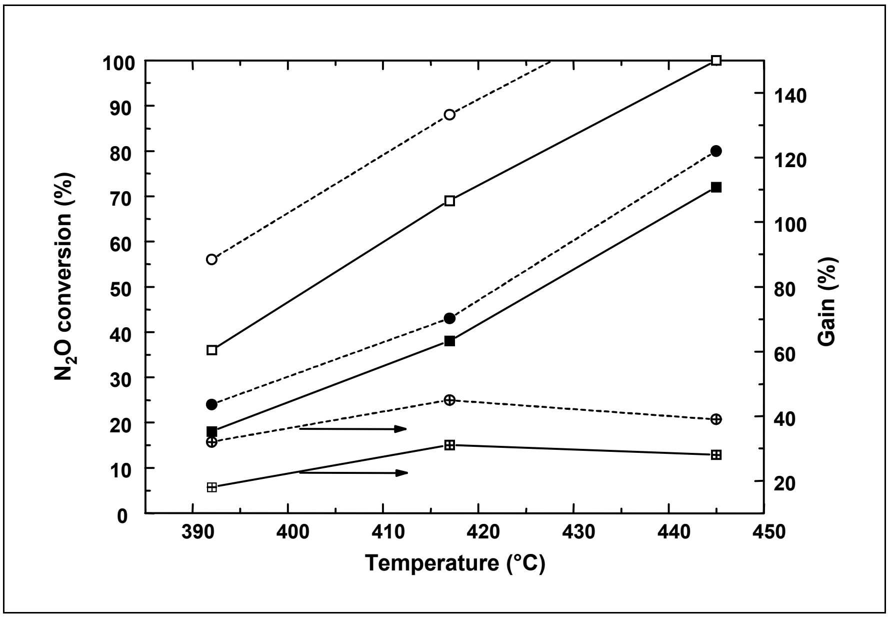


Figure 6.13: Influence of pressure on decomposition of N_2O (solid symbols) and on SCR of N_2O by NH_3 (unfilled symbols) for batch 7033

DeN_2O pilot conditions: Pressure = (λ) 3.8 bar abs. or (ν) 2.1 bar abs., VVH = 12000/h, $N_2O \approx 1700$ ppm, NO ≈ 700 ppm, $NO_2 \approx 700$ ppm, $O_2 = 2.5$ % and $H_2O \approx 1$ %.

An increase in the pressure favours the reduction of N_2O by NH_3.

6.3.5 Behaviour of catalyst in catalytic tests

Several points concerning the behaviour of the catalyst in the catalytic tests need to be verified: the mechanical strength of the extruded elements and the granulates, and the maintaining of the N_2O conversion over time.

6.3.5.1 Mechanical strength

The changes in the mechanical properties of the catalyst during its operation can be observed through measurement of the head loss (ΔP) of the reactor. Table 6.6 indicates the head losses measured under certain operating conditions for all the catalysts.

Batch	VVH (/h)	P (bar abs.)	ΔP (bar)
7033	12000	2.1	0.31
	12000	3.8	0.27
	12000	3.2	
	9000	3.2	0.67
	20000	3.2	0.17
7465	20000	3.2	0.05
7615	20000	3.2	0.08
7976	20000	3.2	0.08
GP1	20000	3.2	0.10
GP2	20000	3.2	0.10

Table 6.6: Influence of VVH and pressure on the head loss of the catalyst under standard catalytic test conditions

The VVH and the pressure have a great influence on the head loss undergone by the catalyst of batch A 7033. The head loss increases with the VVH, but seems to decrease with the pressure. In the most unfavourable case, a value of 0.67 bar of head loss is observed.

These different head losses, which appeared over time, are probably the consequence of a disaggregation and compacting of the catalytic load in the reactor.

For the other catalytic loads, head losses of 0.05 to 0.10 bar were measured, with variations of 0.02 bar for all the tests performed. These head losses are low and denote a good mechanical strength of the catalytic loads, whatever the mode of manufacturing (extruded elements and granulates).

To confirm this result, the catalytic loads of batches A 7033, A 7465 and A 7976 were separated and sieved. It was thus possible to determine the granulometric distributions of the extruded elements on the upper part of the reactor Figure 6.14.

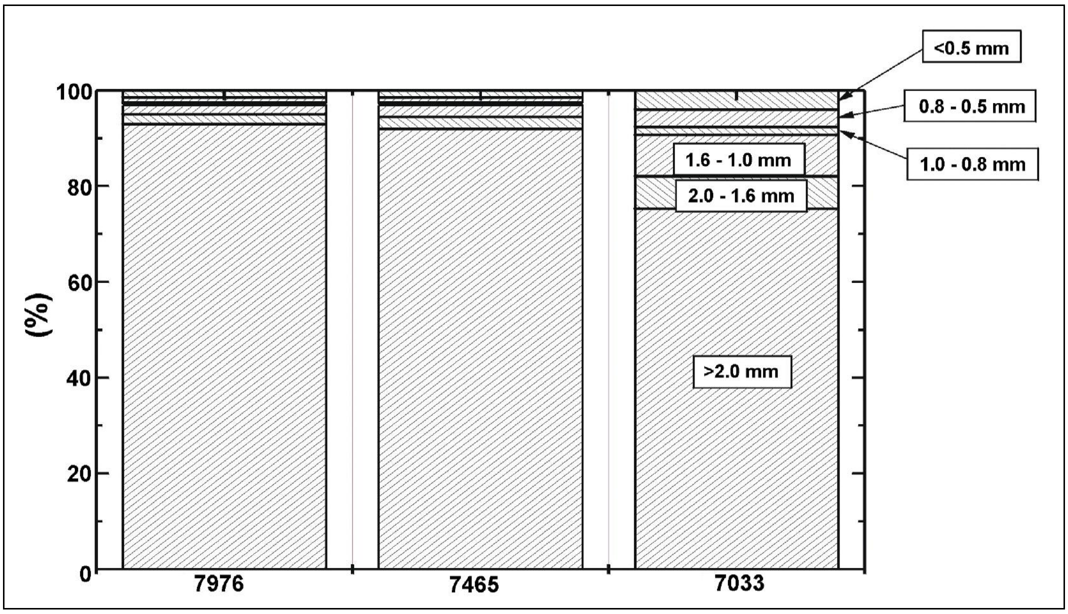


Figure 6.14: Granulometric distribution of extruded elements of different catalytic loads of zeolite

Fe-FER used in the DeN_2O pilot. The granulometric distributions were produced for the following extruded element diameters: >2.0 mm, 2.0 – 1.6 mm, 1.6 – 1.0 mm, 1.0 – 0.8 mm, 0.8 – 0.5 mm and <0.5 mm.

Compared to the first catalytic load (batch A 7033), catalytic load A 7465 presents practically no grains with diameters lower than 2.0 mm: the load did not split. This observation corroborates the low head loss obtained after the various catalytic tests. This observation was confirmed with batches A 7976, GP1 and GP 2.

6.3.5.2 Conservation of catalytic activity

The different catalytic loads of Fe-FER and Fe-BEA were subjected to an accelerated ageing in the selective catalytic reduction of NO_X and N_2O by NH_3.

For batch A 7033, the first stage of accelerated ageing was carried out at 397 °C with 4 % water (line 1 in Table 6.7). After 6 days of testing, a reduction in activity of 16 % (41 % → 25 %) was observed on the conversion of N_2O; the conversion of NO_X was not affected by the conditions of the test.

T = 397 °C		6d	1d	1d	1d	1d
N_2O conversion (%)	41	25	25	31	31	35
T = 425 °C		8d	10d	1d	10d	
N_2O conversion (%)	40	36	24	37	40	

Table 6.7: Ageing test during SCR of nitrous oxide for batch A7033

Conditions: $N_2O \approx 1700$ ppm, $NO_X \approx 1700$ ppm, $O_2 = 2.5$ %, $H_2O = 4$ %, P = 3.5 bar abs. and VVH = 18000/h.

Subsequently, when the test is repeated under normal conditions (1 % water), a resumption of activity appears: 6 % in 2 days then 4 % in 2 days. This resumption of activity probably results from the desorption of the species adsorbed, such as the various forms of nitrates (ammonium, aluminium, iron, etc); the formation of these species is greatly favoured in the presence of water.

Subjected to a second accelerated ageing test at a temperature of 425 °C, the same catalytic load denoted a loss of activity of 4 % after 8 days, and 16 % overall after 18 days. Compared to the test performed at 397 °C, the accelerated ageing is less marked at high temperatures: the formation of strongly adsorbed species is unfavourable.

After stopping of the addition of water (4 % → 1 %), a gain in activity of 13 % was observed after only 1 day, and the initial activity of 40 % conversion of N_2O is obtained. Again after 10 days of operation the adsorbed species desorb easily at 425 °C. In addition, there does not seem to be any modification of the structure of the zeolite and/or formation of iron oxide aggregates which would be prejudicial to good catalytic resistance. If such phenomena occurred, it would not have been possible to obtain the initial activity after an accelerated ageing test, but harsher operating conditions ($T \geq 500$ °C) can lead irreversibly to a loss of activity.

On the other catalytic loads (batch A 7465, A 7615, A 7976, GP1 and GP2), the accelerated ageing was carried out under identical conditions at 450 °C with 4 % water for 1 month, Table 6.7.

Conversion of N_2O (%)	**Initial**	**30d**	**30d**
7465	17	15	18
7615	10	10	10
7976	70	60	67
GP1	41	40	40
GP2	47	45	44

Table 6.8: Ageing tests during SCR of nitrous oxide

Conditions: $N_2O \approx 1700$ ppm, $NO_X \approx 1700$ ppm, $O_2 = 2.5$ %, P = 3.2 bar abs. and VVH = 20000/h.

Batch A 7465 can be taken as an example. At the start of the test, the conversion of N_2O by NH_3 was 17 %. After a month of accelerated ageing, it was still 15 %. Judging from this low conversion deviation, we can assume that there is only a slight deterioration of the catalytic activity of this load.

Returned to the initial conditions and after treating for one month the gaseous effluents loaded with N_2O and NO_X by NH_3, an 18 % conversion was observed: the ageing test did not affect the catalytic activity in a lasting way.

These observations were made on all the catalysts (except for batch 7033).

The conversion of the NO_X by NH_3 was invariably 99 % throughout the duration of these tests.

The Fe-FER and Fe-BEA type catalysts do not therefore appear to lose their activity after an extensive ageing test.

6.3.6 Conclusion of MT tests

In direct decomposition of nitrous oxide (N_2O) under conditions similar to industrial $DeNO_X$ reactors (VVH = 20000/h, Pressure = 3.5 bar absolute, $N_2O \approx 1700$ ppm, $NO \approx 700$ ppm, $NO_2 \approx 700$ ppm, $O_2 = 2.5$ % and $H_2O \approx 1$ %), a 20 % N_2O conversion is obtained at around 390 °C and 70 % at around 450 °C.

With the addition of ammonia (NH_3), a gain in activity is obtained under the standard conditions above: 70 % conversion of N_2O at 390 °C and 90 % at 425 °C. In addition, the presence of ammonia allows almost total reduction of the NO_X by SCR. This catalyst is bi-functional: treatment of the NO_X and of the N_2O.

The following observations could be made on the catalytic loads tested:

- in SCR by NH_3, an increase in the pressure allows a conversion gain to be obtained,
- the absence of NO in the flow to be treated is unfavourable to SCR of N_2O by NH_3
- too high a reaction temperature leads to oxidation of the ammonia
- under the operating conditions of the pilot, VVH variations affect the conversion profiles only very slightly.

As regards the stability of the conversion of N_2O and NO_X in the different tests, the Fe-FER and Fe-BEA type catalysts do not seem to lose their catalytic activity after an extensive accelerated ageing test.

6.4 Economic evaluation and comparison

This gives a solution combining catalytic decomposition of N_2O at high temperature and selective catalytic reduction with ammonia

6.4.1 Hypotheses used

Different sets of hypotheses were used to make these economic evaluations. They are explained below.

- Current emissions from the nitric acid workshop:

2.25 kg of NO_2/tonne of 100 % HNO_3 produced,
6.45 kg of N_2O/tonne of 100 % HNO_3 produced.

- Flow of effluents: (300000 tonne x 3300 Nm3/tonne of 100 % HNO_3)/365 x 24 = 113013 Nm3/h rounded to 120000 Nm3/h

- Volume of catalyst:

Hypothesis 1 GP: 15 m^3
Hypothesis 2 on the bases of the performances of the IRMA formulation A 7976
VVH (ratio of flow to the volume of catalyst): 20000/h hence a required volume of catalyst of 6 m^3.

Hypothesis 3 GP 12 m^3

- N2O conversion: 88 %
- NOX conversion: 99 %
- Stoichiometry $NH_3/(NO_X + N_2O)$: 1
- T = 425 °C

6.4.1.1 Investment

<u>Hypothesis 1</u>
Main equipment

- reactor: FRF 1.8 M
- gas/gas exchanger: FRF 1.18 M
- evaporator/superheater/gas mixer/NH3: FRF 0.754 M

Sub-total: FRF 3.734 M.

Others:

- indivisible equipment: FRF 4.329 M
- assembly work FRF 6.88 M
- engineering: FRF 2.82 M
- Unforeseen elements: FRF 2.099 M

Sub-total: FRF 16.128 M

Hypothesis 2

ADEME experience with this type of investment generally shows a global equipment cost which is double that of the main equipment, which would then bring the total amount of investment to FRF 7.46 M which has been rounded up to FRF 10 M given the unforeseen elements in integration on a site.
This investment sum of FRF 10 M will be taken into account in calculation hypothesis 2.

Hypothesis 3

This case is in fact broken down into two scenarios:
3.1: heating of the gases is necessary and the volume of catalyst used is 12 m^3
In this case, the amount of the investment has been evaluated at FRF 19.2 M by Grande Paroisse.
3.2: this corresponds to scenario 3.1 without heating of the gases, a situation which can be encountered in certain nitric acid workshops.
Grande Paroisse then estimates the initial investment at FRF 13 M.

Annualisation of the investment is obtained by means of the following formula:

A=B1*((B2*(1+B2)^B3)/((1+B2)^B3-1))
With A: annualisation of the investment
B1: Initial investment
B2: Rate of updating (6 %)
B3: Period of distribution of the investment (10 year)

	Hyp 1	Hyp 2	Hyp 3.1	Hyp 3.2
Initial investment (in MFRF)	19862	10	19219	13119
Annualisation (in MFRF)	2.7	1.358	2.611	1.782

Table 6.9: Investment hypotheses

6.4.1.2 Price of catalyst

Different hypotheses were used for the cost per unit volume of the catalyst and its renewal period in order to evaluate the influence on the annualisation.

Hypothesis	Volume (in m^3)	Cost (in F/l)	Initial total cost (in F)	Frequency of renewal (in years)	Annualisation of cost of catalyst (in F)
1	15	656	9839355	3	3681000
2.1	6	500	3000000	3	1122000
2.2	6	500	3000000	5	712000
2.3	6	500	3000000	10	407604
3.1/3.2	12	500	6000000	3	2244000

Table 6.10: Costs per unit volume

6.4.1.3 Consumption of ammonia

For all the scenarios, a stoichiometry of 1 was considered with respect to gross emission levels of 2.25 kg of NO_2/tonne of 100 % HNO_3 produced and 6.45 kg of N_2O/tonne of 100 % HNO_3 produced, or 675 tonne of NO_2 and 1935 tonne of N_2O, giving an ammonia consumption of (675/46) x 17 + (1935/44) x 17 = 249.5 + 747.6 = 997 tonne annually
Cost of ammonia: 1 180 F/tonne
Annual cost: 997 x 1180 = 1 176 594 F
Emissions of NO_X (in NO_2) prevented annually: 675 x 0.99 = 668.25 tonne
Emissions of N_2O prevented annually: 1935 x 0.88 = 1702 tonne

6.4.2 Summary

	Hyp 1	Hyp 2.1	Hyp 2.2	Hyp 2.3	Hyp 3.1	Hyp 3.2	Hypothesis 2.1 with possible subsidy of 30 %
Initial investment (in MFRF)	19.862	10	10	10	19.219	13.119	7
Annualisation (in MFRF)	2.7	1.358	1.358	1.358	2.611	1.782	0.9506
Annual cost of catalyst (in MFRF)	3.68	1.122	0.712	0.408	2.244	2.244	0.785
Consumption of ammonia (in MFRF)	1.177	1.177	1.177	1.177	1.177	1.177	1.177
Total annualisation (in MFRF)	7.557	3.657	3.247	2.943	6.032	5.203	2.913
Tonnage of NO_X in NO_2 and N_2O prevented annually	2370	2370	2370	2370	2370	2370	2 370
Cost per tonne of NO_X in NO_2 or N_2O prevented annually in F (in euro)	3189 (486)	1543 (235)	1370 (208)	1242 (189)	2545 (388)	2195 (335)	1229 (187)
Cost per tonne of CO_2 equivalent prevented for N_2O in F	10.29	4.98	4.42	4.01	8.21	7.08	3.96
Cost per tonne of CO_2 equivalent prevented for N_2O in euro	1.57	0.76	0.67	0.61	1.25	1.08	0.60
Deduction of TGAP in F/tonne	- 373	- 373	- 373	- 373	- 373	- 373	- 373
Additional cost per tonne of NO_X in NO_2 or N_2O prevented annually in F	2816	1170	997	869	2172	1822	856
Additional cost per tonne of CO_2 equivalent prevented for N_2O in F	9.08	3.77	3.22	2.80	7.01	5.88	2.76
Additional cost per tonne of CO_2 equivalent prevented for N_2O in euro	1.38	0.58	0.49	0.43	1.07	0.90	0.42

Table 6.11: Cost summary

These costs must be compared with the indicative average costs recorded for other sectors in euro/tonne of NO_2 equivalent prevented (see extract from NOXCONF 2001 technical summary below) or treatment costs evoked for N_2O (0.5 to 3 euro per tonne of CO_2 equivalent prevented). This will be with a solution combining a high-temperature catalytic decomposition treatment for N_2O and a selective catalytic reduction with ammonia for nitrogen oxides.

Values indicative of cost of treatment of NO_X in various sectors

(extract from NO_XCONF 2001)

Cost in euro per tonne	Min	Max
HNO_3 SCR (CRI)	420	450
GIC 800 MWth + SCR	1500	2500
200 mg/m^3 refineries (French example)	1850	2350
SCR cement (Austrian evaluation)	966	1594
Waste (1 French example/SCR)	9000	
Dutch reference value for waste	3900	4400
SCR glass (2 - 1 to 0.5 g/m^3)	1000	3000
SCR glass (1 - 0.7 to 0.5 g/m^3)	3000	7000
Glass (example: Euroglas)	650	1600
Overall Dutch reference value	4600	
Swedish tax level	5000	
65 mg/m^3 Japanese refinery	3800	5640
Californian exchange value	8200	

For this second solution, BASF indicates for a 500 t/day 100 % HNO_3 unit the need to install 1 m^3 of catalyst at a cost of 250000 euro for a guarantee of approximately 2 years and a N_2O elimination efficiency of approximately 80 % (see NOXCONF 2001).

For the reference unit, it is probable that a volume of 2 m^3 will be necessary.

It is also advisable to carry out adaptation work on the unit to integrate the catalyst.

The cost of these modifications is evaluated at FRF 3 M for the unit serving as a reference in the various calculations.

Furthermore, effects on the efficiency of the unit must not be ruled out.

The cost of N_2O elimination for the catalyst would then be at least:

Initial investment (in M FRF)	3
Annualisation (in M FRF)	0.408
Annual cost of catalyst (in M FRF)	1.789
Total annualisation (in M FRF)	2.197
Tonnage of N_2O prevented annually	1362
Cost per tonne of N_2O prevented annually in FRF	1613
Cost per tonne of CO_2 equivalent prevented for N_2O in FRF	5.2
Cost per tonne of CO_2 equivalent prevented for N_2O in euro	0.79
Deduction of TGAP in F/tonne	- 373
Additional cost per tonne of NO_X in NO_2 or N_2O prevented annually in FRF	1240
Additional cost per tonne of CO_2 equivalent prevented for N_2O in FRF	4
Additional cost per tonne of CO_2 equivalent prevented for N_2O in euro	0.61

Table 6.12: Costs of N_2O elimination

In addition, the treatment of the NO_X was taken into account with the following hypotheses:

- Investment: FRF 9.970 M
- Catalyst: FRF 2.624 M
- Annual consumption of ammonia: FRF 212 530
  i.e. an annualisation of the investment considering a ten-year resistance of the catalyst (experience of the other units) of 1 711 000 F and a total annual cost of 1 923 530 F, i.e. a cost per tonne of NO_X prevented of 1 932 500/(600) = 3 205 F

It can be noted that the volume of catalyst used in the two methods of treatment is roughly equivalent. The performance objectives are not exactly the same, however.

Judging from this information, the new method of treatment which has just been developed for combined NO_X/N_2O treatment leads to an average cost of NO_X and N_2O treatment of between 1242 and 3189 F per tonne, depending on the hypotheses, to be compared with the cost of the alternative method (high-temperature catalytic decomposition of N_2O and NH_3 SCR of NO and NO_2) of 2100 F/tonne. It therefore appears to deserve to be considered in certain specific contexts.

To back up this assertion, it should be recalled, finally, that the use of such a method of treatment is indeed likely to receive financial support from ADEME amounting to around 30 % of the initial investment, this being a demonstration operation.

6.5 General conclusion

Selective catalytic reduction (SCR) of N_2O by ammonia have been studied on Fe-FER and Fe-BEA type catalysts, on a pilot on a bypass from a Grand Quevilly nitric acid workshop. Six catalytic loads have been evaluated by varying different parameters: the temperature, the pressure, the volumic velocity per hour and the NO content. From all the results obtained, the Fe-FER and Fe-BEA catalysts are active in SCR of N_2O and NO_X under the conditions of a nitric acid workshop: a conversion of 70 % of N_2O is obtained at 390 °C (90 % respectively at 425 °C) with a total conversion of the NO_X. These catalysts are bi-functional. In addition, accelerated ageing tests have demonstrated the very good stability over time of the zeolitic structures; no deterioration of the most successful loads was detected.

However, the economic benefits of this solution are strongly linked to the configuration of the nitric acid workshop, and particularly to the possibilities of operation at the optimum working temperature for the catalyst. These conditions are encountered more readily in relatively recent workshops.

The average cost of treatment of NO_X and N_2O has been estimated, for a workshop presenting characteristics close to these specifications, at between 1242 and 3189 F per tonne depending on the hypotheses used.

It should be noted, however, that few workshops present these characteristics in France. The need to heat the tail gas obviously greatly penalises this process and also reduces its benefits with regard to the greenhouse effect.

The currently favoured alternative is therefore catalytic decomposition of N_2O at high temperature combined with treatment of NO and NO_2 by selective catalytic reduction with ammonia or extended absorption. For the same workshop, the cost of this option comes to at least 2100 F/tonne of NO_X (in NO_2 equivalent) or N_2O.

This method may nevertheless have an effect on the efficiency of the oxidation reaction of NH_3 to NO (productivity of the workshop) and on the quality of the downstream products.