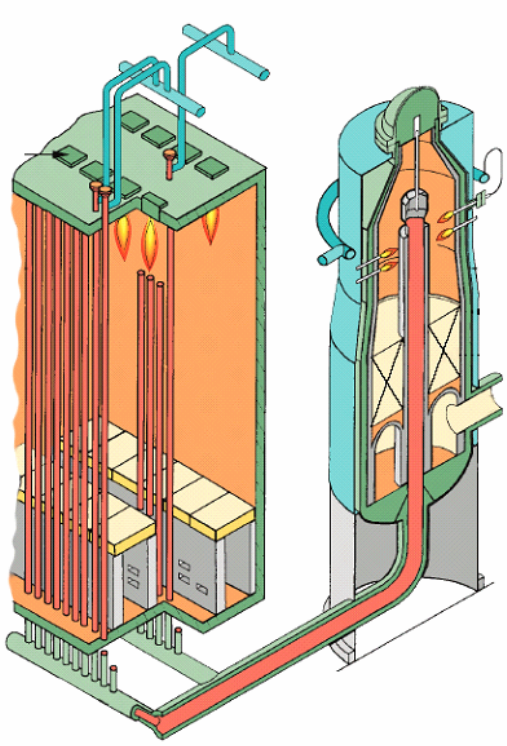
EUROPEAN COMMISSION

Integrated Pollution Prevention and Control

Reference Document on
Best Available Techniques for the Manufacture of

Large Volume Inorganic Chemicals – Ammonia, Acids and Fertilisers

August 2007



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

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

EXECUTIVE SUMMARY

The BAT (Best Available Techniques) Reference Document (BREF) entitled "Reference Document on Best Available Techniques for the Manufacture of Large Volume Inorganic Chemicals – Ammonia, Acids and Fertilisers" reflects an information exchange carried out under Article 16(2) of Council Directive 96/61/EC (IPPC Directive). This executive summary describes the main findings, a summary of the principal BAT conclusions and the associated consumption and emission levels. It should be read in conjunction with the preface, which explains this document's objectives; how it is intended to be used and legal terms. It can be read and understood as a standalone document but, as a summary, it does not present all the complexities of this full document. It is therefore not intended as a substitute for this full document as a tool in BAT decision making.

Scope of this document
This document targets the following sections from Annex 1 to the IPPC Directive:

4.2 (a) ammonia, hydrogen fluoride
4.2 (b) hydrofluoric acid, phosphoric acid, nitric acid, sulphuric acid, oleum
4.3 phosphorus-, nitrogen- or potassium-based fertilisers (simple or compound fertilisers).

Although the main use of ammonia, nitric acid, sulphuric acid and phosphoric acid is the downstream production of fertilisers, the scope of this document is not restricted to the manufacture of fertiliser grade products. By addressing the items listed above, the scope of this document includes the production of synthesis gas for the production of ammonia and the production of sulphuric acid based on SO_2 gases from various processes, e.g. SO_2 gases from non-ferrous metals production or regeneration of spent acids. However, specific and in-depth information on the production of non-ferrous metals can be found in detail in the BREF on Non-ferrous Metals Industries.

I. Overview

The fertiliser industry is essentially concerned with the provision of three major plant nutrients – nitrogen, phosphorus and potassium – in plant available forms. Nitrogen is expressed in the elemental form, N, but phosphorus and potash may be expressed either as the oxide (P_2O_5, K_2O) or as the element (P, K). Sulphur is also supplied in large amounts, partly through the sulphates present in such products as superphosphate and ammonium sulphate. Secondary nutrients (calcium, magnesium, sodium and sulphur) may be supplied incidentally as a result of the production process and its raw materials. Micro-nutrients (boron, cobalt, copper, iron, manganese, molybdenum and zinc) can be incorporated into the major fertilisers or supplied as speciality products. 97 % of nitrogen fertilisers are derived from ammonia and 70 % of phosphate fertilisers are derived from phosphoric acid. NH_3, HNO_3, H_2SO_4 and H_3PO_4 belong to the quantitatively most important industrial chemicals and are mainly used for the production of fertilisers, but also for various other process, e.g. in chemical industry. However, HF production is not typically associated with fertiliser production, and main applications are as a raw material for the production of fluorocarbons, and in the steel, glass and chemical industries.

Figure I gives an overview of the boundaries and links between the LVIC-AAF industries. Accordingly, it is no surprise that often a suitable combination of productions (and not only fertiliser production) is carried out on one integrated site, typically focused on the production of nitrogen-based fertilisers or phosphate fertilisers.

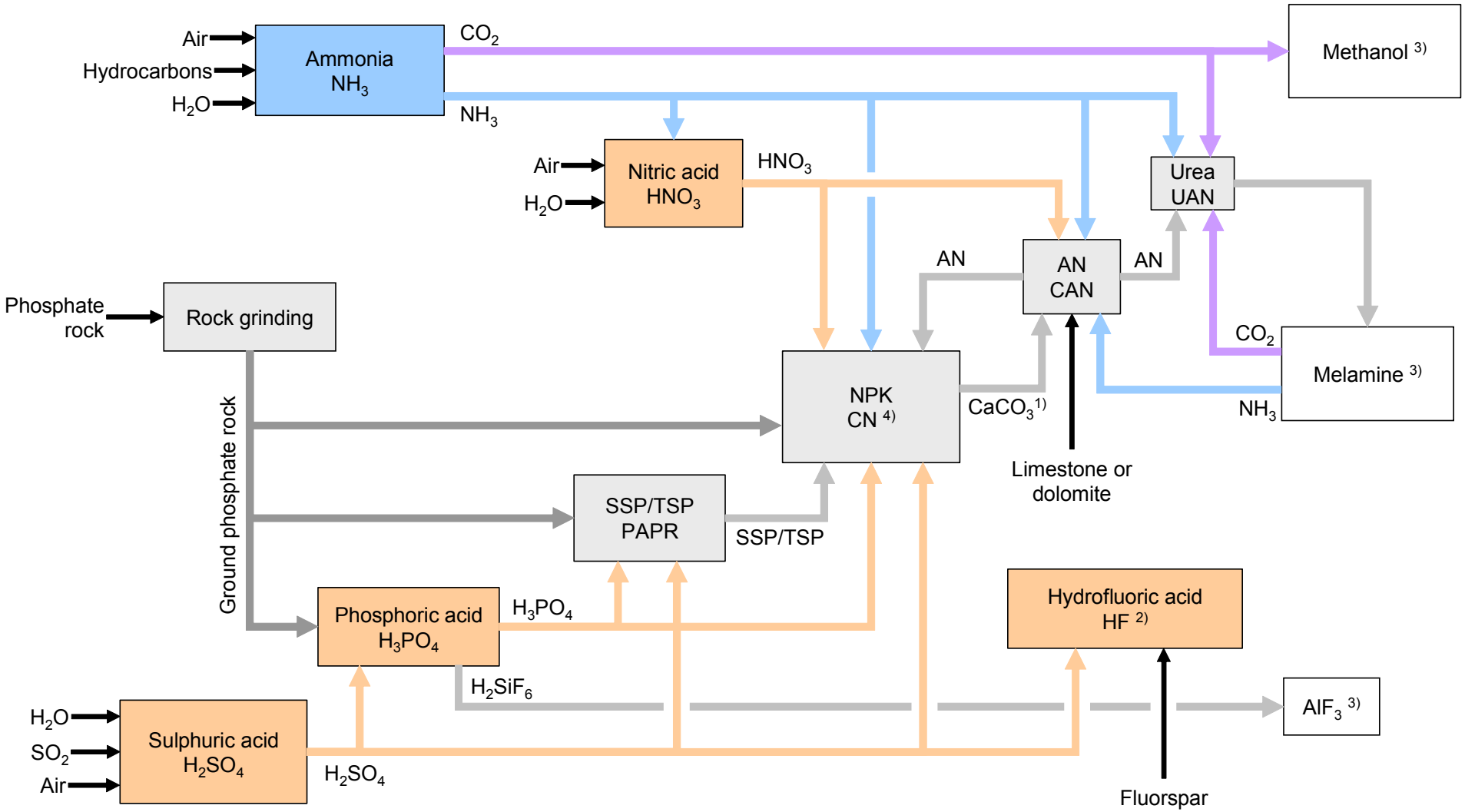


Figure I: Overview of boundaries and links between the LVIC-AAF industries
[1] only with NPK production using the nitrophosphate route [2] not typically produced on fertiliser sites [3] not described in this document
[4] CN is $Ca(NO_3)_2$, and is alternatively produced by neutralisation of HNO_3 with lime (not described in this document)

II. Production and environmental issues

Generally, LVIC-AAF production is carried out in dedicated equipment and specific processes which are a result of decades of development. However, NPK, AN/CAN and phosphate fertilisers can be produced in the same line of equipment and abatement system. The production capacities generally vary from some hundred to up to more than 3000 tonnes per day. The nitrogenous fertiliser plant is especially a major consumer of energy for meeting various heating requirements and mechanical energy for driving different equipment, such as compressors, pumps and fans. Often, the bigger equipment is driven by steam turbines and the smaller one by electrical motors. Electrical power is taken from the public grid or generated on-site. The steam is supplied by boiler plants, cogeneration plants or is produced in waste heat boilers using energy from ammonia, nitric acid or sulphuric acid production.

Fertiliser production currently accounts for about 2 – 3 % of the total global energy consumption. For Western Europe, the corresponding figure is about 1 %. Nitrogen fertilisers account for a large majority of this consumption. Most of the energy for fertiliser production is required by the fixation of atmospheric nitrogen to manufacture ammonia. Considerable energy is also required for the conversion of ammonia to urea. Amongst the LVIC-AAF industries, the production of sulphuric acid and nitric acid are candidates for exporting energy as high, medium, or low pressure steam or as hot water.

The main pollutants emitted to air are NO_x, SO_2, HF, NH_3 and dust, which are, depending on the particular source, emitted at high volume flows. In the production of HNO_3, considerable amounts of the greenhouse gas N_2O are generated.

Some by-products, e.g. phosphogypsum, are generated in high volumes. These by-products show potential for valorisation, but transport costs, contamination with impurities and the competition with, e.g. natural resources, restrict the successful marketing. Hence, excess volumes require disposal.

III. Best available techniques

Common issues

BAT is to carry out regular energy audits for the whole production site, to monitor key performance parameters and to establish and to maintain mass balances for nitrogen, P_2O_5, steam, water and CO_2. Minimisation of energy losses is carried out by generally avoiding steam pressure reduction without using the energy or by adjusting the whole steam system in order to minimise the generation of excess steam. Excess thermal energy should be used on-site or off-site and, if local factors prevent that, as a last option, steam might be used for generating only electrical power.

BAT is to improve the environmental performance of the production site by a combination of recycling or re-routing mass streams, efficiently sharing equipment, increasing heat integration, preheating of combustion air, maintaining heat exchanger efficiency, reducing waste water volumes and loads by recycling condensates, process and scrubbing waters, applying advanced process control systems and by maintenance.

Production of ammonia

BAT for new installations is to apply conventional reforming or reduced primary reforming or heat exchange autothermal reforming. In order to achieve the NO_x concentration emission levels given in Table I, techniques such as SNCR at the primary reformer (if the furnace allows the required temperature/retention time windows), low NO_x burners, ammonia removal from purge and flash gases or low temperature desulphurisation for autothermal heat exchange reforming, should be applied.

BAT is to carry out routine energy audits. Techniques to achieve the energy consumption levels given in Table II, are extended preheating of the hydrocarbon feed, preheating of combustion air, installation of a second generation gas turbine, modifications of the furnace burners (to assure an adequate distribution of gas turbine exhaust over the burners), rearrangement of the convection coils and addition of additional surface, pre-reforming in combination with a suitable steam saving project. Other options are improved CO_2 removal, low temperature desulphurisation, isothermal shift conversion (mainly for new installations), use of smaller catalyst particles in ammonia converters, low pressure ammonia synthesis catalyst, use of sulphur resistant catalyst for shift reaction of syngas from partial oxidation, liquid nitrogen wash for final purification of the synthesis gas, indirect cooling of the ammonia synthesis reactor, hydrogen recovery from the purge gas of the ammonia synthesis or the implementation of an advanced process control system. In partial oxidation, sulphur is recovered from flue-gases, e.g. by applying a combination of a Claus unit with tail gas treatment to achieve BAT associated emission levels and efficiencies given in the BREF on Oil and Gas Refineries. BAT is to remove NH_3 from process condensates, e.g. by stripping. NH_3 is recovered from purge and flash gases in a closed loop. The full text provides guidance on how to handle startup/shutdown and other abnormal operating conditions.

Production of nitric acid

BAT is to use recoverable energy: co-generated steam and/or electrical power. BAT is to reduce emissions of N_2O and to achieve the emission factors or emission concentration levels given in Table III by applying a combination of the following techniques:

- optimising the filtration of raw materials
- optimising the mixing of raw materials
- optimising the gas distribution over the catalyst
- monitoring catalyst performance and adjusting the campaign length
- optimisation of the NH_3/air ratio
- optimising the pressure and temperature of the oxidation step
- N_2O decomposition by extension of the reactor chamber in new plants
- catalytic N_2O decomposition in the reactor chamber
- combined NO_x and N_2O abatement in tail gases.

Split view: Industry and one Member State do not agree with the N_2O emission levels associated with the application of BAT *for existing plants* due to the limited experience with the De-N_2O techniques presented in Sections 3.4.6 and 3.4.7, the variance in the results obtained from pre-selected test installations, and the many technical and operational constraints for applying these techniques in the nitric acid plants in operation in Europe today. In their opinion, the applied catalysts are still under development, although already placed on the market. Industry also claims that the levels should relate to averages achieved in the lifetime of the De-N_2O catalyst, although this lifetime is not known yet. Industry and one Member State claim that the BAT range should include 2.5 kg N_2O/tonne 100 % HNO_3 for existing plants.

BAT is to reduce emissions during startup and shutdown conditions. BAT is to reduce emissions of NO_x and to achieve the emission levels given in Table IV by applying one or a combination of the following techniques:

- optimisation of the absorption stage
- combined NO_x and N_2O abatement in tail gases
- SCR
- addition of H_2O_2 to the last absorption stage.

Production of sulphuric acid

BAT is to use recoverable energy: co-generated steam, electrical power, hot water. The options to achieve the conversion rates and emission levels given in Table V are the application of double contact/double absorption, single contact/single absorption, the addition of a 5th catalyst

bed, using a cesium promoted catalyst in bed 4 or 5, the change over from single to double absorption, wet or combined wet/dry processes, regular screening and replacement of the catalyst (especially in catalyst bed 1), the replacement of brick-arch converters by stainless steel converters, improving raw gas cleaning (metallurgical plants), improving air filtration, e.g. by two stage filtration (sulphur burning), improving sulphur filtration, e.g. by applying polishing filters (sulphur burning), maintaining heat exchanger efficiency or tail gas scrubbing (provided that by-products can be recycled on-site).

BAT is to continuously monitor the SO_2 levels required to determine the SO_2 conversion rate and the SO_2 emission level. The options to achieve SO_3/H_2SO_4 mist emission levels (see Table VI) are the use of sulphur with a low impurity content (in case of sulphur burning), adequate drying of inlet gas and combustion air (only for dry contact processes), the use of a larger condensation area (only for the wet catalysis process), adequate acid distribution and circulation rate, applying high performance candle filters after absorption, controlling concentration and temperature of the absorber acid or applying recovery/abatement techniques in wet processes, such as ESP, WESP or wet scrubbing. BAT is to minimise or abate NO_x emissions. BAT is to recycle exhaust gases from product H_2SO_4 stripping to the contact process.

Phosphate rock grinding and prevention of rock dust dispersion

BAT is to reduce dust emissions from rock grinding, e.g. by application of fabric filters or ceramic filters and to achieve dust emission levels of 2.5 – 10 mg/Nm^3. BAT is to prevent dispersion of phosphate rock dust by using covered conveyor belts, indoor storage, and frequently cleaning/sweeping the plant grounds and the quay.

Production of phosphoric acid

BAT for existing installations using a wet process is to achieve P_2O_5 efficiencies of 94.0 – 98.5 %, e.g. by applying one or a combination of the following techniques:

- dihydrate process or improved dihydrate process
- increasing the residence time
- recrystallisation process
- repulping
- double-stage filtration
- recycling the water from the phosphogypsum pile
- selection of phosphate rock.

BAT for new installations is to achieve P_2O_5 efficiencies of 98.0 % or higher, e.g. by applying a hemi-dihydrate recrystallisation process with double-stage filtration. BAT for the wet process is to minimise the emissions of P_2O_5 by applying techniques like entrainment separators (where vacuum flash coolers and/or vacuum evaporators are used), liquid ring pumps (with recycling of the ring liquid to the process) or scrubbing with recycling of the scrubbing liquid.

BAT is to reduce fluoride emissions by the application of scrubbers with suitable scrubbing liquids and to achieve fluoride emission levels of 1 – 5 mg/Nm^3 expressed as HF. BAT for wet processes is to market the generated phosphogypsum and fluosilicic acid, and, if there is no market, to dispose of it. Piling of phosphogypsum requires precautionary measures and recycling of water from these piles. BAT for wet processes is to prevent fluoride emissions to water, e.g. by the application of an indirect condensation system or by a scrubbing with recycling or marketing the scrubbing liquid. BAT is to treat waste water by applying a combination of the following techniques:

- neutralisation with lime
- filtration and optionally sedimentation
- recycling of solids to the phosphogypsum pile.

Plant concept	NO_x emission as NO_2
	mg/Nm^3
Advanced conventional reforming processes and processes with reduced primary reforming	90 – 230 [x]
Heat exchange autothermal reforming	a) 80 b) 20
a) Process air heater b) Auxiliary boiler [x] Low end of the range: best existing performers and new installations	
No direct correlation between concentration levels and emission factors could be established. However, emission factors of 0.29 – 0.32 kg/tonne NH_3 are seen as a benchmark for conventional reforming processes and processes with reduced primary reforming. For heat exchange autothermal reforming, an emission factor of 0.175 kg/tonne NH_3 is seen as a benchmark.	

Table I: NO_x emission levels associated with BAT for the production of ammonia

Plant concept	Net energy consumption [x]
	GJ(LHV)/tonne NH_3
Conventional reforming processes, processes with reduced primary reforming or heat exchange autothermal reforming	27.6 – 31.8
[x] For interpretation of the given energy consumption levels, please refer to the full text. As a consequence, the levels might vary up to ± 1.5 GJ. Generally, the levels relate to steady state operation as it would be typically experienced during a performance test directly following a revamp or an overhaul at intended capacity.	

Table II: Energy consumption levels associated with BAT for the production of ammonia

		N_2O emission level [x]	
		kg/tonne 100 % HNO_3	ppmv
M/M, M/H and H/H	New plants	0.12 – 0.6	20 – 100
	Existing plants	0.12 – 1.85	20 – 300
L/M plants		No conclusion drawn	
[x] The levels relate to the average emission levels achieved in a campaign of the oxidation catalyst			

Table III: N_2O emission levels associated with the application of BAT for the production of HNO_3
Note: there is a split view on the emission levels for existing plants (see text above)

	NO_x emission level as NO_2	
	kg/tonne 100 % HNO_3	ppmv
New plants	--	5 – 75
Existing plants	--	5 – 90 [x]
NH_3 slip from SCR	--	<5
[x] Up to 150 ppmv, where safety aspects due to deposits of AN restrict the effect of SCR or with addition of H_2O_2 instead of applying SCR		

Table IV: NO_x emission levels associated with the application of BAT for the production of HNO_3

Conversion process type		Daily averages	
		Conversion rate [x]	SO_2 in mg/Nm^3 [xx]
Sulphur burning, double contact/double absorption	Existing installations	99.8 – 99.92 %	30 – 680
	New installations	99.9 – 99.92 %	30 – 340
Other double contact/double absorption plants		99.7 – 99.92 %	200 – 680
Single contact/single absorption			100 – 450
Other			15 – 170

[x] These conversion rates relate to the conversion including the absorption tower, they do not include the effect of tail gas scrubbing

[xx] These levels might include the effect of tail gas scrubbing

Table V: Conversion rates and SO_2 emission levels associated with BAT for production of H_2SO_4

	Emission level as H_2SO_4
All processes	10 – 35 mg/Nm^3
Yearly averages	

Table VI: SO_3/H_2SO_4 emission levels associated with BAT for production of H_2SO_4

	GJ/tonne HF	Remark
Fuel for kiln heating	4 – 6.8	Existing installations
	4 – 5	New installations, production of anhydrous HF
	4.5 – 6	New installations, production of anhydrous HF and HF solutions

Table VII: Achievable consumption levels associated with BAT for the production of HF

	kg/tonne HF	mg/Nm^3	Remark
SO_2	0.001 – 0.01		Yearly averages
Fluorides as HF		0.6 – 5	

Table VIII: Achievable emission levels associated with BAT for the production of HF

	Parameter	Level mg/Nm^3	Removal efficiency in %
Phosphate rock digestion, sand washing, CNTH filtration	NO_x as NO_2	100 – 425	
	Fluoride as HF	0.3 – 5	
Neutralisation, granulation, drying, coating, cooling	NH_3	5 – 30 [x]	
	Fluoride as HF	1 – 5 [xx]	
	Dust	10 – 25	>80
	HCl	4 – 23	

[x] The lower part of the range is achieved with nitric acid as scrubbing medium, the upper part of the range is achieved with other acids as scrubbing medium. Depending on the actual NPK grade produced (e.g. DAP), even by applying multistage scrubbing, higher emission levels might be expected

[xx] in the case of DAP production with multistage scrubbing with H_3PO_4, levels of up to 10 mg/Nm^3 might be expected

Table IX: Emission levels to air associated with the application of BAT for the production of NPK

Hydrofluoric acid

The options to achieve fuel consumption levels within the ranges given in Table VII are preheating the feed H_2SO_4, optimised kiln design and optimised temperature profile control for the rotary kiln, using a pre-reactor system, energy recovery from kiln heating or spar calcination.

BAT for the treatment of tail gases from the fluorspar process is to apply, e.g. water scrubbing and/or alkaline scrubbing and to achieve the emission levels given in Table VIII. BAT is to reduce dust emissions from fluorspar drying, transfer and storage and to achieve dust emission levels of 3 – 19 mg/Nm^3.

Split view: Part of industry claims that the dust emission levels are not achievable, because changing the bags in the applied fabric filters more than one time per year would not be economically viable.

Waste water from wet scrubbing is treated, e.g. by neutralisation with lime, addition of coagulation agents, filtration and optionally sedimentation. BAT for the fluorspar process is to market the generated anhydrite and fluosilicic acid, and if there is no market, to dispose of it, e.g. by landfilling.

Production of NPK fertilisers

BAT is to improve the environmental performance of the finishing section, e.g. by applying plate bank product cooling, recycling of warm air, selecting proper size of screens and mills, e.g. roller or chain mills, applying surge hoppers for granulation recycle control or applying online product size distribution measurement for granulation recycle control. BAT is to minimise the NO_x load in exhaust gases from phosphate rock digestion, for example, by accurate temperature control, a proper rock/acid ratio, phosphate rock selection or by controlling other relevant process parameters.

BAT is to reduce emissions to air from phosphate rock digestion, sand washing and CNTH filtration by applying, e.g. multistage scrubbing, and to achieve emission levels given in Table IX. BAT is to reduce emission levels to air from neutralisation, granulation, drying, coating, cooling by applying the following techniques and to achieve the emission levels or removal efficiencies given in Table IX:

- dust removal, such as cyclones and/or fabric filters
- wet scrubbing, e.g. combined scrubbing.

BAT is to minimise waste water volumes by recycling washing and rinsing waters and scrubbing liquors into the process, e.g. and by using residual heat for waste water evaporation. BAT is to treat the remaining waste water volumes.

Production of urea and UAN

BAT is to improve the environmental performance of the finishing section, for example, by applying plate bank product cooling, redirecting urea fines to the concentrated urea solution, selecting proper size of screens and mills, e.g. roller or chain mills, applying surge hoppers for granulation recycle control or applying product size distribution measurement and control. BAT is to optimise the total energy consumption for urea production by applying one or a combination of the following techniques:

- for existing stripping installations, continue applying stripping technology
- for new installations, applying total recycling stripping processes
- for existing conventional total recycling installations, only in case of a substantial urea plant capacity increase, upgrading to stripping technology
- increasing heat integration of stripping plants
- applying combined condensation and reaction technology.

BAT is to treat all exhaust gases from the wet sections by scrubbing, taking into account the lower explosion limit and to recycle the resulting ammonia solutions to the process.

BAT is to reduce ammonia and dust emissions from prilling or granulation and to achieve ammonia emission levels of 3 – 35 mg/Nm^3, e.g. by scrubbing or optimising the operation conditions of prilling towers, and to re-use scrubber liquids on-site. If the scrubbing liquid can be re-used, then preferably by acidic scrubbing, if not, by water scrubbing. In optimising the emission levels to the values mentioned above, it is assumed that dust emission levels of 15 – 55 mg/Nm^3 are achieved, even with water scrubbing.

Where process water with or without treatment is not re-used, BAT is to treat process water, e.g. by desorption and hydrolysation and to achieve the levels given in Table X. If, in existing plants, the levels cannot be achieved, it is BAT to apply subsequent biological waste water treatment. It is also BAT to monitor the key performance parameters as described in the full text.

		NH_3	**Urea**	
After process water treatment	New plants	1	1	ppm w/w
	Existing plants	<10	<5	

Table X: BAT levels for the treatment of process water from urea production

Production of AN/CAN

BAT is to optimise the neutralisation/evaporation stage by a combination of the following techniques:

- using heat of reaction to preheat the HNO_3 and/or to vapourise NH_3
- operating the neutralisation at an elevated pressure and exporting steam
- using the generated steam for evaporation of the ANS
- recovering residual heat for chilling process water
- using the generated steam for the treatment of process condensates
- using the heat of reaction for additional water evaporation.

BAT is to effectively and reliably control pH, flow and temperature. The options to improve the environmental performance of the finishing section are applying plate bank product cooling, recycling of warm air, selecting proper size of screens and mills, e.g. roller or chain mills, applying surge hoppers for granulation recycle control or applying product size distribution measurement and control.

BAT is to reduce dust emissions from dolomite grinding to levels <10 mg/Nm^3 by applying, e.g. fabric filters. Because of an insufficient data basis, no conclusions could be drawn for emissions to air from neutralisation, evaporation, granulation, prilling, drying, cooling and conditioning.

BAT is to recycle process water on site or off site and to treat the remaining waste water in a biological treatment plant or using any other technique achieving an equivalent removal efficiency.

Production of SSP/TSP

BAT for waste water treatment is to apply BAT given in the BREF on Common Waste Water and Waste Gas Treatment/Management Systems in the Chemical Sector. BAT is to improve environmental performance of the finishing section by one or a combination of the following techniques:

- applying plate bank product cooling
- recycling of warm air
- selecting proper size of screens and mills, e.g. roller or chain mills
- applying surge hoppers for granulation recycle control
- applying online product size distribution measurement for granulation recycle control.

BAT is to reduce fluoride emissions by the application of scrubbers with suitable scrubbing liquids and to achieve fluoride emission levels of 0.5 – 5 mg/Nm^3 expressed as HF. BAT is to reduce waste water volumes by the recycling of scrubbing liquids, where, besides the manufacture of SSP or TSP, acidulated phosphate rock (PAPR) is also produced. BAT for the production of SSP/TSP and multi purpose production is to reduce emissions to air from neutralisation, granulation, drying, coating, cooling by applying the following techniques and to achieve the emission levels or removal efficiencies given in Table XI:

- cyclones and/or fabric filters
- wet scrubbing, e.g. combined scrubbing.

	Parameter	Level mg/Nm^3	Removal efficiency in %
Neutralisation, granulation, drying, coating, cooling	NH_3	5 – 30 [x]	
	Fluoride as HF	1 – 5 [xx]	
	Dust	10 – 25	> 80
	HCl	4 – 23	

[x] The lower part of the range is achieved with nitric acid as scrubbing medium, the upper part of the range is achieved with other acids as scrubbing medium. Depending on the actual NPK grade produced (e.g. DAP), even by applying multistage scrubbing, higher emission levels might be expected

[xx] In the case of DAP production with multistage scrubbing with H_3PO_4, levels of up to 10 mg/Nm^3 might be expected

Table XI: Emission levels to air associated with the application of BAT for production of SSP/TSP

IV. Concluding remarks

The information exchange on Best Available Techniques for the Manufacture of Large Volume Inorganic Chemicals – Ammonia, Acids and Fertilisers was carried out from 2001 to 2006. This document was developed based on about 600 comments to the first draft and about 1100 comments to the second draft and a series of additional meetings to finalise the work. Finally, a high degree of consensus was reached. Two split views were recorded.

The EC is launching and supporting, through its RTD programmes, a series of projects dealing with clean technologies, emerging effluent treatment and recycling technologies and management strategies. Potentially these projects could provide a useful contribution to future BREF reviews. Readers are therefore invited to inform the EIPPCB of any research results which are relevant to the scope of this document (see also the preface of this document).

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 forms part of a series presenting the results of an exchange of information between EU Member States and industries concerned on best available technique (BAT), associated monitoring, and developments in them. It is published by the European Commission pursuant to Article 16(2) of the Directive, and must therefore be taken into account in accordance with Annex IV of the Directive when determining "best available techniques".

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 world-wide 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.

Chapters X.1 and X.2 provide general information on the industrial sector concerned and on the industrial processes used within the sector. Chapters X.3 provide data and information concerning current emission and consumption levels reflecting the situation in existing installations at the time of writing.

Chapters X.4 describe 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.

Chapters X.5 present 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. In the case of 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, and these judgements will often be 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 5 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:

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Best Available Techniques Reference Document on the manufacture of Large Volume Inorganic Chemicals (Ammonia, Acids and Fertilisers)

EXECUTIVE SUMMARY I

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SCOPE

This document on Large Volume Inorganic Chemicals – Ammonia, Acids and Fertilisers (LVIC-AAF) targets the following sections from Annex 1 to the IPPC Directive:

4.2 (a) ammonia, hydrogen fluoride
4.2 (b) hydrofluoric acid, phosphoric acid, nitric acid, sulphuric acid, oleum
4.3 phosphorus-, nitrogen- or potassium-based fertilisers (simple or compound fertilisers).

Although the main use of ammonia, nitric acid, sulphuric acid and phosphoric acid is the downstream production of fertilisers, the scope of this document is not restricted to production of fertiliser grade products.

For clarification, it is stated that by addressing the items listed above, the scope of this document includes:

- the production of synthesis gas for the production of ammonia
- the production of sulphuric acid based on SO_2 gases from various processes, e.g. SO_2 gases from non-ferrous metals production or regeneration of spent acids.

However, specific and in-depth information on the production of non-ferrous metals can be found in detail in the BREF on Non-ferrous Metals Industries [61, European Commission, 2003].

The scope of this document does not include the following:

- reconcentration or purification of spent sulphuric acids
- production of foodgrade phosphates.

1 OVERVIEW TO THE PRODUCTION OF LVIC-AAF

1.1 General information

1.1.1 Overview

The fertiliser industry is essentially concerned with the provision of three major plant nutrients – nitrogen, phosphorus and potassium – in plant available forms. Nitrogen is expressed in the elemental form, N, but phosphorus and potash may be expressed either as the oxide (P_2O_5, K_2O) or as the element (P, K). Sulphur is also supplied in large amounts, partly through the sulphates present in such products as superphosphate and ammonium sulphate. Secondary nutrients may be supplied incidentally as a result of the production process and its raw materials. Micro-nutrients (trace elements) can be incorporated into the major fertilisers or supplied as speciality products [27, UNEP, 1998]. Table 1.1 gives an overview of production of ammonia, acids and fertilisers, raw materials and the major environmental issues. HF production is not typically associated with fertiliser production.

Raw material	Production of	Major issues
Hydrocarbon feed, water, air	**NH_3**	Energy consumption Air: NO_x Waste water
NH_3, CO_2	**Urea, UAN**	Energy consumption Air: NH_3, dust Waste water: NH_3, urea
Air, NH_3	**HNO_3**	Energy export Air: N_2O, NO_x
SO_2 Air	**H_2SO_4**	Energy export Air: SO_2, SO_3/H_2SO_4 mist
Phosphate rock, H_2SO_4	**H_3PO_4**	Air: HF, H_2SiF_6 Phosphogypsum Waste water
Fluorspar, H_2SO_4	**HF**	Air: HF, dust Anhydrite Waste water
Phosphate rock, H_2SO_4, H_3PO_4	**TSP/SSP**	Air: HF, dust Waste water
NH_3, HNO_3	**AN**	Air: NH_3, dust Waste water
AN, $CaCO_3$	**CAN**	Air: NH_3, dust Waste water
Phosphate rock, SSP/TSP NH_3 H_2SO_4, H_3PO_4, HNO_3 Various other	**NPK [x]**	Air: NH_3, NO_x, HF, HCl, dust Waste water
CNTH, NH_3	**CN**	Air: NO_x, dust
[x] raw materials and emissions depend on the particular NPK produced		

Table 1.1: Overview of products, raw materials and the major environmental issues
This table has been based on the other chapters of this document

97 % of nitrogen fertilisers are derived from ammonia and 70 % of phosphate fertilisers are derived from phosphoric acid. During the past 30 years, a very large proportion of additional production has been of phosphoric acid based fertilisers. Potash is used as such. As a consequence, these three materials, ammonia, phosphoric acid and potash, give a very good picture of the progression of the fertiliser industry. The energy required for nitrogen fertiliser production (see also Section 1.1.2.1) is fairly evenly distributed around the planet, although there has been a trend towards production in locations where cheap natural gas is available. There has also been a trend towards the production of nitrogen fertilisers in high-demand developing countries. The location of nitrogen production in developing countries therefore reflects partly the relocation nearer to sources of low-cost gas, as in the Near East and the Caribbean, but also towards the main consuming regions, such as South Asia and China. In future, it will be these regions where the new capacities will be realised. In 1974, the developing countries accounted for 27 % of ammonia capacity. By 1998, their share had increased to 51 % (see also Section 2.1). West Europe's share fell from 13 % in 1988 to 9 % in 2000 [2, IFA, 2005].

Phosphoric acid is obtained by a reaction between phosphate rock and an acid, mostly sulphuric acid (see Section 5.2). Over the past two decades there has been a distinct trend towards the processing of phosphate rock in countries with substantial natural resources of this material, especially in North Africa and the US, but also in the Middle East, South and West Africa and China. This trend is expected to continue. In Western Europe, phosphoric acid capacity and output have fallen by 52 % since 1988. The main producers of phosphate rock and phosphate fertilisers are the US, the former USSR, China, the Maghreb countries, Egypt, Senegal, Togo and South Africa, and the Middle East. Several of these countries are developing countries and the phosphate industry makes an important contribution to their economies [2, IFA, 2005].

Potash is produced in the few countries where the ores are located. Russia and Belarus account for about 33 % of the world's production capacity, North America – mostly Canada – for 40 %, Western Europe for 17 % and Israel and Jordan for 8 %, these few regions thus accounting for a total of 98 % of world capacities [2, IFA, 2005].

With the exception of HF, the main application of the products addressed in Table 1.1 is as fertiliser or in the fertiliser industry. Table 1.2 gives examples for non fertiliser related applications of some LVIC-AAF products.

Product	Application, non fertiliser related
HNO_3	Nitrating agent in the preparation of explosives and organic intermediates, chemical in metallurgy
H_2SO_4	Acidic dehydrating reaction medium in organic chemical and petrochemical processes, production of TiO_2 pigments, hydrochloric acid, and hydrofluoric acid, pickling and descaling steel, for leaching copper, uranium, and vanadium ores in hydrometallurgical ore processing, and in the preparation of electrolytic baths for non-ferrous metal purification and plating
HF	see Section 6.1
AN	Porous ammonium nitrate prills are still an important component of explosives
Urea	Production of melamine, preparation of urea-formaldehyde resins, feed for cattle and other ruminants (mainly in the US), for $DeNO_x$-processes

Table 1.2: Examples for non fertiliser related applications of some LVIC-AAF products [15, Ullmanns, 2001]

1.1.2 Environmental issues

1.1.2.1 Energy consumption and emission of greenhouse gases

For emissions of N_2O from the production of nitric acid, see Section 3.1 and Table 3.7.

Energy consumption has become an environmental issue because of the ecological impact of energy production and transport, and because of the emission of greenhouse gases from fuel burning. Fertiliser production currently accounts for about 2 – 3 % of the total global energy consumption. For Western Europe, the corresponding figure is about 1 %. Nitrogen fertilisers account for a large majority of this consumption. Most of the energy for fertiliser production is required by the fixation of atmospheric nitrogen to **manufacture ammonia**. Considerable energy is also required for the **conversion of ammonia to urea**. For the manufacture of ammonium nitrate, the conversion of ammonia to nitric acid provides a net energy gain which can be used, for example, to produce electrical energy via a steam turbine. The neutralisation of ammonia with nitric acid to produce ammonium nitrate also releases energy. In the case of phosphate fertilisers, energy is required for the mining of the ore, for the production of phosphoric acid, for the further processing into finished products and for pollution control [27, UNEP, 1998].

Although fertiliser production will always consume large amounts of energy in processes requiring high temperatures and pressures, the industry has become more energy efficient through improved design. Ammonia factories built in 1990 used some 30 per cent less energy per tonne of nitrogen than those designed around 1970. Energy use in a new plant, using natural gas in a reforming process, including raw materials, can now be lower than 30 GJ/tonne NH_3, compared with 75 GJ/tonne for the processes prevalent in the early 1960s. Partial oxidation processes use considerably more energy than reforming processes. In 1995, the average for all plants in the US fertiliser industry was about 40 GJ/tonne [27, UNEP, 1998].

1.1.2.2 Energy export

Amongst the AAF industries the production of **sulphuric acid** and **nitric acid** are candidates for exporting energy as high, medium, or low pressure steam or as hot water. If all thermal energy is converted to electrical power via a steam turbine, the net energy export will be reduced by approximately 65 %.

See also Sections 2.3.1.1, 3.2.6 and 4.4.15, Table 4.17, Table 4.18, Table 4.19 and Table 4.20.

Production of	Export as	Remarks
HNO_3	HP steam	Plants optimised for maximum energy export tend to have low temperatures in tail gases. 1. This might entail a safety issue, due to the potential for formation of AN in the expander turbine and the stack, see Section 3.4.10 2. This might interfere with the selection and applicability of tail gas treatment systems, see Section 3.4.10 and 3.4.6
H_2SO_4	HP steam LP steam Hot water	The potential for energy export depends on the combination of the SO_2 source, the SO_2 level in the inlet gas and the applied conversion process. The energy export can be increased significantly, if the waste heat from the acid cooling can be recovered and used
NH_3	HP steam	Ammonia plants can be designed to export energy and at the same time improving the net energy consumption

Table 1.3: Considerations on energy export
This table is based on the referenced sections

1.1.2.3 High exhaust gas volume flows

The main pollutants emitted to air are NO_x, SO_2, HF and dust (see again Table 1.1). However, the assessment of emissions from various sources needs to take into account the actual emission volume flow, which can differ significantly from source to source. To give an impression, Table 1.4 shows some examples for emission volume flows.

Source	Volume flow	Unit
Prilling, various productions	90000 – 2000000 [x]	Nm^3/hour
Other finishing sections, various productions	92000 – 340000	
Tail gas from nitric acid plants	20000 – 300000 [x]	
Tail gas from sulphuric acid plants	25000 – 125000 [x]	
Phosphate rock digestion	8000 – 25000	
Den, crusher, and enclosed conveyor belt (SSP/TSP)	25000	
Vent from urea synthesis section	420	
[x] [154, TWG on LVIC-AAF, 2006]		

Table 1.4: Examples for emission volume flows
The examples are taken from this document

1.1.2.4 Large volume by-products

The following large volume by-products are generated:

- **phosphogypsum** from the production of H_3PO_4
- **fluosilicic acid** from scrubbing of exhaust gases containing HF or SiF_4, relevant in all activities which include phosphate rock digestion and the production of HF
- **anhydrite** from the production of HF.

For example, 4 – 5 tonnes of phosphogysum are generated per tonne P_2O_5 manufactured in the production of H_3PO_4. Hence, if Europe's production capacity (2.25 Mtonnes per year according to Table 5.1) for the wet process was fully used, about 9 – 11 Mtonnes per year of phosphogypsum would be generated.

All these large volume by-products show the potential for valorisation, but transport costs, contamination with impurities and the competition with, e.g. natural resources, restrict the successful marketing. Hence, excess volumes are disposed of, e.g. by landfilling.

Concerning disposal and valorisation of phosphogypsum, see Section 5.4.13.
Concerning recovery and valorisation of fluosilicic acid, see Sections 5.4.7, 6.4.4 and 10.4.3.
Concerning valorisation of anhydrite, see Section 6.4.3.

1.1.2.5 Issues arising from impurities in raw materials

Raw materials with the potential for importing undesired compounds into the LVIC-AAF plant are:

- phosphate rock (see Section 5.2.2.1.1)
- fluorspar (see Section 6.2.2)
- H_2SO_4, e.g. technical quality from non-ferrous metal industries, also known as "fatal acid" (see Sections 5.2.2.1.2 and 10.2.2).

The impurities affect the quality of products and by-products, increase pollutant concentrations in raw gases (e.g. NO_x and HF) or might cause odour nuisance.

One issue is the radioactivity in different phosphate rocks (see also Table 5.4 and Table 5.8) and health and safety aspects arising from such radioactivity. Phosphate rock is the feedstock for the production of H_3PO_4, SSP, TSP and phosphate present in multinutrient fertilisers. It has a natural radioactivity. However, the radioactivity levels measured are considered to be lower than the background levels [154, TWG on LVIC-AAF, 2006].

Concerning phosphate rock selection, see Sections 5.4.9 and 5.4.10.

1.1.2.6 Safety issues

Special attention needs to be given to safety issues rising from the production of fertilisers, which might, in turn, lead to considerable environmental effects.

Hazardous situations may result from the improper storage, loading and use of some raw materials, especially compounds containing nitrogen (such as ammonia and nitric acid). For more information related to storage and loading, see [5, European Commission, 2005].

Urea

Typical ammonia emission sources in the synthesis phase are non-condensable vent streams from the ammonia recovery sections and separators. These process vent streams are the result of inerts present in the CO_2, and passivation air added to prevent corrosion. These process vent streams consist of hydrogen (H_2), oxygen (O_2), nitrogen (N_2) and in most cases ammonia (NH_3) and carbon dioxide (CO_2). Particular amounts of H_2, O_2 and NH_3 may lead to the formation of an explosive gas mixture. The risk can be reduced by catalytic combustion of H_2 present in the CO_2 feedstock to values below 300 ppm or by diluting the vent streams with CO_2 or N_2 [154, TWG on LVIC-AAF, 2006].

See Section 8.4.5 for the Safe NH_3 washing from inerts.

AN or AN based NPK fertilisers

Self-sustaining decomposition (SSD) is the phenomenon that a fertiliser containing nitrate locally starts to decompose and this decomposition propagates through the total mass without further external heating (however, in most cases it starts with some external source of heat). The SSD of AN at atmospheric pressure requires a fixed matrix, on which the reaction of molten AN takes place, and a catalyst. AN does not show SSD by itself. A number of materials have a strong catalytic effect on the SSD of AN or materials containing AN, including acids, chlorides, organic materials, chromates, dichromates, certain metals (such as zinc, copper and lead) and salts of manganese, copper and nickel. Some AN based NPK fertilisers also meet both requirements (fixed matrix and catalyst), making the SSD of these fertilisers possible. However,

the SSD of NPK does not lead to detonation. SSD might lead to the release of large amounts of toxic gases and vapour (such as NO_x up to 300 times the volume of the solid fertiliser). This could theoretically lead to a physical explosion when the gases cannot escape from a closed object.

After solidification of the fresh fertiliser, heat development in some cases is still rather high. A few days after solidification, some of the fertilisers (e.g. SSP and TSP) are still curing. Some of the processes taking place during curing are exothermic (e.g. neutralisation). Generally, the temperature rises less than 10 °C [154, TWG on LVIC-AAF, 2006].

See Section 9.2.2 about the safety issues of AN production.

Deposits of AN in HNO_3 plants

For safety concerns related to deposits of AN in HNO_3 plants, see Sections 3.4.1, 3.4.10, 3.4.11 and 3.5.

1.2 Integrated production sites

1.2.1 Overview

Figure 1.4 gives an overview of the boundaries and links between the LVIC-AAF industries. Accordingly, it is no surprise that often a suitable combination of productions (and not only fertiliser production) is carried out on one integrated site.

Besides economic driving force, integration offers various environmental benefits:

- more options to efficiently recycle material streams
- efficient share of equipment, e.g. the NH_3 vaporiser
- efficient generation and use of utilities
- increased heat integration
- efficient share of treatment facilities, e.g. neutralisation or biological treatment of waste waters
- reduced bulk storage and, hence, less emissions from storage
- reduced loading/unloading of raw materials and, hence, less emissions from loading /unloading
- more options for recycling condensates, process and scrubbing waters, which in turn can enable the use of more efficient scrubbing liquids, e.g. acidic instead of water
- less transport, reducing emissions to air and risk of major accidents.

However, these advantages are partially offset by the following considerations:

- integration might decrease the operational flexibility
- problems in one plant might affect other plants
- shutdown for maintenance might cause shutdown of dependent processes
- integration increases management, control and logistical requirements.

1.2.2 Some examples

Only very large sites include production of the whole range of fertilisers. Typically, an integrated site is focused on the production of nitrogen (or AN) based fertilisers or phosphate fertilisers. Figure 1.1, Figure 1.2 and Figure 1.3 give typical examples for portfolios and relative production capacities of nitrogen-based and phosphate-based plants.

Urea is produced only when integrated with an **ammonia** plant. The ammonia plant provides the required feed (NH_3 and CO_2, even in the required molar ratio) and might also, if designed for energy export, contribute to the steam requirements of the urea plant. For more details on the production of urea, see Section 8.2. For an example of integration of **HNO_3 with AN** production, see Section 1.4.1. An advanced example for integrated production is the operation of an **"ODDA"** plant for the manufacture of NPK by the nitrophosphate route (see Section 7.2.2.1). Because of the required starting materials and the generation of co-products, the nitrophosphate route is usually realised when integrated with ammonia, HNO_3 and CAN production. The liquid ammonia is also used to economically cool the nitrophosphoric acid section. For more details on the nitrophosphate route, see Section 7.2.

Another typical combination is the production of **H_2SO_4 and H_3PO_4**. The produced H_2SO_4 is used as a raw material for H_3PO_4 and, additionally, the energy available from the sulphuric acid plant is used to generate electricity in steam turbines and to concentrate weak H_3PO_4 to intermediate concentrations in a vacuum evaporation section. The production of H_2SO_4 can also be integrated with the production of **non-ferrous metals (copper, lead or zinc),** the production of **TiO_2** or with **organic chemical industries** through the recovery of spent acids, e.g. from nitrations and sulfonation.

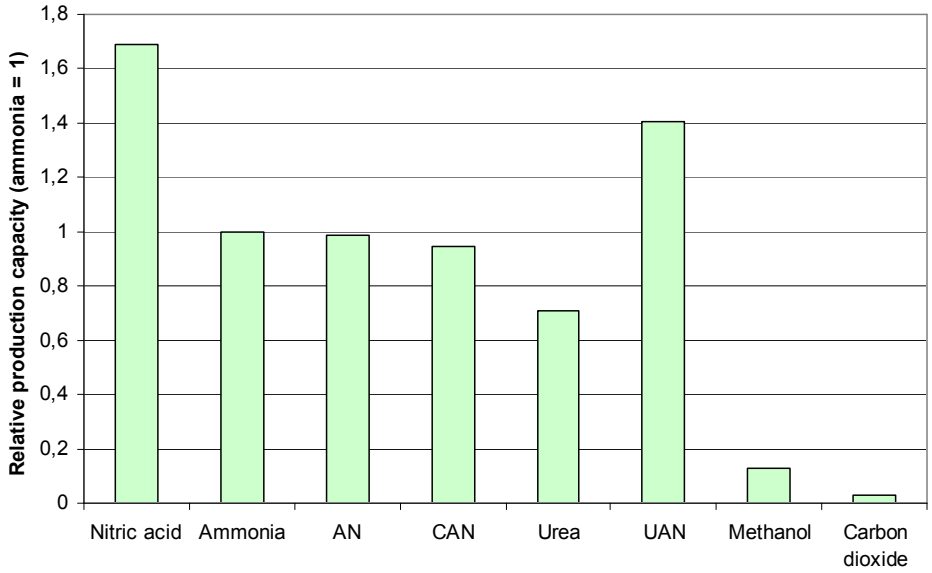

Figure 1.1: Example A for portfolio and relative capacities of a nitrogen-based fertiliser site The example plant also produces other chemicals, such as urea formaldehyde, formalin and aluminium sulphate

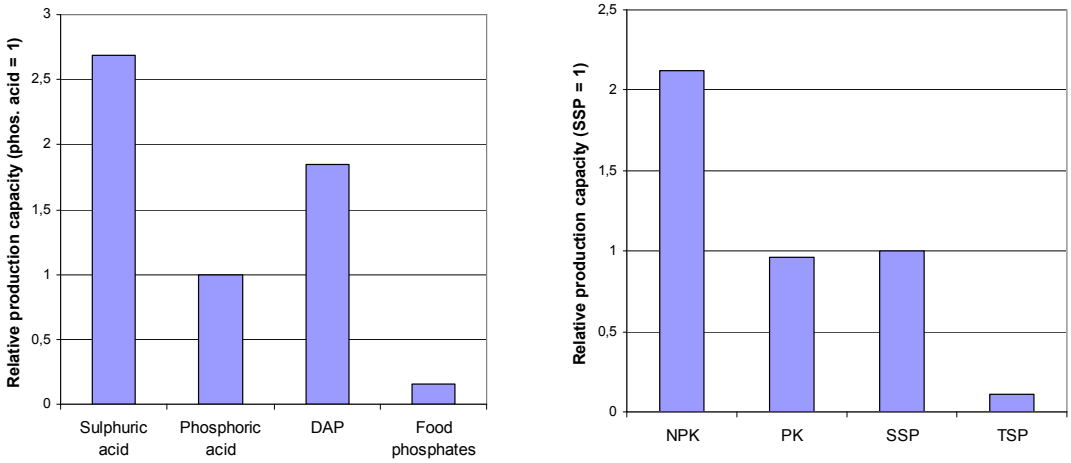

Figure 1.2: Two examples for portfolio and relative capacities of phosphate-based fertiliser sites The example plant on the left also produces AlF_3

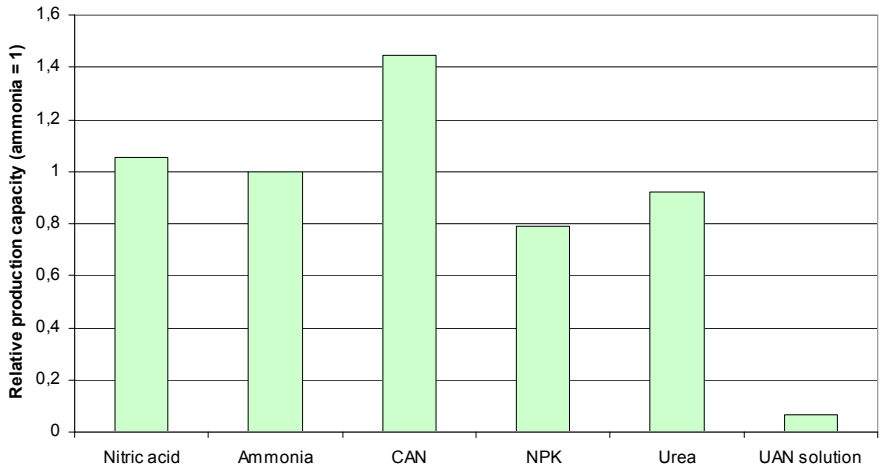

Figure 1.3: Example B for portfolio and relative capacities of a nitrogen-based fertiliser site The example plant produces melamine and CO_2 on the same site

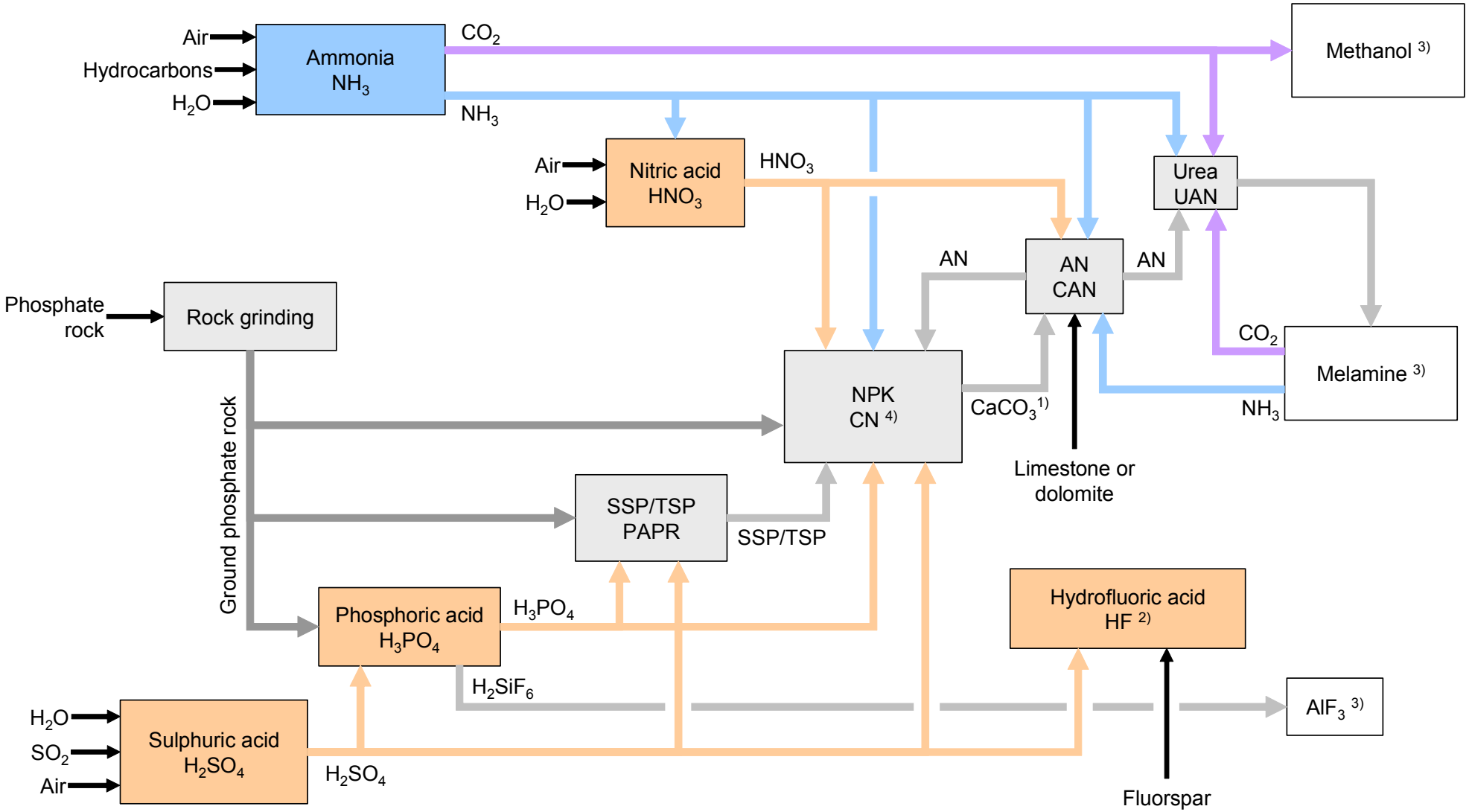

Figure 1.4: Overview of boundaries and links between the LVIC-AAF industries
The figure is based on [9, Austrian UBA, 2002, 107, Kongshaug, 1998]. For an explanation of the abbreviations, see Section 13 "Glossary".
[1] only with NPK production using the nitrophosphate route [2] not typically produced on fertiliser sites [3] not described in this document
[4] CN is $Ca(NO_3)_2$, and is alternatively produced by neutralisation of HNO_3 with lime (not described in this document)

1.2.3 Supply of steam and electricity

The nitrogenous fertiliser plant is especially a major consumer of energy for meeting various heating requirements and mechanical energy for driving different equipment, such as compressors, pumps and fans. Often, the bigger equipment is driven by steam turbines and the smaller one by electrical motors.

Electrical power is taken from the public grid or generated on-site.

The steam is supplied by boiler plants, cogeneration plants or is produced in waste heat boilers using energy from ammonia, nitric acid or sulphuric acid production.

For detailed information on generation of steam and electrical power, see [10, European Commission, 2005].

1.2.3.1 Steam turbines and steam grid

Figure 1.5 shows an example for a steam system (or steam grid) on a fertiliser plant. The steam extracted from the turbines is used to provide process steam at required pressures. Major examples for steam turbine driven equipment are:

- the synthesis gas compressor of the ammonia plant
- refrigeration compressors
- the CO_2 compressor of the urea plant
- the air compressors of the sulphur burner in sulphuric acid plants.

Condensing turbines (in Figure 1.5 marked with a cross) are used to balance the load on the different steam headers. Reduction of pressure without generating power is generally avoided, however, to take care of power/steam mismatches, startup conditions and emergencies, a system for pressure reduction and de-superheating ("PRDS valve") is installed.

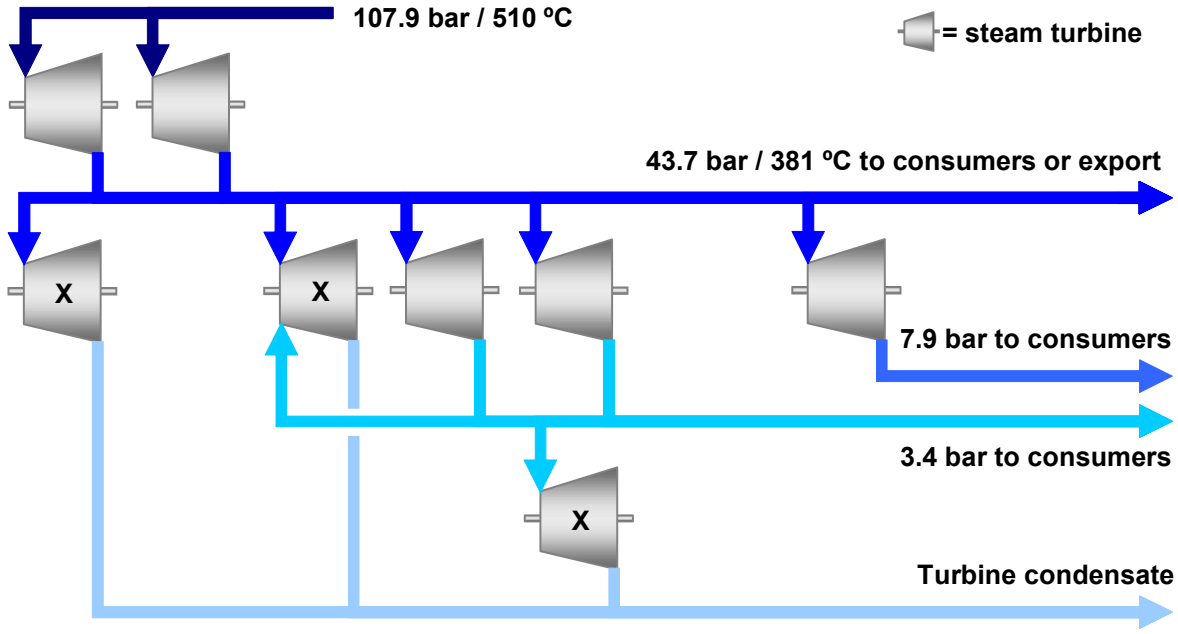

Figure 1.5: Example for a steam system (or steam grid) on a fertiliser plant
In this example, 360 tonnes/hour steam are provided by the ammonia plant.
The figure is based on [163, Haldor Topsoe, 2001]

1.2.3.2 Exporters and consumers on an integrated production site

Table 1.5 gives an overview of net exporters and consumers of energy in an integrated production site.

Exporters	Potential for export, depending on design	Potential for autothermal operation	Consumers
H_2SO_4 HNO_3	NH_3 AN neutralisation/ evaporation	Phosphate rock digestion (for H_3PO_4, SSP/TSP, NPK) AN granulation	NH_3 Urea H_3PO_4 evaporation AN evaporation HF Rock grinding Finishing sections (granulation, prilling, drying, cooling)

Table 1.5: Overview of net exporters and net consumers of energy on an integrated site

1.3 Overview of emissions and consumption levels

For emissions from specific production, please see Sections X.3 of this document.

1.4 Common techniques to consider in the determination of BAT

This section sets out techniques considered generally to have potential for achieving a high level of environmental protection in the industries within the scope of the document. Management systems, process-integrated techniques and end-of-pipe measures are included, but a certain amount of overlap exists between these three when seeking the optimum results.

Prevention, control, minimisation and re-cycling procedures are considered as well as the re-use of materials and energy.

Techniques may be presented singly or as combinations to achieve the objectives of IPPC. Annex IV to the Directive lists a number of general considerations to be taken into account when determining BAT and techniques within this chapter will address one or more of these considerations. As far as possible a standard structure is used to outline each technique, to enable comparison of techniques and an objective assessment against the definition of BAT given in the Directive.

The content of this section is not an exhaustive list of techniques and others may exist or be developed which may be equally valid within the framework of BAT.

Generally, a standard structure is used to outline each technique, as shown in Table 1.6:

Type of information considered	Type of information included
Description	Technical description of the technique
Achieved environmental benefits	Main environmental impact(s) to be addressed by the technique (process or abatement), including emission values achieved and efficiency performance. Environmental benefits of the technique in comparison with others
Cross-media effects	Any side-effects and disadvantages caused by implementation of the technique. Details on the environmental problems of the technique in comparison with others
Operational data	Performance data on emissions/wastes and consumption (raw materials, water and energy). Any other useful information on how to operate, maintain and control the technique, including safety aspects, operability constraints of the technique, output quality, etc.
Applicability	Consideration of the factors involved in applying and retrofitting the technique (e.g. space availability, process specific)
Economics	Information on costs (investment and operation) and any possible savings (e.g. reduced raw material consumption, waste charges) also as related to the capacity of the technique
Driving force for implementation	Reasons for implementation of the technique (e.g. other legislation, improvement in production quality)
References to literature and example plants	Literature for more detailed information on the technique. Reference to a plant where the technique is reported to be used

Table 1.6: Information breakdown for each technique described in this section

1.4.1 Increase process integration (1)

Description

In the example plant, the integration of the nitric acid and the AN plant has been increased (for an overview of nitric acid production, see Section 3.2; for an overview of AN production, see Section 9.2). The following measures have been realised:

- gaseous (superheated) NH_3 is a common raw material, both plants can share one NH_3 vapouriser, operated with process steam from the AN plant
- LP steam available in the AN plant can be used heating boiler feed-water (BFW) from 43 ºC to about 100 ºC through two heat exchangers (see Figure 1.6)
- the hot BFW can then also be used to preheat the tail gas of the nitric acid plant
- process condensate from the AN plant is recycled to the absorption column of the nitric acid plant.

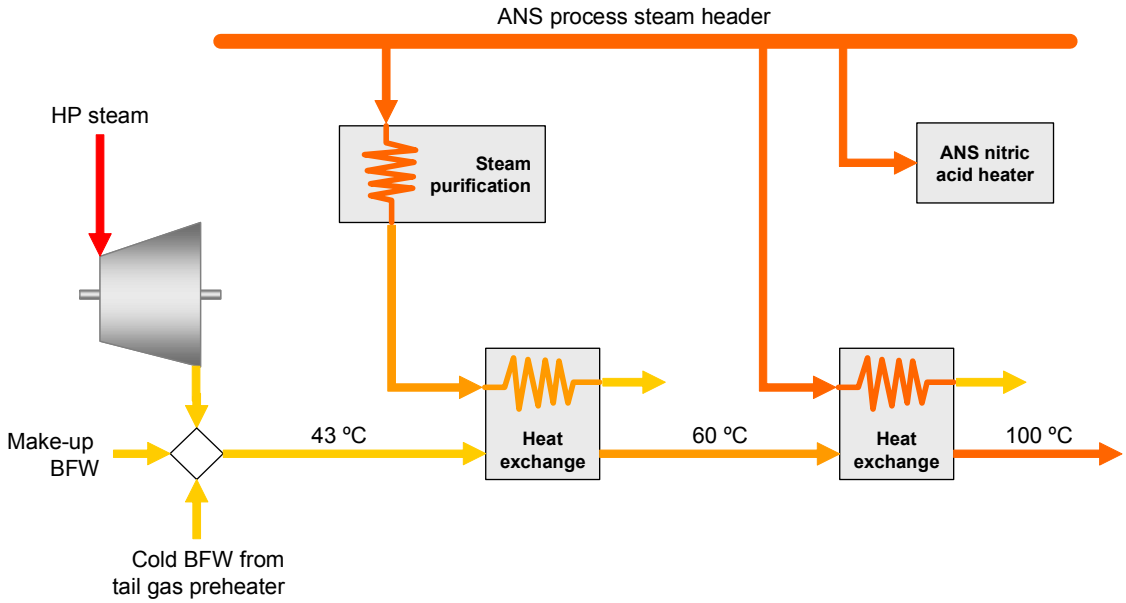

Figure 1.6: Heating of BFW with steam from the AN plant
[140, Peudpièce, 2006]

Achieved environmental benefits

- improved energy efficiency
- reduced emissions to water
- savings in demineralised water.

Cross-media effects

None believed to be likely.

Operational data

No information provided.

Applicability

Generally applicable. Especially applicable where processes are interdependent anyway. However, the options for improvement will depend on the particular case.

On an integrated site, it has to be considered that changes in one plant might affect parameters of other plants. This applies also to changes with environmental driving forces [154, TWG on LVIC-AAF, 2006].

Economics

Cost benefits through:

- improved energy efficiency
- less consumption of demineralised water
- lower investment by using a common ammonia vapouriser.

In the example, savings in operation costs of more than EUR 1000000/year are achieved.

Driving force for implementation

Cost benefits and reduced emissions to water.

References to literature and example plants

[140, Peudpièce, 2006], Grande Paroisse, Rouen

1.4.2 Increase process integration (2)

Description

On the example fertiliser site, the off-gases from the primary and secondary decomposers of the urea plant contain NH_3 and CO_2. ***In the former configuration***:

- after removal of CO_2 in MEA solution, NH_3 was recycled to the process. For recycling, the NH_3 vapours are cooled and compressed to 18.6 bar using water cooled condensers and two reciprocating compressors

- at the same time, in the NPK plant, NH_3 at 0 ºC is drawn from storage and vapourised to 5.9 bar using LP steam and used for neutralisation of H_3PO_4.

In the new configuration NH_3 is compressed to 5.9 bar only in the urea section and then exported from the urea to the NPK section.

Achieved environmental benefits

- reduced consumption of electric power for compression
- LP savings.

Cross-media effects

None believed to be likely.

Operational data

No information provided.

Applicability

Generally applicable. However, the options for improvement will depend on the particular case.

On an integrated site, it has to be considered that changes in one plant might affect parameters of other plants. This applies also to changes with environmental driving forces [154, TWG on LVIC-AAF, 2006].

Economics

Cost benefits. Payback time: 2 months.

Driving force for implementation

Cost benefits.

References to literature and example plants

[173, GreenBusinessCentre, 2002]

1.4.3 Handling excess steam

Description

Steam at various pressures is used and generated on an integrated production site for heating requirements and for driving various mechanical equipment. Depending on the specific production site, excess steam might be generated. This is handled according to the following priorities:

1. generally, avoid pressure reduction without using the energy
2. try and adjust the whole steam system in order to minimise excess steam generation by minimising the overall consumption
3. use of excess steam on-site or off-site
4. as a last option, using steam for generating only electrical power, if local factors prevent the use of excess thermal energy on-site or off-site.

For an example of using LP steam for cooling, see Section 9.4.2 "Recovery of residual heat for chilling process water".

Achieved environmental benefits

- reduced energy consumption.

Cross-media effects

None believed to be likely.

Operational data

No information provided.

Applicability

Generally applicable.

Economics

No information provided, but cost benefits can be assumed.

Driving force for implementation

Reduced energy consumption and cost benefits.

References to literature and example plants

[154, TWG on LVIC-AAF, 2006]

1.4.4 Replacing old PRDS valves

Description

Reduction of steam pressure without generating power is generally avoided, however, to take care of power/steam mismatches, startup conditions and emergencies, a system for pressure reduction and de-superheating ("PRDS valve") is installed.

The former PRDS valve needed to be maintained with a minimum flow of 150 kg/hour, so that the valve opens immediately when required. This flow caused erosion of the valve internals leading to a even higher steam flow, and resulted ultimately in a continuous venting of steam.

The new PRDS system with drag type valves only requires a flow of 20 kg/hour to ensure quick opening and erosion is reduced drastically.

Achieved environmental benefits

- reduced energy consumption.

Cross-media effects

None believed to be likely.

Operational data

No information provided.

Applicability

Generally applicable.

Economics

Cost benefits. Payback time: 8 months.

Driving force for implementation

Cost benefits.

References to literature and example plants

[173, GreenBusinessCentre, 2002]

1.4.5 Optimisation/maintenance of vacuum pumps

Description

Various vacuum pumps are used on a fertiliser production site. The selection of the right size and maintenance are essential for achieving efficient operation.

In the example, two vacuum pumps of 500 m^3/hour capacity and 0.3 bar vacuum were in use, one with valve throttling. The capacity had decreased due to uneven wearing and the vacuum line joints were found to be leaking. After maintenance, the vacuum is produced with only one pump.

Achieved environmental benefits

- reduced energy consumption
- in the simple example, a saving of 15 kW was achieved.

Cross-media effects

None believed to be likely.

Operational data

No information provided.

Applicability

Generally applicable.

Economics

Cost benefits can be assumed.

Driving force for implementation

Cost benefits.

References to literature and example plants

[173, GreenBusinessCentre, 2002]

1.4.6 Mass balances

Description

Mass balances are important tools for understanding a complex production site and the development of priorities for improvement strategies. Mass balances for the following items are considered:

- nutrients: nitrogen (e.g. raw materials, products, NH_3 emissions, scrubbing liquors)
- nutrients: P_2O_5 (e.g. raw materials, products, dust emissions, phosphogypsum)
- steam (including pressures and temperatures)
- water (e.g. BFW, cooling water, process water, condensates, scrubbing liquors)
- CO_2 (for an example, see Table 1.7)
- raw material input (e.g. use of lime arising from the CNTH conversion for CAN production).

	Input [x]	Output [x]		
		For re-use	Released	
Ammonia plant 1			203.9	From heating
		348.8		
Ammonia plant 2			72.9	From heating
			75.8	From CO_2 desorption
		97.2		
CO_2 plant	57.1			
ODDA plant	63.1		5.7	
Urea plant	279.1			
Melamine plant		66.9	25.1	
		Total released	**383.4**	
[x] levels in 1000 tonnes CO_2 per year				

Table 1.7: Example for a CO_2 balance
This table is based on Figure 4 of [9, Austrian UBA, 2002]

An example of a water balance for the production of NPK fertilisers is given in [9, Austrian UBA, 2002].

Achieved environmental benefits

- enables the development of improvement strategies.

Cross-media effects

None believed to be likely.

Operational data

No information provided.

Applicability

Generally applicable.

Economics

Additional costs for monitoring and establishing/maintaining data sets. Cost benefits from implemented improvement.

Driving force for implementation

Cost benefits.

References to literature and example plants

[9, Austrian UBA, 2002]

1.4.7 Recovery of NO_x from exhaust gases

Description

In the example plant (production of explosives), NO_x is recovered from exhaust gases from the reaction, feed tanks, centrifugation and buffers by scrubbing (see Figure 1.7). The first three absorption towers are operated with water, the last with H_2O_2. H_2O_2 is used to oxidise NO:

$$NO + NO_2 + 2\ H_2O_2 \rightarrow 2\ HNO_3 + H_2O$$

$$2\ NO_2 + H_2O_2 \rightarrow 2\ HNO_3$$

This improves the absorption efficiency drastically and the emitted NO_x consists of >98 % NO_2.

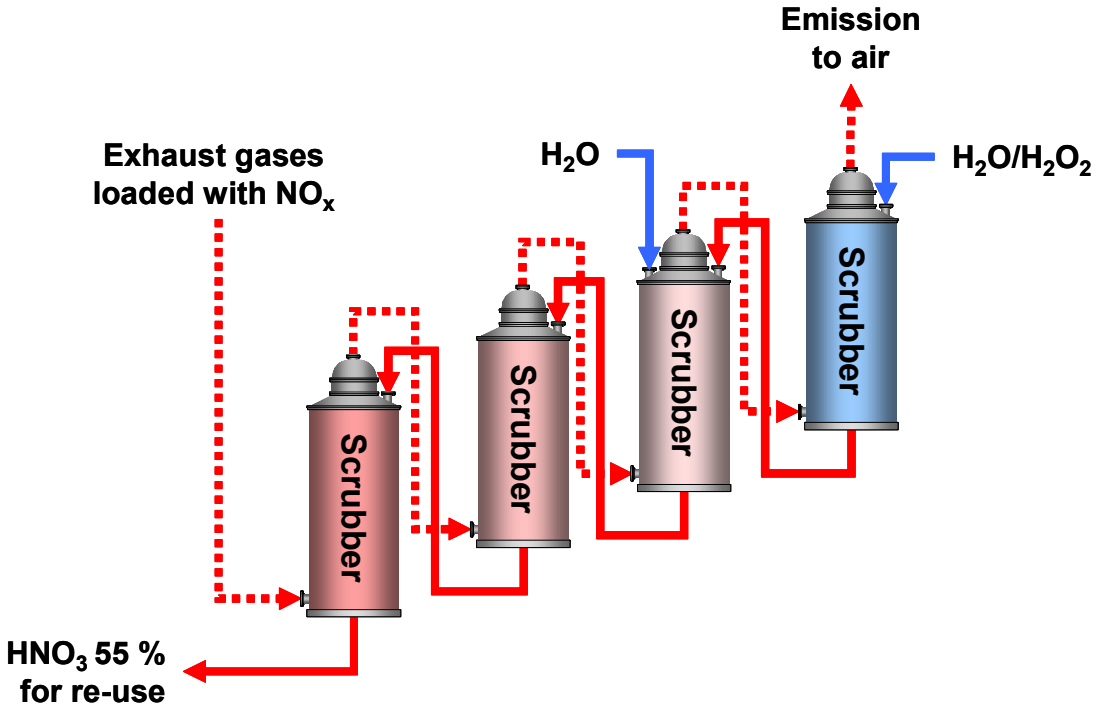

Figure 1.7: Recovery of NO_x from exhaust gases with a scrubber cascade

Achieved environmental benefits

- efficient recovery of NO_x from exhaust gases
- emission levels of 113 – 220 mg/Nm^3 have been achieved.

Cross-media effects

Energy and H_2O_2 consumption.

Operational data

Operational data of the example:

- volume flow to scrubber cascade: 7700 m^3/hour
- scrubbing medium in the last scrubber: H_2O_2 15 %.

Applicability

Especially applicable in cases where even sophisticated scrubbing systems do not achieve comparable emission levels. However, the only information provided about the application of H_2O_2 for NO_x recovery in the LVIC-AAF industries relates to the manufacture of nitric acid, see Section 3.4.10.

Economics

No specific information provided. Additional costs for H_2O_2, benefits from the recovery of N compounds.

Driving force for implementation

See "Achieved environmental benefits".

References to literature and example plants

[15, Ullmanns, 2001, 153, European Commission, 2006]. Two example plants (production of explosives) apply this technique for recovery of NO_x from various exhaust gases.

1.4.8 Techniques described elsewhere in this document

Description

A number of techniques considered for the determination of product specific BAT have potential for a wider applicability within the LVIC-AAF industries:

- Section 2.4.6 “Energy audits”
- Section 2.4.7 “Advanced process control”
- Section 2.4.10 “SNCR at the primary reformer”
- Section 2.4.12 “Preheating of combustion air”
- Section 2.4.23 “Low NO_x burners”
- Section 3.4.9 “Selective catalytic reduction of NO_x (SCR)”
- Section 4.4.13 “Maintaining heat exchanger efficiency”
- Section 8.4.13 “Monitoring of key performance parameters”.

Achieved environmental benefits

See the referenced sections.

Cross-media effects

See the referenced sections.

Operational data

See the referenced sections.

Applicability

See the referenced sections.

Economics

See the referenced sections.

Driving force for implementation

See the referenced sections.

References to literature and example plants

See the referenced sections.

1.4.9 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, i.e.:

- 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.e.:

(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 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, i.e.:

- 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, i.e.:

- 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.

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 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 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 force 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)

1.5 Common BAT

In understanding this section 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 sector
- examination of the techniques most relevant to address these key issues
- identification of the best environmental performance levels, on the basis of the available data in the European Union and worldwide
- examination of the conditions under which these performance levels were achieved; such as costs, cross-media effects, and the main driving forces involved in implementation of the 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 the 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 chapter. These give a rough indication about the magnitude of the 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 BAT reference documents 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.

1.5.1 Common BAT for the LVIC-AAF industries

For a specific production, BAT is to apply the specific BAT given in the specific Sections X.5.

BAT is to carry out regular energy audits for the whole production site (see Sections 1.4.8).

BAT is to monitor key performance parameters and to establish and to maintain mass balances (see Sections 1.4.6 and 1.4.8) for:

- nitrogen
- P_2O_5
- steam
- water
- CO_2.

BAT is to minimise energy losses by (see Section 1.4.3).

- generally, avoiding steam pressure reduction without using the energy
- adjusting the whole steam system in order to minimise excess steam generation
- using excess thermal energy on-site or off-site
- as a last option, using steam for generating only electrical power, if local factors prevent the use of excess thermal energy on-site or off-site.

BAT is to improve the environmental performance of the production site by a combination of the following techniques:

- recycling or re-routing mass streams (for examples, see Sections 1.4.1 and 1.4.2)
- efficiently sharing equipment (for an example, see Section 1.4.1)
- increasing heat integration (for an example, see Section 1.4.1)
- preheating of combustion air (see Section 1.4.8)
- maintaining heat exchanger efficiency (see Section 1.4.8)
- reducing waste water volumes and loads by recycling condensates, process and scrubbing waters (for an example, see Sections 1.4.1)
- applying advanced process control systems (see Section 1.4.8)
- maintenance (for examples, see Sections 1.4.4 and 1.4.5).

1.5.2 BAT for 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 Section 1.4.9)

- 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.

2 AMMONIA

2.1 General information

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.

In 2003, the world production capacity was 109 million tonnes ammonia. Most of the production capacity was located in the following regions [2, IFA, 2005]:

- Asia (46 % of world capacity)
- East Europe and central Asia (14 %)
- North America (11 %)
- West Europe (9 %), with this share falling from a level of 13 % in 1988
- Middle East (7 %)
- Latin America (6 %)
- Central Europe (4 %)
- Africa (1 %)
- Oceania (1 %).

In 1974, the developing countries accounted for 27 % of ammonia capacity. By 1998, their share had increased to 51 %. In these countries, ammonia is used to produce urea for rice growing.

A modern ammonia plant has a typical capacity of 1000 – 2000 tonnes/day and new plants are commonly designed for up to 2200 tonnes/day. The European Union's ammonia industry produces approximately 11 million tonnes ammonia per year (2001), from around 50 plants. Data on the location of these plants, their capacity, age and the type of feedstock used, are given in Table 2.1.

With rising feedstock prices and hard competition in the market, many producers have looked for possibilities to "revamp" or modernise their older, less efficient plants so that they can stay competitive. Most revamp projects have been combined with a moderate capacity increase because some of the original equipment was oversized and only specific bottlenecks had to be eliminated, not entailing excessive cost. As the market possibilities for a company do not increase in steps of 1000 or 1500 t/day but slowly and continuously, such a moderate capacity addition involves less risk and is more economical than building a new plant.

For integration of ammonia production with other production, see Chapter 1.

	Location	Company	Capacity (t/d)	First commissioned	Status	Feedstock
AT	Linz	AMI	1000 520	1974 1967	Rev. 1987 – 1990	NG NG
BE	Antwerp	BASF	1800	1991		
	Tertre	Kemira GrowHow	1200	1968	Rev. 1996/04	NG
CZ	Litvinov	Chemopetrol	1150	1972		NG
EE	Kothla-Jarve	Nitrofert	500	1979		NG
FR	Grandpuits	Grande Paroisse	1150	1970		NG
	Rouen	Grande Paroisse	1150	1969	Rev.	NG
	Gonfreville	Yara	1000	1969		NG
	Pardies	Yara	450	1961		NG/Hydrogen
	Ottmarsheim	Pec Rhin-BASF	650	1967 – 1968	Rev. 1996	NG
DE	Ludwigshafen	BASF	1200/1360	1971/1982		NG
	Köln	Innovene	900	1969 – 1970	Rev.	NG
	Brunsbüttel	Yara	2000	1978	Rev. 1989	Vacuum residues
	Lutherstadt Wittenberg	SKW Piesteritz	2 x 1650	1974 – 75	Rev.	NG
	Gelsenkirchen	Ruhr Öl GmbH	1250	1973		Vacuum residues
EL	Thessaloniki	EKO Chemicals A.E.	400	1966/1976		Naphtha
	Nea Karvali	Phosphoric Fert Industry	400	1986		NG
HU	Pétfürdo	Nitrogénművek Rt.	1070	1975		NG
IT	Ferrara	Yara	1500	1977		NG
	Nera Montoro	Yara	400	1970		NG
LT	Jonava	Achema	1400	1978		NG
LV	Krievu sala	Gazprom	1770			
NL	Geleen	DSM Agro BV	1360/1360	1971/1984		NG
	Sluiskil	Yara	C: 900	1971	Rev.	NG
			D: 1500	1984		NG
			E: 1750	1987		NG
PL	Pulawy	Zaklady Azotowe Pulawy	2 x 1340	1966		NG
	Police	POLICE	2 x 750	1985		NG
	Kedzierzyn	ZAK	500	1954		NG
	Wloclawek	ANWIL	750	1972		NG
	Tarnów	ZAK	530	1964		NG
PT	Barreiro	Quimigal Adubos S.A.	900	1984	Rev. planned	Residues[(a)]
ES	Sabinanigo	Energía e Industrias Aragonesas	40	1925	Rev. 1980/95	H_2 and N_2 [(b)]
	Palos	Fertiberia S.A.	1130	1976	Rev. 1986/89	NG
	Puertollano	Fertiberia S.A.	600	1970	Rev. 1988/92	NG
SK	Sala Nad Vahom	Duslo	1070	1990		NG
UK	Billingham, Cleveland	TERRA Nitrogen	1150[(c)]	1977		NG
	Severnside	TERRA Nitrogen	2 x 400	1988		NG
	Ince, Cheshire	Kemira GrowHow	1050	1970	Rev.	NG
	Hull	Kemira GrowHow	815	1989		H_2 and N_2 [(b)]

NG Natural gas
Rev. Revamped
[(a)] visbreaker residues, vacuum residues
[(b)] from other plant
[(c)] name plate capacity, current ~1500

Table 2.1: Ammonia production plants in the European Union
Based on [3, European Commission, 1997]

2.2 Applied processes and techniques

Note: process parameters presented in the following sections, such as temperatures and pressures, might deviate in specific cases.

2.2.1 Overview

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 fossil fuels. Depending of the type of fossil fuel, two different methods are mainly applied to produce the hydrogen for ammonia production: steam reforming or partial oxidation.

For a detailed description of conventional steam reforming, see Section 2.2.3.
For a detailed description of partial oxidation, see Section 2.2.4.
About advanced conventional steam reforming, processes with reduced primary reforming, and heat exchange autothermal reforming, see Sections 2.4.1, 2.4.2, 2.4.3.
For a description of ammonia production using water electrolysis, see Section 2.4.26.

As it can be seen from Table 2.2, currently, about 80 % of the ammonia production capacity worldwide is provided by the well-developed steam reforming 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
Water	Water electrolysis	0.5

Table 2.2: Applied processes and feed stocks in the production of ammonia
The third column shows the related share of world capacity (1990)
[3, European Commission, 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 2.3 suggest that, compared to the steam reforming process, there is a potential for improvement of the energy efficiency of partial oxidation processes.

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

Table 2.3: Cost differences and total energy demands for ammonia production
[3, European Commission, 1997]

2.2.2 Output from ammonia production

2.2.2.1 Ammonia

A typical size for a single stream ammonia production plant is 1000 – 1500 tonnes/day (300000 – 500000 tonnes/year) [1, EFMA, 2000]. The product is stored if not utilised.

Commercial anhydrous ammonia has two grades of purity:

- anhydrous ammonia min. 99.7 wt-%, water content approximately 0.2 wt-%
- anhydrous ammonia min. 99.9 wt-%.

2.2.2.2 Carbon dioxide

Carbon dioxide is produced in accordance with stoichiometric conversion and can be recovered for further use as feedstock in a urea plant, for use in fertiliser production (ODDA process) and/or methanol production or liquefaction, 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 – 1.40 kg/kg NH_3, dependent on the degree of air reforming (the figures do not include carbon dioxide in the combustion gases). 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.

In ***partial oxidation*** of residual oils, CO_2 production is 2 – 2.6 kg/kg NH_3, dependent on the feedstock C/H ratio [1, EFMA, 2000].

2.2.2.3 Sulphur

In partial oxidation, 87 – 95 % of the sulphur content of the gasifier feed is recovered in a Claus unit.

2.2.2.4 Steam

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.

2.2.3 Conventional steam reforming

Figure 2.1 gives an overview of conventional steam reforming. The individual process stages are described in the following subsections.

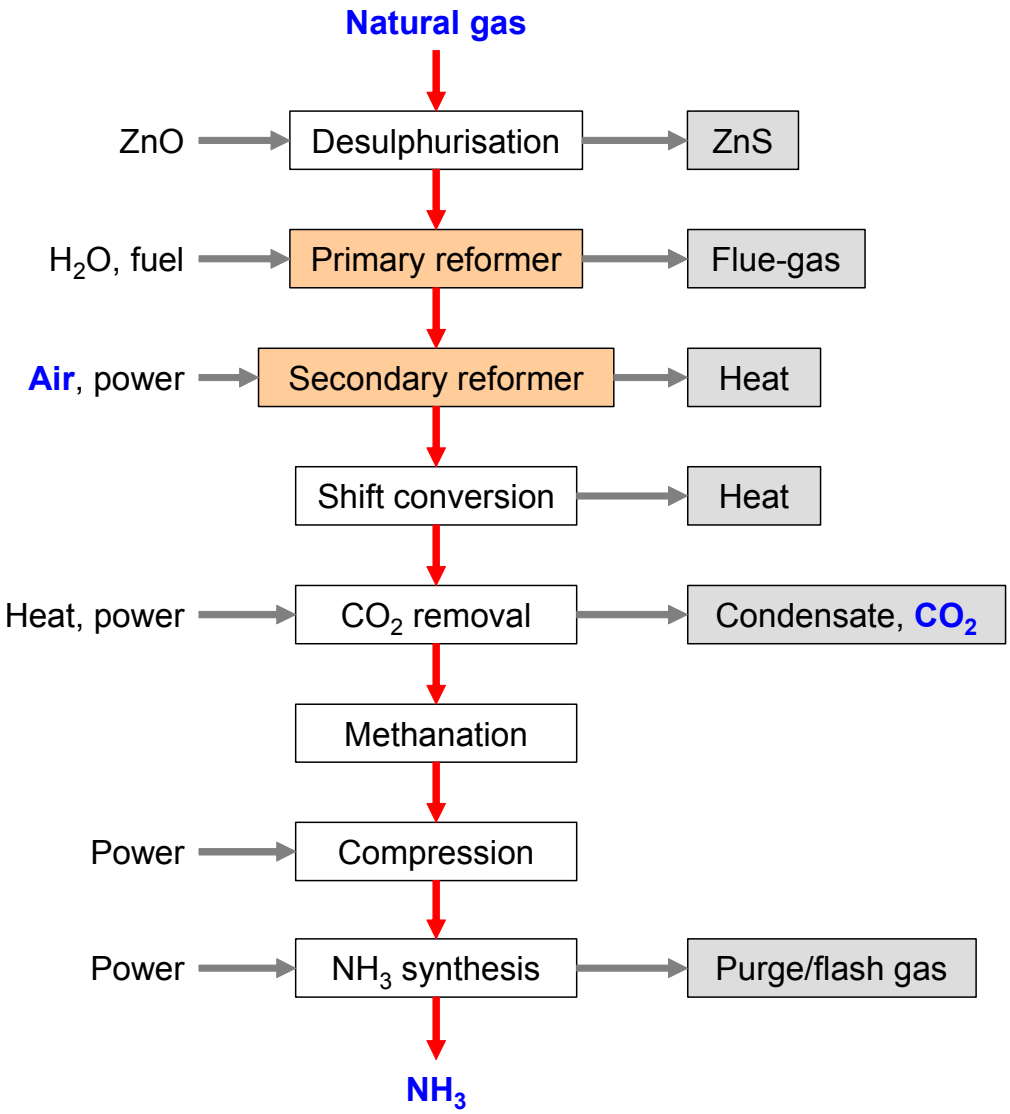

Figure 2.1: NH_3 production by conventional steam reforming
[1, EFMA, 2000]

2.2.3.1 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 concentration of less than 0.15 mg S/Nm^3 feed gas. 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 = alkyl group):

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

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

2.2.3.2 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:

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

Gas from the desulphuriser is mixed with steam and the preheated mixture enters the primary reformer at a temperature in the range of 400 – 600 °C.

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 pre-reformer 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.

About half of the heat is utilised for the reforming reaction, the rest remains in the flue-gas and is utilised in the convection section of the reformer to preheat several process streams.

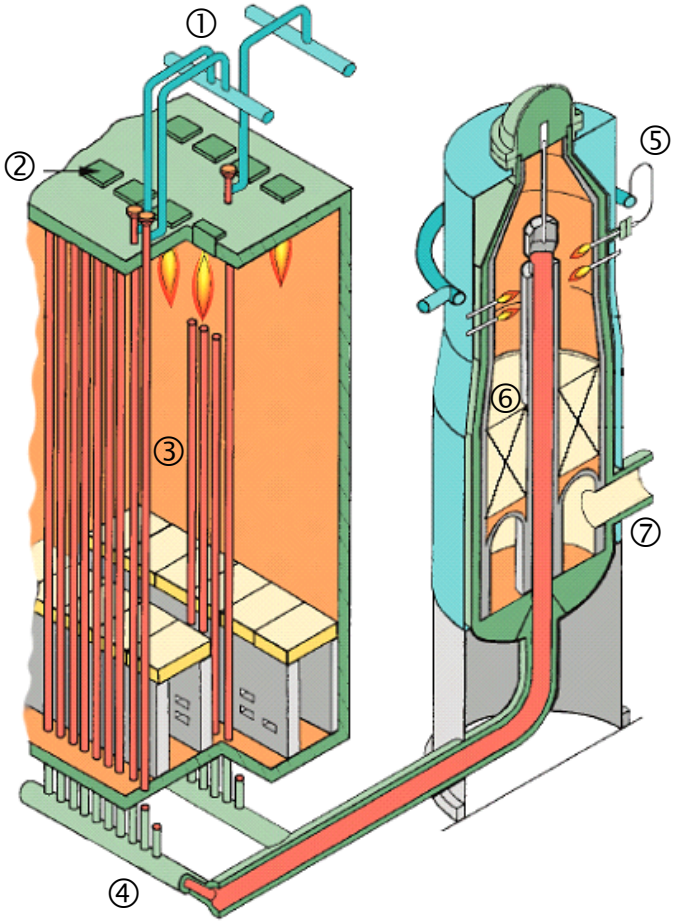

Figure 2.2: Example of a reformer radiant section and a secondary reformer
① inlet manifold, ② burners, ③ reformer tubes, ④ outlet manifold, ⑤ process air inlet, ⑥ catalyst bed, ⑦ gas outlet
[12, Uhde, 2004]

2.2.3.3 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 catalysts containing nickel.

The process air is compressed and heated in the primary reformer convection section to around 500 – 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 approximately 1000 °C. Heat is removed in a waste heat steam boiler, a superheater/boiler or a boiler/preheater, cooling the gas to approximately 330 – 380 °C.

2.2.3.4 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 350 – 380 °C and then over a copper oxide/zinc oxide catalyst at approximately 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.

2.2.3.5 CO_2 removal

This process step removes the CO_2 from the reaction gas and the quantity corresponds to nearly all the carbon introduced as feed gas into the overall process. The residual CO_2 content is usually in the range of 50 – 3000 ppmv. 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. Table 2.4 gives an overview.

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
Processes with 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 2.4: Overview of some CO_2 removal processes
[4, European Commission, 2000]

2.2.3.6 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:

$$CO + 3H_2 \rightarrow CH_4 + H_2O \quad \Delta H = -206 \text{ kJ/mol}$$
$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \quad \Delta H = -165 \text{ kJ/mol}$$

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.

2.2.3.7 Compression

Modern ammonia plants use centrifugal compressors to pressurise the synthesis gas to the required level (100 – 250 bar, 350 – 550 °C) for ammonia synthesis. Molecular sieves are sometimes 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.

2.2.3.8 NH_3 synthesis

The synthesis of ammonia takes place on an iron catalyst at pressures usually in the range of 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 a lower energy consumption to be achieved (see Section 2.4.17).

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, inerts and unreacted gases. The size of this purge stream controls the level of inerts in the loop, keeping these to approximately 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.

2.2.3.9 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 in most cases energy is exported 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.

2.2.4 Partial oxidation

The partial oxidation process is used for the gasification of heavy feedstocks such as residual oils and coal. Figure 2.3 gives an overview of the process steps. 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. Ammonia plants which incinerate waste require compliance with the waste incineration Directive 76/2000/EC and the emissions of dioxins may be a concern.

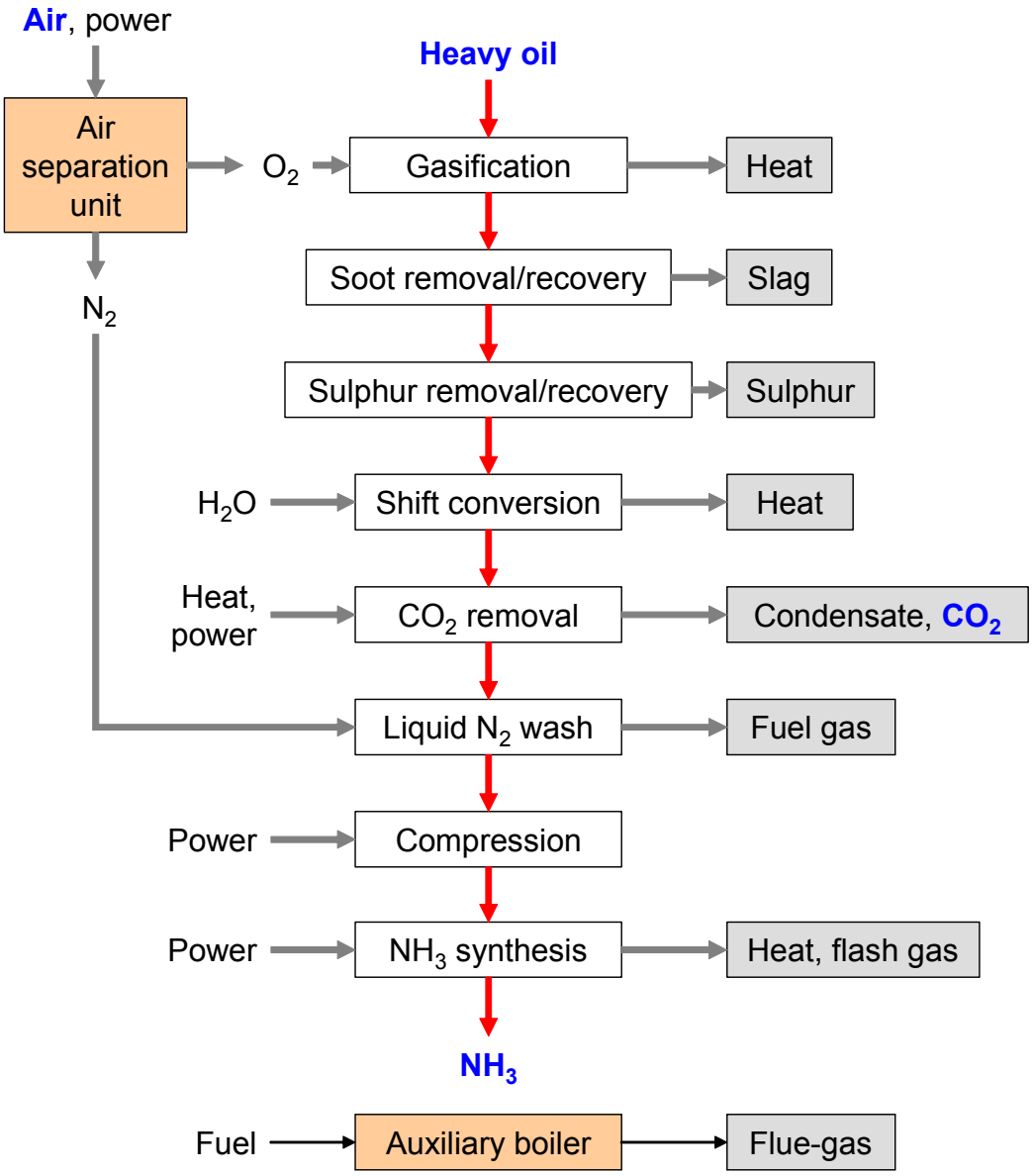

Figure 2.3: NH_3 production by partial oxidation
[1, EFMA, 2000]

2.2.4.1 Air separation plant

The air separation plant 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.

2.2.4.2 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 approximately 3 – 5 % CO_2, approximately 0.2 % CH_4 and 0.5 % soot depending on the quality of the feedstock. 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.

2.2.4.3 Soot removal

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 of after a biological treatment. A paste containing vanadium and nickel is recovered and sold to the metallurgical industry.

2.2.4.4 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, containing 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.

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:

$$C + ½\ O_2 \rightarrow CO \qquad \Delta H_o = -100.6\ kJ/mol$$
$$C + H_2O \rightarrow CO + H_2 \qquad \Delta H_o = 175.4\ kJ/mol$$

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.

2.2.4.5 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.

2.2.4.6 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 of between 2 and 3 % can be attained. Over the past twenty years, sulphur resistant catalysts containing cobalt-molybdenum 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.

2.2.4.7 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.

2.2.4.8 Liquid nitrogen wash

For the final purification, normally liquid nitrogen at approximately -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 and H_2O are separated from the inlet gas by molecular sieve adsorption. The resulting synthesis gas is very pure and purging in the synthesis loop is minimised. The rejected waste gas fraction serves as a fuel.

2.2.4.9 Ammonia synthesis

The ammonia synthesis loop is identical to the synthesis for steam reforming, see Section 2.2.3.8.

2.2.4.10 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 air, oxygen needed in the gasifier, nitrogen used in the liquid nitrogen wash, ammonia used in the refrigeration system, and the make-up gas and recycle gas in the ammonia synthesis loop. Steam turbines and occasionally electrical energy are used to drive these compressors.

2.2.5 Startup/shutdown and catalyst replacement

Startup/shutdown operations, trip-conditions, leaks and fugitive sources cause periodic emissions. The initial startup 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 startup or trips is estimated to be 10 – 20 kg/hour as NO_2 [3, European Commission, 1997]. The ammonia plant is started up in stages. Nitrogen, heated by a 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 startup heater. The full startup sequence may take one or two days. Shutdown is a reverse of the startup procedure. Ammonia plants tend to run continuously for extended periods of time with only minor interruptions that require a partial shutdown. Shutdown due to technical failure happens on average 5.7 times per year. These procedures need atmospheric venting of large volumes of gases. The flows are usually less than half the full capacity flowrate. The main pollution control issue is how to dispose of these gases. One practice is to vent at 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.

All the ***catalysts*** in the plant require ***replacement*** at the end of their useful life. The life of each catalyst varies considerably with plant design [7, UK EA, 1999]. 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.

2.2.6 Storage and transfer equipment

For more detailed information about storage of bulk and dangerous materials, including specific information on storage of ammonia, see [5, European Commission, 2005] and references within.

Liquefied ammonia from production plants is either used directly in downstream plants or transferred to storage tanks.

Ammonia is usually stored by using one or other of the following methods [1, 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 approximately 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.

2.3 Current emission and consumption levels

2.3.1 Energy consumption

Table 2.6 shows the reported energy consumption levels for the production of ammonia. An example for the breakdown of energy flow is indicated in Table 2.5.

Energy flow	Share %
Product ammonia	71.9
Unrecovered process heat	10.5
Air compressor turbine	7.8
Syngas compressor turbine	5.7
Flue-gas heat	2.4
Refrigeration compressor turbine	1.8
Miscellaneous	0.6
Overall	**100**

Table 2.5: Example for energy flows in an ammonia production plant (1350 tonnes/day, fired primary reformer) [13, Barton and Hunns, 2000]

2.3.1.1 Comparison of energy consumption figures

The comparison of energy consumption figures without precise knowledge of design and evaluation criteria can be misleading. First, the state of the ammonia product should be noted. Relative to the delivery of liquid ammonia to battery limits at ambient temperature, the production of 3 bar ammonia vapour at the same temperature would save 0.6 GJ/tonne NH_3, while delivery as liquid at -33 °C would need an extra 0.3 GJ/tonne NH_3. The temperature of the available cooling medium has a considerable influence. Increasing the cooling water temperature from 20 to 30 °C increases energy consumption by 0.7 GJ/tonne NH_3. A detailed energy balance, listing all imports and exports, together with the caloric conversion factors used for steam and power is needed for a fair comparison of plants. Additionally, energy export can have a beneficial effect on the net energy consumption. Gas composition is also of some importance. Nitrogen content is marginally beneficial: 10 mol % nitrogen leads to a saving of about 0.1 GJ/tonne NH_3, whereas a content of 10 mol % carbon dioxide would add 0.2 GJ/tonne NH_3 to the total consumption value [15, Ullmanns, 2001].

Production process	Feedstock	Fuel	Net	Remark	Source
	GJ(LHV)/tonne NH_3				
Steam reforming in general	22 – 25	4 – 9			[6, German UBA, 2000] and references within to [48, EFMA, 1995] (updated in 2000)
			29.3		
			32 – 35		
			28.8 – 31.5		[1, EFMA, 2000]
			33.4	Before energy optimisation (1350 tonnes/day, commissioned in 1993). After implementation of improvement schemes: estimated 29.4 GJ/tonne	[13, Barton and Hunns, 2000]
			30.6	After revamp (1100 tonnes/day, commissioned 1971)	[14, Austrian Energy Agency, 1998]
			27.6 – 30.1	Depending on local conditions, e.g. cooling water temperature	[12, Uhde, 2004]
			31.5	IFFCO Aonla Unit 1	[26, Dipankar Das, 1998]
			31.0	Tata Fertilizers, Babrala	
			32.7	Nagarjuna Fertilizers	
Conventional steam reforming	22.1	7.2 – 9.0			[1, EFMA, 2000]
Advanced conventional processes			29.2	Major characteristics: CO_2 removal with improved solvents Indirect cooling of the ammonia reactor Use of smaller catalyst particles Preheating of combustion air Hydrogen recovery from purge gas of the ammonia reactor	[3, European Commission, 1997] [7, UK EA, 1999]
Reduced primary reforming	23.4	5.4 – 7.2			[1, EFMA, 2000]
	26	6 – 8			[6, German UBA, 2000]

Production process	Feedstock	Fuel	Net	Remark	Source
	GJ(LHV)/tonne NH_3				
			28.9	Major characteristics: CO_2 removal with improved solvents Indirect cooling of the ammonia reactor Use of gas turbine to drive process air compressor	[3, European Commission, 1997] [7, UK EA, 1999]
Heat exchange autothermal reforming	24.8	3.6 – 7.2			[1, EFMA, 2000]
	27.5	4 – 8			[6, German UBA, 2000]
			31.8[x]	Major characteristics: Low temperature desulphurisation Isothermal shift conversion Use of Co-promoted ammonia synthesis gas catalyst CO_2 removal systems with solid adsorbent Supplying process steam by feed gas saturation with process condensates	[3, European Commission, 1997]
Partial oxidation	28.8	5.4 – 9.0	35.1 – 37.8		[1, EFMA, 2000]
	29 – 34	6 – 20			[6, German UBA, 2000] and references within to [48, EFMA, 1995] (updated in 2000)
			36		
			39 – 42		
			38.7	Major characteristics: Claus unit Liquid nitrogen wash for final purification of synthesis gas from partial oxidation	[3, European Commission, 1997]
[x] The net energy consumption level is influenced by the site specific conversion factor for the imported electricity and plant throughput					

Table 2.6: Reported energy consumption levels for the production of ammonia

2.3.2 NO_x emissions

Table 2.7 shows the reported NO_x emission levels for the production of ammonia.

Production process	Emission levels			Remark	Source
	NO_x expressed as NO_2, dry gas				
	mg/Nm^3	ppmv	kg/t NH_3		
Steam reforming with fired primary reformer	200 – 400	98 – 195	0.6 – 1.3		[1, EFMA, 2000]
	142 – 162			Primary reformer equipped with SNCR, reduction efficiency 30 – 50 %, ammonia slip <1 – 5 mg/Nm^3	[9, Austrian UBA, 2002]
	470			Before 1992, without additional measures	DSM, Geleen (AFA-3)
	200			1992 – 2003, with SNCR	
	150 – 160			2003, replacement of all 12 convection burners with low NO_x burners	
	280			Achieved with SNCR	Kemira, Tertre
Steam reforming in general	200 - 400		0.6 – 1.3		[6, German UBA, 2000] and references within
	200		0.45	Estimated 10 – 20 kg NO_x/hour from flaring synthesis gas under startup or trip	
Advanced conventional processes	157		0.32	Ammonia removal from purge and flash gases in the ammonia synthesis section Low NO_x burners	[3, European Commission, 1997]
	155 129		0.315 0.286	Levels of 2000 and 2004. Low NO_X burners.	[33, VITO, 2005]

Production process	Emission levels			Remark		Source
	NO_x expressed as NO_2, dry gas					
	mg/Nm^3	ppmv	kg/t NH_3			
Reduced primary reforming	90		0.27	NO_x emission levels in the range of 0.3 kg/t are achieved only if air[x] preheating is carried out with waste gas from a gas turbine where low oxygen and high CO_2 concentrations exist. If considerable air preheating is applied and no gas turbine waste gases can be used, the NO_x emission is of the range of 130 mg/Nm^3 or 0.39 kg/tonne NH_3 Ammonia removal from purge and flash gases in the ammonia synthesis section Low NO_x burners		[3, European Commission, 1997]
Heat exchange autothermal reforming	80 % reduced emission compared to fired primary reforming					[1, EFMA, 2000]
	80		0.175 [xx]	Process air heater	Ammonia removal from purge and flash gases in the ammonia synthesis section	[3, European Commission, 1997]
	20			Auxiliary boiler		
Partial oxidation	< 700			Auxiliary boiler		[1, EFMA, 2000]
	560		1.04	Auxiliary boiler with low NO_x burner		[3, European Commission, 1997]
	185		0.41	Superheater with low NO_x burner		
	200 – 450			Superheater		
	350		0.056	Thermal post-combustion after Claus unit		
	200 – 450		0.2 – 0.5	Superheater		[6, German UBA, 2000]
	700		1.3	Auxiliary boiler		
	500		0.562	Superheater		[28, Comments on D2, 2004]
	900		334	Thermal post-combustion		

[x] the source does not specify if process or combustion air is preheated

[xx] total, including equivalent from electricity import

Table 2.7: Reported NO_x emission levels for the production of ammonia

2.3.3 Other consumption levels

Process			Unit	Remark	Reference
Process steam	Steam reforming	0.6 – 0.7	kg/kg NH_3	At stoichiometric conversion	[1, EFMA, 2000, 6, German UBA, 2000, 9, Austrian UBA, 2002]
		1.5		Total supply at a S/C ratio of 3.0	
		1.6		For each production line of Agrolinz Melamin	
	Partial oxidation	1.2		Total supply	
Process air	Conventional steam reforming	1.1	kg air/kg NH_3	Equal to 0.85 kg N_2/kg NH_3. The levels are 50 – 100 % higher for reduced primary reforming	
	Partial oxidation	4		Air fed to the air separation unit	
Boiler feed-water		0.7 – 1.5	kg/kg NH_3	Only the process steam consumption has to be replenished by outside water, assuming all steam condensates are recycled. The amounts depend 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	
Solvents	CO_2 removal	0.02 – 0.04	kg/tonne NH_3	Solvents are mainly losses by leaks. The level equals approx. 2 kg/hour for a typical capacity plant.	
Additives				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	
Catalyst replacement	Hydro-desulphurisation	1	m^3/year	Approximate consumption figures, based on average filling volumes and normally recommended operating periods, for a gas-based conventional reforming plant. The usage refers to a 1500 t/d capacity. Actual usage in existing and new plants may differ considerably	
	Sulphur removal	5			
	Primary reforming	5			
	Secondary reforming	4			
	High temperature shift	10			
	Low temperature shift	20			
	Methanation	2			
	Synthesis	10			

Table 2.8: Other reported consumption levels for the production of ammonia

2.3.4 Other emission levels

Table 2.9 shows other emission levels reported for the production of ammonia.

Parameter	Process	Emission level			Remark	Reference
		mg/Nm^3	kg/t NH_3	ppmv		
CH_4	From CO_2 desorption	10			Selexol process	[9, Austrian UBA, 2002]
CH_4		72			Benfield process	
CO		125				
CO		0.4			Selexol process	
SO_2	From primary reformer	<0.1			At sulphur levels of <0.5 mg/Nm^3 in the natural gas. With higher sulphur content in the natural gas, higher SO_2 levels can be expected	
SO_2	Gas based conventional primary steam reformer	0.1 – 2	<0.01		Depending on fuel, can be calculated by a mass balance	[1, EFMA, 2000]
CO		<10	<0.03			
CO_2			500		8 % in the flue-gas	
CO	Partial oxidation			30		
Dust		<50				
H_2S				0.3		
Methanol				<100		
CO	Partial oxidation, superheater	95	0.105	100		Yara, Brunsbüttel [28, Comments on D2, 2004]
Methanol		876	1.526			
H_2S		0.1				
SO_2		7				

Parameter	Process	Emission level			Remark	Reference
		mg/Nm^3	kg/t NH_3	ppmv		
Methanol	Partial oxidation, CO_2 removal			600		
SO_2	Partial oxidation, thermal post combustion	4500	1.676			
CO	Partial oxidation, thermal post combustion	100	0.034			Yara, Brunsbüttel
BOD	Partial oxidation, process condensate				80 mg/l, inlet of the treatment plant	[28, Comments on D2, 2004]
Particulates	Partial oxidation, superheater	10				[3, European Commission, 1997]
Methanol		140				
H_2S		0.5				
CO	Partial oxidation, superheater	7	0.016			
Methanol		94	0.210			
H_2S		0.3	0.001			
CO	Partial oxidation, auxiliary boiler	8	0.016		Low NO_x burners	
Particulates		4.3	0.008			
Hydrocarbons		9	0.017			
SO_2		1060	1.98			
SO_2	Partial oxidation, Claus unit				2 % of the S-content in fuel	
SO_2	Partial oxidation, thermal oxidiser after Claus unit	1340	2.18			
CO		5	0.001			
Particulates		4	0.008			
Hydrocarbons		9	0.001			
NH_3	Partial oxidation, emission to water		0.130			
Particulates	Primary reformer	5				

Parameter	Process	Emission level			Remark	Reference
		mg/Nm^3	kg/t NH_3	ppmv		
NH_3	Ammonia synthesis, after purge gas washer	75	0.040			
	Fugitive emissions				1 tonne NH_3/year	
	Advanced conventional process, emission to water		0.028		Stripping of process condensates and recycling to boiler feed-water	[3, European Commission, 1997]
	Reduced primary reforming, emission to water				Negligible	
	Heat exchange autothermal reforming, emission to water		0.080		Supplying process steam by feed gas saturation with process condensates	
	Emissions to water before installation of a stripping unit		0.7		25 m^3/hour	[9, Austrian UBA, 2002]
			0.8		49 m^3/hour	
	NH_3 slip from SNCR at primary reformer	1.1 – 5.1			Measured 4 times/year	
	Purge gas from ammonia synthesis				18 kg NH_3/year	
	Ammonia synthesis, emissions to air		0.014			[6, German UBA, 2000]
			0.011			
			0.032			
CO			0.006			
Hydrocarbons			0.009			
Waste	In general		0.2		Catalysts and molecular sieves	[3, European Commission, 1997]
			0.07		Spent catalysts, 13 tonnes/year	[9, Austrian UBA, 2002]
			0.09		Spent catalysts, 31 tonnes/year	

Table 2.9: Other emission levels reported for the production of ammonia

2.4 Techniques to consider in the determination of BAT

Conventional steam reforming is described in Section 2.2.3.
Partial oxidation is described in Section 2.2.4.

2.4.1 Advanced conventional processes

Description

The different process steps for the conventional steam reforming process are integrated 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. 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)
- 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 and superheat steam
- 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 from the ammonia synthesis loop and using it to raise high pressure steam
- applying a highly 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.

Achieved environmental benefits

In comparison with conventional processes, the following environmental benefits are achieved:

- reduced reformer firing, lower NO_x emissions
- energy savings.

For achievable emission and consumption levels, see:

- Table 2.6 for energy consumption
- Table 2.7 for NO_x emissions
- and Table 2.8 and Table 2.9 for other levels.

Cross-media effects

- still relatively high NO_x emissions.

Operational data

See Description.

Applicability

Applicable in new and existing plants. The applicability in existing plants requires an assessment of the specific case.

Economics

Cost benefits can be presumed.

Driving force for implementation

Plant optimisation and cost benefits.

References to literature and example plants

[1, EFMA, 2000, 3, European Commission, 1997]

2.4.2 Processes with reduced primary reforming and increased process air

Description

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. Table 2.10 shows the characteristic modifications in comparison with the conventional process.

Process step	Description
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 approximately 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 the steam to carbon ratio, compared to the conventional concept.
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. The slightly higher methane slip in this type of process is acceptable because most of the methane will be removed in a cryogenic 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. See Table 2.6.
Cryogenic final purification	In the purifier process, excess nitrogen, most of the 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, helium and methane. 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 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 waste gas fraction containing methane.
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 ammonia synthesis loop.

Table 2.10: Characteristics of processes with reduced primary reforming

Achieved environmental benefits

The main improvements are:

- lower NO_x formation
- minimisation of energy consumption
- increased firing efficiency in the primary reformer
- prolonged life of catalyst tubes and outlet header
- higher conversion per pass and reduced purge flow result in a more efficient ammonia synthesis loop.

For achievable emission and consumption levels, see:

- Table 2.6 for energy consumption
- Table 2.7 for NO_x emissions
- and Table 2.8 and Table 2.9 for other levels.

Cross-media effects

- increased energy consumption for compression due to higher process air requirements.

Operational data

See Description.

Applicability

Applicable for new plants.

Economics

Cost benefits can be assumed.

Driving force for implementation

Plant optimisation and cost benefits.

References to literature and example plants

[1, EFMA, 2000, 3, European Commission, 1997]

2.4.3 Heat exchange autothermal reforming

Description

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 reformer furnace. Surplus air or oxygen-enriched air is required in the secondary reformer to meet the heat balance in this autothermal design.

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 synthesis gas 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 a new ruthenium-based catalyst.

Achieved environmental benefits

- emissions to the air 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.

For achievable emission and consumption levels, see:

- Table 2.6 for energy consumption
- Table 2.7 for NO_x emissions
- and Table 2.8 and Table 2.9 for other levels.

Cross-media effects

- energy may need to be imported to drive mechanical equipment
- higher total energy consumption in comparison with other steam reforming concepts.

Operational data

No specific information provided.

Applicability

Applicable for new plants.

Economics

No specific information provided.

Driving force for implementation

This plant concept allows the building of a plant which can be started up quickly.

References to literature and example plants

[1, EFMA, 2000, 3, European Commission, 1997], so far seven installations of capacities from 350 to 1070 tonnes per day have been built and operated.

2.4.4 Revamp: increase capacity and energy efficiency

Description

The revamp of a 20 year old reduced primary reforming ammonia plant (1100 tonnes/day) is aimed to improve the efficiency of the primary reformer furnace/gas turbine combination by extensive preheating of the mixed feed going to the furnace and by the installation of a highly efficient gas turbine of which the operating conditions can be adapted to suit the oxygen requirements of the furnace. Table 2.11 gives an overview of the implemented measures.

Measure	Description
Extended preheating of the hydrocarbon/steam feed	To reduce the fuel gas consumption, the duty of the radiant section was decreased by extended preheating of the hydrocarbon/steam mixture before it reaches the catalyst tubes. This was done by installing a new highly alloyed mixed feed preheat coil in the convection section of the furnace. In this way, radiant heat is substituted by heat available in the convection section at a sufficiently high temperature level.
New gas turbine	A second key factor in achieving the fuel gas savings was the installation of a second generation gas turbine. The amount of oxygen available in the exhaust gases from this machine matches closely the oxygen requirements of the primary reformer furnace. In this way, the flow through the radiant box of the furnace is minimised and allows the high temperatures required in the fire box with less fuel gas consumption.
Modifications of the burners	Due to the low oxygen surplus, the furnace burners have required modifications to assure an adequate distribution of gas turbine exhaust over the burners. This is important to obtain complete combustion of the furnace fuel and to assure a uniform heat release in the fire box. This last issue is critical for the lifetime of the catalyst tubes, as local overheating of the tubes might cause premature tube failure. After revamp, the power of the new gas turbine is sufficient to drive the process air compressor, so the helper steam turbine was eliminated. The gas turbine exhaust gases show temperatures of about 520 °C and all exhaust is sent through the radiant section to provide sufficient oxygen for combustion in the furnace.
Rearrangement of the convection coils and add additional surface	Because of the reduced fired duty and because a larger share of the total heat is absorbed in the reforming process (mixed feed preheat coil + radiant tubes), a lower heat load is available for the rest of the convection section. For this reason, all convection coils in the heat recovery section were rechecked for the revamped process requirements and, where necessary, additional surface was added. The rearrangement of the convection coils which is an integral part of the proposed furnace revamp, also serves another objective: the heat conservation is further optimised by reducing the stack losses.
Maintenance	About 50 % of the efficiency increase is achieved by re-establishing the original state of the plant, e.g. closing leaks.

Table 2.11: Some implemented measures to revamp the 20 year old plant

Achieved environmental benefits

- reduced NO_x emissions <200 mg/Nm^3 due to low oxygen surplus
- energy consumption reduction (before and after the revamp) from 36.0 to 31.1 GJ/tonne (fuel + feed)
- net energy consumption after revamp: 30.6 GJ/tonne.

Cross-media effects

None believed to be likely.

Operational data

No specific data provided.

Applicability

This is an integrated technique applicable in existing steam reforming plants.

Economics

Total investment: EUR 5700000

The expected pay-back time was less than one year.

Driving force for implementation

Environmental and cost benefits.

References to literature and example plants

[14, Austrian Energy Agency, 1998], [74, Versteele and Crowley, 1997], Yara ammonia unit C, Sluiskil

2.4.5 Pre-reforming

Description

A pre-reformer installed prior to the primary reformer, in combination with a suitable steam saving project, reduces energy consumption and reduces marginally the NO_x emissions. 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. The primary reforming duty is reduced as less firing is needed (less NO_x emissions) allowing, at the same time, a lower S/C ratio (energy saving) to be achieved.

Achieved environmental benefits

- up to 5 – 10 % heat load reduction (reduced energy consumption)
- reduced emissions to air.

Cross-media effects

None believed to be likely.

Operational data

No information provided.

Applicability

This is an integrated technique applicable in new and existing conventional steam reforming plants and reduced primary reforming plants.

Economics

Combined improvements in NO_x reduction and the usage of surplus steam from an adjacent source leads to an overall cost saving.

Driving force for implementation

Conversion of steam savings to fuel gas savings.

References to literature and example plants

[3, European Commission, 1997], [73, Riezebos, 2000]

2.4.6 Energy audits

Description

The purpose of an energy audit is to characterise the energy consumption of a large, complex process plant and identify opportunities to improve the energy efficiency. The implementation of a fully detailed energy audit involves a significant amount of time and effort and so it is usual to proceed through a series of structured stages. These stages identify the potential for improvement with minimal expenditure and provide a series of points at which decisions can be made to proceed with further study, depending on the potential savings that have been identified. A staged approach to an energy audit would normally include the following steps:

Stage 1 – preliminary benchmarking

This provides a quick initial assessment of the potential for improving energy consumption. This is done by answering some basic questions about plant performance, modification history and utility consumption. Comparison with industry standards gives a broad indication of the scope for improving the energy consumption of the unit.

Stage 2 – exploratory audit

This involves a more complete understanding of the plant operation, including the determination of the heat and material balance for the plant. This audit will identify a number of simple changes that are likely to give a quick improvement in plant performance. It will also identify a number of other areas that are likely to need further study.

Stage 3 – in-depth energy audit

The third stage of the energy audit process involves a more detailed assessment of the plant operation and the scope for improvement. An in-depth audit comprises:

- data collection
- base case modelling
- on-site discussions
- development and evaluation of relevant modifications
- review and reporting.

Achieved environmental benefits

- provides the basis for improvement strategies.

Cross-media effects

None believed to be likely.

Operational data

No information provided.

Applicability

Generally applicable.

[18, J. Pach, 2004]: The *routine* assessment of energy efficiency includes:

- daily or weekly calculation of energy consumption
- monthly or quarterly reconciliation of ammonia production
- routine monitoring of the key unit operations to identify abnormal losses
- routine review of steam availability and demand
- repair and maintenance of insulation
- identification of suitable opportunities for improved energy efficiency.

The following daily energy checklist is used by an example plant:

Ammonia plant energy checklist				
		Production date:		
Description	Unit	Standard	Actual	Remarks
Reforming section				
Excess oxygen (O_2AT11)	%	0.8 – 1.2		
Burner flame condition		Flat, no smoke		
CO_2 removal system/methanation				
Steam required/actual	tonnes/hour			
Lean solution flow required/actual	m^3/hour			
Steam system				
SiO_2 in blowdown as per lab	ppm			
KS vent condition (visual)		No steam		
O_2PV302 op	%	0		
KS/HS let down op	%	<1		
Process gas venting, if any				
Flare condition (visual)		No flame		
Specific energy				
Specific energy (feed)	GJ/tonne	24.33		
Specific energy (fuel)		6.53		
Specific energy (feed + fuel)		30.86		
Specific energy including utilities, target		32.38		
Checked by:		Reviewed by:		

Table 2.12: Example for a daily energy checklist for an ammonia plant

Economics

No information provided.

Driving force for implementation

Environmental and cost benefits.

References to literature and example plants

[13, Barton and Hunns, 2000, 18, J. Pach, 2004, 71, Maxwell and Wallace, 1993]

2.4.7 Advanced process control

Description

An advanced process control (APC) system has been successfully implemented on the ammonia plant in 2004. The APC is model-based or model predictive and the implementation did not have a significant negative effect on operation nor was a plant shutdown caused or required. With the APC on-line in the example plant, the production is stable at record-high levels.

The APC provides ***weighted and hierarchical*** optimisation. ***Hierarchical*** means that there are different classes of optimisation problems. Only when one class has been solved and further degrees of freedom are available, the next lower priority class will be solved. Thanks to this feature, the APC is able to support control strategies adapted to specific scenarios, e.g. where plant safety takes priority over quality or where quality takes priority over energy saving. ***Weighted*** means, that within an optimisation problem, one of the variables is more important than another (e.g. because it costs more).

Achieved environmental benefits

In the referenced example plant, the benefits on production capacity and/or energy consumption are significant.

Cross-media effects

None believed to be likely.

Operational data

No information provided.

Applicability

Generally applicable. The implementation of the same APC was expected to start for the company's ammonia unit D in 2005 and was in planning for more units.

Economics

Significant cost benefits. In the example plant, the payback actually started already during the initial phase of project where the complete control and operating strategy of the plant was revised and reconsidered.

Driving force for implementation

Cost benefits in the example plant.

References to literature and example plants

[19, IPCOS, 2004], Yara ammonia unit E, Sluiskil

2.4.8 Use of gas turbine to drive the process air compressor

Description

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 might increase NO_x formation.

Achieved environmental benefits

- considerable energy savings.

Cross-media effects

- potential increase of NO_x emissions.

Operational data

No information provided.

Applicability

This is an integrated technique applicable to new steam reforming plants, and is a typical technique applied in reduced primary reforming plants.

Economics

No information provided.

Driving force for implementation

Cost savings.

References to literature and example plants

[3, European Commission, 1997]

2.4.9 Combined Claus unit and tail gas treatment

Description

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 streams containing H_2S. To further recover sulphur, subsequent tail gas treatment is applied.

For more detailed information about Claus units and subsequent tail gas treatment, see [8, European Commission, 2002].

Achieved environmental benefits

- recovery of sulphur with efficiencies of 98.66 to 99.99 % related to the combination of Claus unit and tail gas treatment [8, European Commission, 2002].

Cross-media effects

See [8, European Commission, 2002].

Operational data

See [8, European Commission, 2002].

Applicability

This technique is applicable to new and existing partial oxidation plants.

Economics

See [8, European Commission, 2002].

Driving force for implementation

See [8, European Commission, 2002].

References to literature and example plants

[3, European Commission, 1997, 8, European Commission, 2002]

2.4.10 SNCR at the primary reformer

Description

The selective non-catalytic reduction (SNCR) process is a secondary measure to reduce nitrogen oxides already formed in the flue-gas of a combustion unit. Within the SNCR unit, the injection of the additive and the reaction of nitrogen oxides to nitrogen and water take place. It is operated without a catalyst at a temperature of between 850 and 1100 °C. At ammonia plants, normally ammonia is used as the reducing agent, as it is available on-site.

The temperature window is of considerable importance as, above this, ammonia is oxidised and so even more NO_x is produced, and below this, the conversion rate is too low and unconverted ammonia is emitted to air. Moreover, with load changes the temperature pattern in the convection section will change. To adjust the required temperature window with the ammonia injection, several levels of injection are necessary.

The reaction of nitrogen oxides and ammonia/urea into water and nitrogen is strongly dependent on temperature and retention time within the required temperature range, as well as on the ammonia to nitrogen oxides ratio. As already mentioned, the temperature window for ammonia and caustic ammonia is 850 to 1000 °C, the optimum temperature being 870 °C. In comparison, the temperature window when using urea is wider (800 to 1100 °C) with an optimal temperature at 1000 °C.

The retention time within the required temperature window is in the range 0.2 – 0.5 seconds. Once more, optimisation is required as regards the molar ratio of NH_3 to NO_x. The NO_x removal rate is favoured by an increased ratio, but in the meantime the ammonia slip increases too, leading to increased pollution of subsequent units (e.g. heat exchangers, flue-gas ducts). In order to neutralise these two contrary effects, a NH_3 to NO_x ratio between 1.5 and 2.5 has been found to be the optimum.

Achieved environmental benefits

Generally, with SNCR a reduction rate of 40 – 70 % is achievable [11, European Commission, 2003].

Austrian ammonia plants, which are equipped with SNCR at the primary reformer, achieve NO_x reduction rates of 30 – 50 % and emission levels of 140 – 160 mg/Nm^3. The limit for the ammonia slip is 10 mg/Nm^3 [9, Austrian UBA, 2002].

Ammonia slip is 1 – 5 mg/Nm^3 [17, 2nd TWG meeting, 2004].

Cross-media effects

Most problems with SNCR applications are related to non-uniform distribution of the additive within the combustion chamber. Therefore, optimisation of the distribution system is required. Special distribution systems are used to gain an optimal distribution of ammonia and flue-gas.

In order to achieve a high abatement rate and a low NH_3 slip, additive and NO_x in the flue-gas must undergo sufficient mixing.

- potential for N_2O formation
- NH_3 consumption.

Operational data

See Description.

Applicability

In general, SNCR is applicable to new and existing ammonia plants. In particular SNCR is considered as an efficient reduction measure for existing plants. SNCR is an option for retrofitting the primary reformer, as it can be implemented at existing plants.

Retrofitting is considered suitable in the case of Kellogg furnaces, and unlikely to be possible with Foster Wheeler furnaces. Some furnaces will not provide the right temperature range/retention times [17, 2nd TWG meeting, 2004].

Economics

As the reducing agent is available on-site, equipment costs and operating costs are lower in comparison to other combustion plants. At ammonia plants, equipment for an additive storage unit is not necessary.

Driving force for implementation

Reduced NO_x emissions.

References to literature and example plants

- the two ammonia production lines of Agrolinz Melamin were equipped with SNCR between 1998 and 2000
- DSM, Geleen
- Kemira, Tertre.

[9, Austrian UBA, 2002, 10, European Commission, 2005, 11, European Commission, 2003]

2.4.11 Improved CO_2 removal systems

Description

The CO_2 formed in the gasification process and in the shift conversion process 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 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.

Achieved environmental benefits

Energy savings of 30 – 60 MJ/kmol CO_2 (about 0.8 – 1.9 GJ/tonne NH_3) is possible.

Cross-media effects

None believed likely.

Operational data

No information provided.

Applicability

This integrated technique applies to all new and existing steam reforming ammonia plants.

Economics

Cost benefits can be assumed.

Driving force for implementation

Cost benefits.

References to literature and example plants

[3, European Commission, 1997]

2.4.12 Preheating of combustion air

Description

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. If considerable air preheat is applied and no gas turbine waste gases can be used, a value of 90 mg/Nm^3; 270 g/tonne NH_3 could be raised to 130 mg/Nm^3; 390 g/tonne NH_3.

Achieved environmental benefits

- energy savings.

Cross-media effects

Increased NO_x emissions.

Operational data

No information provided.

Applicability

This is an integrated technique applicable to new and existing steam reforming plants.

Economics

Cost benefits.

Driving force for implementation

Cost benefits.

References to literature and example plants

[3, European Commission, 1997]

2.4.13 Low temperature desulphurisation

Description

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, instead of direct firing. In this way, NO_x emissions from the desulphurisation unit are avoided.

Achieved environmental benefits

- energy savings
- prevention of an additional emission source.

Cross-media effects

None believed likely.

Operational data

No information provided.

Applicability

An integrated technique applicable in the desulphurisation section of new and existing autothermal heat exchange reforming plants.

Economics

Cost benefits can be assumed.

Driving force for implementation

Cost benefits.

References to literature and example plants

[3, European Commission, 1997]

2.4.14 Isothermal shift conversion

Description

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 (330 – 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 conventional high temperature shift catalyst containing chromium 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. The Fischer-Tropsch synthesis is the reaction of hydrogen with carbon monoxide, carbon dioxide or mixtures of these carbon oxides (synthesis) to yield one or more carbon compounds, e.g. hydrocarbons, alcohols, esters, acids, ketones and aldehydes.

Achieved environmental benefits

- energy saving
- no necessity for the disposal of a chromium spent catalyst
- startup time of the one-step isothermal shift is reduced compared to the conventional two-step shift systems, resulting in lower emissions.

Cross-media effects

None believed likely.

Operational data

No information provided.

Applicability

This integrated technique is mainly applicable in new autothermal heat exchange reforming plants.

Economics

No information provided.

Driving force for implementation

Energy saving.

References to literature and example plants

[3, European Commission, 1997]

2.4.15 Use of smaller catalyst particles in ammonia converters

Description

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. The downside is an increased pressure drop, which could have an adverse effect on the energy savings.

Achieved environmental benefits

- energy savings.

Cross-media effects

None believed likely.

Operational data

No information provided.

Applicability

This is an integrated technique applicable to new and existing steam reforming and partial oxidation plants.

Economics

Cost benefits can be assumed.

Driving force for implementation

Cost benefits.

References to literature and example plants

[3, European Commission, 1997]

2.4.16 Stripping and recycling of process condensates

Description

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

Reduction of emissions to water.

Cross-media effects

Energy consumption for stripping.

Operational data

No information provided.

Applicability

This technique is applicable to new and existing steam reforming and partial oxidation plants.

Economics

Costs are estimated to be EUR 2.9 – 3.3 million for retrofit in existing plants with a capacity of 1500 tonnes/day.

Driving force for implementation

Reduction of emissions to water.

References to literature and example plants

[1, EFMA, 2000, 3, European Commission, 1997]

2.4.17 Low pressure catalyst for ammonia synthesis

Description

A new ammonia synthesis catalyst containing ruthenium and an alkali promoter on a graphite support has 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.

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

An energy reduction of up to 1.2 GJ/tonne NH_3 can be achieved, but it might be offset by the necessity to spend energy for ammonia refrigeration.

Cross-media effects

Not believed likely.

Operational data

No information provided.

Applicability

This is an integrated technique applicable to new and existing steam reforming and partial oxidation plants.

Economics

No information provided, but cost benefits can be assumed.

Driving force for implementation

Cost benefits.

References to literature and example plants

[3, European Commission, 1997]

2.4.18 Use of sulphur resistant catalysts for shift reaction of syngas 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 wash 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

- energy savings.

Cross-media effects

Not believed likely.

Operational data

No information provided.

Applicability

This is an integrated technique applicable to new partial oxidation plants.

Economics

No information provided, but cost benefits can be assumed.

Driving force for implementation

Cost benefits.

References to literature and example plants

[3, European Commission, 1997]

2.4.19 Liquid nitrogen wash for final purification of the synthesis gas

Description

The synthesis gas is scrubbed countercurrently 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 unnecessary and a high conversion rate per pass is achievable.

Achieved environmental benefits

- eliminates purge gas
- increases the efficiency of the synthesis loop.

Cross-media effects

Not believed likely.

Operational data

No information provided.

Applicability

This is an integrated technique applicable to new partial oxidation plants.

Economics

No information provided, but cost benefits can be assumed.

Driving force for implementation

Cost benefits.

References to literature and example plants

[3, European Commission, 1997]

2.4.20 Indirect cooling of the ammonia synthesis reactor

Description

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

- energy savings
- higher ammonia conversion rate per pass
- reduced catalyst volumes.

Cross-media effects

None believed to be likely.

Operational data

No information provided.

Applicability

This is an integrated technique applicable to new and existing steam reforming and partial oxidation plants.

Economics

Cost savings can be assumed.

Driving force for implementation

Cost savings.

References to literature and example plants

[3, European Commission, 1997]

2.4.21 Hydrogen recovery from the purge gas of the ammonia synthesis loop

Description

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 synthesis loop.

This hydrogen recovery can be performed using different technologies, such as cryogenic separation, membrane technology or pressure swing adsorption (PSA).

Achieved environmental benefits

- energy savings.

Cross-media effects

None believed likely.

Operational data

No information provided.

Applicability

This is a technique applicable to new and existing high pressure synthesis loop steam reforming plants.

Economics

Cost benefits can be assumed.

Driving force for implementation

Cost benefits.

References to literature and example plants

[3, European Commission, 1997]

2.4.22 Ammonia removal from purge and flash gases in a closed loop

Description

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. The scrubbed gases are burnt in the reforming section. The obtained NH_3 solution is recycled to other processes or distilled to recover pure NH_3.

Achieved environmental benefits

Reduced NO_x emissions, reduced NH_3 emissions.

Cross-media effects

Additional energy consumption.

Operational data

No information provided.

Applicability

This integrated technique is primarily applicable in new and existing conventional steam reforming plants. It is unlikely to be applicable for very small flash gas streams, when the cross-media effect (energy consumption) outweighs the environmental benefit (reduced NO_x emissions).

Economics

No information provided.

Driving force for implementation

Reduced NO_x emissions, reduced NH_3 emissions.

References to literature and example plants

[1, EFMA, 2000, 3, European Commission, 1997]

2.4.23 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. 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.

For a more detailed description of low NO_x burners, see [10, European Commission, 2005].

Achieved environmental benefits

NO_x reduction rates of up to 70 % [10, European Commission, 2005].

Cross-media effects

None believed to be likely.

Operational data

No information provided.

Applicability

This is an integrated technique applicable to new and existing steam reforming and partial oxidation plants.

Economics

The cost of the burners can be estimated to the cost of standard configuration + 10 % or, if waste gas recirculation is realised, + 15 to 30 % [3, European Commission, 1997]. The cost for retrofitting can be significant.

Driving force for implementation

Reduction of NO_x emissions.

References to literature and example plants

[3, European Commission, 1997, 10, European Commission, 2005], DSM, Gelen

2.4.24 Metal recovery and controlled disposal of spent catalysts

Description

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

Allows the recovery and re-use of materials.

Cross-media effects

None believed likely.

Operational data

No information provided.

Applicability

This management concept is applicable to all ammonia plants.

Economics

Benefits from selling spent catalysts.

Driving force for implementation

Safe disposal or recovery.

References to literature and example plants

[3, European Commission, 1997]

2.4.25 Handling of startup, shutdown and abnormal operating conditions

Description

During startup and shutdown higher emissions occur than during normal operation. The initial startup is usually the most severe because of its duration. Ammonia plants are started up or shutdown in a controlled sequence, which results in reformed and synthesis gases to be vented through various vents of the plant. It may also be necessary to vent natural gas during the startup of the desulphurisation section (see also Section 2.2.5).

Options to minimise emissions include the following:

- minimisation of the startup and shutdown time by using interlocks and a logical operational sequence
- use of recycled inert gases for preheating
- application of maximum allowed prudent preheat rates for equipment and catalysts
- reduction of the low temperature shift catalyst with an inert gas carrier
- taking the synloop into operation as quickly as possible
- flaring of non treatable vent gases.

Increased emissions can result from emergency shutdowns due to equipment failure, upsets in process conditions, human error, and force majeure. Proper risk analysis is carried out to provide the necessary preventive or control sequence in case of emergency. Instrument interlocks, emergency backup equipment such as batteries, sparing of equipment, instrument voting systems, adequate system inventory, computer control, and scrubbers are all used to avoid or minimise emissions during an emergency. Proper shutdown procedures are established to prevent formation of the toxic nickel carbonyl from gases containing carbon monoxide. These gases are normally excluded from methanators containing nickel catalysts at any temperature below 150 °C (below this temperature, nickel carbonyl is formed).

Achieved environmental benefits

Reduced emissions.

Cross-media effects

None believed likely.

Operational data

No information provided.

Applicability

Generally applicable.

Economics

No information provided.

Driving force for implementation

Emission reduction.

References to literature and example plants

[3, European Commission, 1997]

2.4.26 Ammonia production using hydrogen from water electrolysis

Description

Electrolytically produced hydrogen can be used directly for the production of ammonia, and such operations existed in the mid 1990s 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 carried out 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.

Achieved environmental benefits

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

Cross-media effects

None believed likely.

Operational data

No specific information provided.

Applicability

Ammonia production based on water electrolysis is currently carried out in plants of up to 500 tonnes/day. The process is generally not considered economically viable. However, under certain local circumstances (depending on the local price for electric power), it can still be an interesting and competitive technology, in particular when renewable electric power is abundantly available.

Economics

The process is generally not considered economically viable due to the actual price for electric power.

Driving force for implementation

Local considerations.

References to literature and example plants

[1, EFMA, 2000, 3, European Commission, 1997]

2.5 BAT for ammonia

BAT is to apply the common BAT given in Section 1.5.

BAT for storage is to apply BAT given in [5, European Commission, 2005].

BAT for new installations is to apply one of the following plant concepts:

- conventional reforming (see Section 2.4.1)
- reduced primary reforming (see Section 2.4.2)
- heat exchange autothermal reforming.

BAT is to apply one or a combination of the following techniques, and to achieve the NO_x concentration emission levels given in Table 2.13:

- SNCR at the primary reformer, if the furnace allows the required temperature/retention time windows (see Section 2.4.10)
- low NO_x burners (see Section 2.4.23)
- ammonia removal from purge and flash gases (see Section 2.4.22)
- low temperature desulphurisation for autothermal heat exchange reforming (see Section 2.4.13).

Plant concept	**NO_x emission as NO_2**
	mg/Nm^3
Advanced conventional reforming processes and processes with reduced primary reforming	90 – 230 [x]
Heat exchange autothermal reforming	a) 80 b) 20
a) Process air heater b) Auxiliary boiler [x] Low end of the range: best existing performers and new installations	
No direct correlation between concentration levels and emission factors could be established. However, emission factors of 0.29 – 0.32 kg/tonne NH_3 are seen as a benchmark for conventional reforming processes and processes with reduced primary reforming. For heat exchange autothermal reforming, an emission factor of 0.175 kg/tonne NH_3 is seen as a benchmark.	

Table 2.13: NO_x emission levels associated with BAT

BAT is to carry out routine energy audits (see Section 2.4.6).

BAT is to apply a combination of the following techniques and to achieve energy consumption levels given in Table 2.14:

- extended preheating of the hydrocarbon feed (see Section 2.4.4)
- preheating of combustion air (see Section 2.4.12)
- installation of a second generation gas turbine (Section 2.4.4 and 2.4.8)
- modifications of the furnace burners to assure an adequate distribution of gas turbine exhaust over the burners (see Section 2.4.4)
- rearrangement of the convection coils and addition of additional surface (see Section 2.4.4)
- pre-reforming in combination with a suitable steam saving project (see Section 2.4.5)
- improved CO_2 removal (see Section 2.4.11)
- low temperature desulphurisation (see Section 2.4.13)
- isothermal shift conversion (mainly for new installations, see Section 2.4.14)
- use of smaller catalyst particles in ammonia converters (see Section 2.4.15)
- low pressure ammonia synthesis catalyst (see Section 2.4.17)
- use of a sulphur resistant catalyst for shift reaction of syngas from partial oxidation (see Section 2.4.18)
- liquid nitrogen wash for final purification of the synthesis gas (see Section 2.4.19)
- indirect cooling of the ammonia synthesis reactor (see Section 2.4.20)
- hydrogen recovery from the purge gas of the ammonia synthesis (see Section 2.4.21)
- implementation of an advanced process control system (see Section 2.4.7).

Plant concept	**Net energy consumption** [x]
	GJ(LHV)/tonne NH_3
Conventional reforming processes, processes with reduced primary reforming or heat exchange autothermal reforming	27.6 – 31.8
[x] For interpretation of the given energy consumption levels, see Section 2.3.1.1. As a consequence, the levels might vary up to ± 1.5 GJ. Generally, the levels relate to steady state operation as would be typically experienced during a performance test directly following a revamp or an overhaul at intended capacity.	

Table 2.14: Energy consumption levels associated with BAT

BAT for partial oxidation is to recover sulphur from flue-gases, e.g. by applying a combination of Claus unit and tail gas treatment and to achieve BAT associated emission levels and efficiencies given in [8, European Commission, 2002], see Section 2.4.9.

BAT is to remove NH_3 from process condensates, e.g. by stripping.

BAT is to recover NH_3 from purge and flash gases in closed loop.

BAT is to handle startup/shutdown and other abnormal operating conditions according to Section 2.4.25.

3 NITRIC ACID

3.1 General information

Nitric acid is one of the most important and quantitatively one of the top ten industrial chemicals. Production levelled off in the 1990s because of the increased use of the downstream product urea. In 2003, 16.6 million tonnes HNO_3 were produced in Europe [102, EFMA, 2000].

In the EU-25, Switzerland and Norway about 100 European nitric acid plants are in operation in 2006. The capacity ranges from 150 – 2500 tonnes/day [154, TWG on LVIC-AAF, 2006].

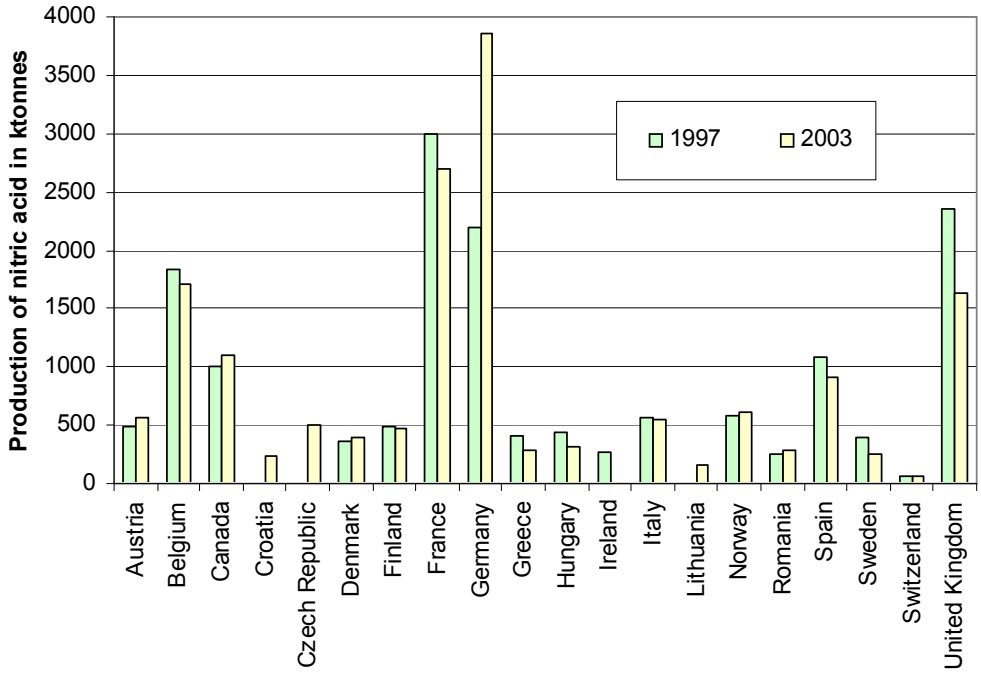

Figure 3.1: HNO_3 production levels in some European countries in 1997 and 2003 [117, UNFCCC, 2006]

Most of the nitric acid produced is used for inorganic fertilisers; it is mostly neutralised with ammonia to form ammonium nitrate [15, Ullmanns, 2001]. Other uses for nitric acid are in the manufacture of AN explosives, and chemicals, such as caprolactam, adipic acid, dinitro toluene or nitrobenzene. A weak acid (relating to the greater part of the production of nitric acid) or a strong acid can be produced, depending on the application required: weak acid (50 – 65 % w/w) is suitable for use in the production of fertilisers, but stronger acid (up to 99 % w/w) is required for many organic reactions. Concentrated nitric acid can be manufactured directly and indirectly. The direct process is quite different from the process to produce weak nitric acid; the indirect process uses weak nitric acid as one of the starting materials.

The other plant type operates with a dual pressure process in order to increase the efficiency. Older dual plants operate with low pressure/medium pressure, while more modern dual plants operate with medium pressure/high pressure.

Generation of the greenhouse gas N_2O as a by-product

Oxidation of ammonia generates NO, with N_2O as a by-product. Increases in combustion pressure from 1 to 5 bar in the last decades has slightly increased the N_2O emission level. According to [107, Kongshaug, 1998], the average European plant emits 6 kg of N_2O per tonne of HNO_3 corresponding to about 2 tonnes CO_2-eq. per tonne of 100 % HNO_3.

3.2 Applied processes and techniques

The following description is for a typical plant. Details might vary from plant to plant.

3.2.1 Overview

Figure 3.2 gives an overview of the production of HNO_3. The four relevant plant types are distinguished according to the pressures applied in the oxidation and absorption stage as presented in Table 3.1.

Type	Applied pressure in bar		Abbreviation
	Oxidation	Absorption	
Dual Low/Medium	<1.7	1.7 – 6.5	L/M
Mono Medium/Medium	1.7 – 6.5		M/M
Dual Medium/High	1.7 – 6.5	6.5 – 13	M/H
Mono High/High	6.5 – 13		H/H

Table 3.1: Different plant types for the production of HNO_3
This table is based on [88, infoMil, 1999, 102, EFMA, 2000, 104, Schöffel, 2001]

To create a higher pressure in the absorption section, 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.

3.2.2 Raw material preparation

The liquid 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, in order not to negatively affect the catalyst of the following oxidation step. 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. NH_3 is mixed with the air in a ratio of approximately 1:10 (bearing in mind the LEL) and (optionally) filtered.

3.2.3 Oxidation of NH_3

NH_3 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:

$$4\ NH_3 + 5\ O_2 \leftrightarrow 4\ NO + 6\ H_2O$$

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

$$4\ NH_3 + 3\ O_2 \leftrightarrow 2\ N_2 + 6\ H_2O$$

$$4\ NH_3 + 4\ O_2 \leftrightarrow 2\ N_2O + 6\ H_2O$$

The yield of nitric oxide (NO) depends on pressure and temperature as indicated in Table 3.2.

Pressure in bar	Temperature (°C)	NO yield (%)
<1.7	810 – 850	97
1.7 – 6.5	850 – 900	96
>6.5	900 – 940	95

Table 3.2: NO dependence on pressure and temperature [102, EFMA, 2000]

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 approximately 90 % platinum alloyed with rhodium for greater strength and sometimes containing palladium.

The enthalpy of the hot reaction gas is used to produce steam and/or preheat the tail gas. After this, the reaction gas has a temperature of 100 to 200 °C, depending on the process and it is then further cooled with water. The water formed in the oxidation reactions is condensed in a cooler-condenser and transferred to the absorption column.

3.2.4 Oxidation of NO and absorption in H_2O

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

$$2\ NO + O_2 \leftrightarrow 2\ NO_2$$

For this purpose, secondary air is added to the gas mixture obtained from the ammonia oxidation. Demineralised water, steam condensate or process condensate is added at the top of the absorption column. The weak acid solution (approximately 43 %) produced in the cooler condenser is also added to the absorption column. The NO_2 in the absorption column is contacted countercurrently with flowing H_2O, reacting to give HNO_3 and NO:

$$3\ NO_2 + H_2O \leftrightarrow 2\ HNO_3 + NO$$

The oxidation, absorption of the nitrogen dioxide and its reaction to nitric acid and nitric oxide take place simultaneously in the gaseous and liquid phases. Both reactions (oxidation and HNO_3 formation) depend on pressure and temperature and are favoured by higher pressure and lower temperature.

The formation of HNO_3 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 50 – 65 wt-% 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 approximately 20 – 30 ºC. This gas mixture is commonly referred to as tail gas and is heated by heat exchange. The hot tail gas is led through a NO_X abatement system and through a tail gas expander for energy recovery. The resulting expanded tail gas (in most cases with a temperature above 100 °C to prevent the deposition of ammonium nitrate and ammonium nitrite) is vented through a stack.

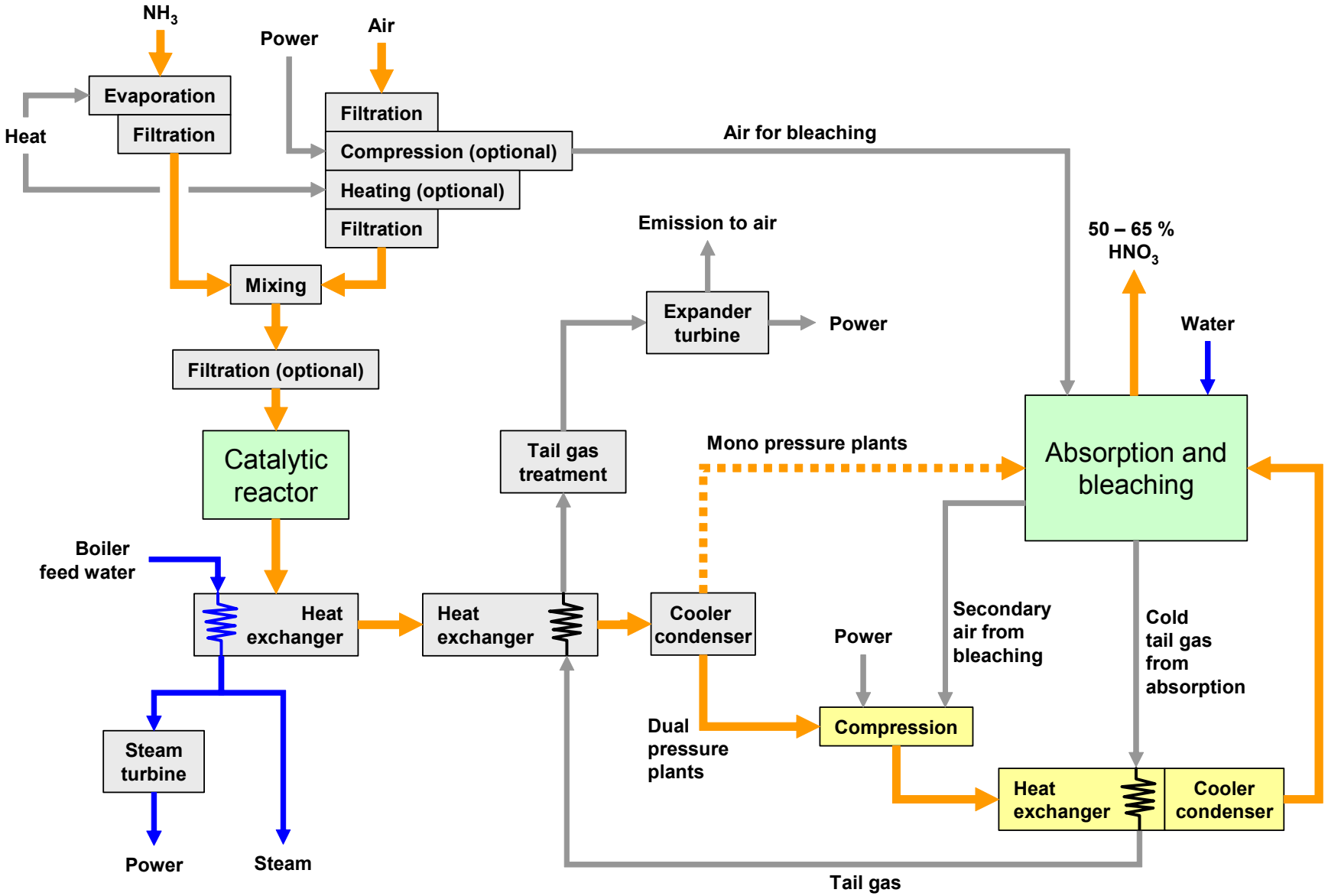

Figure 3.2: Overview of the production of HNO_3
This figure is based on [88, infoMil, 1999, 102, EFMA, 2000]

3.2.5 Tail gas properties and emission reduction

The tail gas composition depends on the applied process conditions. Table 3.3 gives an overview of tail gas properties.

Parameter	Level	Unit
NO_x as NO_2	200 – 4000	mg/Nm^3
NO/NO_2 ratio	about 1/1	molar ratio
N_2O	600 – 3000	mg/Nm^3
O_2	1 – 4	% v/v
H_2O	0.3 – 0.7	% v/v
Pressure	3 – 12	bar
Temperature after absorption	20 – 30	°C
Temperature after reheating	200 – 500	°C
Volume flow	20000 – 100000	Nm^3/hour
	3100 – 3300 [x]	Nm^3/tonne 100 % HNO_3

Table 3.3: Tail gas properties after the absorption stage
[94, Austrian UBA, 2001], [x] [112, Gry, 2001]

The most common treatment techniques for tail gases from nitric acid plants are:

- SCR (for NO_x abatement, see Section 3.4.9)
- NSCR (for NO_x and N_2O abatement, see Section 3.4.8.

More recent strategies to reduce NO_x or N_2O emissions include:

- optimisation of the oxidation stage (see Sections 3.4.1, 3.4.2, 3.4.3 and 3.4.5)
- catalytic decomposition of N_2O, applied already in the oxidation reactor, directly after the oxidation catalyst (see Section 3.4.6)
- optimisation of the absorption stage (see Section 3.4.4)
- combined catalytic NO_x/N_2O abatement with intermediate injection of NH_3, applied to the tail gas in front of the expander turbine (see Section 3.4.7).

3.2.6 Energy export

The nitric acid process has undergone significant energy improvements during the last decades from atmospheric plants, via M/M units to M/H plants. The reaction from NH_3 to HNO_3 theoretically releases 6.3 GJ/tonne 100 % HNO_3. However, energy losses in gas compressors and cooling (water) reduce the net steam export. If all thermal energy is converted to electrical power in a steam turbine, the net energy export will be reduced by approximately 65 %.

	GJ/tonne 100 % HNO_3	Remark
Modern M/H plant	2.4	As HP steam
Average net export of European plants	1.6	
Best plants 30 years ago	1.1	

Table 3.4: Overview of energy export from HNO_3 production
[94, Austrian UBA, 2001, 107, Kongshaug, 1998]

3.2.7 Production of concentrated nitric acid

Direct processes for the production of concentrated nitric acid are based on the production of liquid N_2O_4, which reacts under pressure with oxygen and dilute nitric acid to form HNO_3.

$$2\ N_2O_4 + O_2 + 2\ H_2O \rightarrow 4\ HNO_3$$

Nitrogen oxides, which are formed in an ammonia combustion unit operated at low pressure, are completely oxidised into NO_2 (oxidation step and post-oxidation step). NO_2 is washed out with concentrated nitric acid (absorption step) and by process condensate and dilute nitric acid (final absorber step). NO_2 (or its dimer N_2O_4) is stripped from the concentrated acid (bleaching) and liquefied. Concentrated acid is formed from liquid N_2O_4, oxygen and dilute nitric acid (from the final absorption step) in a reactor at a pressure of approximately 50 bar. Concentrated nitric acid is recirculated to the absorption and final oxidation steps, part of nitric acid is withdrawn as product acid. Waste gas is discharged from the final absorption step. NO_x concentration of the waste gas depends on the temperature of the final absorption step. Process condensates and dilute nitric acid arising from catalytic ammonia oxidation, oxidation and post oxidation step are re-used. However, more process condensate is formed than can be used for production of concentrated acid. A part of the process condensates has to be used for other production or treated as waste water.

Indirect processes are based on extractive distillation and rectification of weak nitric acid. Sulphuric acid or magnesium nitrate is used as the dehydrating agent. With sulphuric acid processes, weak nitric acid is preheated and distilled with H_2SO_4. With magnesium nitrate processes, a solution of $Mg(NO_3)_2$ is used to extract water from the nitric acid. Dehydrating agents are restored under vacuum. Process condensates which demand an adequate waste water treatment arise from concentrating the dehydrating agent. Vapour withdrawn from the head of the distillation or extraction column is condensed to form concentrated nitric acid. Waste gases contain nitric acid vapour and are scrubbed with dilute nitric acid.

3.3 Current emission and consumption levels

Table 3.5 and Table 3.6 give an overview/examples for consumption levels of HNO_3 production. Figure 3.3 shows the empirical correlation between specific N_2O emission levels and N_2O concentrations in tail gases. Table 3.7 shows the reported N_2O levels and Table 3.8 the reported NO_x levels.

	M/M	H/H	M/H	Unit
Operating pressure	6	10	4.6/12	bar
Ammonia	286	290	283	kg/tonne 100 % HNO_3
Electrical power	9	13	8.5	kWh/tonne 100 % HNO_3
Platinum primary losses	0.15	0.26	0.13	g/tonne 100 % HNO_3
Heating steam 8 bar, saturated	0.05	0.35	0.05	tonnes/tonne 100 % HNO_3
Excess steam, 40 bar, 450 ºC	0.75	0.58	0.65	tonnes/tonne 100 % HNO_3
Cooling water [x]	100	125	105	tonnes/tonne 100 % HNO_3
[x] ΔT = 10 K, including water for steam turbine condenser				

Table 3.5: Examples for consumption levels for steam turbine-driven HNO_3 plants and tail gas containing <50 ppm NO_x [94, Austrian UBA, 2001]

Energy consumption	M/H	L/M	Unit
Capacity	300000	180000	tonnes/year
Compression with electric actuation	5		MWh/hour
Compression with steam actuation		20 [xx]	tonnes steam/hour
Other energy consumption	0.55	0.60	MWh/hour
Steam production	43 [x]	25 [xx]	tonnes steam/hour
[x] 42 bar/520 ºC		[xx] 23 bar/350 ºC	

Table 3.6: Examples for energy consumption and steam production for a M/H and a L/M plant [94, Austrian UBA, 2001]

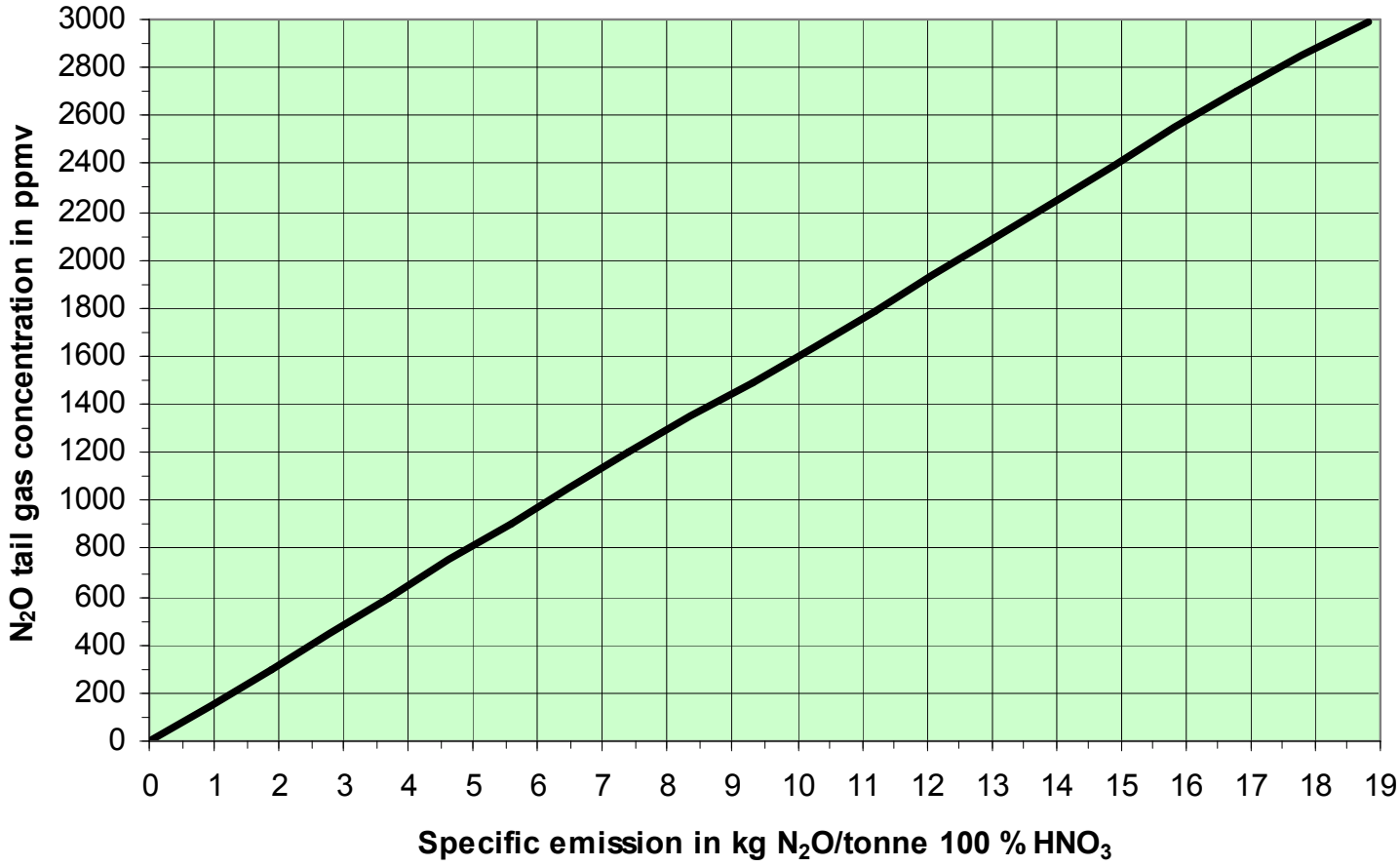

Figure 3.3: Empirical correlation between specific N_2O emission levels and N_2O concentrations in tail gases [96, Maurer and Groves, 2004]

Process type	N_2O emission level		Remark	Reference
	kg/tonne 100 % HNO_3	ppmv		
With NSCR		300		[96, Maurer and Groves, 2004]
Variation within a campaign until gauze exchange	5.6 – 9	900 – 1500	With medium pressure burner. Correlating with N_2O yield of 1.5 – 2.5 %	
All plants	*1.9 – 21.6*	300 – 3500		[102, EFMA, 2000]
Norsk Hydro	2.5	*400*	Modern integrated plant	[86, IPCC, 2000]
Low pressure oxidation	4 – 5	*650 – 810*		
Medium pressure oxidation	6 – 7.5	*970 – 1220*		
EU designed dual pressure plants	8 – 10	*1300 – 1620*		
A few, outdated plants	10 – 19	*1620 – 3080*		
19 Yara plants	3 – 9	*490 – 1500*		[80, Jenssen, 2004]
Atmospheric plants	5	*810*		
Medium pressure oxidation	7	*1140*		
High pressure plants	5 – 9	*810 – 1500*		
EU average	6	*970*		
Depending on the process conditions	*3.1 – 12.3*	500 – 2000		[98, ADEME, 2003]
EU representative level	6 – 8	*970 – 1300*		[99, IRMA, 2003]
EU average	7	*1140*		[87, infoMil, 2001]
Dual M/H plant	*0.12 – 0.25*	20 – 40	Combined tail gas abatement system since 2003	[100, AMI, 2006]

Process type	N_2O emission level		Remark	Reference
	kg/tonne 100 % HNO_3	ppmv		
	4.9 – 8.6	800 – 1400	Before 2003, 3.3/8 bar	[94, Austrian UBA, 2001]
Dual L/M plant	*3.4 – 4.9*	550 – 800	0/3.8 bar	[94, Austrian UBA, 2001] [100, AMI, 2006]
Mono M/M plant	*4.9*	800	Campaign average. Improved oxidation catalyst by Heraeus (see Section 3.4.3), 4.5 bar, 250 ºC in front of the expander	SKW Piesteritz
Mono M/M plant	*6.2 – 7.4*	1000 – 1200	230 ºC in front of the expander	Sasol Nitro, South Africa
Dual M/H plant	*7.7*	1250	Capacity: 584000 tonnes/year, 5/10 bar	YARA, Sluiskil 6
Dual M/H plant	*9*	1500	Capacity: 500000 tonnes/year, 5/11 bar, 500 ºC in front of expander	DSM Geleen
Mono M/M plant	*7.1*	1150	Capacity: 210000 tonnes/year, 5 bar, 450 ºC in front of expander	DSM Geleen [103, Brink, 2000]
Dual M/H plant	*7.7*	1250	Capacity: 730000 tonnes/year, 4/11 bar	YARA, Sluiskil 7
Mono M/M plant	*5.7*	920	Capacity: 255000 tonnes/year, 4 bar, 400 ºC in front of expander	DSM IJmuiden [103, Brink, 2000]
Dual M/H plant	*9*	1500	Capacity: 245000 tonnes/year, 4/10 bar	DSM IJmuiden
Mono M/M plant	*3.8*	613	Capacity: 80000 tonnes/year, 2.6 – 3.6 bar	Kemira Agro Pernis [x]
Mono H/H plant	*0.2*	27	Capacity: 400000 tonnes/year, NSCR, 9 bar	Kemira Agro Rozenburg [x]
Dual M/H plant	*5.3*	860	Capacity: 1100 tonnes/day, 3.5/12.8 bar, gauze age at time of measurement: 5 months	Agropolychim, Devnia
Medium pressure plant	*1.9*	300	Heraeus secondary catalyst	GP Rouen AN6
Dual M/M (KD6)	*5.5*		Heraeus secondary catalyst	Lovochemie, Lovosice
			Heraeus secondary catalyst	Agropolychim
Dual M/H (Uhde 2)	7.2	1350	Capacity 750 tonnes/day	Kemira GrowHow, Tertre

Process type	N_2O emission level		Remark	Reference
	kg/tonne 100 % HNO_3	ppmv		
Dual M/M (Uhde 3)	7.1	1150	Capacity 550 tonnes/day	
Dual H/H (Dupont)	0.2	33	Capacity 850 tonnes/day, NSCR	
Dual M/H (SZ2)	*1.8*	285	BASF secondary catalyst, 12 cm (6.7 kg before reduction)	BASF, Antwerp
Dual M/H (SZ3)	*1.7*	272	BASF secondary catalyst, 12 cm (6.7 kg before reduction)	
Dual M/H	*6.7*			
Dual H/H	*0.01*		NSCR	
M/H	*2.0*	325	YARA secondary catalyst, 50% filling (7 kg before reduction)	YARA, Ambès
	3.3	535	YARA secondary catalyst, 40% filling (7 kg before reduction)	
M/H	*2.8*	445	YARA secondary catalyst, 25% filling (5.2 kg before reduction)	YARA, Montoir
	0.8	130	YARA secondary catalyst, 75% filling (5.2 kg before reduction)	
[x] Plant closed				

Table 3.7: Reported N_2O emission levels from the production of HNO_3

Process type	NO_x emission level		$DeNO_x$ system		Remark	Reference
	mg/Nm^3	ppmv	Type	Efficiency %		
Dual M/H plant Line E		5	Combined	99	Combined tail gas abatement system since 09/2003, 3.3/8 bar, 300000 tonnes/year, no NH_3 slip	[100, AMI, 2006] [108, Groves, 2006]
	180 – 190	90	SCR	82	Before 2003, 3.3/8 bar, 300000 tonnes/year, NH_3 slip 0.26 – 2.6 mg/Nm^3	[94, Austrian UBA, 2001]
Dual L/M plant Line F	320 – 330	155 – 160	SCR	92 – 95	0/3.8 bar, 180000 tonnes/year, NH_3 slip 0.05 – 0.1 mg/Nm^3	[94, Austrian UBA, 2001] [100, AMI, 2006]
	158	90			Optimisation of the SCR in 2006	
Dual M/H plant	164 – 185	80 – 90	- -	- -	5/11 bar, 2000 tonnes/day, low cooling water temperatures	YARA, Porsgrunn
Dual M/H plant	410	200	- -	- -	Capacity: 584000 tonnes/year, 5/10 bar	YARA, Sluiskil 6
Dual M/H plant	348	170	- -	- -	Capacity: 500000 tonnes/year, 5/11 bar, 500 ºC in front of expander	DSM Geleen
Mono M/M plant	154	75	SCR	97	Capacity: 210000 tonnes/year, 5 bar, 450 ºC in front of expander	DSM Geleen
Dual M/H plant	369	180			Capacity: 730000 tonnes/year, 4/11 bar	YARA, Sluiskil 7
Mono M/M plant	410	200	SCR	87	Capacity: 255000 tonnes/year, 4 bar, 400 ºC in front of expander	DSM IJmuiden
Dual M/H plant	410	200			Capacity: 245000 tonnes/year, 4/10 bar	DSM IJmuiden
Mono M/M plant	492	240	SCR	87	Capacity: 75000 tonnes/year, 2.6 – 3.6 bar	Kemira Agro Pernis [x]
Mono H/H plant	205	100	NSCR	95	Capacity: 400000 tonnes/year, 8.4 bar	Kemira Agro Rozenburg [x]
Dual L/M plant	205	100	SCR	80	Capacity: about 73000 tonnes/ year, 0/3.5 bar	Kemira Agro Denmark
		<200	SCR	90	Capacity: 500 tonnes/day, absorption at 3.67 bar, SCR commissioned in 1990	Kemira Agro, Willebroek [x]

Process type	NO_x emission level		$DeNO_x$ system		Remark	Reference
	mg/Nm^3	ppmv	Type	Efficiency %		
Dual M/H plant	145 – 161	70	SCR	50 – 67	Capacity: 650 tonnes/day, 5/10 bar, 350 ºC in front of expander (yearly average)	BASF Antwerp
Two dual M/H plants	145 – 161	<100	SCR	70 – 76	Capacity: 2 x 945 tonnes/day, 5/10 bar, NH_3 slip <10 ppm, 350 ºC in front of expander (yearly average)	
Mono H/H plant	156	75	NSCR		Mono 9.5 bar, temperature after SNCR is about 620 ºC (yearly average)	
Four L/M plants		<150	SCR	67 – 81	Capacity: 4 x 270 tonnes/day, oxidation pressure 1.3 bar, absorption at 7.3 bar, SCR commissioned in 1975/1977	BASF Ludwigshafen
		165	SCR	87	Capacity: 225 tonnes/day, absorption at 3.3 bar, SCR commissioned in 1976	CFK Köln
		<200	SCR	60	Capacity 270 tonnes/day, absorption at 4.5 bar, SCR commissioned in1979	GUANO, Krefeld
		<200	SCR	83	Capacity: 180 tonnes/day, absorption at 7.0 bar, SCR commissioned in 1983	GUANO, Nordenham
Two plants		200	SCR	90 – 92	Capacity: 225 tonnes/day, absorption at 3.4 and 3.2 bar, SCR commissioned in 1979/1980	SUPRA Landskrona [x]
		<200	SCR	64	Capacity: 300 tonnes/day, absorption at 4.5 bar, SCR commissioned in 1982	SUPRA, Koeping
		<500	SCR	75 – 83	Capacity: 390 tonnes/day, absorption at 1.5 bar, SCR commissioned in 1982	SUPRA, Koeping
		<200	SCR	60	Capacity: 360 tonnes/day, absorption at 4.9 bar, SCR commissioned in 1982	Quimigal, Alverca

Process type	NO_x emission level		$DeNO_x$ system		Remark	Reference
	mg/Nm^3	ppmv	Type	Efficiency %		
		<200	SCR	60	Capacity: 360 tonnes/day, absorption at 4.9 bar, SCR commissioned in 1982	Quimigal, Lavradio
		<500	SCR	41	Capacity: 920 tonnes/day, absorption at 7.0 bar, SCR commissioned in 1982	PEC, Ottmarsheim
		<200	SCR	60	Capacity: 450 tonnes/day, absorption at 4.7 bar, SCR commissioned in 1983	YARA, Rjukan [x]
		<200	SCR	71 – 80	Capacity: 900 tonnes/day, absorption at 4.7 bar, SCR commissioned in 1985	YARA, Ravenna
		<200	SCR	80	Capacity: 170 tonnes/day, absorption at 6.26 bar, SCR commissioned in 1988	YARA, Ravenna
		<200	SCR	92	Capacity: 172 tonnes/day, absorption at 6.35 bar, SCR commissioned in 1987	YARA, Ravenna
		300	SCR	88	Capacity: 670 tonnes/day, absorption at 3.7 bar, SCR commissioned in 1985	YARA, IJmuiden
		<170	SCR	76	Capacity: 500 tonnes/day, absorption at 4.6 bar, SCR commissioned in 1986	DuPont, Orange (USA)
		<200	SCR	80	Capacity: 300 tonnes/day, absorption at 3.8 bar, SCR commissioned in 1987	Lonza, Visp.
		<200	SCR	90	Capacity: 500 tonnes/day, absorption at 3.57 bar, SCR commissioned in 1990	RADICI, Novara
		<100	SCR	80	Capacity: 225 tonnes/day, absorption at 11.2 bar, SCR commissioned in 1991	FCC, Pascagoula (USA)

Process type	NO_x emission level		$DeNO_x$ system		Remark	Reference
	mg/Nm^3	ppmv	Type	Efficiency %		
		<100	SCR	90	Capacity: 245 tonnes/day, absorption at 11.2 bar, SCR commissioned in 1992	BP Lima (USA)
Mono M/M plant	410	200	SCR	83	Capacity: 65000 tonnes per year, 4.5 bar	SMX Sasolburg
Dual M/H plant		170 – 200	- -		Capacity: 1100 tonnes/day, 3.5/12.8 bar, absorption at 20 – 40 ºC	Agropolychim, Devnia
3 plants		70	SCR			Hu-Chems, Korea
Mono H/H plants, UKL-7 (GIAP)	103	50	SCR or NSCR	95	Capacities: 120000 tonnes per year, 7 bar, NH_3 slip of about 50 ppm	[88, infoMil, 1999]
Dual M/H plants, AK-72 (GIAP)	103	50	SRC or NSCR	93	Capacities: 380000 tonnes per year, 4/10 bar, NH_3 slip of about 50 ppm	
M/H (Uhde 2)		190 – 200	- -		Capacity 750 tonnes/day	Kemira GrowHow, Tertre
M/M (Uhde 3)		150 – 180	SCR	*75 – 90*	Capacity 550 tonnes/day	
H/H (Dupont)		150 – 180	NSCR	*75 – 90*	Capacity 850 tonnes/day	
[x] Plant closed						

Table 3.8: Reported NO_x emission levels from the production of HNO_3

3.4 Techniques to consider in the determination of BAT

3.4.1 Oxidation catalyst performance and campaign length

Description

Catalyst performance is negatively affected by:

- poisoning by air pollution and contamination from the ammonia
- poor ammonia-air mixing
- poor gas distribution across the catalyst.

This may reduce the NO yield by up to 10 %. Additionally, local ammonia excesses in the burner are a plant safety risk (based on LEL) and could also cause the catalyst gauze to overheat. To minimise these effects, some plants use magnetic filters to remove any rust from ammonia, static mixers to give a high quality mixture and an additional filtration step applied to the ammonia/air mixture. Burner heads often contain a perforated plate or honeycomb grid to ensure good distribution. The gas velocity over the catalyst gauze must be steady.

Gauze composition. 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(III)oxide could accumulate at the catalyst surface and decrease catalytic activity. Palladium is also used in catalyst alloys to reduce costs. Adding up to 5 % palladium, resulting in no significant differences in the nitrogen monoxide yield, and has the benefit that palladium costs are lower than platinum or rhodium.

Effect of the campaign length on N_2O formation

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. However, catalyst loss is inevitable and the catalyst gauze has to be exchanged periodically. Table 3.9 gives an overview of various parameters in relation to the applied pressure. The campaign lengths vary from 1.5 to 12 months.

For a medium pressure burner, a fresh gauze yields <1.5 % N_2O resulting in a tail gas concentration <1000 ppm. This can rise to 1500 ppm at the end of a campaign, corresponding to a 2.5 % of ammonia being converted to N_2O [96, Maurer and Groves, 2004]. Figure 3.4 shows the N_2O generation in relation to the progress of a campaign according to [118, French Standardization, 2003].

A sudden increase of N_2O levels can indicate that damage to the catalyst gauze has occurred, thus allowing ammonia to bypass the gauzes. Potential consequences include AN formation in cooler parts of the plant and overheating of downstream equipment.

Hence, monitoring the catalyst performance (e.g. by monitoring N_2O levels) is essential and the campaign length can be chosen accordingly.

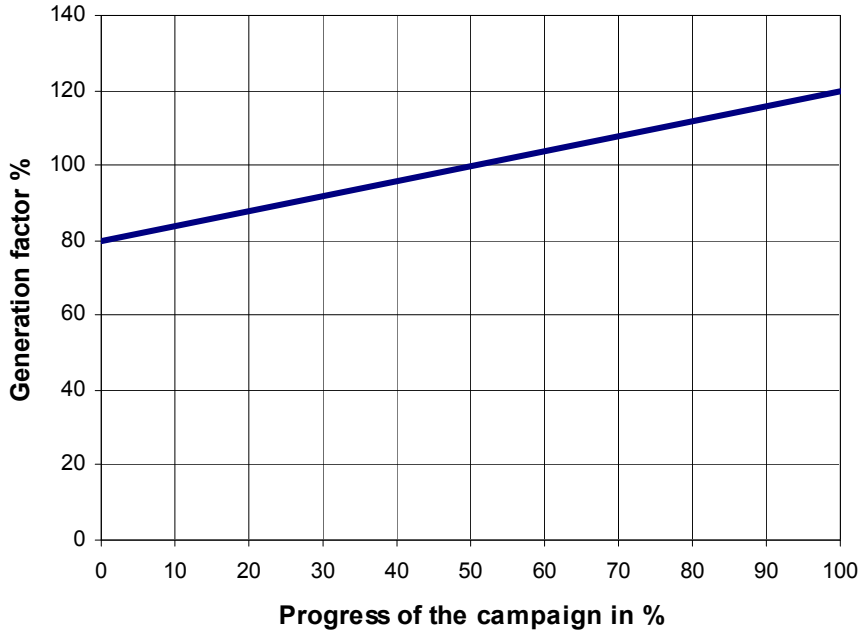

Figure 3.4: N_2O generation in relation to the progress of a campaign [118, French Standardization, 2003]

Pressure of NH_3 oxidation	1	3 – 7	8 – 12	bar
Catalyst layer	3 – 5	6 – 10	20 – 50	
Gas velocity	0.4 – 1.0	1 – 3	2 – 4	Meter/second
Temperature	840 – 850	850 – 900	900 – 950	ºC
Catalyst loss	0.04 – 0.06	0.10 – 0.16	0.25 – 0.32	g/tonne HNO_3
Campaign length	8 – 12	4 – 7	1.5 – 3	Months

Table 3.9: Parameters of ammonia oxidation related to applied pressures [88, infoMil, 1999, 94, Austrian UBA, 2001]

Achieved environmental benefits

- optimised NO yield
- minimisation of N_2O formation.

Cross-media effects

None believed likely.

Operational data

See Table 3.9.

Applicability

Generally applicable.

Taking into account recent developments in oxidation catalyst manufacture, the catalyst gauzes are replaced regularly about 1 – 4 times a year [154, TWG on LVIC-AAF, 2006].

Economics

- additional costs for monitoring
- additional costs for catalyst exchange if campaigns are shortened
- benefit from improved NO yield.

Driving force for implementation

Increased NO yield and reduced N_2O emissions.

References to literature and example plants

[87, infoMil, 2001, 96, Maurer and Groves, 2004, 102, EFMA, 2000]

3.4.2 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. Additionally, a high NO yield is favoured by low pressure (as low as possible) and optimum temperature (750 – 900 °C).

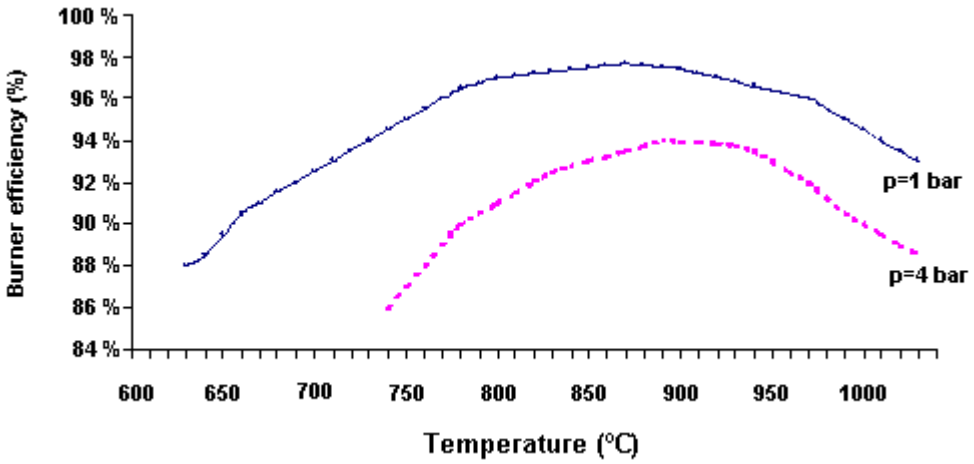

Figure 3.5: Indicative relation of the ammonia burner efficiency and temperature at 1 and 4 bar [88, infoMil, 1999]

Ammonia/air ratio. From an engineering point of view, the combustion of ammonia is one of the most efficient catalytic industrial reactions (the theoretical maximum conversion would be 98 % in a one bar plant). 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.

Operating at ***low pressure*** increases the conversion of NH_3 to NO according to the laws of thermodynamics.

A high reaction ***temperature*** enhances ammonia combustion, but decreases the conversion efficiency due to the increased generation of N_2 and N_2O. The oxidation generally takes place at temperatures of 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 increase. The reaction mechanism tends to be more selective towards nitrogen and N_2O formation at lower catalyst temperature. 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. The reaction temperature is directly related to the ammonia/air ratio: a 1 % increase in the proportion of ammonia increases the temperature by approximately 68 °C.

Achieved environmental benefits

- optimised NO yield
- minimisation of N_2O formation.

Cross-media effects

None believed likely.

Operational data

See description.

Applicability

Generally applicable. There are limitations for changes in existing plants but in new plants adaptation is easier. The above parameters; NH_3/air ratio, temperature and pressure 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 specific information provided.

Driving force for implementation

Increased NO yield and reduced N_2O emissions.

References to literature and example plants

[88, infoMil, 1999]

All plants throughout the world can be expected to optimise the operating conditions for maximising an NO yield. The NO yield affects the production: as a result, the NO yield must be as high as possible within the technical and economical possibilities of the plant, however the conversion to NO is limited to 98 % maximum, with the remaining conversion being to N_2O and N_2.

3.4.3 Alternative oxidation catalysts

Description

- ***improved platinum catalysts*** show modifications in composition and 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. Simultaneously, an extension of the campaign length is possible. Examples are the FTC and FTCplus catalysts by Heraeus or oxidation catalyst from Umicore [87, infoMil, 2001, 105, Müller, 2003, 145, Nitrogen2003, 2003]

- alternatively, ***Co_3O_4 based catalysts*** have been available for 30 years. Some sources claim higher ammonia conversion efficiencies (94 – 95 %), whilst others say this is only 88 – 92 % in a high pressure plant. Normally, the NO yield in an existing nitric acid plant will be approximately between 93 and 97 %. Additionally, the lifetime of the catalyst is longer, reducing the number of plant shut-downs and lower pressure drop is observed. High temperatures and reduction of Co_3O_4 to CoO leads to catalyst deactivation

- in the republics of the CIS, ***two-step catalysts*** are used extensively. 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.

Achieved environmental benefits

- the example plant achieved a reduction of 30 – 50 % N_2O with an improved platinum-based Heraeus catalyst [105, Müller, 2003]. An M/M example plant achieves, with this catalyst, N_2O emission levels of 500 – 1000 ppm in half year campaigns, on average about 800 ppm. The other example plant (M/M) achieves 600 – 700 ppm N_2O

- a reduction of up to 30 % N_2O may be achieved with an improved platinum-based catalyst [87, infoMil, 2001]

- it has been demonstrated that alternative oxidation catalysts produce up to 80 – 90 % less N_2O than platinum-based catalysts, however the benefits might be offset by a lower NO yield and hence increase NH_3 consumption

- the use of two-step catalysts reduces the amount of platinum used by between 40 – 50 % and platinum losses are reduced by 15 – 30 % under similar conditions.

Cross-media effects

None believed likely.

Operational data

See description.

Applicability

As optimised platinum catalysts or alternative 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

For new plants, alternative catalysts can be an option. For existing plants, retrofit costs are reported to be in 1999 USD 1.5 – 2 million (about EUR 1425000 – 1900000 in 2001). The lower NO yield should also be taken into account as it has a significant cost effect.

Savings of EUR 0.50 – 2.00 per tonne of HNO_3 have been achieved [145, Nitrogen2003, 2003].

Driving force for implementation

Process optimisation and minimised N_2O formation.

References to literature and example plants

[87, infoMil, 2001, 94, Austrian UBA, 2001, 105, Müller, 2003]

- SKW Piesteritz GmbH: improved platinum-based Heraeus catalyst
- Grande Paroisse, Rouen: improved platinum-based Heraeus catalyst
- Incitec (Australia) and Simplot (Canada) use a cobalt oxide catalyst
- two-step catalysts are widely used in the republics of the CIS.

3.4.4 Optimisation of the absorption stage

Description

See also Section 3.4.10 "Addition of H_2O_2 to the last absorption stage".

Optimising the absorption step results in an efficient formation of the nitric acid and it minimises 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"). Various parameters effect the absorption efficiency, mainly:

1. **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. The effect of pressure on the absorption stage is illustrated in Table 3.10. Figure 3.6 shows applied absorption pressures in relation to the related tail gas levels.

2. **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.

3. **Optimal contact between NO_x, O_2 and H_2O** — 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.

	M/H	L/M	Unit
Absorption pressure	8	3.8	bar
Absorption temperature	25	25	ºC
Absorption efficiency	99.6	98.2	%
NO_x concentration before SCR	≤ 500	2000 – 3000	ppm

Table 3.10: Parameters of the absorption stages in a M/H and a L/M plant [94, Austrian UBA, 2001]

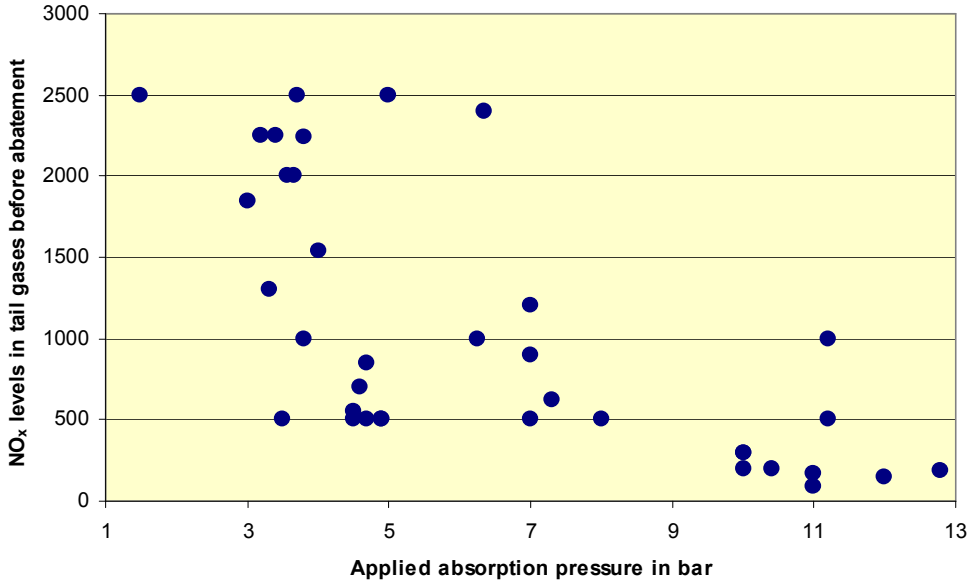

Figure 3.6: Applied absorption pressures and related NO_x levels in tail gases
This figure is based on data given in Table 3.8.

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 monopressure processes, ammonia oxidation and NO_2 absorption take place at the same pressure. In general, three types of monopressure plants are possible: low pressure (<1.7 bar), medium pressure (1.7 – 6.5 bar) and high pressure (6.5 – 13 bar). 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.

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. 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 approximately 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.

High efficiency absorption (HEA). During NO_2 absorption nitrous acid (HNO_2) may be formed as follows:

$$2\ HNO_2 + O_2 \leftrightarrow 2\ HNO_3$$

$$3\ HNO_2 \leftrightarrow HNO_3 + H_2O + 2\ NO$$

The 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

- tail gas levels of 40 – 50 ppm NO_x (82 – 103 mg NO_x/m^3) are technically feasible (15 bar, production of a typical low strength nitric acid, completely optimised absorption columns)
- the combination of technical and economic viability of a new absorption column, combined with the high absorption pressure, can result in values of 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

- high absorption pressures can reduced steam export
- extended absorption with an adjusted form of cooling can be expected to use more energy. Cooling systems are necessary to reach the lower temperatures, hence heat losses to the environment may increase, discharge of warm water may have negative effect on receiving water bodies
- H/H systems show a lower NO yield and generate more N_2O.

Operational data

See description.

Applicability

High pressure systems. In existing plants, the pressure in the absorption unit can be raised within certain technical limits. Generally applicable for new plants, usually designed as an M/H plant.

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. 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. Also refrigeration equipment and associated pipework will need additional expenditure. Haifa Chemicals Ltd. added a second absorption column to the existing set-up (7 bar).

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.

ZAK, Tarnow decided to replace its existing eight production lines by one M/H line (5/15 bar) of 700 tonne HNO_3/day. The Instytut Nawozow Sztucznych (INS) – which is an academic institute that is working for this plant – developed a computer program to optimise the design of this new absorption column. This program could also simulate the performance of the absorption column. Table 3.11 shows the results of the high absorption pressure and the optimum design (structure of the sieve plates, distance between the sieve plates, size of the column).

		Option 1	Option 2	Option 3
		Design values, low steam export	Low HNO_3 concentration, low steam export	Most economic option, high steam export
Absorption pressure in bar		15	15	12
Produced HNO_3 concentration in %		65	56	60
NO_x tail gas level	ppm	100	40	130 – 170
	mg/Nm^3	205	82	267 – 349

Table 3.11: Theoretical study of the optimisation of the absorption stage design at ZAK, Tarnow [88, infoMil, 1999]

The nitric acid plant of ***Yara, Porsgrunn*** was built in 1992 and has a capacity of 2000 tonne HNO_3/day. It is a M/H plant (5/11 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/Nm^3) were achieved without using an additional abatement system.

The nitric acid plant of ***Agropolychim, Devnia*** was built in 2003, has a capacity of 1100 tonnes/day and is designed as a M/H plant (3.5/12.8 bar). At absorption temperatures of 20 – 40 ºC, NO_x levels of 170 – 200 ppm are achieved.

Economics

- monopressure operation has been shown in the past to give special economical advantages. Capital costs are lower, because only one compression unit is required. 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 tonnes 100 % HNO_3/day) it is more realistic to build a dual pressure plant
- 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 approximately 15 – 20 % higher than the investment for a monopressure plant. 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 were in 1998 USD 0.6/tonne HNO_3 produced (about EUR 0.55/tonne HNO_3 produced, figures based on a 365 tonne 100 % HNO_3/day plant).

Driving force for implementation

Optimised HNO_3 yield and lower NO_x emissions.

Reference literature and example plants

[88, infoMil, 1999, 94, Austrian UBA, 2001], ZAK, Tarnow; Yara, Porsgrunn, Agropolychim, Devnia, Haifa Chemicals Ltd.

3.4.5 N_2O decomposition by extension of the reactor chamber

Description

Yara 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 approximately 3.5 m extra in length between the platinum catalyst and the first heat exchanger. For illustration, see Figure 3.7. Due to the longer residence time of 1 – 3 seconds, a N_2O reduction of 70 – 85 % might be obtained, since N_2O is metastable at higher temperatures and decomposes to N_2 and O_2.

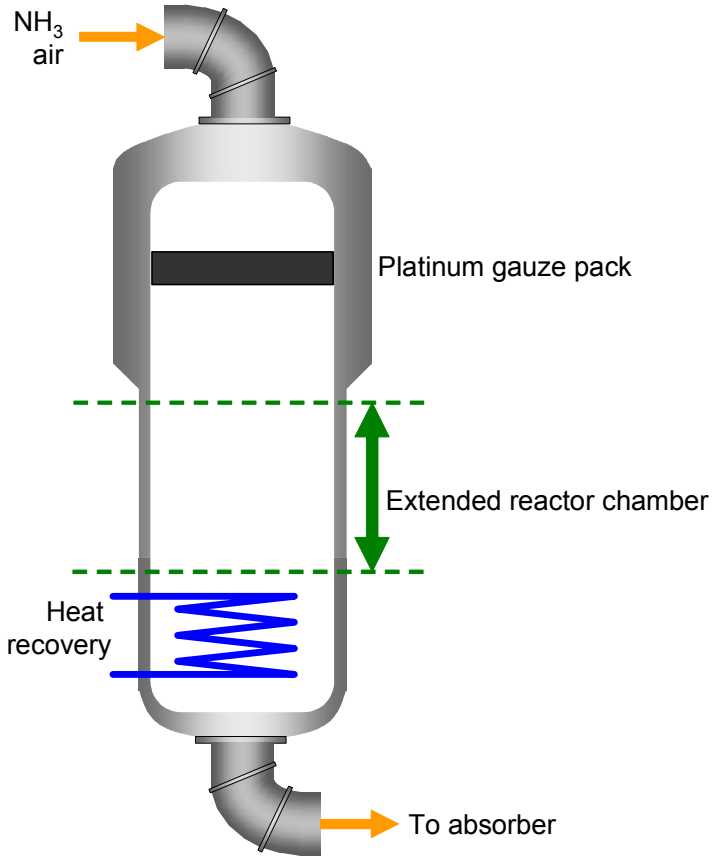

Figure 3.7: Decomposition of N_2O by extension of the reactor chamber
Figure based on [87, infoMil, 2001]

Achieved environmental benefits

The example plant achieves an N_2O emission level of 2 – 3 kg/tonne 100 % HNO_3 [80, Jenssen, 2004, 104, Schöffel, 2001] or about 400 ppm [17, 2nd TWG meeting, 2004].

Cross-media effects

None believed likely.

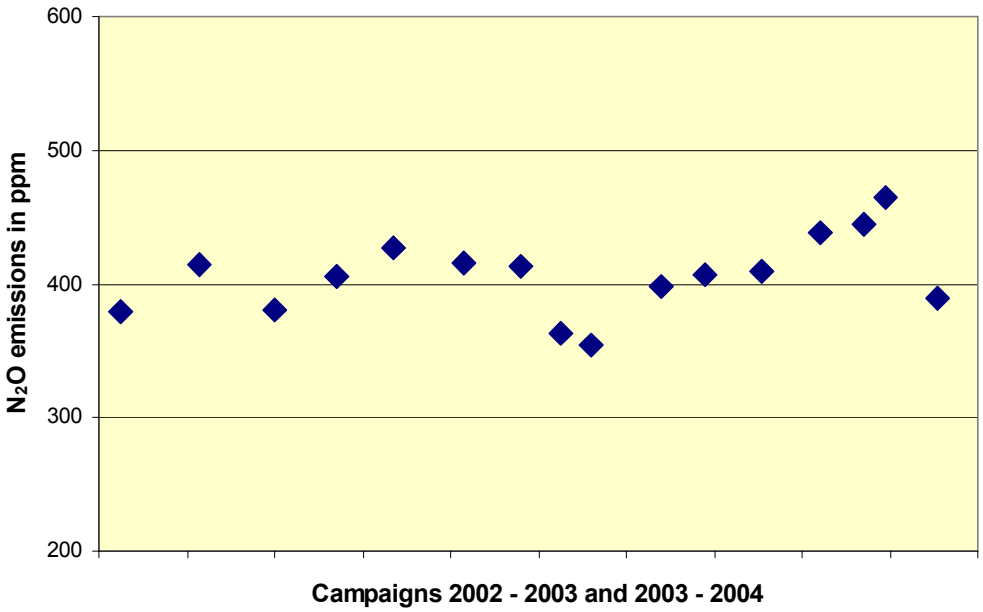

Figure 3.8: Achieved N_2O emission levels at the example plant [17, 2nd TWG meeting, 2004]. The example plant operates a 5 bar oxidation with a gauze temperature of 890 ºC. The reactor chamber is extended by 4 metres.

Operational data

For a modern dual pressure plant, a correlation between the chamber extension in metres and the N_2O decomposition rate in % is given in [104, Schöffel, 2001], assuming a temperature gradient along the decomposition chamber. For example, a decomposition rate of 80 % is predicted to be achieved by an extension of about 7 metres.

Applicability

Applicable to new plants. Not applicable to low pressure plants. Hydro Agri (Yara) installed this system successfully without measurable effects on the NO yield in Porsgrunn (Norway).

Retrofitting the technique in existing plants is not considered because of the "excessive" costs [104, Schöffel, 2001].

The applicability is restricted actually to a maximum reactor diameter lower than 4 metres, because of the lack of mechanical support of the oxidation catalyst [154, TWG on LVIC-AAF, 2006].

Economics

- low additional investment costs for new plants
- much higher investment cost for existing plants
- negligible additional operational costs.

Driving force for implementation

Reduction of N_2O emissions.

References to literature and example plants

[17, 2nd TWG meeting, 2004, 80, Jenssen, 2004, 87, infoMil, 2001, 104, Schöffel, 2001], Yara, Porsgrunn (1991).

3.4.6 Catalytic N_2O decomposition in the oxidation reactor

Description

N_2O can be decomposed just after being formed, by a selective De-N_2O catalyst in the high temperature zone (between 800 and 950 ºC). This is realised by placing the catalyst right below the platinum gauze. Most nitric acid burners are fitted with a basket filled with Raschig rings giving structural support to the gauzes, and the De-N_2O catalyst can be introduced by partial replacement of the Raschig rings. Hence, usually, no modification of the basket is required and the gauze pack can be installed as usual.

According to [109, Lenoir, 2006], a catalyst layer of 50 – 200 mm achieves a high decomposition rate with low additional pressure drop. However, with increasing oxidation pressure, the pressure drop over the catalyst will increase.

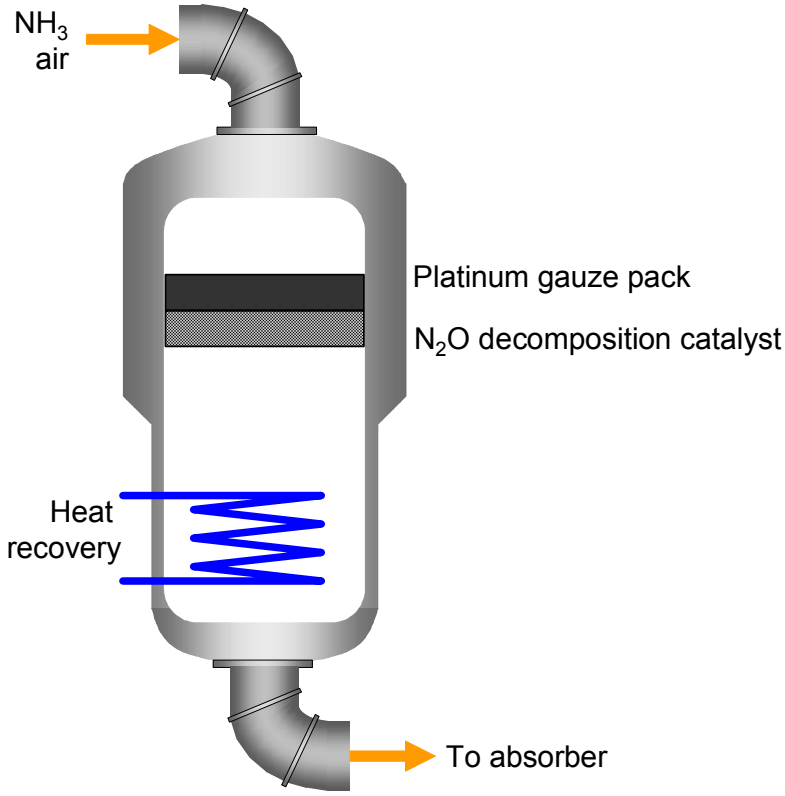

Figure 3.9: Catalytic N_2O decomposition in the oxidation reactor
Figure based on [87, infoMil, 2001]

Achieved environmental benefits

Depending on the catalyst filling height and the assessed time period, N_2O average emissions levels of 130 – 325 ppm are achieved, see Table 3.12.

Cross-media effects

None believed likely.

Operational data

Various catalysts are actually available, e.g.

1. Catalyst developed by Yara [109, Lenoir, 2006]:

    - cerium oxide-based catalyst with cobalt as the active component
    - multicored cylindrical pellets 9 x 9 mm
    - bulk density of 1.1 – 1.3 g/m^3
    - radial crushing strength >20 Newton
    - increasing efficiency with increasing pressure and temperature
    - no losses in NO yield.

2. Catalyst developed by BASF [111, NCIC, 2004, 149, BASF, 2006]:

    - various types available, "O3-85"-types
    - composition (w/w): CuO 20 %, ZnO 16 %, plus Al_2O_3 and promoters
    - various shapes
    - operational for low, medium and high pressure oxidation
    - no measurable loss in NO yield.

3. Catalyst developed by Heraeus [113, Sasol, 2006, 116, Jantsch, 2006]:

    - precious metal deposited over ceramic
    - no measurable effect on NO yield
    - N_2O level adjustable by variation of the catalyst layer thickness.

Applicability

Applicable to new and existing plants. Table 3.12 shows example plants.

In atmospheric pressure plants, the extra pressure drop in the reactor reduces the plant capacity [149, BASF, 2006].

Depending on the particular case, limitations for the application of a N_2O decomposition catalyst might arise with respect to the following factors [149, BASF, 2006]:

- some plants might require modifications to build in a basket
- basket design and actual basket condition
- available height in the burner basket for filling with a De-N_2O catalyst, heights might vary from about 5 – 14 cm
- potential for gas slip at the reactor wall
- gas temperature, pressure and velocity
- additional pressure drop, depending on the catalyst size and shape
- additional load on the statics of the reactor through added weight and additional pressure drop.

Economics

- additional costs for the catalyst
- easy and cost-effective to install, using the existing basket without any further modifications
- an NO_x abatement system is still required in most cases.

According to [89, Kuiper, 2001], a comparison of various N_2O reduction strategies (including Yara, BASF and Uhde approach) does not show a significant difference in cost effectiveness and the cost per tonne HNO_3. The costs are estimated at EUR 0.71 – 0.87 per tonne CO_2-eq. reduced and EUR 0.98 – 1.20 per tonne HNO_3 produced.

References to literature and example plants

[87, infoMil, 2001, 104, Schöffel, 2001, 106, Yara, 2006, 109, Lenoir, 2006, 110, F&C, 2005, 111, NCIC, 2004, 113, Sasol, 2006], for example plants, see Table 3.12.

Plant	Type	N_2O emission level		Baseline N_2O kg/tonne 100 % HNO_3	Remark
		kg/tonne	ppm		
YARA , Ambès	M/M	2.0	325	7	Implemented from May 2002 to June 2003. Achieved with 50 % catalyst filling
	M/M	3.3	535		Implemented from January 2004 to March 2006. Achieved with 40 % catalyst filling
YARA, Montoir	M/H	2.8	445	5.2	Implemented in August 2003, 25 % catalyst filling
	M/H	0.8	130		Implemented in Augut 2005, new catalyst, 75 % filling
YARA, Pardies	M/M				
BASF, Ludwigshafen	L/M				Implemented in 1999. The DeN_2O catalyst was removed in 2002 because of capacity loss. Now under development
BASF, Antwerp SZ2	M/H	1.8	285	6.7	Implemented in 2005/2006, 12 cm catalyst filling, new catalyst
BASF, Antwerp SZ3	M/H	1.7	272		Implemented in 2005/2006, 12 cm catalyst filling, new catalyst
Lovochemie KD6	M/M	5.5	890		Achieved with Heraeus catalyst
Grande Paroisse, Rouen	M/H	1.9	300		Achieved with Heraeus catalyst in combination with an improved oxidation catalyst (FTCplus)
Ube Industries, Yamaguchi					BASF catalyst, 2001
F&C Ltd, Israel	H/H				YARA catalyst, in planning
NCIC Ltd, China	M/?				BASF catalyst, in planning
NFL Ltd, India	M/?				BASF catalyst, in planning
Sasol					Heraeus catalyst, in planning

Table 3.12: Example plants applying catalytic N_2O decomposition in the oxidation reactor
[87, infoMil, 2001, 106, Yara, 2006, 109, Lenoir, 2006, 110, F&C, 2005, 111, NCIC, 2004, 113, Sasol, 2006, 154, TWG on LVIC-AAF, 2006]

3.4.7 Combined NO_x and N_2O abatement in tail gases

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 approximately 420 – 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 (De-N_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 (De-N_2O/De-NO_x step) NO_x is reduced by injection of NH_3. Further decomposition of N_2O also takes place.

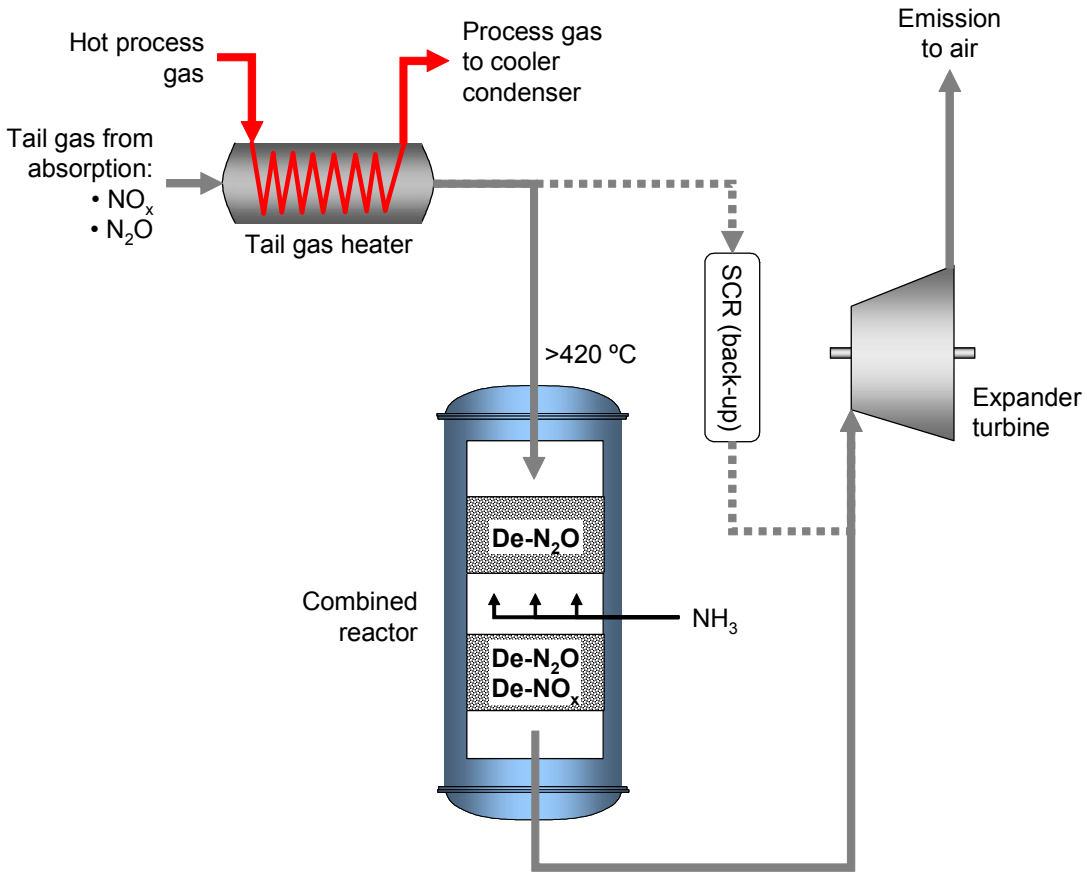

Figure 3.10: Combined NO_x and N_2O abatement
[82, Uhde/AMI, 2004]

Achieved environmental benefits

- simultaneous abatement of N_2O and NO_x
- N_2O removal efficiency of 98 – 99 %
- achievable emission levels of 0.12 – 0.25 kg N_2O per tonne 100 % HNO_3 or 20 – 40 ppm
- NO_x removal efficiency of 99 %
- NO_x emission levels <5 ppm [108, Groves, 2006]
- no NH_3 slip.

For illustration of the achieved emission reduction in the years 2003 – 2005 in the example plant, see Figure 3.11.

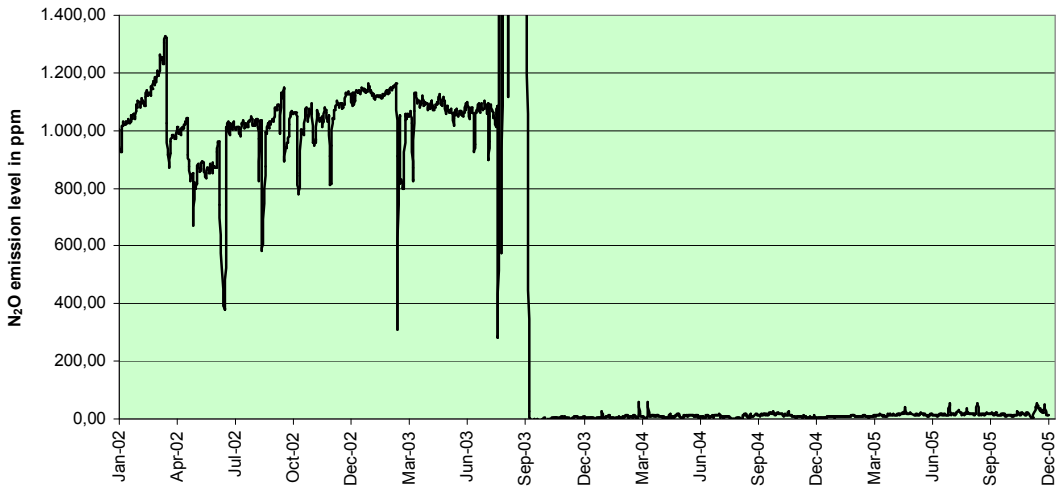

Figure 3.11: N_2O emission before and after commissioning of the combined tail gas treatment [100, AMI, 2006]

Cross-media effects

Ammonia consumption.

Operational data

Data of the example plant:

- type: M/H plant (3.3/8 bar)
- capacity: 1000 tonnes/day
- volume flow: 120000 Nm^3/hour
- NO_x in tail gas: ≤ 500 ppm
- N_2O in tail gas: 800 – 1400 ppm, typically 1000 – 1100 ppm
- the gauzes are changed approximately twice a year, absorption stage operated at 25 ºC.

Applicability

Generally applicable to new nitric acid plants. Applicable to existing nitric acid plants with tail gas temperatures ≥ 420 ºC without major reconstruction of the plant. According to [104, Schöffel, 2001], the following plant types show the required tail gas temperatures (or higher):

- ***M/H*** plants of recent construction
- ***H/H*** plants (there are only a few in Europe).

Examples with high tail gas temperature are given in [88, infoMil, 1999, 103, Brink, 2000]:

- the ***M/M*** plant of DSM in Geleen (450 ºC, commissioned in 1968)
- the ***M/M*** plant of DSM in IJmuiden (400 ºC, commissioned in 1966)
- the ***M/H*** plant of DSM in IJmuiden (500 ºC, commissioned in 1987)
- the ***M/H*** plant of DSM in Geleen (500 ºC, commissioned in 1989).

According to [119, Hu-Chems, 2006], tail gas temperatures can be increased within certain limitations, by removing heat transfer surface from the process cooler and installing an internal bypass, in the example from 387 to 435º C.

Economics

Investment costs. The cost of the AMI unit was EUR 2100000. Because of the experience gained with the AMI unit, reduction of the investment cost is expected for future units for this nitric acid plant capacity to around EUR 1700000 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. +10 K; decomposition of N_2O is an exothermic reaction). Specific catalyst costs and the lifetime of the catalyst are not available, therefore total operating costs and specific cost calculations are not known.

According to [89, Kuiper, 2001], a comparison of various N_2O reduction strategies (including Yara, BASF and Uhde approach) does not show a significant difference in cost effectiveness and the cost per tonne HNO_3. The costs are estimated at EUR 0.71 – 0.87 per tonne CO_2-eq. reduced and EUR 0.98 – 1.20 per tonne HNO_3 produced.

Driving force for implementation

Reduction of N_2O emissions.

References to literature and example plants

[82, Uhde/AMI, 2004, 83, Maurer and Groves, 2005, 84, Schwefer, 2005, 85, Uhde, 2004, 92, Maurer and Merkel, 2003, 93, Uhde, 2005, 94, Austrian UBA, 2001, 95, Wiesenberger, 2004, 96, Maurer and Groves, 2004, 100, AMI, 2006, 108, Groves, 2006],

AMI, Linz (change over from SCR to combined treatment in 09/2003)

3.4.8 Non-selective catalytic reduction of NO_x and N_2O in tail gases

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 De-NO_x system, NSCR also considerably reduces the emissions of N_2O. This process is called non-selective, because the fuel first depletes all of the free oxygen present in the tail gas and then 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). An excess of reducing agent is required to reduce nitrogen oxides and nitrous oxide to nitrogen. Catalysts for NSCR are usually based on platinum, vanadium pentoxide, iron oxide or titanium; catalyst supports are typically made of alumina 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 (approximately 0.5 vol-% 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.

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

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

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.

Achieved environmental benefits

- simultaneous abatement of N_2O and NO_x
- reduction of N_2O of at least 95 %, reducing emissions to well below 50 ppm N_2O
- reduction of NO_x emission to 100 – 150 ppm (205 – 308 mg/m^3).

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 (about 12 g/m^3)
- 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.

Operational data

See description.

Applicability

Generally applicable. Application in an existing plant will demand major adjustments, making the installation of an NSCR less feasible.

Economics

According to [87, infoMil, 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/hour. In the example plant, 290 m^3 natural gas/hour are necessary to reduce the NO_x concentration from 2000 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/hour (EUR 26.8/hour) 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 ºC) reduce the lifetime of the catalyst to 3 – 5 years.

Driving force for implementation

Reduction of NO_x and N_2O emissions.

References to literature and example plants

[80, Jenssen, 2004, 87, infoMil, 2001, 88, infoMil, 1999, 94, Austrian UBA, 2001]

H/H plant of BASF, Antwerp.

Kemira Agro Rozenburg (the Netherlands) used a NSCR as a De-NO_x facility. The plant had a capacity of 400000 tonnes 100 % HNO_3/year and operated at 9 bar (H/H). The plant was designed to be combined with an NSCR, reducing the emission of N_2O to 27 ppm (53 mg/m^3). Kemira Agro Rozenburg closed in December 2000 [87, infoMil, 2001]. The NSCR showed the following characteristics:

- NO_x before abatement, 2000 ppm (4100 mg/m^3)
- NO_x after abatement, 100 ppm (205 mg/m^3)
- fuel used, natural gas
- emissions of CH_4, 0.4 tonnes/year
- emissions of CO, 0.7 tonnes/year
- emissions of CO_2, 6216 tonnes/year
- emissions of VOC (not methane), 0.3 tonnes/year.

After the closure of Kemira Rozenburg, the NSCR equipment was reinstalled in Tertre, Belgium [33, VITO, 2005]:

- NO_x before abatement, 2000 ppm
- NO_x after abatement, 150 – 190 ppm
- fuel used, natural gas.

3.4.9 Selective catalytic reduction of NO_x (SCR)

Description

For a more extensive description of SCR, see [11, European Commission, 2003]. 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:

$$6\ NO + 4\ NH_3 \leftrightarrow 5\ N_2 + 6\ H_2O$$

$$6\ NO_2 + 8\ NH_3 \leftrightarrow 7\ N_2 + 12\ H_2O$$

$$NO + NO_2 + 2\ NH_3 \leftrightarrow 2\ N_2 + 3\ H_2O$$

$$4\ NO + O_2 + 4\ NH_3 \leftrightarrow 4\ N_2 + 6\ H_2O$$

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. The tail gas needs heating to the operational temperature depending on the catalyst being used, i.e. between 120 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_2 in the NO_x, varies between 50 – 75 %, and this significantly affects the catalyst behaviour. As a result of this, some catalysts used in power plants cannot be used in nitric acid plants.

Achieved environmental benefits

- a NO_x conversion of 80 – 97 % can be achieved [11, European Commission, 2003]
- achievable emission levels are 74 – 100 ppm [11, European Commission, 2003]
- ammonia reacts preferentially with nitrogen oxides so less reducing agent is needed compared to NSCR, however, energy might be recovered in the case of NSCR.

For achieved emissions levels, see also Table 3.8. See also Section 3.4.7 "Combined NO_x and N_2O abatement in tail gases".

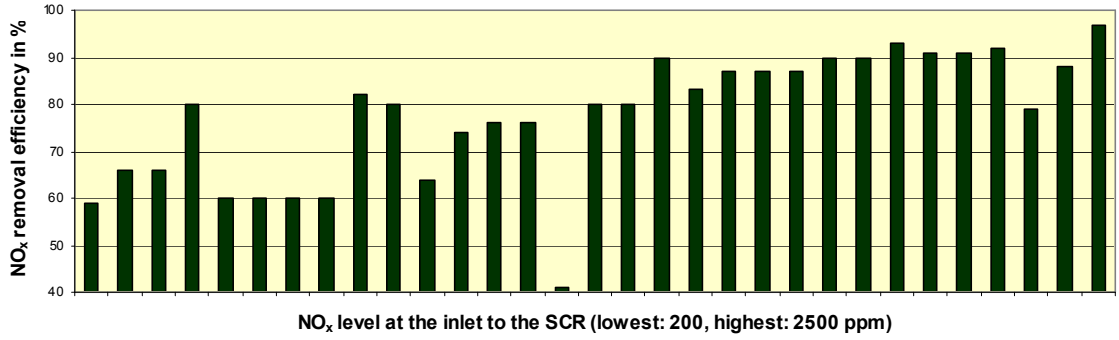

Figure 3.12: NO_x removal efficiencies of SCR units applied in HNO_3 plants
The efficiencies are related to the NO_x inlet concentrations of the plant. This figure is based on data given in Table 3.8

Cross-media effects

- ammonia consumption depending on the amount of NO_x reduced
- ammonia slip, usually less than 10 ppm (7.6 mg/Nm^3)
- older catalysts in particular could produce some N_2O.

Operational data

- optimum operating temperature varying from 200 to 350 °C
- pressure drop before the expander unit of 0.01 – 0.1 bar
- the tail gas temperature after reduction of 200 – 360 °C is significantly lower than in the case of NSCR (650 – 800 °C), allowing the use of simpler, cheaper construction materials.

Applicability

Generally applicable. In principle, SCR facilities can be applied in both new and existing nitric plants and can operate at all pressures.

Due to safety concerns, an SCR facility is usually not operated at inlet gas temperatures of below 180 ºC [154, TWG on LVIC-AAF, 2006].

Economics

Based on an M/H plant with a production output of 1000 tonnes 100 % HNO_3/day and an operating time of 8400 hours/year, the costs of an SCR are as follows:

- capital costs: EUR 2000000
- annual costs: EUR 300000
- total costs: approximately USD 1.3/tonne HNO_3 produced in 1998 (in 1998 about EUR 1.16/tonne HNO_3 produced).

Assuming a catalyst price of between USD 35000 and 53000 per m^3 (about EUR 32000 – 49000 per m^3), excluding technical and maintenance costs, a catalyst volume of 3.75 m^3 at a flowrate of 48235 m^3/hour, ammonia consumption of 77 kg NH_3/hour and a NO_x reduction from 2000 to 150 ppm (from 4100 to 308 mg/Nm^3), the following costs can be calculated:

- fuel operating costs: USD 15.40/hour (about EUR 14.20/hour)
- or USD 1.03/tonne 100 % HNO_3 produced (about EUR 0.95).

(Based on a price of USD 200/tonne NH_3 (= EUR 185/tonne NH_3) and an average flow of 3230 m^3/tonne 100 % HNO_3 and 8640 operating hours/year at a flow of 48235 m^3/hour = 129 ktonne 100 % HNO_3/year).

Driving force for implementation

Reduction of NO_x emissions.

References to literature and example plants

[11, European Commission, 2003, 88, infoMil, 1999, 94, Austrian UBA, 2001]

3.4.10 Addition of H_2O_2 to the last absorption stage

Description

Haifa Chemicals is required to reduce the NO_x emissions from their nitric acid plants by the end of 2006. For an overview of the company's nitric acid lines, see Table 3.13. After turning down the application of SCR for line 2 due to safety considerations, the addition of H_2O_2 to the last absorption stage has been tested and operated on full scale.

Safety concerns arise where the tail gas cools down in the expander to levels of <85 ºC and NO_x (remaining levels after SCR) and NH_3 (potential slip from the SCR) are present. With such a low temperature, the formation of an ammonium nitrate/nitrite layer on the expander blades and in the stack has to be considered.

Instead of applying an SCR, H_2O_2 is added to the second absorption tower of line 2 in order to increase the absorption efficiency, but at the same time to keep the H_2O_2 consumption on economic levels.

	Line 1	**Line 2**
Absorption pressure	4 bar	7 bar
Temperature before expander	210 ºC	175 ºC
Temperature after expander	120 ºC	35 ºC
NO_x level before additional measures	2000 ppm [x]	500 ppm [xx]
NO_x level including additional measures	80 ppm (SCR) [x]	150 ppm (H_2O_2)
Reference: Haifa Chemicals Ltd. (Israel) [x] due to the variation of the cooling water temperature (in Israel), the levels vary from about 1400 ppm (in winter) to about 2500 ppm (in summer). However, the SCR restrains the emission level by controlling the ammonia dosing accordingly [xx] before addition of a second absorption tower, the level was 1000 ppm		

Table 3.13: Overview of the two nitric acid lines of the example plant

Achieved environmental benefits

- in the example plant, NO_x emission levels of 150 ppm are achievable
- increased HNO_3 yield.

Cross-media effects

- consumption of H_2O_2.

Operational data

HNO_3 in the first absorption tower: 60 – 62 %
HNO_3 in the second absorption tower: about 8 %.

Applicability

Generally applicable.

Economics

Investment cost:	USD 500000 for 384 tonnes/day 100% HNO_3 (127000 tonnes/year).
Specific cost:	USD 2.5 per tonne HNO_3.

Driving force for implementation

Reduction of NO_x emissions in plants with very low tail gas temperatures, safety concerns.

References to literature and example plants

Roister Clarck Nitrogen, US
Agrium Kenewick, US
Apach Nitrogen, US (for startup and shutdown)
Haifa Chemicals Ltd., Israel

3.4.11 NO_X reduction during startup/shutdown

See also Section 3.4.10 "Addition of H_2O_2 to the last absorption stage".

Description

The process for producing nitric acid is unstable at startup and shutdown. At startup, 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.

During normal operation, the percentage NO_2 in the NO_x varies between 50 – 75 %. Especially during startup, 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.

Various techniques are available to reduce NO_X emissions during startup and shutdown, but investments are often high compared to the amount of NO_x reduction achievable. Extra NO_x emissions due to startup 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.

Potential end-of-pipe measures during startup include:

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 startup 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, down-times for the SCR will reduce.

Installing a scrubber. Excessive emissions at startup can be minimised by the use of caustic, sodium carbonate or ammonia alkali scrubber.

Installation of a tower with a dry adsorbent material. NO_x reduction at startup can be achieved by using a dry adsorbent, e.g. silica gel or molecular sieves.

The above procedures are less suitable during shutdowns, as pressure and temperature quickly reduce.

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 startup 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 startup 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 a NO_X reduction of at least 70 % during startup can be expected.

Installation of a tower with a dry absorbent material. Figures are not known but a NO_X reduction of at least 70 % during startup 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.

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 startup. 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.

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 it has to be disposed of as waste.

Installation of a tower with a dry adsorbent material. The spent adsorbent material is a waste for disposal.

Operational data

No specific information provided.

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 to 450 °C.

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 space 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.

Economics

Generally, most end-of-pipe technologies to reduce startup and shutdown emissions are quite expensive in comparison to the NO_x reduction.

Heating the tail gas. Equipment costs for a burner are approximately NLG 200000 (about EUR 91000). Installing a furnace (equipment and engineering) will cost at least NLG 1000000 (EUR 450000). Other economics are not known.

Installing a low temperature SCR. Capital costs of a complete SCR facility are at least NLG 1000000 (about EUR 450000). To reduce only the startup emissions, the costs of an SCR are unacceptable in most cases. Other economics are not known.

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.

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.

Driving force for implementation

Reduction of the visual appearance from the reddish-brown or yellow stack gas.

Reference literature and example plants

[88, infoMil, 1999]

3.5 BAT for nitric acid

BAT is to apply the common BAT given in Section 1.5.

BAT for storage is to apply BAT given in [5, European Commission, 2005].

BAT is to use recoverable energy: co-generated steam and/or electrical power.

BAT is to reduce emissions of N_2O and to achieve the emission factors or emission concentration levels given in Table 3.14 by applying a combination of the following techniques:

- optimising the filtration of raw materials, see Section 3.4.1
- optimising the mixing of raw materials, see Section 3.4.1
- optimising the gas distribution over the catalyst, see Section 3.4.1
- monitoring catalyst performance and adjusting the campaign length, see Section 3.4.1
- optimisation of the NH_3/air ratio, see Section 3.4.2
- optimise pressure and temperature of the oxidation step, see Section 3.4.2
- N_2O decomposition by extension of the reactor chamber in new plants, see Section 3.4.5
- catalytic N_2O decomposition in the reactor chamber, see Section 3.4.6
- combined NO_x and N_2O abatement in tail gases, see Section 3.4.7.

		N_2O emission level [x]	
		kg/tonne 100 % HNO_3	**ppmv**
M/M, M/H and H/H	New plants	0.12 – 0.6	20 – 100
	Existing plants	0.12 – 1.85	20 – 300
L/M plants		No conclusion drawn	
[x] the levels relate to the average emission levels achieved in a campaign of the oxidation catalyst			

Table 3.14: N_2O emission levels associated with the application of BAT for the production of HNO_3

Split view: Industry and one Member State do not agree with the N_2O emission levels associated with the application of BAT *for existing plants* due to the limited experience with the De-N_2O techniques presented in Sections 3.4.6 and 3.4.7, the variance in the results obtained from pre-selected test installations, and the many technical and operational constraints for applying these techniques in the nitric acid plants in operation in Europe today. In their opinion, the applied catalysts are still under development, although already placed on the market. Industry also claims that the levels should relate to averages achieved in the lifetime of the De-N_2O catalyst, although this is not known yet. Industry and one Member State claim that the BAT range should include 2.5 kg N_2O/tonne 100 % HNO_3 for existing plants.

BAT is to reduce emissions of NO_x and to achieve the emission levels given in Table 3.15 by applying one or a combination of the following techniques:

- optimisation of the absorption stage, see Section 3.4.4
- combined NO_x and N_2O abatement in tail gases, see Section 3.4.7
- SCR, see Section 3.4.9
- addition of H_2O_2 to the last absorption stage, see Section 3.4.10.

BAT is to reduce emissions during startup and shutdown conditions (e.g. see Sections 3.4.10 and 3.4.11).

	NO_x emission level as NO_2	
	kg/tonne 100 % HNO_3	**ppmv**
New plants	--	5 – 75
Existing plants	--	5 – 90 [x]
NH_3 slip from SCR	--	<5
[x] up to 150 ppmv, where safety aspects due to deposits of AN restrict the effect of SCR or with addition of H_2O_2 instead of applying SCR		

Table 3.15: NO_x emission levels associated with the application of BAT for the production of HNO_3

3.6 Emerging techniques for nitric acid

3.6.1 Combined NO_x and N_2O abatement with addition of hydrocarbons

Description

See also Section 3.4.7. In contrast to the technique described there, NO_x is eliminated by reaction with ammonia in a first step (comparable to an SCR system). In a second step, N_2O is removed by catalytic reduction with a hydrocarbon, such as natural gas or propane as shown in Figure 3.13.

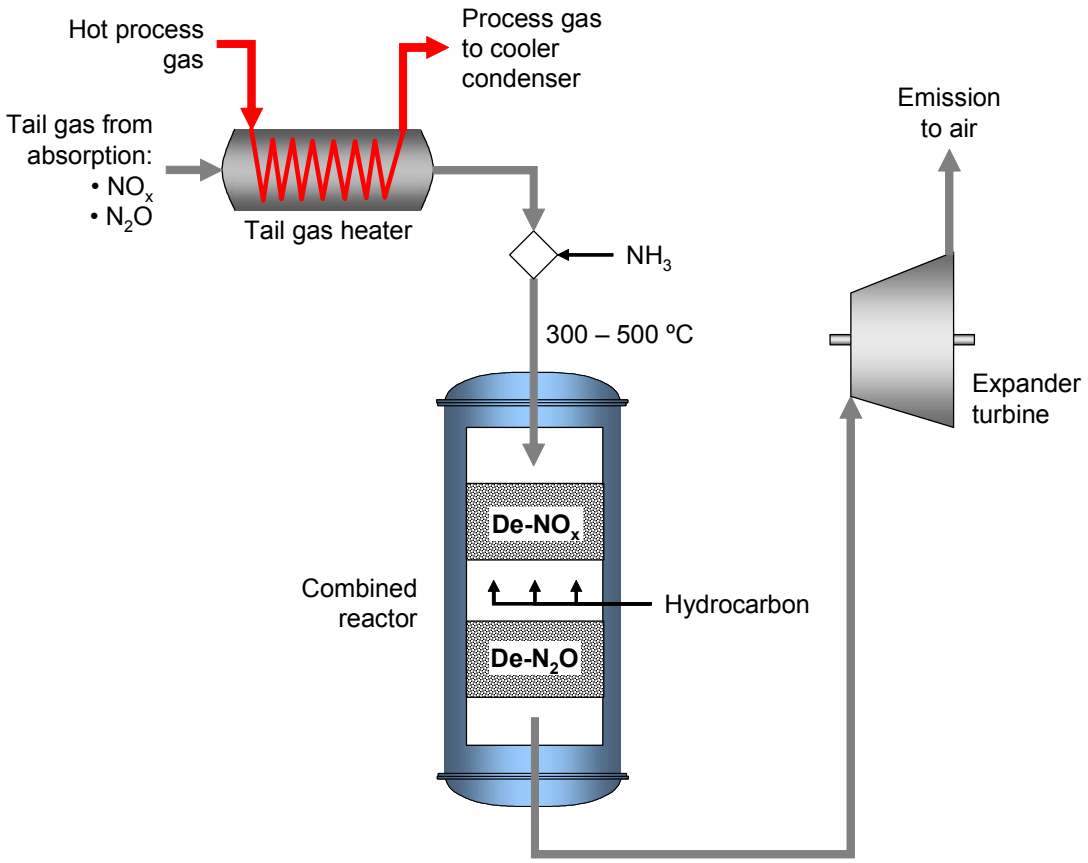

Figure 3.13: Overview of the combined treatment of NO_x and N_2O with hydrocarbons

Achieved environmental benefits

- simultaneous abatement of N_2O and NO_x to levels similar to those given in Section 3.4.7 are expected
- expected N_2O reduction of about 97 %.

Cross-media effects

- consumption of hydrocarbons and NH_3
- no information is available on other potential pollutants (e.g. CO).

Operational data

No specific information provided.

Applicability

Applicable to plants with tail gas temperatures in the range of 300 – 500 °C. Current developments aim at widening this temperature window. Within certain limitations, tail gas temperatures can be adjusted by removing heat transfer surface from the process cooler and/or installing internal bypasses.

Economics

No specific information provided.

Driving force for implementation

Reduction of N_2O emissions.

Reference literature and example plants

[146, Uhde, 2006]

Abu Qir Fertilizer Company, Egypt, to be completed in September 2006
Hu-Chems Fine Chemical Coorperation, South Korea, to be completed in 2007

4 SULPHURIC ACID

4.1 General information

More H_2SO_4 is produced than any other chemical in the world. In Western Europe in 1997, over 19 Mtonnes were produced, the total production worldwide being estimated at around 150 Mtonnes. About half of the world's output is produced in North America, Western Europe and Japan. Table 4.1 shows the production levels for some European countries. For the EU-25, the sulphuric acid production capacity is estimated in 2004 to about 22 Mtonnes per year [17, 2nd TWG meeting, 2004]. In the EU-25, sulphuric acid was produced in 95 plants in 2004. Figure 4.1 shows the plant size distribution. Table 4.2 lists the sulphuric acid producers as compiled by ESA.

Mtonnes H_2SO_4	1994	1997	2000	2006
Belgium/Luxembourg	1515	2160	2238	1942
Finland	1373	1570	1655	1760
France	2227	2242	2269	1755
Germany	3380	3496	4898	4595
Greece	630	0675	688	815
Italy	1228	1590	1042	1616
Netherlands	1073	1040	988	988
Norway	585	666	569	315
Spain	2348	2810	2418	3500
Sweden	518	630	629	1010
United Kingdom	1225	1205	1058	447

Table 4.1: H_2SO_4 production levels for some European countries [58, TAK-S, 2003]

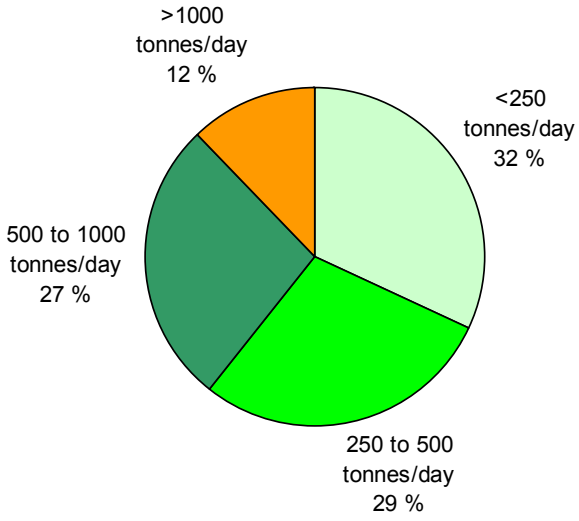

Figure 4.1: Plant size distribution in the EU-25 in 2004 [17, 2nd TWG meeting, 2004]

Country	Company	Location	Capacity (tonnes per year)	SO_2 source	Product
Austria	Donau Chemie AG	Pischelsdorf	230000	Sulphur	H_2SO_4
	Lenzing AG	Lenzing	90000	Sulphur	H_2SO_4
Belgium	BASF Antwerpen NV	Antwerpen	230000	Sulphur	H_2SO_4 & oleum
	Lanxess Antwerpen NV	Antwerpen	340000	Sulphur	H_2SO_4 & oleum
	Prayon SA	Engis	165000	Sulphur	H_2SO_4
	PVS Chemicals Belgium NV	Gent	70000	Sulphur	H_2SO_4 & oleum
	Misa Eco Services Sulfuriqu	Gent (Rieme)	250000	Sulph./spent acid/waste	H_2SO_4/oleum/Na bisulphite
	Sadaci	Gent	22000	Smelter gas	H_2SO_4
	Tessenderlo Group	Ham	365000	Sulphur	H_2SO_4
	Umicore	Hoboken	76000	Smelter gas	H_2SO_4
		Balen	384000	Smelter gas	H_2SO_4
Bulgaria	Cumerio	Pirdop	1000000	Smelter gas	
	KCM	Plovdiv	110000	Smelter gas	
	OCK	Kardjali	35000	Smelter gas	
Switzerland	SF Chemie	Basel	85000	Sulphur	H_2SO_4 & oleum
Croatia	Petrolkemija	Kutina	495000	Sulphur	
Czech Republic	Synthesia	Pardubice	76000	Sulphur/spent acid	
Germany	Xstrata Zink GmbH	Nordenham	210000	Smelter gas	H_2SO_4
	Berzelius Stolberg GmbH	Stolberg	100000	Smelter gas	H_2SO_4
	BASF	Ludwigshafen	610000	Sulphur	H_2SO_4 & oleum
	Lanxess AG	Leverkusen	160000	Sulphur	H_2SO_4
		Leverkusen	20000	Regenerated	H_2SO_4
		Dormagen	94000	Regenerated	H_2SO_4
	Degussa AG	Marl	50000	Sulphur	H_2SO_4
		Wesseling	120000	Sulphur	H_2SO_4
		Worms	230000	Regenerated	H_2SO_4
		Mannheim	65000		H_2SO_4
	Deutsche Steinkohle AG	Bottrop	15000	Sulphur	H_2SO_4 & oleum
	DOMO Caproleuna GmbH	Leuna	260000	Sulphur	H_2SO_4 & oleum

Country	Company	Location	Capacity (tonnes per year)	SO_2 source	Product
	Grillo-Werke AG	Frankfurt	258000	Sulphur	H_2SO_4 & oleum
	Tronox	Uerdingen	65000	Pyrite	H_2SO_4 & oleum
			25000	Sulphur	
	Metaleurop Weser GmbH	Nordenham	50000	Smelter gas	H_2SO_4 & oleum
	Norddeutsche Affinerie AG	Hamburg	1300000	Smelter gas	H_2SO_4 & oleum
	PVS Chemicals Germany GmbH	Kelheim	120000	Sulphur	H_2SO_4 & oleum
	Ruhr-Zink	Datteln	200000	Smelter gas	H_2SO_4
	Sachtleben Chemie GmbH	Duisburg	500000	sulphur, pyrites, recycling of filtersalt	H_2SO_4 & oleum
Spain	Atlantic Copper	Huelva	1350000	Copper smelter	H_2SO_4
	Asturiana de Zinc	Avilés(Asturias)	730000	Zinc smelter	H_2SO_4 & oleum
	Fertiberia SA	Huelva	890000	Sulphur	H_2SO_4
	UBE Chemicals	Castellón	90000	Sulphur	H_2SO_4
	Befesa Desulfuracion SA	Luchana-Barakaldo	320000	Sulphur	H_2SO_4 & oleum
Finland	Boliden Harjavalta Oy	Harjavalta	660000	Copper & nickel smelter	H_2SO_4
	Kemira Oy	Kokkola	320000	Zinc roaster	H_2SO_4 & oleum
	Kemira GrowHow	Siilinjärvi	530000	Pyrite	H_2SO_4
	Kemira Oy	Pori	220000	Sulphur	H_2SO_4
France	Rhodia Eco Services Sulfurique	Les Roches	250000	Sulphur/spent acid	H_2SO_4 & regeneration
	Lyondell	Le Havre	275000	Sulphur	H_2SO_4
		Thann	45000	Sulphur	H_2SO_4
	Huntsman	Calais	300000	Sulphur	H_2SO_4
		St. Mihiel	300000	Sulphur	H_2SO_4
	Grand Paroisse	Bordeaux	90000	Sulphur	H_2SO_4 & oleum
	Albemarle	Port de Bouc	20000	Sulphur	H_2SO_4
	Arkema	Pierre Bénite	165000	Sulphur	H_2SO_4 & oleum
		Pau	35000	Sulphur	H_2SO_4
		Carling	155000	Sulphur	H_2SO_4 & regeneration

Country	Company	Location	Capacity (tonnes per year)	SO_2 source	Product
	Umicore	Auby	200000	Smelter gas	H_2SO_4
	Clariant	Lamotte	130000	Sulphur	H_2SO_4, oleum & SO_2
Greece	Phosphoric Fertilizers Industry SA	Kavala	180000	Sulphur	H_2SO_4
			280000	Sulphur	H_2SO_4
		Thessaloniki	130000	Sulphur	
			225000	Sulphur	
Italy	Nuova Solmine S.p.A	Scalino(GR)	600000	Sulphur	H_2SO_4 & oleum
	Nuova Solmine	Serravalle Scrivia (AL)	60000	Regenerated	H_2SO_4 & oleum
	Marchi Industriale	Marano Veneziano(VE)	90000	Sulphur	H_2SO_4 & oleum
	Portovesme s.r.l.	Porto Vesme(CA)	400000	Smelter gas	H_2SO_4
	ENI S.p.a	Gela(CL)	180000	Smelter gas	H_2SO_4
			120000	Not disclosed	H_2SO_4
	ERG-Priolo	Priolo(SR)	30000	Regenerated	H_2SO_4
	Ilva-TA	Taranto(TA)	20000	Not disclosed	H_2SO_4
	Fluorsid	Macchiareddu (CA)	100000	Sulphur	H_2SO_4
Macedonia	Zletlovo	Titov Veles	132000	Ex sintering	
The Netherlands	Zinifex Budel Zink BV	Budel	380000	Smelter gas	H_2SO_4
	DSM Fibre Intermediates B.V.	Geleen	400000	Sulphur	Oleum
	Climax	Rotterdam	40000	Smelter gas	H_2SO_4
	Corus	Velsen	18000	Smelter gas	H_2SO_4
Norway	New Boliden	Odda	195000	Smelter gas	H_2SO_4
	Falconbridge Nikkelverk A/S	Kristiansand	110000	Ni sulphide mattes	H_2SO_4
Portugal	Quimitecnica SA	Barreiro-Lavradio	25000	Desulphurisation ammonia plant	H_2SO_4
Romania	Sofert	Bacau	200000	Sulphur	
Sweden	Kemira Kemi AB	Helsingborg	360000	Sulphur	H_2SO_4 & oleum
	New Boliden	Skelleftehamn	640000	Copper & lead	H_2SO_4

Country	Company	Location	Capacity (tonnes per year)	SO_2 source	Product
				smelting	
Serbia	RHMK Trepca	Mitrovica		Lead & zinc smelter	
	Sabac	Sabac		Lead & smelter	
Slovenia	Cinkarna Celje d.d.	Celje	150000	Sulphur	H_2SO_4
United Kingdom	Degussa	Knottingley(Yorks)	30000	Sulphur	H_2SO_4
	INEOS Enterprises	Runncorn Site	280000	Sulphur	H_2SO_4 & oleum
	Rhodia Eco Services Ltd	Staveley	117000	Sulphur	H_2SO_4 & oleum
Turkey	Bagfas	Bandyrma	500000	Sulphur	
	Tugsas	Samsun	214000	Pyrite	
	Etibor	Bandyrma	240000	Pyrite	
	Black Sea Copper	Samsun	282000	Smelter gas	

Table 4.2: Sulphuric acid producers organised in ESA or associated to ESA
[154, TWG on LVIC-AAF]

Figure 4.2 gives an overview of the main feedstock, consumers and cycles of the H_2SO_4 economy. Table 4.3 shows the distribution of H_2SO_4 production according to the SO_2 source. The phosphate fertiliser industry is by far the most important user. Other applications of H_2SO_4 are in petroleum refining, pigment production, steel pickling, non-ferrous metals extraction and the manufacture of explosives, detergents (organic sulphonation processes), plastics and manmade fibres. The chemical industry also uses varying amounts of H_2SO_4 in specialised production applications for dyes, pharmaceuticals and fluorine chemicals.

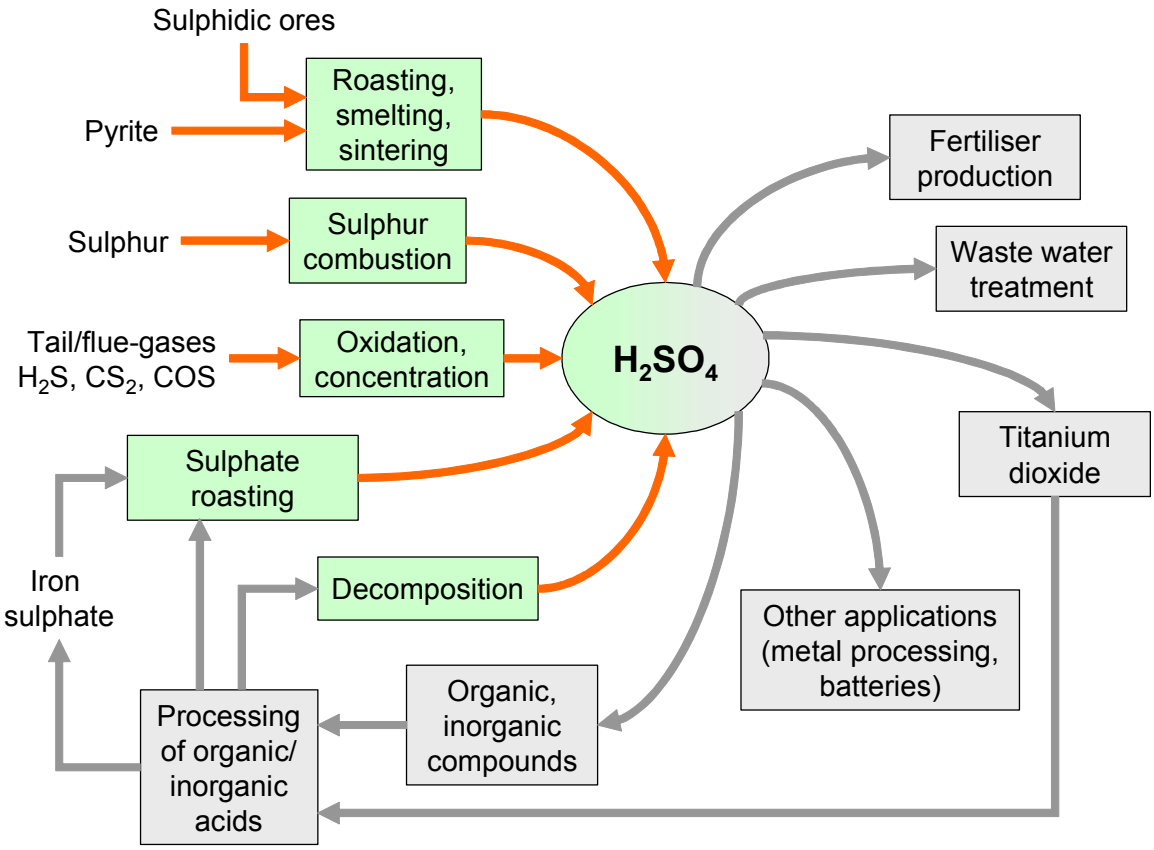

Figure 4.2: Overview of the main feedstock, consumers and cycles of the H_2SO_4 economy This figure is based on [58, TAK-S, 2003]

SO_2 source	% distribution
Sulphur	43.7
Non-ferrous metals	39.0
H_2SO_4 regeneration	7.5
Pyrite	4.2
Recovery & others	5.6

Table 4.3: Distribution of the H_2SO_4 production 2005 according to the SO_2 source [154, TWG on LVIC-AAF]. This table relates to production in the EU-25, Norway and Switzerland.

4.2 Applied processes and techniques

4.2.1 Overview

For an overview of the production of H_2SO_4, see Figure 4.3. H_2SO_4 is produced from SO_2, which is derived from various sources (see Section 4.2.3), such as combustion of elemental sulphur or roasting of metal sulphides. SO_2 is then converted into SO_3 in a gas phase chemical equilibrium reaction, using a catalyst:

$$SO_2 + ½\ O_2 \leftrightarrow SO_3 \qquad \Delta H_0 = -99\ kJ/mole$$

The conversion rate is defined as follows:

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

Both thermodynamic and stoichiometric 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, 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.

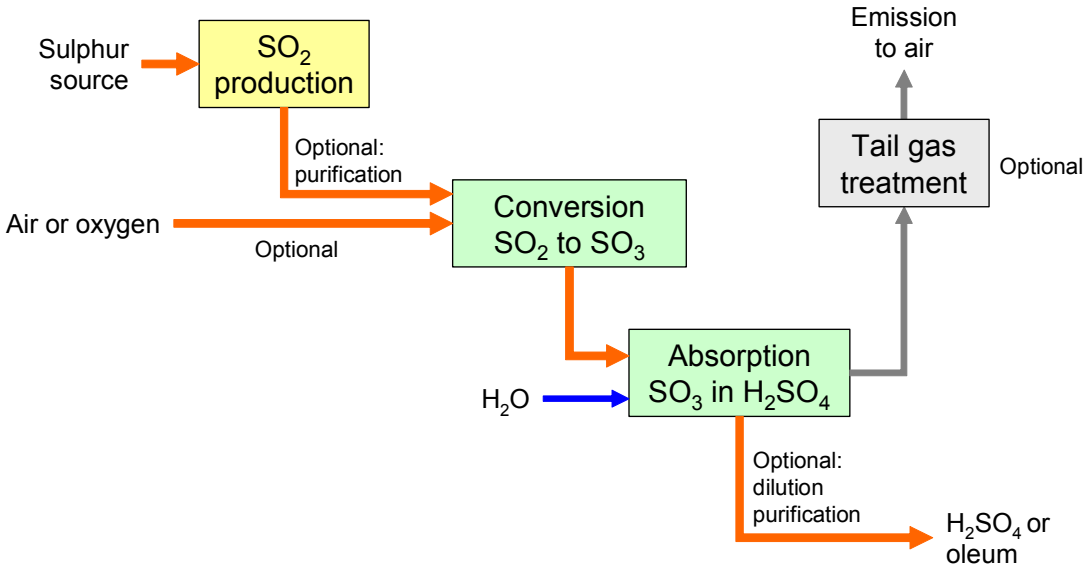

Figure 4.3: Overview of the production of H_2SO_4
This figure is based on [58, TAK-S, 2003]

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.

Two general converter types have been in use extensively in the past:

- the brick-arch support and
- the cast iron beams and columns design (still very popular in North America).

Newer converter types are:

- central core tube converters
- converters with one or more integrated heat exchangers (with the heat exchanger placed in the core tube or "wrapped" around the outer shell of the converter vessel).

In conventional converters, the shell is generally made of boiler quality steel, with internal brick lining and mostly additional aluminium spraying to protect the material from scaling. A great advantage of the brick lined vessel is its high heat capacity, which enables long shutdown times without preheating. The disadvantage is that older brick-arches can be porous and, hence, process gas partially bypasses the intermediate absorber (see also Section 4.4.6 "Replacement of brick-arch converters").

Newer converter designs are made of the 304 or 321 type stainless steel to ensure long term stability. The higher cost of stainless steel is compensated by less weight, simply through a thinner wall thickness. Figure 4.4 illustrates the design of brick-arch and core tube converters.

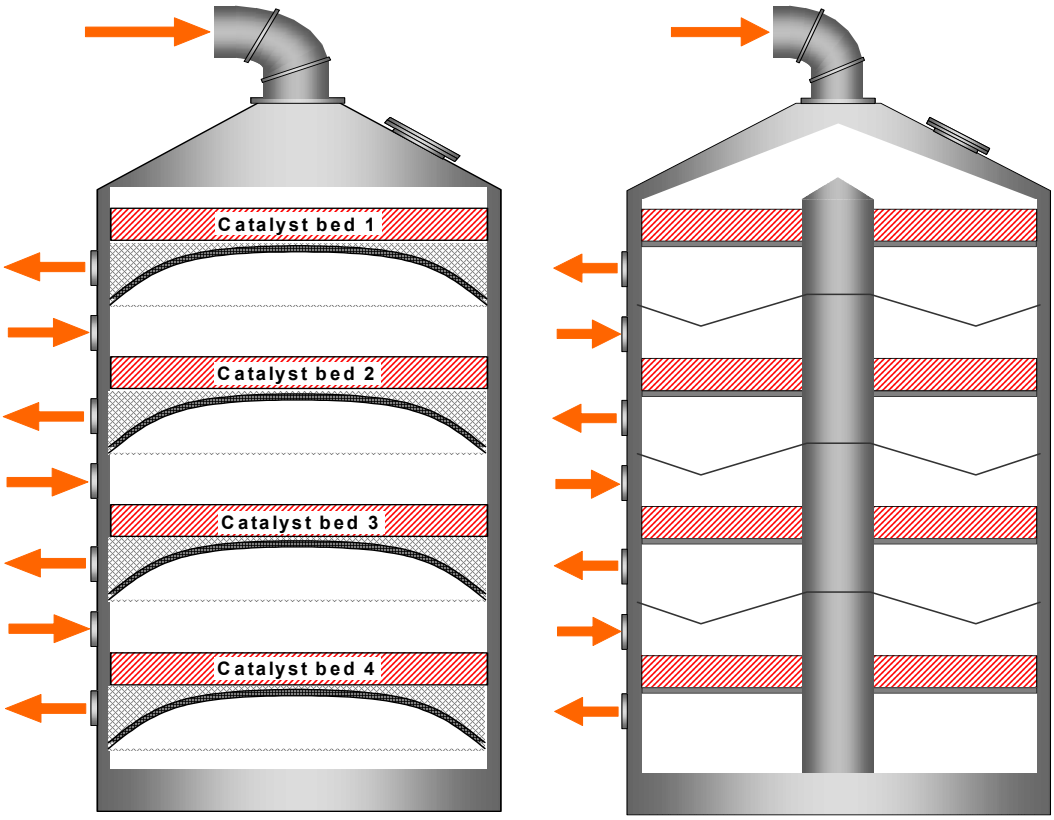

Figure 4.4: Schematic of a brick-arch converter (left) and a core tube converter (right)
These figures are based on [67, Daum, 2000]

Finally, sulphuric acid is obtained from the absorption of SO_3 and water into H_2SO_4 (with a concentration of at least 98 %). For an example of a final absorber, see Figure 4.5. 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 – 120 ºC)
- 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.

For the correlation between SO_2 levels, specific SO_2 loads in tail gases and conversion rates, see Section 4.3.

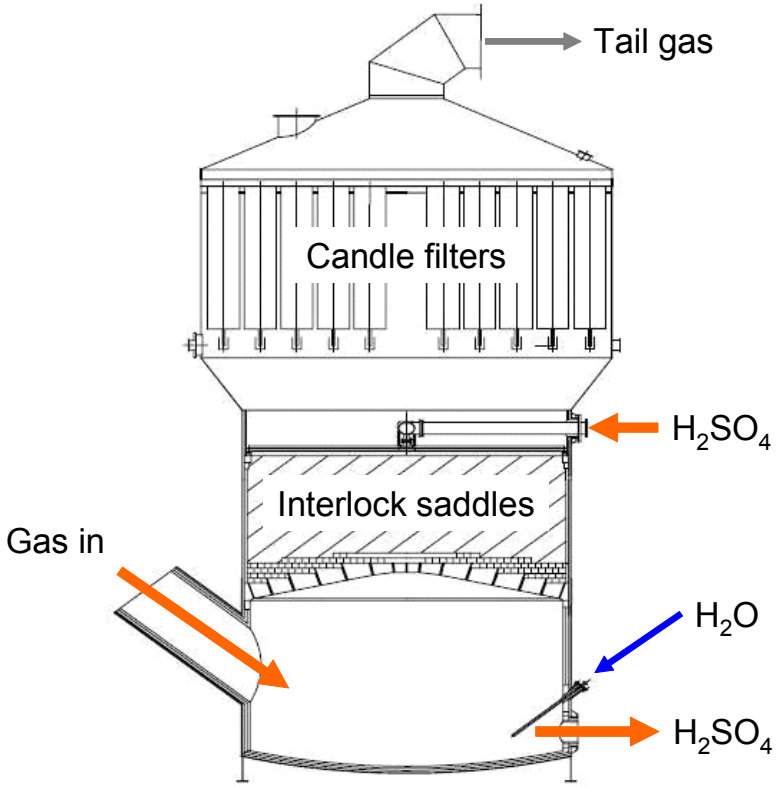

Figure 4.5: Example for a final absorber
This figure is based on [68, Outukumpu, 2006]

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.

Figure 4.6 gives an impression of a sulphuric acid plant. The example shows a double contact/double absorption plant based on sulphur combustion:

1. solid sulphur storage
2. sulphur melting
3. liquid sulphur filtration
4. liquid sulphur storage
5. air filter and silencer
6. air dryer
7. sulphur combustion, two burners with individual air supply
8. steam drum, feed-water tank, waste heat boiler
9. converter
10. intermediate absorber
11. final absorber
12. stack
13. heat exchangers, economisers and superheater.

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. For a more detailed description of individual processes, see:

- Section 4.4.1 ”Single contact/single absorption process”
- Section 4.4.2 “Double contact/double absorption process”
- Section 4.4.8 “Wet catalysis process”
- Section 4.4.9 “Combined wet/dry catalysis process”.

For tail gas treatment, see Sections 4.4.19 to 4.4.22.

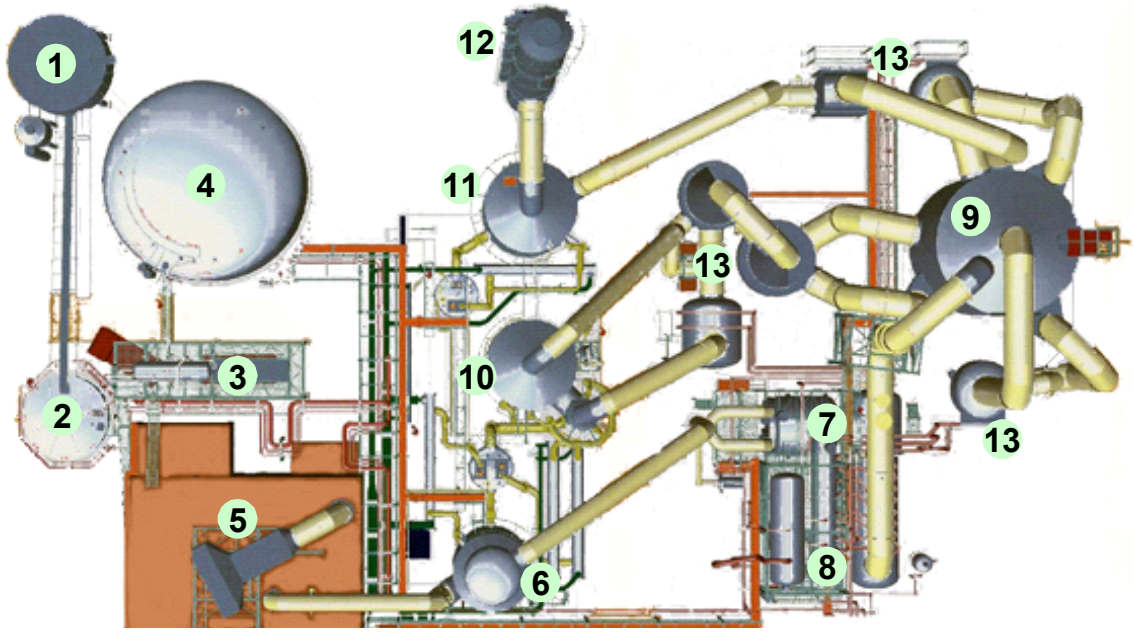

Figure 4.6: Example for a sulphuric acid plant (top view)
[68, Outukumpu, 2006]

4.2.2 Catalysts

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 % w/w 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.

In industrial practice, the lower temperature range is 410 – 440 ºC for conventional catalysts and 380 – 410 ºC for caesium treated catalysts. The upper temperature range is 600 – 650 ºC, above this, catalytic activity can be permanently lost due to internal surface area reduction. The average operating life for the catalyst is approximately 10 years. Operating life is generally determined as a result of catalyst losses during screening of the catalyst, which has to be carried out periodically to remove dust.

See also Sections 4.4.4 “Application of a Cs-promoted catalyst” and 4.4.12 “Prevention of catalyst activity loss”.

4.2.3 Sulphur sources and SO_2 production

Table 4.5 gives an overview of the major sulphur sources for the manufacture of H_2SO_4 and some characteristic features of the gas containing SO_2 arising from these sources.

4.2.3.1 Sulphur combustion

Elemental sulphur is derived from desulphurisation of natural gas or crude oil by the Claus process. Elemental sulphur is delivered to the plant preferably liquid but also solid (at temperatures of 140 – 150 °C) and, if necessary, filtered prior to combustion.

The combustion is carried out in one-stage or two-stage units between 900 and 1500 °C. The combustion unit consists of a combustion chamber followed by a waste heat boiler. The SO_2 content of the combustion gases is generally as much as 18 % v/v and the O_2 content is low (but higher than 3 %). The inlet gases content to the conversion process is generally between 7 – 13 % SO_2, if necessary adjusted by dilution with air.

4.2.3.2 Regeneration of spent acids

Spent acids arise from processes where H_2SO_4 or oleum is used as a catalyst (alkylation, nitration, sulphonation, etc.) or from other processes where H_2SO_4 is used to clean, dry, or eliminate water.

The **thermal decomposition** of spent sulphuric acids to sulphur dioxide is carried out under oxidative conditions in a furnace at a temperature of about 1000 °C. The process is described by the following equation:

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

Spent acids are atomised into small droplets to achieve good thermal decomposition. The required energy is provided by the injection of hot flue-gases. The additional volume leads to dilution of the SO_2 content. This dilution can be reduced by preheating of the combustion air or by enriching with O_2.

The **reductive decomposition** of spent sulphuric acid to sulphur dioxide is carried out by heating the spent sulphuric acid and contained residues in a rotary kiln on a coke bed to temperatures of 400 – 1000 °C. The spent sulphuric acid is decomposed to SO_2. Organic compounds are partially reduced to coke but contribute, due to the reductive conditions, as CO and VOCs to the exhaust gas. Inorganic materials, such as Mg, Fe, Pb and heavy metal compounds remain in the coke. The exhaust gases are treated by thermal oxidation at temperatures of 1100 – 1300 °C with sufficient residence times.

The SO_2 content in the combustion gases depends mainly on the composition of the spent acids (content of water and organics), and it can vary from 2 to 15 %. Sulphur can be fed to adjust the SO_2 content and to minimise variations. Most of the energy from the combustion gases is recovered as steam in a waste heat boiler. The exhaust gases are cleaned downstream, demisted, dried and reheated before passing to the converter.

Another option is the production of liquid SO_2 or sodium bisulphite as a co-product of the sulphuric acid plant.

4.2.3.3 Pyrite roasting

Fluidised bed roasters are the preferred equipment for pyrite roasting. They are superior to other types of equipment in terms of process technology, throughput rates and economy. When roasting pyrite to get SO_2 gas, two by-products, iron oxide and energy, are produced. One tonne of acid requires 0.5 tonne pyrite.

Due to the heterogeneous character of the raw material pyrite, the SO_2 content in the gases is slightly variable over time (generally 6 – 14 %, O_2 free). The gases are always treated in three to four cleaning steps with cyclones, bag filters, scrubbers and electrostatic precipitators. Waste water from the scrubbing is treated before discharge. The clean gas is diluted with air to 6 – 10 % and dried before entering the conversion process.

4.2.3.4 Spent acid from TiO_2 production and roasting of metal sulphates

Spent acid from TiO_2 production is reconcentrated by applying vacuum and heating, using the heat from the subsequent H_2SO_4 plant. While the concentrated H_2SO_4 is recycled to TiO_2 production, the precipitated metal sulphates are decomposed.

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 approximately 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 driers or fluidised bed driers to a monohydrate or mixed hydrate during the first step. In the second step, the material is decomposed at approximately 900 °C. Gases from this process contain approximately 7 % v/v SO_2. 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 gas containing SO_2 leaving the furnace is cooled in a waste heat boiler to approximately 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 can also be processed in a fluidised bed reactor or a furnace. In individual cases, iron sulphate is also decomposed in multiple-hearth furnaces with flue-gases from fuel oil or natural gas combustion.

4.2.3.5 Non-ferrous metal production

Examples are metallurgical processes like roasting, smelting or sintering of ores in order to yield metals, such as Cu, Zn or Pb. For a detailed description of non-ferrous metal production, see [61, European Commission, 2003].

Non-ferrous metal smelting accounts for 39 % of H_2SO_4 production (see also Table 4.3). Many metal sulphides when roasted during metallurgical processes, produce gases containing 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. Often, smelters must be overdesigned in flow capacity for adjusting the high and fluctuating metallurgical gas flow coming from the smelter. Furthermore, there is a minimum concentration of SO_2 that can be treated without increasing the number of stages in the plant. Table 4.4 shows some characteristics of metallurgical processes and the effects on the H_2SO_4 production.

Variation of the SO_2 concentration per hour	Effect on the conversion rate in % absolute	Fluctuation of SO_2 and/O_2
>4 % v/v	-0.4	extremely high
2 – 4 % v/v	-0.3	very high
1 – 2 % v/v	-0.2	high
<1 % v/v	-0.1	slightly
	-0.2 % for the time of cleaning and control	
	-0.2 % for the time of gas volume flow variation >10 %	

Table 4.4: Some characteristics of metallurgical processes and their effect on H_2SO_4 production [154, TWG on LVIC-AAF, 2006]

For copper plants, it is typical to find not only fluctuations in the concentration of SO_2 in converters, but also fluctuations in the gas flow. The reason is that about 30 % of converter operating time is used for charging and slag tapping. Pyrometallurgical copper extraction is based on the decomposition of complex iron-copper sulphite minerals into copper sulphides, followed by selective oxidation, separation of the iron portion as slag, and final 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 ends up as SO_2. A concentrate of $CuFeS_2$ produces almost one tonne of sulphur (2 tonnes of SO_2) per tonnes of copper extracted.

The development of copper processes has been dominated by two objectives. One is to economise on energy, making the maximum use of reaction heat obtained from the process. 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 gas is purified by cooling, scrubbing and electrostatic cleaning in order to remove dust and SO_3.

4.2.3.6 Other raw gas sources

A variety of gases containing sulphur can be used directly or after suitable processing as raw gases to produce H_2SO_4. These include:

- various gases arising from combustion or catalytic conversion of H_2S and/or CS_2 or COS

  Examples are H_2S rich tail gases from **coke ovens**, **synthesis gas production, gasifiers and HDS units at refineries, tail gases from Claus units** or the manufacture of **viscose**. The resulting SO_2 raw gases also contain water, which requires drying prior to H_2SO_4 production or specific wet catalysis processes (see Sections 4.4.8 and 4.4.9).

- flue-gases from combustion of fuels containing sulphur [10, European Commission, 2005]

  One example is the "**Wellman-Lord"** process that removes SO_2 from flue-gases and yields an SO_2 rich gas for H_2SO_4 production. The process is based on absorption and desorption of SO_2 in $NaSO_3$ solutions.

  Another example is the "**Bergbau-Forschung"** or "**activated carbon"** process, also for removing SO_2 from flue-gases. The process is based on adsorption and desorption of SO_2 on activated carbon and yields a SO_2/steam mixture, which is used for the downstream wet catalysis H_2SO_4 plant (see Sections 4.4.8 and 4.4.9).

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

In these cases, the driving force for the production of H_2SO_4 can be understood as the recovery of sulphur compounds from tail gases or as emission abatement technique.

Sulphur source/SO_2 production process		SO_2 in raw gas % v/v	SO_2 before contact process % v/v	Variation of SO_2 content with time	Characteristic features
Elemental sulphur		9 – 12	9 – 12	Very low	Cleaning of raw gases is not required
Pyrite		<15	8 – 10	Low	Cleaning of raw gases is required; high amounts of burning residues, which are usually not utilised
Non-ferrous metal products	Copper Lead (sinter) Lead roasting/smelting	1 – 20 2 – 6 7 – 20	1 – 12 2 – 6 7 – 12	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; increase of SO_2 content by application of air enriched with O_2
	Zinc	5 – 10	5 – 10	Rather low	Cleaning of raw gases is required
Fe(II) sulphate		6 – 15	6 – 12	High	$FeSO_4$ is processed together with diluted acid from the production of pigments
Waste acid with organic 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 → thermal post-combustion
H_2S gases [xx]		0.3 – 10 [x]	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
Exhaust gases of sulphurous fossil fuel		0.1 – 6	Depending on process	Low to high	Low SO_2 content, high waste gas volumes

[x] Higher SO_2 contents with burning of sulphur

[xx] coke oven gas, spinning bath waste gas, gases from processing of natural gas and crude oil

Table 4.5: Major sulphur sources and their features
[57, Austrian UBA, 2001, 154, TWG on LVIC-AAF]

4.2.4 Product H_2SO_4 treatment

Table 4.6 gives an overview of the potential treatment of the product H_2SO_4.

Treatment	Description			Exhaust gas contaminants	Applicability
Dilution	The acid produced, generally 94 %, 96 % or 98.5 – 99.5 %, is diluted with water or steam condensate to the usual commercial concentrations/usage concentrations (25 to 99 % H_2SO_4). Dilution is carried out batchwise ("acid into water not vice versa!") or continuously by inline mixing.			None	
SO_2 stripping	The hot acid is stripped with air in order to reduce the concentration of dissolved SO_2 to levels below 30 mg/kg. The exhaust gas is returned to the contact process.			None	
Particulate removal	After plant shutdown for maintenance, the sulphuric acid can contain particulate contaminants, arising from insoluble iron sulphate or silicates from linings or filling materials. The removal is carried out with conventional equipment. Filtration is also carried out in fill lines to road tankers or rail cars.			None	
De-nitrification	Equivalent amounts of reducing chemicals are added in order to react with $NOHSO_4$ (nitosyl sulphuric acid) to nitrogen or N_xO_x compounds.	Urea	Absorber/tank	N_2	Limited to <80 % H_2SO_4
		Dihydrazine sulphate (40 % solution)	Absorber/tank	N_2, N_2O	For acid and oleum
		Amidosulphonic acid (15 % solution), hydroxilammonium sulphate	Absorber/tank	N_2	Limited to 50 – 99.5 % H_2SO_4
		Acid saturated with SO_2	78 % H_2SO_4/ separate tower	N_2, NO_x	Limited by the water balance
Decolourisation "Acid bleaching"	Acid from smelter or recycling plants may contain carbon compounds and result in black colour.	H_2O_2	Absorber/tanks	None	Generally applicable
Mercury removal	Bolchem method	In 99 % acid, the mercury compounds are oxidised to HgO. After dilution to approx. 80 %, the Hg is precipitated with thiosulphate solution as HgS and removed with a filter press. Hg concentrations of 0.05 ppm are achieved, depending on the NO_x content of the acid. Depending on the water balance, purified acid is also used for blending absorber acid.			
SuperLig method	Absorption of Hg in ion exchangers containing crown ethers	Hg concentrations of approx. 0.1 ppm are achieved.			
Toho zinc method	Addition of KI to 93 % acid and precipitation as HgI_2	Requires acid temperatures of approx. 0 ºC.			

Table 4.6: Overview of potential treatment of the product H_2SO_4
[58, TAK-S, 2003]

4.3 Current emission and consumption levels

Figure 4.7 and Figure 4.8 show the correlation between SO_2 levels in tail gases and the SO_2 conversion rates. Figure 4.9 shows the correlation between the specific SO_2 loads in tail gases and the SO_2 conversion rates. Table 4.7 shows achieved SO_2 conversion rates and SO_2 emission levels. Table 4.8 shows achieved SO_2 emission levels to air, Table 4.9 gives some example data for waste waters from H_2SO_4 production before waste water treatment and Table 4.10 shows solid wastes from production of H_2SO_4.

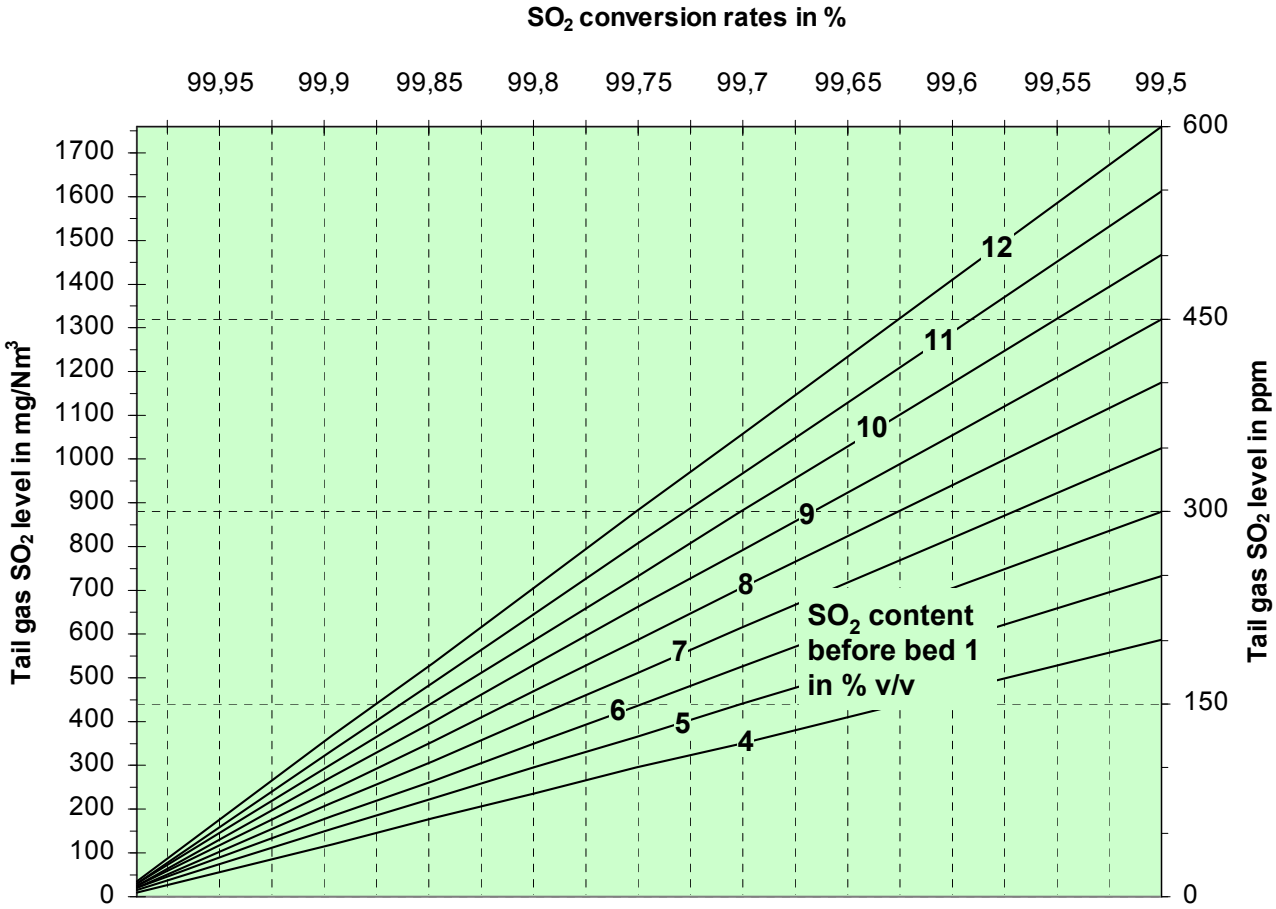

Figure 4.7: Conversion rates of 99.5 to 99.9 % and tail gas SO_2 levels in relation to the SO_2 content before bed 1
This figure is based on [57, Austrian UBA, 2001, 58, TAK-S, 2003] and relates mainly to double contact/double absorption processes, see Section 4.4.2.
Note: for the conversion from ppm to mg/Nm^3, a factor of 2.93 is used

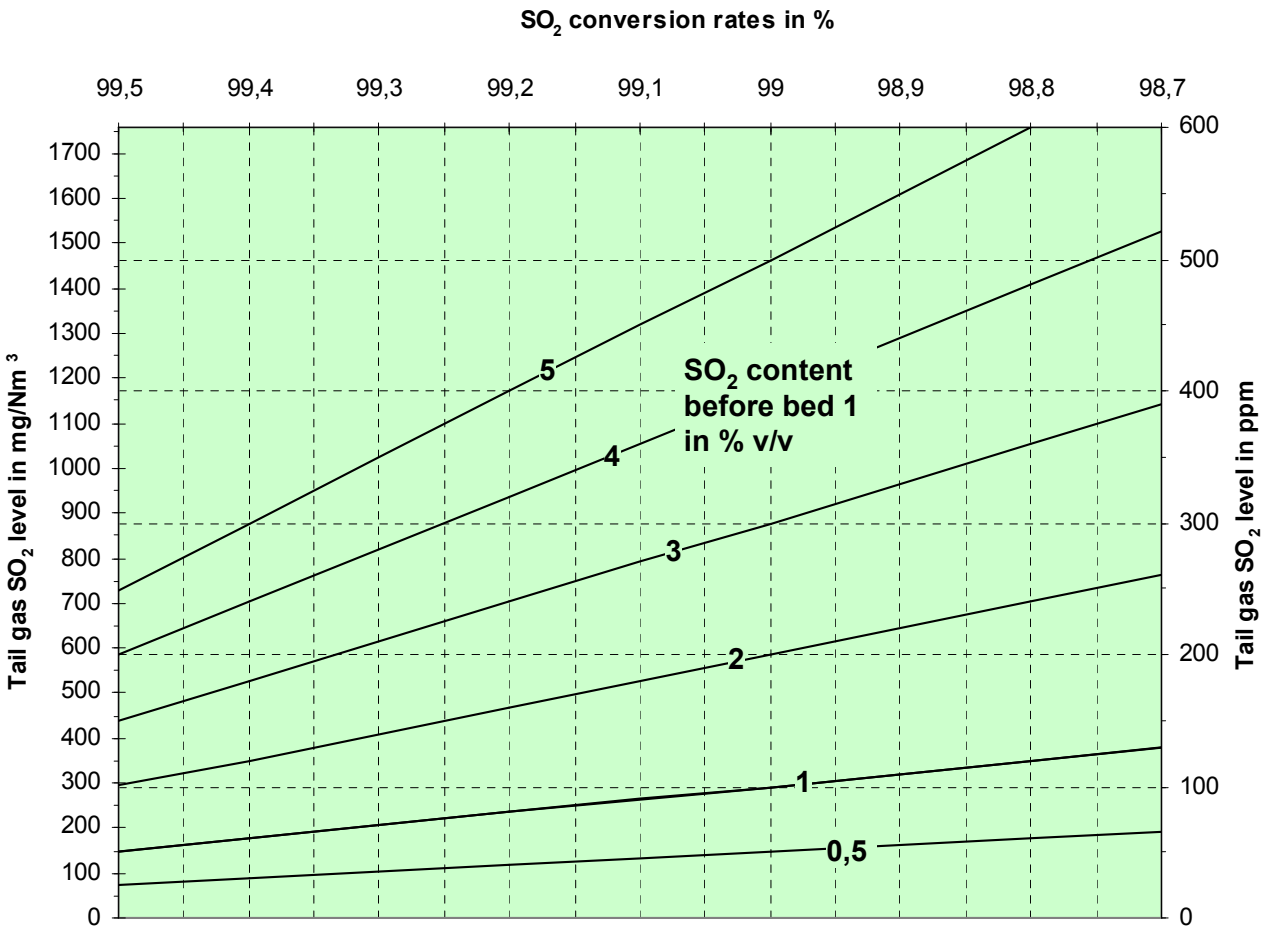

Figure 4.8: Conversion rates of 98.7 to 99.5 % and tail gas SO_2 levels in relation to the SO_2 content before bed 1
This figure is based on [57, Austrian UBA, 2001, 58, TAK-S, 2003] and relates mainly to other than double contact/double absorption processes

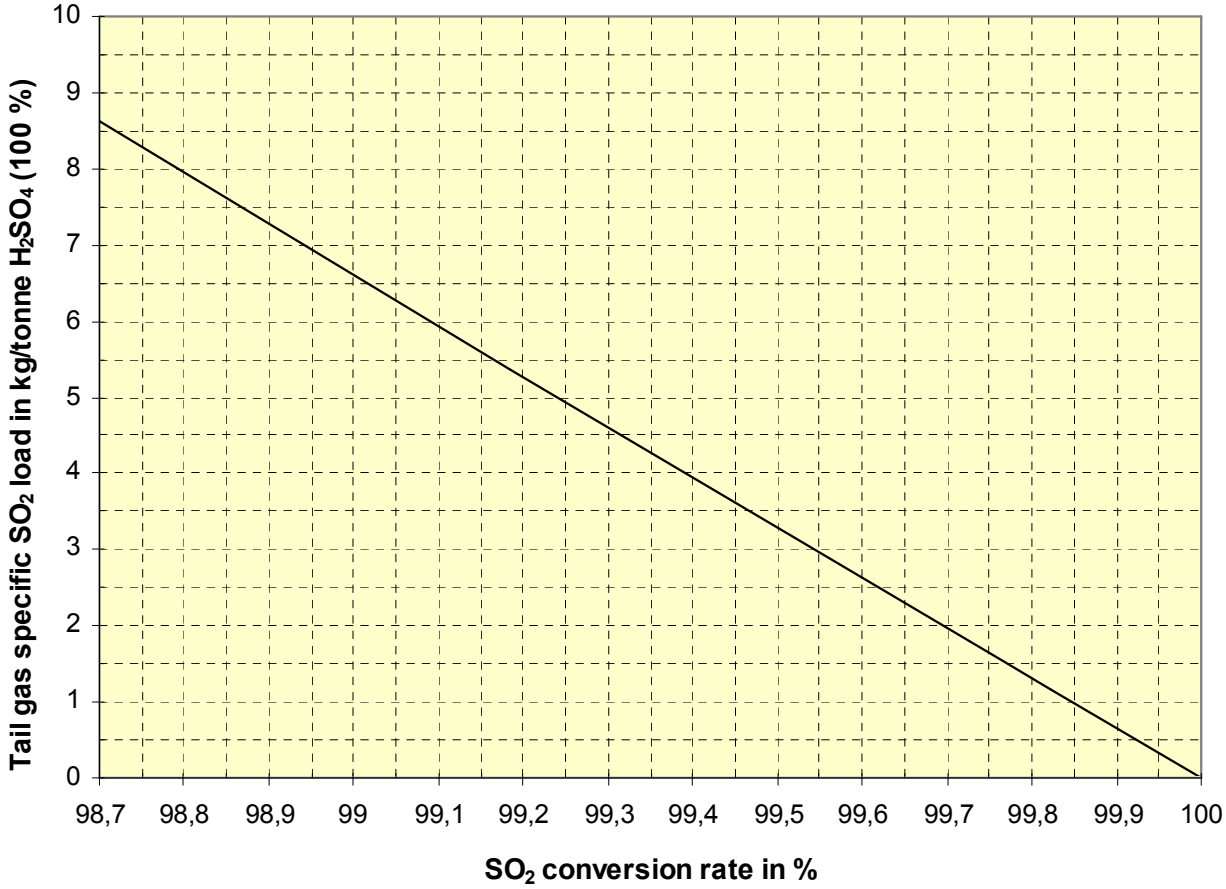

Figure 4.9: Correlation between SO_2 conversion rates and specific SO_2 loads in tail gases
This figure is based on [57, Austrian UBA, 2001, 58, TAK-S, 2003]

Capacity in tonnes of 100 % H_2SO_4/day	SO_2 source	Process type/ abatement system	Number of beds	Cs promoted catalyst?	Inlet SO_2 % v/v	Variation of inlet SO_2	Conversion rate %	SO_2 emission		Reference
								mg/m^3	kg/tonne H_2SO_4	
20	H_2S in coke oven gas	Single contact	4	●	2		99.5	430	4.5	VOEST Linz
690	Elemental sulphur	Double contact	4		9.5		99.7 – 99.8	600 – 700	2.1	Donau Chemie
66	Elemental sulphur + rich gases from viscose production	Combined wet/dry double contact	4		8		99.8	500	1.18	Lenzing AG
146	Elemental sulphur + lean and rich gases from viscose production	Wet catalytic process + H_2O_2 scrubber	2		5.9		98.8 99.9 [xxx]	170		Lenzing AG (new line)
270	Elemental sulphur	Double contact	4		11 – 11.5		99.8	810	1.4	Lenzing AG
17	Rich gases from viscose production	Wet catalytic process (single catalyst layer), WESP	1		8400 mg/Nm^3		99	120	9	Glanzstoff Austria
850	Elemental sulphur	Double contact	4	●	10.5 – 11.5		99.7 – 99.8		1.7	INEOS Enterprises
2000	Spent acids, sulphate roasting	Double contact	4		< 8.0		99.5 – 99.7			Sachtleben Chemie GmbH, Duisburg
1300	Copper ore	Double contact	5	●	5 – 12		99.8			Norddeutsche Affinerie
1300	Copper ore	Double contact	4	●	5 – 12		99.7 – 99.8			
1300	Copper ore	Double contact	4	●	5 – 12		99.7 – 99.8			
750	Zinc ore	Double contact	4	●			99.7 – 99.8			Ruhr Zink GmbH
750	Elemental sulphur	Double contact	4				99.7 – 99.8			Grillo Werke, Frankfurt
600	Spent acid, $FeSO_4$, pyrite	Double contact	5				99.7 – 99.8			Kerr McGee, Krefeld
768	Elemental sulphur	Double contact	5				99.8 – 99.9			Domo Caproleuna GmbH

Capacity in tonnes of 100 % H_2SO_4/day	SO_2 source	Process type/ abatement system	Number of beds	Cs promoted catalyst?	Inlet SO_2 % v/v	Variation of inlet SO_2	Conversion rate %	SO_2 emission		Reference
								mg/m^3	kg/tonne H_2SO_4	
400	Spent acids	Double contact + H_2O_2 scrubber	4				99.7 – 99.8	<8 (1100 before the scrubber)		Degussa AG (Röhm), Wesseling
650	Spent acids	Double contact	5				99.6 – 99.7			Degussa AG (Rhöm), Worms
435	Elemental sulphur, spent acid	Double contact	4	●			99.83 – 99.87			Lanxess Deutschland GmbH
980	Elemental sulphur	Double contact	4	●	10 – 11		99.7 – 99.8	400 – 600	0.78 – 1.18	Lanxess, Antwerp
330	Elemental sulphur	Double contact	4		8 – 11		99.6 – 99.7		<2.8	Clariant, Lamotte
1750	Elemental sulphur	Double contact	4		10.5 – 11.5		99.7 – 99.8	700 – 800	1.4 – 1.6	Nuova Solmine
250	Sulphur, SO_2 gas	Double contact	4				99.8			SFChem, Pratteln
590	Zinc ore	Double contact	4		5 – 8.5		99.5 – 99.7			Xstrata Zink GmbH
200	Elemental sulphur	Single contact	4	●			99.1			PVS Chemicals
	Copper smelter	Double contact	4	●	13.1		99.91 (design)			LG Metals, Korea
	Copper smelter	Double contact	4	●	14		99.95 (design)			Kennecott, Utah
320	Lead roasting, QSL and O_2 process	Double contact	4	● (2 beds)	12		99.6 – 99.7	<480		Berzelius Metallhütten GmbH, Stolberg
910										Boliden, Sweden
540	Elemental sulphur	Single contact + tail gas treatment								Enichem, Italy
339										Sarlux
1000	Zinc ore	Double contact	5	●	5 – 7.2	low	99.92	<200		Zinifex, Budel
900	Metallurgical	Double contact		●						Asturiana de Zinc S.A.

Capacity in tonnes of 100 % H_2SO_4/day	SO_2 source	Process type/ abatement system	Number of beds	Cs promoted catalyst?	Inlet SO_2 % v/v	Variation of inlet SO_2	Conversion rate %	SO_2 emission		Reference
								mg/m^3	kg/tonne H_2SO_4	
1000	Elemental sulphur	Double contact + H_2O_2 scrubber	5	●	10		99.92 (99.98 with scrubber)	30 (250 before scrubber)	0.15	Kemira Kemi, Helsingborg
1000	Elemental sulphur	Double contact + heat recovery system	4		11.5	Constant	99.73	1083	1.77	Tessenderlo Chemie
		Single contact + NH_3 scrubber					99.94	150		DSM, Geleen
1500	Elemental sulphur, spent acid	Single contact + NH_3 scrubber	4		6 – 10		99.6	685	2.39	Misa Eco
400	Elemental sulphur	Double contact	5				99.9			Fluorsid, Macchiareddu
1250	Copper ore	Double contact	5		5 – 10.2		99.7 – 99.8			Atlantic copper, Huelva
1735	Copper ore	Double contact	5	●	5 – 9		99.7			
600	Copper ore	Double contact	4		5 – 8.5		99.65	<1200		
2400	Elemental sulphur	Double contact	4		10.5 – 11.5		99.75		1.38	Fertiberia, Huelva
612	Elemental sulphur	Double contact	3/1		10	9 – 11	99.8 – 99.85	<500		BASF, Ludwigshafen
490	Elemental sulphur	Double contact	3/1		10	9 – 11	99.85 – 99.9	<500		
370	Spent acid	Double contact	2/2		7	5 – 8	99.5 – 99.6	<1300		
300	Spent acid	Double contact	2/2		7	5 – 8	99.5 – 99.6	<1300		
735	Elemental sulphur	Double contact	3/1		11.6		99.7 – 99.8			BASF, Antwerp
800	Elemental sulphur	Double contact			11.5		99.6		2.6	Millennium, Le Havre
940	Elemental sulphur		5							Rontealde S.A., Bilbao
537	Complex Pb,CuS batch process	Double contact	4	●	0 – 6.5	Strong	99.5 – 99.7	1200		UMICORE, Hoboken
570	Zn ore	Double contact	4		8 – 8.5		99.5 – 99.7	900 – 1200		UMICORE, Auby

Capacity in tonnes of 100 % H_2SO_4/day	SO_2 source	Process type/ abatement system	Number of beds	Cs promoted catalyst?	Inlet SO_2 % v/v	Variation of inlet SO_2	Conversion rate %	SO_2 emission		Reference
								mg/m³	kg/tonne H_2SO_4	
320	Zn ore	Single contact + ZnO scrubber	4	●	5 – 6.5		98.8 – 99.1 (without scrubber)	600 – 900 (with scrubber)		UMICORE,. Balen K11
850	Zn ore	Double contact	4	●	8.9 – 9.5		99.5 – 99.6	<1200		UMICORE, Balen K12
490	Metallurgical	Double contact + H_2O_2 scrubber								Newmont Gold, USA
400	Metallurgical	Double contact + H_2O_2 scrubber								CPM, Brazil
895	Pb sinter, ZnS roaster	Wet process	2		6.5		98 – 99			OAO Kazzinc
1140	CuS smelter	Wet process	2		6.5		98 – 99			ZAO Karabashmed
170	MoS_2 roaster	Wet process	3		1.40 – 3.75		99.6			Molibdenos y Metales in planning
		NH_3 scrubber						210		[57, Austrian UBA, 2001]
	Elemental sulphur	Double contact	4	●	11.5	constant	99.9	250		[57, Austrian UBA, 2001]
84	H_2S gases from synthesis gas production	Wet process					98			Amoníaco de Portugal

Table 4.7: Achieved SO_2 conversion rates and SO_2 emission levels to air for the manufacture of H_2SO_4

	Emission of SO_3 and acid mist as H_2SO_4		
Abatement system	**mg/m³**	**kg/tonne H_2SO_4**	**Reference**
High performance candle filters	25 – 35		Grillo-Werke AG, Frankfurt
	18		VOEST Linz
	10 – 15	0.01 – 0.02	Donau Chemie
	30	0.07	Lenzing AG
	<50	<0.08	Lenzing AG
WESP	not detectable	not detectable	Glanzstoff Austria
	20 – 30		[57, Austrian UBA, 2001]
Wire mesh filter	<100	<0.14	[58, TAK-S, 2003]
High performance candle filters	<50	<0.07	
Tail gas scrubbing			
ESP	<20	<0.03	
		0.21	[6, German UBA, 2000] (several plants)
		0.053	
		0.056	
		0.017	
		0.061	
		0.031	
		0.094	
		0.08	
	28		
	35		
	42		

Table 4.8: Achieved SO_3 emission levels to air for the manufacture of H_2SO_4

SO_2 source	Spent acid and salts from TiO_2 production	Spent acid and salts from TiO_2 production
	g/tonne	g/tonne
SO_4	2910	2380
Fe	23	90
Pb	0.1	0.38
Ni		0.05
As		0.24
Cd		0.005
Cr		0.38
Zn		1
Cu	0.16	0.1
Hg	0.002	0.02
total N		
COD	445	19

Table 4.9: Examples for waste waters from H_2SO_4 production before waste water treatment [21, German UBA, 2000]

	Solid waste	g/tonne 100 % H_2SO_4
Sulphur burning/single contact	Spent catalyst	10 – 20
Sulphur burning/double contact		
Pyrite roasting	Spent catalyst	about 40
Zn and Pb smelter	Spent catalyst	20 – 40
Complex (Pb,Cu)S batch treatment	Spent catalyst	20 – 40
Cu smelter	15 – 35 % of the installed catalyst and per screening operation	20 – 40
Spent acid decomposition	Spent catalyst	40
	Ashes	400

Table 4.10: Solid wastes from production of H_2SO_4 [62, EFMA, 2000]

4.4 Techniques to consider in the determination of BAT

4.4.1 Single contact/single absorption process

Description

After purification and drying, the SO_2 is converted into SO_3 using a series of 4 catalyst beds, containing alkali and V_2O_5. Afterwards, the SO_3 is absorbed in concentrated sulphuric acid and, if necessary, an oleum absorber is installed upstream. SO_3 reacts with the water contained in the absorber acid to yield H_2SO_4. The absorber acid is kept at the desired concentration of approximately 99 % w/w by addition of water or dilute H_2SO_4.

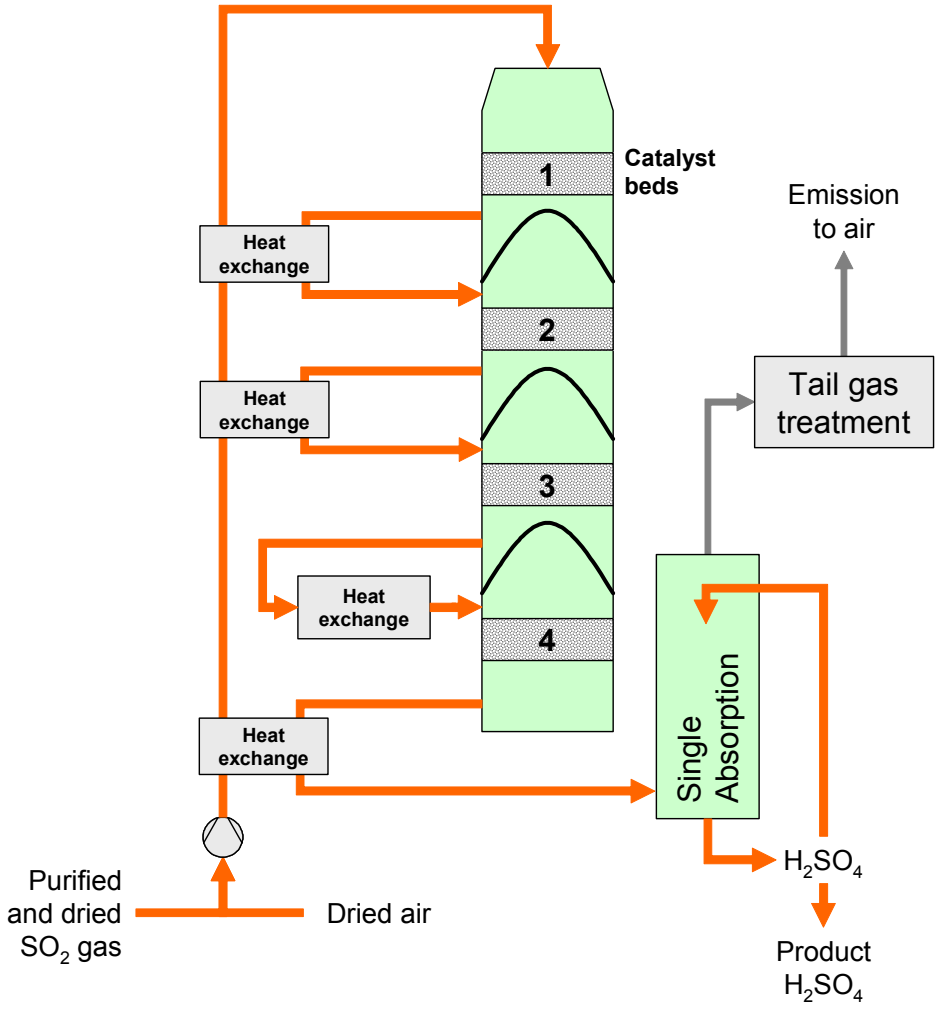

Figure 4.10: Example for a single contact/single absorption process
This figure is based on [59, Outukumpu, 2005] and [57, Austrian UBA, 2001].

Achieved environmental benefits

Note: Conversion rates, tail gas SO_2 concentrations and specific SO_2 load in tail gases are correlated, see Figure 4.7, Figure 4.8 and Figure 4.9.

Conversion rates >98 % are difficult to achieve in existing plants. However, some plants achieve conversion rates of 98.5 % [58, TAK-S, 2003].

Conversion rates of about 97.5 % are achieved without primary or secondary reduction measures [57, Austrian UBA, 2001].

New plants achieve conversion rates of 98 – 99 % [59, Outukumpu, 2005].

Cross-media effects

Without additional measures: relatively high SO_2 emissions due to the low conversion rates.

Operational data

Typical O_2/SO_2 ratio: 1.7.

Applicability

The single contact/single absorption process is generally used for gases with an SO_2 content from 3 – 6 %. New single contact plants are built only for inlet gases with substantial fluctuation of the SO_2 content [58, TAK-S, 2003].

Applicable to inlet gases with SO_2 contents typically <4 % v/v. Applicable only in combination with a primary or secondary emission reduction measure (e.g. a Cs-promoted catalyst or tail gas scrubbing) [57, Austrian UBA, 2001].

Because of the favourable energy balance, a single absorption plant can maintain autothermal operation with SO_2 inlet concentrations >2 % v/v [59, Outukumpu, 2005].

Economics

Lower investment cost in comparison with double contact plants.

Driving force for implementation

Inlet gases with low and/or variable SO_2 content.

References to literature and example plants

[57, Austrian UBA, 2001, 58, TAK-S, 2003], Voest Alpine Stahl

4.4.2 Double contact/double absorption process

Description

In the double contact process, a primary SO_2 conversion of 85 – 95 % is achieved in the first catalysis stage of the converter before entry into an intermediate absorber, depending on the arrangement of the converter beds and the contact time. After cooling of the gases to approximately 190 ºC in a heat exchanger, the SO_3 already formed is absorbed in 98.5 – 99.5 % sulphuric acid. If necessary, an oleum absorber is installed upstream of the intermediate absorber. The absorption of SO_3 shifts the reaction equilibrium significantly towards the formation of more SO_3. This results in a considerably higher conversion rate, if the residual gas is passed through the following converter beds (usually one or two). The SO_3 which is formed in the second catalysis stage is absorbed in the final absorber. Figure 4.11 shows the example of a 2+2 double contact double absorption plant. 2+2 indicates the number of catalyst beds before and after intermediate absorption. 3+1 represents the alternative configuration with 4 beds, 3+2 is the normal configuration with 5 beds (see Section 4.4.3).

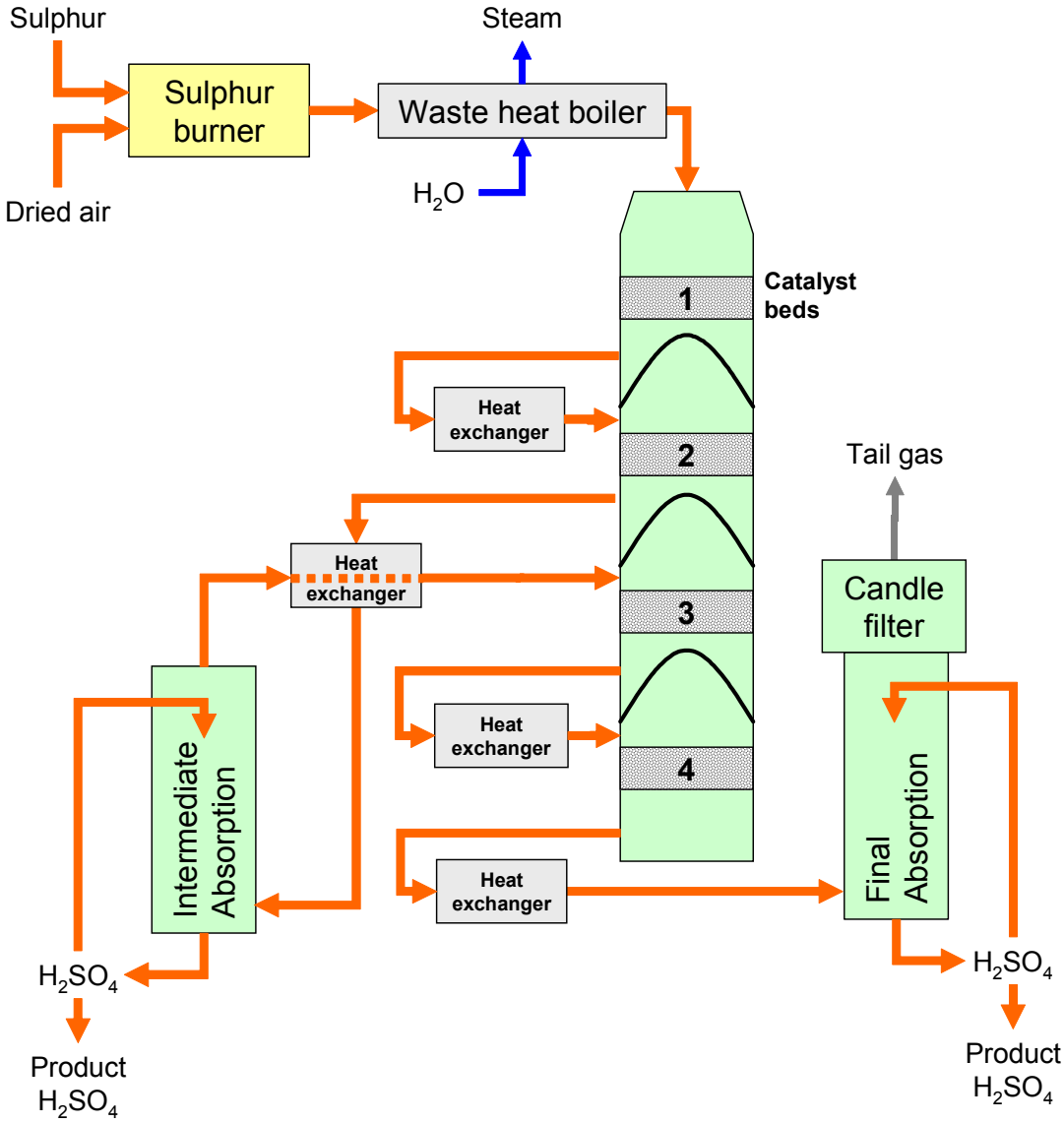

Figure 4.11: Example for a 2+2 double contact/double absorption process
This figure is based on [57, Austrian UBA, 2001].

Achieved environmental benefits

Note: Conversion rates, tail gas SO_2 concentrations and specific SO_2 load in tail gases are correlated, see Figure 4.7, Figure 4.8 and Figure 4.9.

Average daily conversion rates of at least 99.7 – 99.9 % with double contact processes [154, TWG on LVIC-AAF]. Conversion rates of 99.8 % are achievable with four catalyst beds and inlet gas of low variabilility. With four catalyst beds and inlet gases from non-ferrous metal production (higher variability), 99.7 % are achievable [57, Austrian UBA, 2001]. For examples of degree of variation of the SO_2 inlet concentration and the variation of the conversion rate, see Figure 4.12 and Figure 4.13.

For energy recovery and export, see Section 4.4.15.

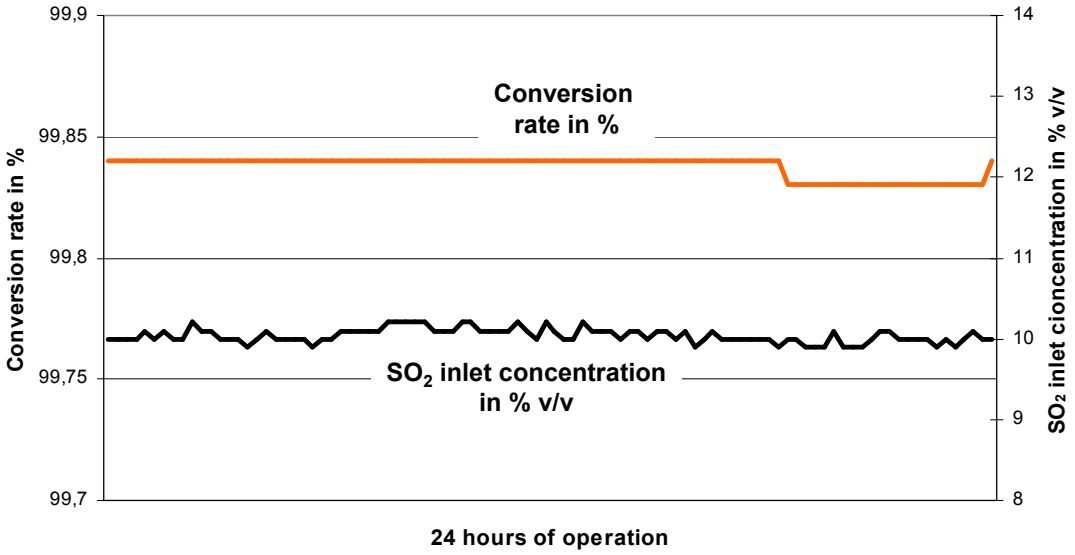

Figure 4.12: SO_2 inlet concentration and conversion rate of production based on sulphur burning [154, TWG on LVIC-AAF, 2006]

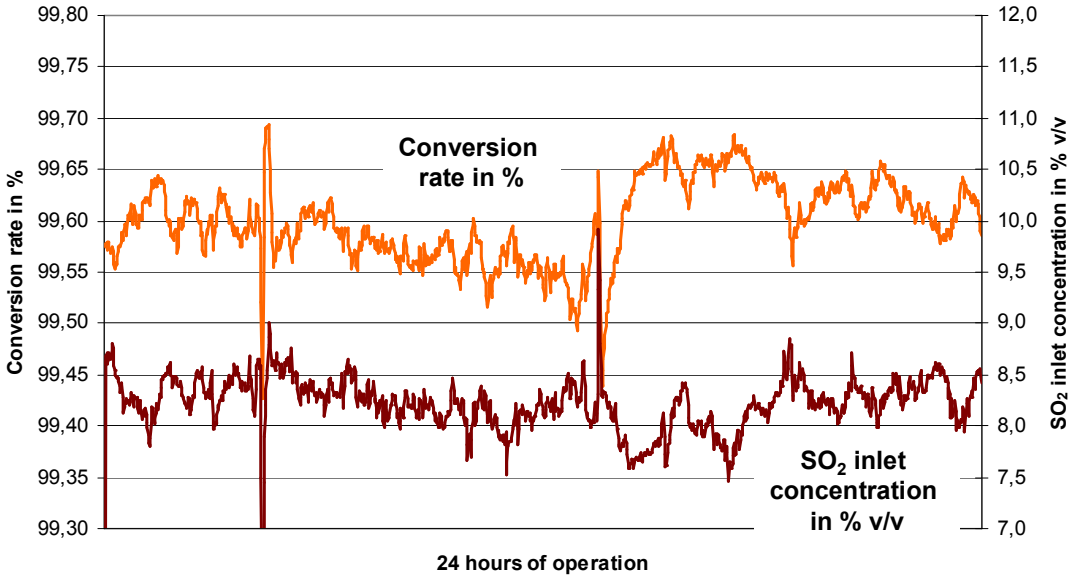

Figure 4.13: SO_2 inlet concentration and conversion rate of production based on Zn roasting [154, TWG on LVIC-AAF, 2006]

Cross-media effects

None believed likely.

Operational data

In general, the process uses gases with an SO_2 content of 10 to 11 % [58, TAK-S, 2003]. The inlet gas temperature is about 400 ºC. Gases with lower temperatures, e.g. metallurgical gases after purification, require reheating from 50 to 400 ºC. This is usually carried out with recovered heat from the conversion process [57, Austrian UBA, 2001].

Applicability

- applicable for SO_2 inlet content of 5 – 12 % v/v [58, TAK-S, 2003]
- applicable for SO_2 inlet content of >4.5 up to 14 % v/v. Below 4.5 % v/v, double contact processes do not work autothermally [59, Outukumpu, 2005].

Pressure contact process. One plant is known to operate a double contact process at an elevated pressure of 5 bar. This increases the conversion rate by shifting the conversion equilibrium and favouring the formation of SO_3. The pressure double contact process achieves 99.8 – 99.85 % conversion; here, the tail gas contains 200 – 250 ppm SO_2. The disadvantages are higher electricity consumption and, at the same time, less steam production. Higher NO_x emissions are caused by higher sulphur combustion temperatures (1800 ºC). In comparison, savings of 10 – 17 % on investment costs are gained. However, the benefits from building a plant for smaller gas volumes (at higher pressure) are offset by more stringent safety regulations and additional costs for pressure resistant materials.

Economics

The double contact/double absorption process is considered as the baseline for inlet gas SO_2 concentrations >4.5 % v/v.

Driving force for implementation

Development of the single contact/single absorption process.

References to literature and example plants

[57, Austrian UBA, 2001, 58, TAK-S, 2003], Donau Chemie AG, Lenzing AG, Degussa AG

4.4.3 Addition of a 5th bed to a double contact process

Description

By retrofitting a double contact plant with a 5th catalyst bed, 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 5th bed is possible, if sufficient room is available. The 5 bed double contact plant is realised as a 3+2 layout (3 catalyst beds prior to the intermediate absorber).

Achieved environmental benefits

Note: Conversion rates, tail gas SO_2 concentrations and specific SO_2 load in tail gases are correlated, see Figure 4.7, Figure 4.8 and Figure 4.9.

- lower SO_2 emissions through higher conversion rates.

Cross-media effects

Higher pressure drop and consequently slightly higher electricity consumption for compression.

Operational data

No specific information provided.

Applicability

Generally applicable for double contact plants, provided that sufficient room is available. At the Hamburger Affinerie AG, the waste gases of a copper smelting process are used for sulphuric acid production (three lines). The third line of 1300 tonnes/day (installed in 1991), consists of five catalyst layers. Extra costs for the 5th catalyst bed were about EUR 1000000. SO_2 emissions of this double contact plant are 300 mg/Nm³ on average, corresponding to an average conversion rate of 99.89 %.

Economics

For cost calculations for retrofitting H_2SO_4 plants, see Table 14.1.

Driving force for implementation

Lower SO_2 emissions.

References to literature and example plants

[57, Austrian UBA, 2001, 58, TAK-S, 2003, 60, Windhager, 1993], Hamburger Affinerie AG, Atlantic Copper, Huelva, Rontealde S.A., Bilbao

			EUR/year
Waste gas volume (Nm^3/hour)	36000		
Operating time (hour/year)	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/hour)	32		
Extra investment costs (EUR)	1090000		
Repayment on investment incl. interest (EUR/year)			**112300**
Period of depreciation (year)	15		
Interest rate (%)	6		
Extra costs of maintenance and wear (EUR/year)			**21800**
Maintenance and wear (% of investment costs)	2		
Energy consumption extra pressure drop for the 5^{th} catalyst layer (mbar)	60		
Extra energy consumption of ventilator (kWh/hour)	92	0.044 EUR/kWh	**33700**
Extra energy consumption of circulating pumps and additional energy consumers (kWh/hour)	42	0.044 EUR/kWh	**15500**
Extra catalyst costs (incl. 6 % interest rate)			**8900**
Extra amount of catalyst for the 5^{th} catalyst layer (m^3)	30		
Lifetime of catalyst (year)	10		
Specific costs of catalyst		2180 EUR/m^3	
Recovered sulphuric acid (kg/hour)	50	0.051 EUR/kg	**-21200**
Estimated annual extra costs (EUR/year)			**171000**
Specific costs related to reduction of SO_2 emissions (EUR/tonne SO_2)			**629**
Specific extra costs related to the production of H_2SO_4 (EUR/tonne H_2SO_4)			**1.18**
Basis: inlet concentration 10.5 % v/v SO_2, production of 145000 tonnes/year			

Table 4.11: Cost estimate for retrofitting a double contact plant with a 5^{th} catalyst bed [57, Austrian UBA, 2001]

4.4.4 Application of a Cs-promoted catalyst

Description

The conversion of SO_2 into SO_3 is thermodynamically favoured by a lower temperature level due to the exothermic reaction. Conventional catalysts are usually operated at temperature levels of about 420 – 660 °C. Cs-promoted catalysts are sufficiently active at lower temperatures (380 – 400 °C) and can therefore be operated at lower temperatures (380 – 620 °C), which increases the SO_2 conversion rate. Cs-promoted catalysts can be used in the first bed to reduce the bed inlet temperature or in the final catalyst bed (at a low inlet temperature).

Achieved environmental benefits

- increased conversion rate by 0.1 % [17, 2nd TWG meeting, 2004]
- a plant in the Czech Republic reports conversion rates of 99.8 – 99.9 % (double contact, 4 beds, Cs-promoted, 150000 tonnes/year), after 4 years the catalyst is due for exchange and the conversion rate has dropped to 99.7 % [17, 2nd TWG meeting, 2004]
- at double contact plants with sulphur burning SO_2 conversion rates of 99.9 % and an emission reduction of 30 – 70 % (compared to conventional catalysts) are achievable. At single contact plants, conversion rates of 99.5 % and emission reduction rates of about 50 – 70 % are achievable.

Cross-media effects

Additional pressure drop of 15 mbar and higher catalyst volume required [58, TAK-S, 2003].

Operational data

No specific information provided.

Applicability

Generally applicable.

At Voest Alpine Stahl Linz GmbH, a single contact plant (processing H_2S gases from a coke oven plant) has been modified by enlargement of the catalyst layers and by application of a Cs-promoted catalyst in the 4th layer. SO_2 emissions could be reduced from about 1500 mg SO_2/Nm^3 to <500 mg/Nm^3. Additionally, oxygen is injected between the third and the fourth catalyst layer.

In the case of an existing heat recovery system, the application of a Cs-promoted catalyst might be counter productive [154, TWG on LVIC-AAF, 2006].

Economics

Although Cs-promoted catalysts are more costly than conventional catalysts, the added expense is at least partially compensated by an increased production:

- Table 4.12 shows an example of costs for the application of Cs-promoted catalysts in bed 4 of a double contact plant
- Table 4.13 shows an example of costs for retrofitting a single contact plant with a Cs-promoted catalyst
- for cost calculations of retrofitting H_2SO_4 plants, see Table 14.1.

Driving force for implementation

Reduction of SO_2 emission levels.

References to literature and example plants

[57, Austrian UBA, 2001, 58, TAK-S, 2003], Voest Alpine Stahl, Kemira Kemi, Atlantic copper Huelva

			EUR/year
Waste gas volume (Nm^3/hour)	36000		
Operating time (hours/year)	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/hour)	29		
Extra investment costs			
Extra costs for catalyst (incl. 6 % interest rate)			**21700**
Extra amount of catalyst for bed 4 (m^3)	40		
Lifetime of catalyst (years)	10		
Specific costs of catalyst		EUR 4000/m^3	
Recovered sulphuric acid (kg/hour)	44	EUR 0.051/kg	**-18800**
Estimated annual extra costs (EUR/year)			**2900**
Specific costs related to reduction of SO_2 emissions (EUR/tonne SO_2)			**12**
Specific extra costs related to the production of H_2SO_4 (EUR/tonne H_2SO_4)			**0.020**
Basis: inlet concentration 10.5 vol-% SO_2, H_2SO_4 production: 145000 tonnes/year, waste gas volume of 36000 Nm^3/hour, increase of the conversion rate from 99.6 % to a range of 99.85 – 99.9 %			

Table 4.12: Costs for the application of Cs-promoted catalyst in bed 4 of a double contact plant [57, Austrian UBA, 2001]

			EUR/year
Waste gas volume (Nm^3/hour)	10000		
Operating time (hour/year)	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/hour)	10		
Extra investment costs (EUR)	580000		
Repayment on investment including interest (EUR/year)	59900		**59900**
Period of depreciation (year)	15		
Interest rate (%)	6		
Extra costs of maintenance and wear (EUR/year)	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 (years)	10		
Specific costs of catalyst		EUR 6200/m^3	
Recovered sulphuric acid (kg/hour)	15	EUR 0.051/kg	**-6550**
Estimated annual costs (EUR/year)			**78400**
Specific costs related to reduction of SO_2 emissions (EUR/tonne SO_2)			**930**
Basis: inlet concentration of 2 % v/v SO_2, waste gas volume of 10000 mg/Nm^3, increase of the conversion rate from 98 to 99.5 %.			

Table 4.13: Cost estimate for retrofitting a single contact plant with a Cs-promoted catalyst [57, Austrian UBA, 2001]

4.4.5 Change over from single to double absorption

Description

If the raw gas of a single contact plant contains more than 4 % v/v SO_2, the plant can be retrofitted into a double contact plant by installing an intermediate absorber.

Achieved environmental benefits

Reduction of SO_2 emissions of about 75 %.

Cross-media effects

- additional pressure drop of 70 mbar, 100 kW higher energy requirements for compression
- loss of recoverable energy.

Operational data

No specific information provided.

Applicability

Applicable to single contact plants with the required inlet gas SO_2 level.

Economics

For cost calculations of retrofitting H_2SO_4 plants, see Table 14.1.

Driving force for implementation

Reduction of SO_2 emissions.

References to literature and example plants

[57, Austrian UBA, 2001, 58, TAK-S, 2003], Rhodia: 2 plants in Europe, UMICORE, Hoboken in 2004

4.4.6 Replacement of brick-arch converters

Description

Brick-arch converters have been extensively used in the past. One advantage is their high heat capacity, which facilitates shutdown and restart of the conversion process. A disadvantage is that the older brick-arches can be porous and, hence, part of the process gas bypasses the intermediate absorber. This results in lower conversion rates. Usually, mending porous brick-arches is not economically viable, and the brick-arch converter is replaced by a modern converter.

Achieved environmental benefits

Increased conversion rate.

Cross-media effects

None believed likely.

Operational data

No specific information provided.

Applicability

Applicable to brick-arch converters. Brick-arch converters have not been built since the 1980s. Hence, in the usual case existing brick-arch converters are about 25 years old or older. Besides the replacement of the brick-arch converter, the replacement of other equipment might be necessary. This will require an assessment of the profitability.

Economics

Replacement of the converter represents a major investment, but the increase of performance provides a payback.

Driving force for implementation

Low performance of the brick-arch system. Reduction of SO_2 emissions.

References to literature and example plants

[17, 2nd TWG meeting, 2004, 68, Outukumpu, 2006]

4.4.7 Increasing the O_2/SO_2 ratio of the inlet gas

Description

The thermodynamic equilibrium limits the conversion and, hence, impacts on the residual SO_2 emission level. This equilibrium very much depends on the oxygen and sulphur dioxide content of the inlet gas, and also the O_2/SO_2 ratio. Modern sulphur burning plants operate with a feed gas of 11.8 % v/v SO_2 and a residual 8.9 % v/v O_2, resulting in an O_2/SO_2 ratio of 0.75. This enables the plant to match emission levels below 2 kg SO_2 per tonne of H_2SO_4 produced (equivalent to a conversion rate of about 99.7 %).

Plants frequently supply high strength SO_2 gas, particularly those using oxygen-enriched air or dilution air to adjust the O_2/SO_2 ratio.

Achieved environmental benefits

A reduction of the SO_2 emissions can be achieved. The example plant achieved an emission reduction of approximately 30 %.

Cross-media effects

- lower energy output
- consumption of oxygen or oxygen-enriched air.

Operational data

No specific information provided.

Applicability

In particular this measure is applicable for existing sulphuric acid plants, if the actual production is lower than the production capacity. At new plants, a higher dimensioning of the plant would have to be considered.

Economics

Table 4.14 gives a cost estimate for increasing the O_2/SO_2 ratio of the inlet gas.

Driving force for implementation

Reduction of SO_2 emissions.

References to literature and example plants

[57, Austrian UBA, 2001, 67, Daum, 2000], Donauchemie GmbH

			EUR/year
Waste gas volume (Nm^3/hour) at a SO_2 content in the inlet gas of 10.5 % v/v	36000		
SO_2 waste gas concentration (mg/Nm^3) at an SO_2 content in the inlet gas of 10.5 % v/v	1200		
Waste gas volume (Nm^3/hour) at an SO_2 content in the inlet gas of 9.5 % v/v	40000		
SO_2 waste gas concentration (mg/Nm^3) at an SO_2 content in the reaction gas of 9.5 % v/v	700		
Operating time (hour/year)	8400		
Reduction of SO_2 emissions (kg/hour)	15		
Extra investment costs			
Extra energy consumption/energy losses	-		
Extra energy consumption for the ventilator at an SO_2 concentration of 9.5 % v/v (kWh/hour)	68	EUR 0.044/kWh	**24900**
Loss of steam production (40 bar) due to an SO_2 concentration of 9.5 % v/v (tonnes/hour)	1.1		
Loss of electric energy corresponding to the loss of steam production (9.5 % v/v SO_2) (kWh/hour)	40	EUR 0.044/kWh	**14650**
Recovered sulphuric acid (kg/hour)	23	EUR 0.051/kg	**-9950**
Estimated annual extra costs (EUR/year)			**29600**
Specific costs related to the reduction of SO_2 emissions (EUR/tonne SO_2)			**232**
Specific extra costs related to the production of H_2SO_4 (EUR/tonne H_2SO_4)			**0.204**
Basis: reduction of the inlet concentration from 10.5 to 9.5 % v/v SO_2, double contact plant, 145000 tonnes H_2SO_4/year; production lower than output capacity. Increase of the waste gas volume from 36000 to 40000 Nm^3/hour, increase of the conversion rate from 99.6 to 99.74 %.			

Table 4.14: Cost estimate for the increase of the O_2/SO_2 ratio
[57, Austrian UBA, 2001]

4.4.8 Wet catalysis process

Description

Wet SO_2 gases (e.g. from the burning of H_2S gases or from the catalytic conversion of H_2S gases) are directly supplied into the contact tower without previous drying. SO_3 formed by the catalytic conversion immediately reacts with the moisture of the gases, thereby forming sulphuric acid. The sulphuric acid is condensed in a condenser installed after the contact tower. Process variants enable an improved condensation and the production of concentrated acid, for example:

- the Concat process is designed to produce H_2SO_4 of higher concentrations from gases with a low SO_2 content. The formed H_2SO_4 is condensed in two steps, a high temperature venturi condenser (this yields 93 % H_2SO_4) and a condenser tower (this yields 70 – 80 % H_2SO_4)
- the Topsøe WSA process is designed to reduce the formation of H_2SO_4 mist. After the conversion of SO_2 into SO_3, the gases are condensed in a falling film evaporator with glass pipes. The formation of mists is prevented by precise temperature control.

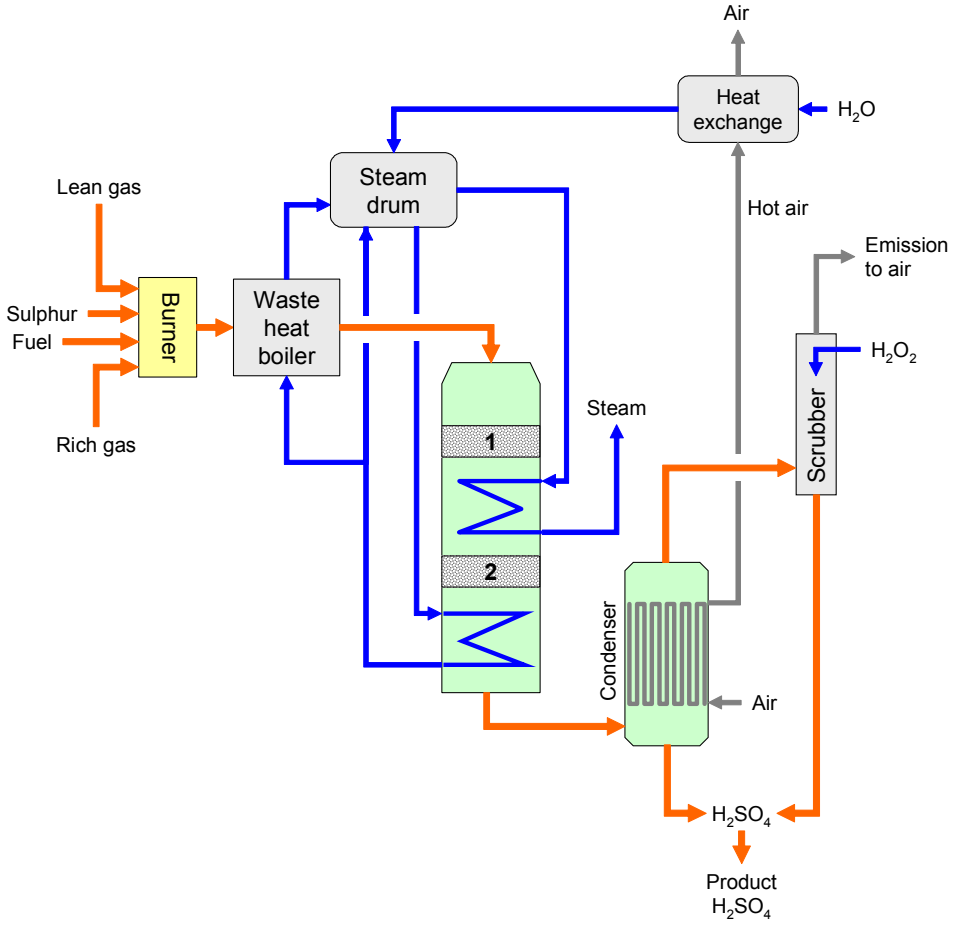

Figure 4.14: Example for a wet catalysis process
Lenzing AG after expansion
[63, Laursen, 2005]

Achieved environmental benefits

Table 4.15 shows examples for the application of wet catalysis processes.

- enables the conversion of the wet SO_2 gases
- emissions from the Concat process: <200 ppm SO_2 and <70 mg/Nm^3 SO_3
- Topsøe WSA process: conversion rates of 99.3 %.

Plant	SO_2 source	Inlet SO_2	Conversion rate	Emission level
		% v/v	%	mg/m^3
Lenzing AG, after expansion	Lean and rich gas from viscose production + elemental sulphur	5.9	98.8 99.9 [x]	170 [x]
PT South Pacific Viscose, Indonesia				
Irving Oil Ltd., Canada	Tail gas from a Claus plant	1	98.1	341
Molymex SA, Mexico	Molybdenum roasting	3.0 – 4.1	98.7 – 99.0	1100 – 1170
Sokolovska Uhelna, Czech Republic	Rectisol regeneration	1.58	97.9	944
[x] including H_2O_2 scrubber				

Table 4.15: Examples for the application of wet catalysis processes [63, Laursen, 2005, 64, Kristiansen and Jensen, 2004]

Cross-media effects

Potential for formation and emission of H_2SO_4 mist.

Operational data

No specific information provided.

Applicability

Applicable to wet SO_2 gases. The potential for the formation of H_2SO_4 mist might require tail gas treatment for example with ESP, WESP or scrubbing [57, Austrian UBA, 2001].

Economics

No specific data provided.

Driving force for implementation

No specific data provided.

References to literature and example plants

[57, Austrian UBA, 2001, 58, TAK-S, 2003, 63, Laursen, 2005, 64, Kristiansen and Jensen, 2004], Glanzstoff Austria, Arzberg power station, KMG Krefeld, Bayer Krefeld, see also Table 4.15.

4.4.9 Combined wet/dry catalysis processes

Description

Combined wet/dry contact processes are double contact/double absorption processes, used in particular for processing gases containing H_2S. If the H_2S content is low, H_2S gases are burned together with elemental sulphur. After reducing the temperature to about 400 °C, the wet combustion gases are directly fed into the contact tower. SO_3 formed by the catalytic conversion immediately reacts with the moisture of the gases and forms sulphuric acid. The sulphuric acid is absorbed in an intermediate absorber installed after the second or third catalyst bed. Remaining SO_2 is converted in the following catalyst bed(s) according to a dry contact process.

The combined wet/dry process uses the same catalyst materials as in a conventional double contact plant.

Achieved environmental benefits

- enables the conversion of wet SO_2 gases
- SO_2 conversion rates up to 99.8 %
- SO_3 emissions of 30 mg/Nm^3.

Cross-media effects

None believed likely.

Operational data

No specific information provided.

Applicability

Applicable to wet SO_2 gases, e.g. with a low H_2S content.

Economics

No specific information provided.

Driving force for implementation

Recovery of sulphur from waste gases..

References to literature and example plants

[57, Austrian UBA, 2001], Lenzing AG

4.4.10 Combination of SCR and wet catalysis

Description

Examples of such processes are the SNOX™ process and the Desonox process.

After particulates removal with a fabric filter or an electrostatic precipitator, the flue-gas is heated in heat exchanger. In the catalytic $DeNO_x$ system, the nitrogen oxides in the flue-gas are reduced selectively with ammonia to yield nitrogen. In the subsequent SO_2 converter, the SO_2 is oxidised catalytically to SO_3, which is recovered in a condenser as concentrated sulphuric acid. Ambient air preheated in the condenser is used as combustion air for the boiler. The combined SCR/wet catalysis plant can be fully automated and can be operated from the main control room of the power plant without requiring additional manpower. There is no hold-up of liquids or solids and response to variations in boiler load is very fast.

Achieved environmental benefits

- enables the direct production of H_2SO_4 from SO_2 in flue-gases
- recovery of 95 % of the sulphur content from the flue-gas.

Cross-media effects

NH_3 consumption.

Operational data

No specific information provided.

Applicability

Applicable to low SO_2 content gases with high volume flows. Usually applied to tail gases from the combustion of fuels containing sulphur. The process is adaptable to new or to retrofit installations.

Economics

No specific information provided.

Driving force for implementation

Lower SO_2 emissions. Cost benefits from selling the co-product H_2SO_4 can be assumed.

References to literature and example plants

[57, Austrian UBA, 2001, 66, Haldor Topsoe, 2000]

4.4.11 Raw gas purification

Description

For production of non-ferrous metals, see also [61, European Commission, 2003].

Raw gases from pyrite roasting, non-ferrous metal production and thermal decomposition of spent acids can contain various contaminants. These are removed prior to H_2SO_4 production in order to prevent the contamination of the product H_2SO_4 or to prevent negative effects on the catalyst performance and lifetime. Table 4.16 gives an overview of the relevant contaminants and their origins.

Contaminant	Origin
Dust	Mainly from roasting of ores, melting and refining processes
Volatile compounds of As, Se, Cd and Hg	From roasting of metal ores
Vapours of volatile metal oxides and chlorides	
Gaseous substances, such as HCl, HF, CO and VOCs	Decomposition of spent acids, roasting of pyrite or in non-ferrous metal processing under reductive conditions
Dioxins/furans [x]	

Table 4.16: Overview of contaminants in raw gases [57, Austrian UBA, 2001], [x] [58, TAK-S, 2003]

The following techniques are applied to remove contaminants from the raw gas:

- dry coarse and fine particulate removal (cyclones, hot gas ESP)
- wet scrubbing (venturi)
- cooling/drying
- reactive F adsorption (optional)
- WESP.

The raw gases are cooled to temperatures of about 320 – 400 ºC and about 85 – 90 % of the dust is removed with a cyclone. Dust is further removed with an ESP to levels of about 20 – 200 mg/Nm^3. Depending on the case, the recovered dust is recycled or disposed of. Wet scrubbing is carried out with 50 % H_2SO_4 as the scrubbing medium in order to remove HCl and HF, and at the same time, to condense volatile compounds of Se and As. Settled solids are removed from the scrubbing liquid and disposed of and the scrubbing liquid is continuously replaced. The spent scrubbing liquid is stripped (SO_2 removal), neutralised and discharged, or alternatively recycled.

After cooling/drying, potential fluoride loads are removed from the gas by reactive adsorbtion in silica beds.

Finally, two-stage WESP is applied to reduce dust levels to <1 mg/Nm^3.

CO is oxidised to CO_2 in the contact process. The remaining amount of contaminants are absorbed in the product H_2SO_4 or released with the stack tail gas.

Achieved environmental benefits

- minimisation of negative effects on catalyst performance and lifetime
- lower emission levels.

Cross-media effects

Auxiliary chemicals and energy consumption.

Operational data

No specific information provided.

Applicability

Generally applicable to raw gases originating from metallurgical processes and decomposition of spent acids.

Economics

No specific information provided.

Driving force for implementation

Purity requirements of the H_2SO_4 process.

References to literature and example plants

[57, Austrian UBA, 2001, 58, TAK-S, 2003]

4.4.12 Prevention of catalyst activity loss

Description

Catalysts suffer from deterioration while in operation. They are exposed to ageing by high temperatures (loss of active components) and plugging by dirt. Some catalysts are occasionally "abused" by sulphur, fuel oil, water or sulphuric acid. At many metallurgical plants, the catalyst is exposed to "poisoning" of the silica carrier by fluorides or volatilisation of the vanadium through chloride attack.

Regular screening and replacement is required, ***particularly at the first bed***, where the catalyst acts with a "fly-catching" effect to segregate residual dust and dirt from the gas. Proper gas cleaning with adequately designed electrostatic mist precipitators will minimise this effect at metallurgical plants, while sulphur burning plants can extend the screening periods substantially by ensuring perfect air filtration (e.g. two stage) and good sulphur filtration, e.g. by using additional polishing filters.

Achieved environmental benefits

A loss of catalyst activity has a detrimental effect on the SO_2 conversion and the SO_2 emissions.

Cross-media effects

None believed likely.

Operational data

No specific information provided.

Applicability

Generally applicable.

The driver for catalyst replacement/screening is usually the increased pressure drop or the necessity of a boiler inspection. Since catalyst replacement/screening requires a plant shutdown, the costs are much higher, in the case of metallurgical plants, because the metallurgical process also has to be stopped [75, MECS, 2006].

Catalyst replacement according to [17, 2nd TWG meeting, 2004]:

First bed:	after 2 – 3 years
Other beds:	after about 10 years.

Catalyst screening (first bed) is carried out after 1 – 3 years, occasionally after 4 years, according to [68, Outukumpu, 2006].

Economics

No specific information provided.

Driving force for implementation

Integrated measure to minimise SO_2 emissions.

References to literature and example plants

[17, 2nd TWG meeting, 2004, 67, Daum, 2000]

4.4.13 Maintaining heat exchanger efficiency

Description

The efficiency of heat exchangers is affected after years of operation by build-up of dirt and corrosion. Maintenance of internal or external heat exchangers ensures that heat is removed efficiently from the converter and, hence, enables optimum catalyst activity. Where heat exchangers cannot be cleaned, replacement has to be considered.

Achieved environmental benefits

- contributes optimum catalyst activity.

Cross-media effects

None believed likely.

Operational data

No specific information provided.

Applicability

Generally applicable.

Economics

No specific information provided.

Driving force for implementation

Integrated measure to minimise SO_2 emissions.

References to literature and example plants

[17, 2nd TWG meeting, 2004]

4.4.14 Monitoring of SO_2 levels

Description

The determination of the SO_2 conversion rate requires monitoring of SO_2 levels at the inlet to the converter and after the final absorption stage (this equals the SO_2 emission level if no tail gas treatment is applied). If tail gas treatment is applied (scrubbing), the SO_2 emission level after tail gas treatment is also monitored. This is carried out with the following frequencies:

- determination of the conversion rates: daily
- monitoring the SO_2 levels: continuously.

Achieved environmental benefits

Conversion rate and emission levels are the main performance indicators.

Cross-media effects

None believed likely.

Operational data

No specific information provided.

Applicability

Generally applicable.

Economics

No specific information provided.

Driving force for implementation

Monitoring of performance indicators.

References to literature and example plants

[17, 2nd TWG meeting, 2004]

4.4.15 Energy recovery and export

Description

Table 4.18 shows energy considerations for double contact plants with different plant setup in comparison with a single contact plant. Table 4.17, Table 4.19 and Table 4.20 show examples for energy balances of double contact processes. Please note that the examples given in Table 4.17 and Table 4.19 include energy release from production of the inlet gas (sulphur burning), the other examples are based on cooled inlet gas.

The input of the starting materials provides the energy for the production of sulphuric acid. An essential feature of the double contact process is the autothermal operation of the plant, which is possible in modern plants with a minimum inlet SO_2 concentration of 4 – 4.5 % v/v. 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 burning gases and from the reaction heat of the contact process. Waste heat released from acid cooling represents about 30 – 40 % of the total process waste heat. A thermal efficiency of 85 – 90 % can be achieved by using waste heat released from the acid cooling for drying processes or for the production of low pressure steam with a special heat recovery system.

For a modern single contact plant, the minimum requirement for autothermal operation is a SO_2 inlet concentration of >2 % v/v [59, Outukumpu, 2005].

If gas cleaning processes are required (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.

Achieved environmental benefits

- a modern double contact plant (sulphur burning) can export about 6 GJ/ tonne H_2SO_4
- roasting of ZnS: production of 0.6 – 1 tonne HP steam (40 bar/400 ºC) per tonne raw material.

Cross-media effects

None believed likely.

Operational data

- input of electrical power: 35 – 50 kWh/tonne H_2SO_4
- pyrite roasting with air releases 13 GJ/tonne pyrite.

Applicability

Generally applicable. The amount of recoverable energy and export options depend on the individual situation (mainly SO_2 source and process). If no energy consumer is available, recovered energy can be partially converted into electrical power.

For recovered heat from acid cooling, there are three main applications [59, Outukumpu, 2005]:

- delivering hot water for municipal/domestic heat supply systems
- phosphoric acid concentration
- delivering hot water for industrial utilisation, such as filter washing, sea water distillation.

Economics

Cost benefits can be presumed.

Driving force for implementation

Cost benefits.

References to literature and example plants

[57, Austrian UBA, 2001, 58, TAK-S, 2003], Tessenderlo, Ham

Energy input		Recovery and losses			
		Item	**Property**	**Recoverable**	**GJ/tonne 100 % H_2SO_4**
Sulphur **97 %**		Sulphur burning and waste heat boiler **37 %**		as HP steam **67 %**	3.1 – 3.4
		Catalyst bed and process gas cooling **30 %**			
		Acid cooling (intermediate absorber, final absorber, gas dryer) **31 %**	85 – 120 °C	For drying processes, as LP steam **31 %**	2.1 – 2.4
		Waste gas (loss) **1.5 %**		-	
Electrical power (compression) **3 %**		Product acid (loss) **0.5 %**		- -	
Basis: sulphur burning, 1000 tonnes/day 100 % H_2SO_4, 11 % v/v SO_2 inlet					

Table 4.17: Energy balance for a double contact process based on sulphur burning [57, Austrian UBA, 2001]

	Energy input/output				
Number of catalyst beds and inlet SO_2 level	2+2 / 11 %	2+2 / 11 % + LP steam option	3+2 / 11 %	2+2 / 5 %	4 / 5 % (single contact)
Process step	GJ/tonne H_2SO_4				
Inlet gas heating	+ 0.992	+ 0.992	+ 0.992	+ 2.119	+ 2.119
Cooling of bed 1	- 0.471	- 0.471	- 0.471	- 0.704	- 0.704
Cooling of bed 2	- 1.018	- 1.018	- 0.278	- 1.766	- 0.199
Intermediate absorption	- 1.190	**- 0.673**	- 1.380	- 1.609	no intermediate absorption
Reheating after intermediate absorption	+ 0.847	+ 0.610	+ 0.815	+ 1.959	
Cooling of bed 3	- 0.195	- 0.195	- 0.888	- 0.061	- 0.046
Cooling of bed 4	- 0.629	- 0.629	- 0.066	- 1.413	- 1.574
Cooling of the 5th bed	no 5th bed	no 5th bed	- 0.589	no 5th bed	no 5th bed
Final absorption	- 0.635	- 0.901	- 0.452	- 0.777	- 0.777
Cooling of product H_2SO_4 to 25 ºC	- 0.096	- 0.096	- 0.096	- 0.096	- 0.096
Potential export of HP and LP steam	- 0.475	**- 1.384**	- 0.486	**Import: 0.133**	- 0.404
Loss by cooling with water or air	- 1.921	- 0.997	- 1.928	- 2.482	- 0.873
(+) energy input by heat exchange	(-) heat recoverable for HP steam production		(-) heat recoverable for LP steam production, 180 ºC		(-) loss to cooling water/air

Table 4.18: Energy considerations of double contact plants with different plant setup in comparison with a single contact plant [58, TAK-S, 2003]

Energy input		Recovery and losses			
		Item	**Property**	**Recoverable**	**GJ/tonne 100 % H_2SO_4**
Sulphur **98 – 98.7 %**		Sulphur burning and waste heat boiler **34 – 37 %**		as HP steam 30 bar **57 – 62 %**	
		Catalyst bed and process gas cooling **24 %**			
		Acid cooling (intermediate absorber) **21 – 24 %**	<120 ºC		
		Acid cooling (final absorber) **7 – 9 %**	<85 ºC		
		Waste gas (loss) **3 %**	75 ºC	-	
Electrical power (compression) **1.3 – 2 %**		Product acid (loss) **1.6 %**	75 ºC	- -	
		Other losses **2 – 3 %**			
Basis: sulphur burning, 500 tonnes/day SO_3, 10.5 % v/v SO_2 inlet					

Table 4.19: Energy balance for a double contact process based on sulphur burning [58, TAK-S, 2003]

Energy input		Recovery and losses			
		Item	**Property**	**Recoverable**	**GJ/tonne 100 % H_2SO_4**
Gas from roasting **94 %**		Acid cooling (intermediate absorber, final absorber, gas dryer) **92 %**	120 – 180 °C	For drying processes, as LP steam **92 %**	about 2.4 [x]
		Waste gas (loss) **5 %**			
		Product acid (loss) **1 %**			
Electrical power (compression) **6 %**		Other (loss) **2 %**			
Basis: metallurgical tail gas with reheating after purification, 1000 tonnes/day 100 % H_2SO_4, 8.5 % v/v SO_2 inlet [x] calculated based on 100 GJ/h and 1000 tonnes H_2SO_4 per day					

Table 4.20: Energy balance of a double contact process based on a metallurgical process [57, Austrian UBA, 2001]

4.4.16 Minimisation and abatement of SO_3 emissions

Description

Emissions of SO_3 or H_2SO_4 mists originate from incomplete absorption (dry contact processes) and especially incomplete condensation (wet catalysis process) are minimised by regular monitoring and control of process parameters, such as:

- constant operation of SO_2 gas production, minimisation of SO_2 level variation
- use of sulphur with a low impurity content (in case of sulphur burning)
- adequate drying of inlet gas and combustion air in dry contact processes
- use of larger condensation area (wet catalysis process)
- optimisation of acid distribution
- high efficiency candle filter and controlling
- circulated quantities
- concentration and temperature of the absorber acid
- monitoring of SO_3/H_2SO_4 mist.

Table 4.21 shows options for further reduction of SO_3/H_2SO_4 emissions.

	Achievable emission levels			
	mg/Nm^3 as H_2SO_4	**kg SO_3/tonne H_2SO_4**	**Investment costs**	**Remarks**
High performance candle filters	<50	<0.14	1500000	
Wet scrubbing				
Wire mesh filter	<100	<0.07	500000	
ESP	<20	<0.03	3000000	
WESP	Not detectable			Especially for wet catalysis processes, recovery of H_2SO_4

Table 4.21: Overview of SO_3/H_2SO_4 recovery/abatement techniques

Achieved environmental benefits

- lower emissions of SO_3 or H_2SO_4 mists.

Cross-media effects

Chemicals and energy consumption with wet scrubbing.

Operational data

No specific information provided.

Applicability

Generally applicable.

Economics

See Table 4.21.

Driving force for implementation

Lower SO_3 emission levels.

References to literature and example plants

[57, Austrian UBA, 2001, 58, TAK-S, 2003]

4.4.17 Minimisation of NO_x emissions

Description

The formation of NO_x has to be considered in the following cases:

- burning of sulphur or gases containing sulphur at higher temperatures
- decomposition of spent acids
- roasting sulphidic ores and pyrite.

NO_x levels can be minimised by applying low NO_x burners.

Achieved environmental benefits

- for sulphur burning, NO_x levels of 20 mg/Nm^3 can be achieved.

Cross-media effects

None believed likely.

Operational data

No specific information provided.

Applicability

Generally applicable.

Economics

No specific data provided.

Driving force for implementation

Lower emissions of NO_x and product quality.

References to literature and example plants

[57, Austrian UBA, 2001]

4.4.18 Treatment of waste waters

Description

Waste water streams arise mainly from wet scrubbing, in particular from the cleaning of metallurgical tail gases, from cleaning pyrite roasting gases and from cleaning gases from spent acid regeneration.

Waste waters are treated by sedimentation, filtration/decantation to remove solids. The waste waters might require neutralisation before discharge.

Achieved environmental benefits

- lower waste water emission levels.

Cross-media effects

None believed likely.

Operational data

No specific information provided.

Applicability

Generally applicable.

Economics

No specific information provided.

Driving force for implementation

Lower waste water emission levels.

References to literature and example plants

[57, Austrian UBA, 2001, 58, TAK-S, 2003]

4.4.19 Tail gas scrubbing with NH_3

Description

SO_2 is scrubbed with an aqueous NH_3 solution and converted into $(NH_4)_2SO_3/SO_4$.

Achieved environmental benefits

- SO_2 emission levels reduced by >88 %
- achieved emission level of 150 mg/Nm^3
- beneficial effects on emissions of SO_3/H_2SO_4 mist are assumed.

Cross-media effects

- chemicals and energy consumption
- generation of NH_4SO_3/SO_4 as a by-product.

Operational data

No specific information provided.

Applicability

Generally applicable, where the by-product can be re-used on-site.

Economics

The investment cost are estimated to be EUR 6000000 [58, TAK-S, 2003].

Driving force for implementation

Emission reduction.

References to literature and example plants

[57, Austrian UBA, 2001, 58, TAK-S, 2003], DSM, Geleen

4.4.20 Tail gas scrubbing with ZnO

Description

SO_2 is scrubbed with an aqueous ZnO solution and converted into $ZnSO_4$.

Achieved environmental benefits

- achievable emission levels of 600 mg/Nm^3
- beneficial effects on emissions of SO_3/H_2SO_4 mist are assumed.

Cross-media effects

- chemicals and energy consumption
- generation of $ZnSO_4$ as a by-product.

Operational data

No specific information provided.

Applicability

Generally applicable, where the by-product can be re-used on-site or sold.

Economics

Investment of EUR 2000000 for 50000 m^3/hour in 2002.

Driving forces for implementation

Emission reduction.

References to literature and example plants

[75, MECS, 2006], UMICORE, Balen

4.4.21 Tail gas treatment: Sulfazide process

Description

In the sulfazide process, the tail gas is moistened with steam and passed through a reactor packed with activated carbon. SO_2, SO_3 and H_2SO_4 are adsorbed and SO_2 oxidised by O_2 to SO_3. The regeneration of the activated carbon with water yields a 20 – 25 % H_2SO_4, which can be recycled to the sulphuric acid plant.

Achieved environmental benefits

- SO_2 emissions are reduced by >90 %
- beneficial effects on emissions of SO_3/H_2SO_4 mist are assumed.

Cross-media effects

Activated carbon and energy consumption.

Operational data

No specific information provided.

Applicability

Generally applicable.

Economics

The investment costs are estimated to be EUR 5500000.

Driving force for implementation

Emissions reduction.

References to literature and example plants

[57, Austrian UBA, 2001, 58, TAK-S, 2003], Kerr McGee, Krefeld (as tail gas treatment for a power plant)

4.4.22 Tail gas scrubbing with H_2O_2

Description

SO_2 can also be converted to SO_3 through oxidation with H_2O_2 or H_2SO_5. The conversion rate is above 99 %. However, using an H_2O_2 process instead of conventional single or double contact processes is not economically viable because of the raw material costs. Still, H_2O_2 or electrochemically generated H_2SO_5 are applied as the scrubbing medium in order to recover SO_2 from tail gases. The scrubbing yields H_2SO_4 which can be recycled to the absorption stage of the H_2SO_4 plant. Hence, this tail gas treatment does not create an additional waste stream or any by-products.

Achieved environmental benefits

- SO_2 removal efficiencies of 98 % [57, Austrian UBA, 2001]
- achievable emission level: 60 mg/Nm^3 [59, Outukumpu, 2005].

Table 4.22 shows some example plants, the applied conversion type, and, where available, the achieved SO_2 levels.

Example plant	Conversion type	SO_2 level in mg/Nm^3		
		Tail gas	Emission	Efficiency
Degussa, Wesseling	Double contact	1100	8	99 %
Lenzing AG	Wet catalysis process	2000	170	91.5 %
Kemira Kemi, Helsingborg	Double contact with 5th catalyst bed	250	30	88 %
Newmont Gold, US	Double contact			
CPM, Brazil	Double contact			

Table 4.22: Achieved SO_2 levels by scrubbing with H_2O_2

Cross-media effects

Chemicals and energy consumption.

Operational data

No specific information provided.

Applicability

Generally applicable.

Economics

[58, TAK-S, 2003] estimates the additional yearly costs for applying an H_2O_2 scrubber after the final absorber of a single contact plant as follows (basis: 1000 tonnes H_2SO_4/day, removal of 10 tonnes SO_2 per day):

Total costs: EUR 1965000.

This includes costs for personnel, depreciation, maintenance, electric power and raw materials.

Driving force for implementation

Lower SO_2 emission levels.

References to literature and example plants

[57, Austrian UBA, 2001, 58, TAK-S, 2003, 62, EFMA, 2000, 63, Laursen, 2005], Röhm GmbH Wesseling, Kemira Kemi Helsingborg (in combination with a 5th bed), Lenzing AG, Newmont Gold (USA), CPM (Brazil)

4.4.23 Removal of Hg from process gases

Description

Acids produced in smelting processes or from recycling plants may contain mercury. Most of the mercury passes into the sulphuric acid plant with the process gas which contains SO_2 and, if it is not washed out through the washing and cooling plant, it will end up in the sulphuric acid product. Besides removal of mercury from the product acid (see Table 4.6), mercury can be removed from process gases. Table 4.23 gives an overview.

Method	Special conditions	Hg concentration after treatment
Boliden-Norzink method	Gas scrubbing with a solution containing Hg^{2+} with formation of Hg_2Cl_2	
(Kalomel)	<0.5 ppm, depending on the attainable temperatures in the washing and cooling plant	
Outokumpu method	Gas scrubbing with hot (approx. 190 °C) sulphuric acid (about 90 %), with formation of Hg_2SO_4	<0.5 ppm
DOWA method	Absorption onto pellets soaked with PbS, with formation of HgS	<0.1 ppm
Sodium thiocyanate method	Washing with thiocyanate solution, with formation of HgS	Unknown
Activated carbon filter	Adsorption of HgO	Unknown
Selenium filter	Formation of HgSe on selenium-doped inert material/zeolites	<0.1 ppm, primarily for SO_2 production

Table 4.23: Overview of the removal of Hg from process gases

Achieved environmental benefits

- less dispersion of Hg with the acid product.

Cross-media effects

Chemicals and energy consumption.

Operational data

No specific information provided.

Applicability

Generally applicable.

Economics

No specific information provided.

Driving force for implementation

Product purity.

References to literature and example plants

[58, TAK-S, 2003]

4.5 BAT for sulphuric acid

BAT is to apply the common BAT given in Section 1.5.

BAT for storage is to apply BAT given in [5, European Commission, 2005].

BAT is to use recoverable energy: co-generated steam, electrical power, hot water (see Section 4.4.15).

BAT is to apply a combination of the following techniques and to achieve the conversion rates and emission levels given in Table 4.24:

- double contact/double absorption (see Section 4.4.2)
- single contact/single absorption (see Section 4.4.1)
- addition of a 5th catalyst bed (see Section 4.4.3)
- using a caesium promoted catalyst in bed 4 or 5 (see Section 4.4.4)
- change over from single to double absorption (see Section 4.4.5)
- wet or combined wet/dry processes (see Sections 4.4.8 and 4.4.9)
- regular screening and replacement of catalyst, especially of catalyst bed 1 (see Section 4.4.12)
- replace brick-arch converters by stainless steel converters (see Section 4.4.6)
- improve raw gas cleaning (metallurgical plants) (see Section 4.4.12)
- improve air filtration, e.g. by two stage filtration (sulphur burning) (see Section 4.4.12)
- improve sulphur filtration, e.g. by applying polishing filters (sulphur burning) (see Section 4.4.12)
- maintaining heat exchanger efficiency (see Section 4.4.13)
- tail gas scrubbing, provided that by-products can be recycled on-site (see Section, 4.4.19, 4.4.20, 4.4.21 and 4.4.22).

Conversion process type		**Daily averages**	
		Conversion rate [x]	**SO_2 in mg/Nm^3** [xx]
Sulphur burning, double contact/double absorption	Existing installations	99.8 – 99.92 %	30 – 680
	New installations	99.9 – 99.92 %	30 – 340
Other double contact/double absorption plants		99.7 – 99.92 %	200 – 680
Single contact/single absorption			100 – 450
Other			15 – 170
[x] these conversion rates relate to the conversion including the absorption tower, they do not include the effect of tail gas scrubbing [xx] these levels might include the effect of tail gas scrubbing			

Table 4.24: Conversion rates and SO_2 emission levels associated with BAT

BAT is to continuously monitor the SO_2 levels required to determine the SO_2 conversion rate and the SO_2 emission level.

BAT is to minimise and reduce SO_3/H_2SO_4 mist emission by applying a combination of the following techniques and to achieve the emission levels given in Table 4.25 (see Section 4.4.16):

- use of sulphur with a low impurity content (in case of sulphur burning)
- adequate drying of inlet gas and combustion air (only for dry contact processes)
- use of larger condensation area (only for wet catalysis process)
- adequate acid distribution and circulation rate
- applying high performance candle filters after absorption
- control concentration and temperature of the absorber acid
- apply recovery/abatement techniques in wet processes, such as ESP, WESP, wet scrubbing.

	Emission level as H_2SO_4
All processes	10 – 35 mg/Nm^3
Yearly averages	

Table 4.25: SO_3/H_2SO_4 emission levels associated with BAT

BAT is to minimise or abate NO_x emissions (see Section 4.4.17).

BAT is to recycle exhaust gases from product H_2SO_4 stripping to the contact process (see Table 4.6).

5 PHOSPHORIC ACID

5.1 General information

[29, RIZA, 2000], for food grade phosphates, see [155, European Commission, 2006].

Phosphoric acid, H_3PO_4, is a colourless, crystalline compound, that is readily soluble in water. The main product is phosphoric acid with a commercial concentration of 52 – 54 % P_2O_5. After sulphuric acid, phosphoric acid is the most important mineral acid in terms of volume and value.

The greatest consumption of phosphoric acid is in the manufacture of phosphate salts as opposed to direct use as acid. Markets are differentiated according to the purity of the acid. The primary application is the production of fertilisers (approximately 80 %) and animal feed supplements (8 %). Purer phosphoric acid is used for the production of industrial phosphates, especially the sodium, potassium, calcium and ammonium salts, and in metal surface treatment. Food grade quality is used for the acidulation of beverages and food grade phosphate salts.

Worldwide phosphoric acid production capacity was 41600 ktonnes in 2004 [154, TWG on LVIC-AAF, 2006]. In Western Europe, the fertiliser consumption strongly declined in the late eighties and the early nineties. For economic reasons, plants are built where there is cheap access to raw materials (either at the phosphate mine or at the source of sulphur or sulphuric acid). In Europe, a large number of relatively small phosphoric acid production plants have closed down, and as a result the structure has increasingly moved towards a small number of large production plants. Between 1980 and 1992, the number of plants in Western Europe reduced from 60 to approximately 20 while the average plant size increased from 80000 tonnes/year to 180000 tonnes P_2O_5/year. An overview of the European phosphoric acid production plants is given in Table 5.1.

Location	Company	Process type	Gypsum disposal	Capacity ktonnes P_2O_5
Belgium	Nilefos	DH	Stacking, fraction sold	130
	Prayon SA	DHH	Stacking 20%, sold 80%	180
Czech Rep.	Fosfa	Thermal		50
Finland	Kemira GrowHow	DH	Stacking	300
France	Grand Quevilly **(closed)**	DH	Stacking	200
Greece	PFI Ltd., Kavala	DH	Stacking	70
	PFI Ltd., Thessaloniki	DH	Stacking	110
Lithuania	AB Lifosa	HH	Stacking	350
Netherlands	Hygro Agri Rotterdam **(closed)**	HDH-2	Sea	160
	Kemira Agro Pernis **(closed)**	HDH-1	Sea	225
	Thermphos	Thermal		155
Poland	Police S.A., Police	DH	Stacking	400
	Fosfory N.F., Gdansk	DH	Stacking	110
	Alwernia S.A.	Thermal		40
	Wizow S.A.	HH	Stacking	50
Spain	Fertiberia S.A.	DH	Stacking	420
	FMC Foret S.A.	DH	Stacking	130

Table 5.1: Overview of the European phosphoric acid plants [154, TWG on LVIC-AAF]

5.2 Applied processes and techniques

5.2.1 Overview

Two different processes using different raw materials can be used in the manufacture of phosphoric acid:

1. the **thermal** process uses elemental phosphorus as the raw material. Here, elemental phosphorus is produced from phosphate rock, coke and silica in an electrical resistance furnace (see Section 5.4.15)
2. **wet** processes, using phosphate minerals, which are decomposed with an acid.

The share of wet phosphoric acid amounts to about 95 % of the total phosphoric acid in the EU. Part of the wet process acid is purified for the manufacture of technical and food grade phosphate salts, usually employing a solvent extraction process. In the EU, the production of phosphoric acid using the solvent extraction purifying route is preferred over the thermal route because of the energy costs.

5.2.2 Wet process

There are three possible subgroups of wet processes depending on which acid is used for the acidulation, i.e. HNO_3, HCl or H_2SO_4. The wet digestion of phosphate rock with H_2SO_4 is the preferred process in terms of volume. For descriptions of specific wet processes using H_2SO_4, see:

- Section 5.4.1, “Dihydrate process”
- Section 5.4.2, “Hemihydrate process”
- Section 5.4.3, “Hemi-dihydrate recrystallisation process, single-stage filtration”
- Section 5.4.4, “Hemi-dihydrate recrystallisation process, double-stage filtration”
- Section 5.4.5, “Di-hemihydrate recrystallisation process, double-stage filtration”.

For a description of the “Nitrophosphate route”, using HNO_3, see Section 7.2.2.1.

Figure 5.1 gives an overview of the production of H_3PO_4 by wet processes. The tri-calcium phosphate from the phosphate rock reacts with concentrated H_2SO_4 to produce H_3PO_4 and the insoluble salt calcium sulphate.

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

The insoluble calcium sulphate is filtered from the H_3PO_4. The reaction between phosphate rock and H_2SO_4 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 recirculated H_3PO_4, thereby converting as much of it as possible to the soluble mono calcium phosphate, followed by precipitation as calcium sulphate with H_2SO_4.

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

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

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.

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. 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 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.

The filtration stage separates the phosphoric acid from the calcium sulphate. About four to five tonnes of gypsum are generated for every tonne (P_2O_5 equivalent) of acid produced. The most common types of filtration equipment are the tilting pan, rotary table or travelling belt.

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 transported 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.

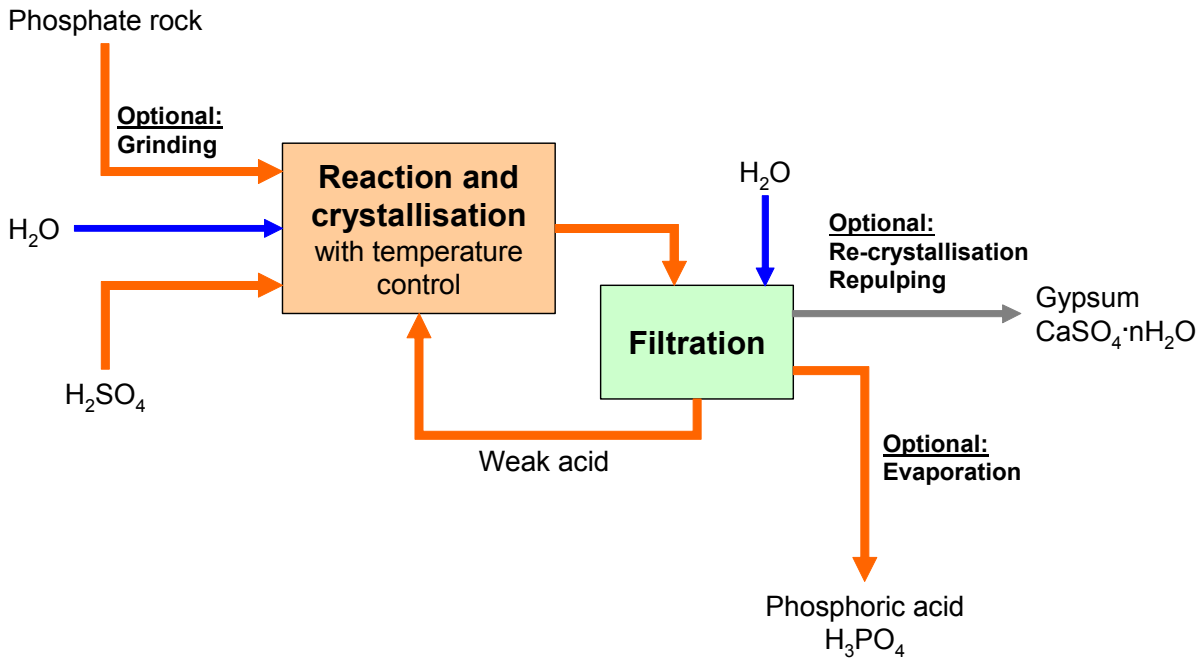

Figure 5.1: Overview of the production of H_3PO_4 (wet process with H_2SO_4)
This figure is based on [29, RIZA, 2000, 31, EFMA, 2000].

5.2.2.1 Raw materials

5.2.2.1.1 Phosphate rock

[31, EFMA, 2000]

Table 5.2 and Table 5.3 give an overview of phosphate rocks from different origins.

Phosphate ores are found in two major geological origins: igneous or sedimentary. 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, 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 the technology needs to be constantly adapted to meet raw materials variations.

According to IFA the supply of phosphate rock in the EU in 2004 was provided by Morocco (47.5 %), Russia (24.3 %), Jordan (8.1 %), Syria (6.2 %), Tunisia (4.9 %), Israel (4.2 %), Algeria (3.8 %) and others (1.0 %) [2, IFA, 2005].

5.2.2.1.2 Sulphuric acid

[29, RIZA, 2000]

The types of H_2SO_4 mainly used as raw material in the production of phosphoric acid are acid produced from elemental sulphur, fatal acid (from non-ferrous metal production) and spent acid.

The amounts of impurities introduced into the process by H_2SO_4 are generally low or negligible compared to the amount introduced by the phosphate rock. Only in the case of mercury and possibly lead, H_2SO_4 may contribute significantly, especially when fatal acid is the main type of H_2SO_4 used. Typical mercury contents are:

- for H_2SO_4 from elemental sulphur <0.01 ppm
- fatal acid 0.1 – 1 ppm.

Origin	Mine/region	Production Mtonnes/year	Reserves [2] Mtonnes	Grade (nominal) % BPL	P_2O_5	CaO	SiO_2	F	CO_2	Al_2O_3	Fe_2O_3	MgO	Na_2O	K_2O	Organics	Organic carbon	SO_3	Cl	SrO
					Composition wt-%														
China																			
Israel	Nahal Zin	4.0	180																
Jordan	El-Hassa																		
Morocco	Khouribga	22.0	5700	73	33.4	50.6	1.9	4	4.5	0.4	0.2	0.3	0.7	0.1	0.3		1.6	0.1	0.1
	Youssoufia																		
	Bu-Cra																		
Russia	Kola[1]	10.5	200	84	38.9	50.5	1.1	3.3	0.2	0.4	0.3	0.1	0.4	0.5		0.1	0.1		2.9
	Kovdor[1]				37.0	52.5	2.0	0.8		0.1	0.2	2.1				0.2			
Senegal	Taiba	2.0	50	80	36.7	50	5	3.7	1.8	1.1	0.9	0.1	0.3	0.1		0.4			
South Africa	Pharlaborwa[1]	2.8	1500	80	36.8	52.1	2.6	2.2	3.5	0.2	0.3	1.1	0.1	0.1	0.1		0.2		0.3
Syria		2.1	100																
Togo		0.8	30	80	36.7	51.2	4.5	3.8	1.6	1	1	0.1	0.2	0.1		0.1	0.3	0.1	
Tunisia	Gafsa	8.1	100																
USA	Florida	34.2	1000	75	34.3	49.8	3.7	3.9	3.1	1.1	1.1	0.3	0.5	0.1	0.5	0.2	0.1		
	North Carolina																		
Others		16.2	1240																
World		128.2	12000																

[1] Igneous [2] Amount which could be economically extracted or produced at the time of determination [9, Austrian UBA, 2002]

Table 5.2: Origin and typical composition of different phosphate rocks (P_2O_5 content is highlighted) based on past analysis [9, Austrian UBA, 2002, 29, RIZA, 2000, 31, EFMA, 2000] and references within, [154, TWG on LVIC-AAF]

Origin	Mine/region	Rare earth metals	U_3O_8	As	Cr	Hg	Pb	Ni	Zn	Cu	Cadmium[2]
		Trace elements ppm									
China											
Israel	Nahal Zin										22
Jordan	El-Hassa										6
Morocco	Khouribga	900	185	13	200	0.1	10	35	200 - 400	40	15
	Youssoufia										
	Bu-Cra										
Russia	Kola[1]	6200	11	0.5	19	<0.1	2		20	37	1.2
	Kovdor[1][3]	1400		2	3	0.001	3	2	5	30	<0.4
Senegal	Taiba		124	18	6	0.2	5				53
South Africa	Pharlaborwa[1]	4800	134	13	1	0.1	11	2	6	102	1.3
Syria											8
Togo				12		0.6					53
Tunisia	Gafsa										62
USA	Florida	600	101	11	60	0.02	17	28	70	13	9
	North Carolina										
Others											
World											

[1] Igneous [2] partially [32, European Commission, 2001] [3] [29, RIZA, 2000]

Table 5.3: Trace elements in phosphate rock of different origin (Cd is highlighted)
Table based on [31, EFMA, 2000]

Origin	Mine/region	U-238	Th-232	Ra-226	Po-210	Pb-210
		Radioactivity Bq/kg				
China						
Israel	Nahal Zin	1325	92	1325	1325	1325
Jordan	El-Hassa					
Morocco	Khouribga					
	Youssoufia					
	Bu-Cra	750	16	750	750	750
Russia	Kola[(1)]	35	90	35	35	35
	Kovdor[(1)]	30	30	12	13	8
Senegal	Taiba					
South Africa	Pharlaborwa[(1)]	110	360	110	110	110
Syria						
Togo						
Tunisia	Gafsa					
USA	Florida	1500	37	1300	1300	1300
	North Carolina					
[(1)] Igneous						

Table 5.4: Radioactivity of different phosphate rocks [29, RIZA, 2000] and references within

5.2.2.2 Grinding

Depending on the phosphate rock properties and the process applied, grinding of the phosphate rock can be necessary. This is usually carried out using ball or rod mills. Both types of mills can operate with wet or dry rock. Some grades of commercial rock do not need grinding, their particle size distribution already being acceptable for the dihydrate reaction section. Most other phosphate rocks require particle size reduction. The energy requirements for grinding depends on the type of phosphate rock and is about 15 – 18 kWh per tonne phosphate rock [9, Austrian UBA, 2002].

5.2.2.3 Recrystallisation

Recrystallisation is applied in order to improve the overall P_2O_5 yield (P_2O_5 efficiency). For descriptions of different recrystallisation processes, see Sections 5.4.3, 5.4.4 and 5.4.5.

5.2.2.4 Evaporation

Currently, almost all evaporators are of the forced circulation design (see Figure 5.2). The forced circulation evaporator consists of a heat exchanger, vapour or flash chamber, condenser, vacuum pump, acid circulating pump and associated pipework. A fluosilicic acid scrubber is usually included with the 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.

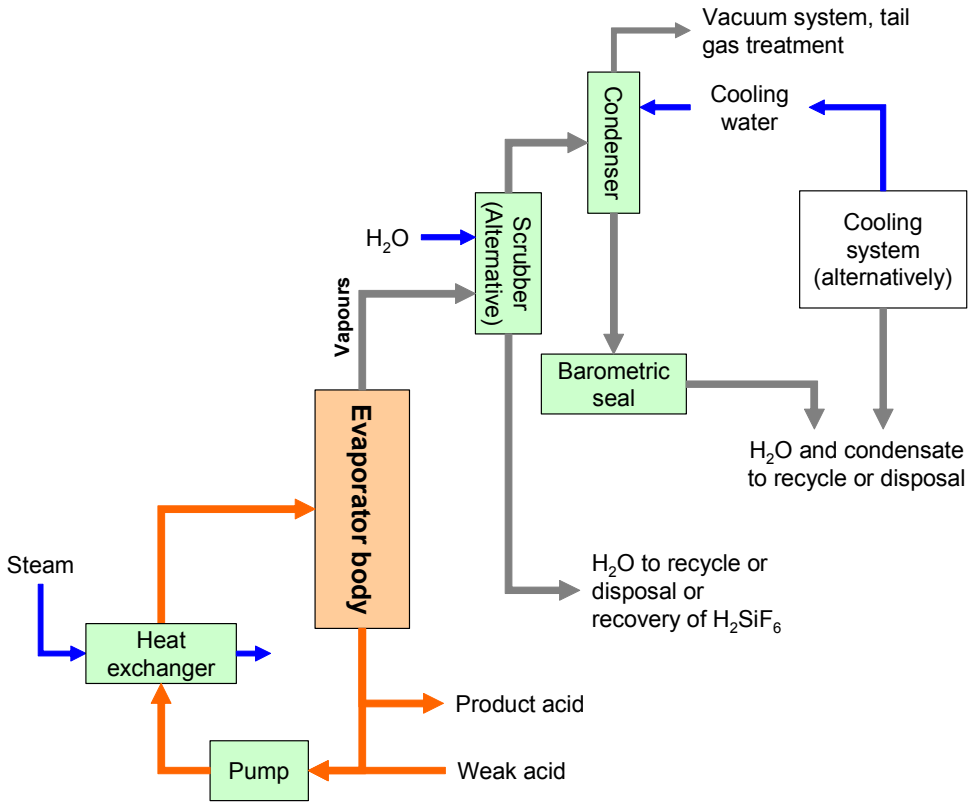

Figure 5.2: Forced circulation evaporator for the concentration of H_3PO_4
This figure is based on [15, Ullmanns, 2001, 31, EFMA, 2000]

5.2.2.5 Co-product phosphogypsum

Gypsum (calcium sulphate) is an unavoidable co-product in wet phosphoric acid production ("phosphogypsum"); for every tonne of phosphoric acid (P_2O_5) around 4 – 5 tonnes of gypsum is produced. Phosphate rock contains a range of impurities which are distributed between the product acid and the calcium sulphate. Because of the volume of the gypsum production and the type and level of impurities in the gypsum, this co-product constitutes an environmental challenge.

5.2.2.6 Co-product fluosilicic 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 fluosilicic 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 system.

5.3 Current emission and consumption levels

The following data all relate to the wet process route based on the use of H_2SO_4. For emission and consumption levels from the thermal process, see Section 5.4.15. Table 5.5 shows the reported consumption levels for the production of phosphoric acid, Table 5.6 emissions to air, Table 5.7 emissions to water and Table 5.8 emissions from the disposal of solids to water.

Consumption of	Per tonne P_2O_5	Remarks		Source
Phosphate rock	2.6 – 3.5 tonnes	Depending on the rock composition		[31, EFMA, 2000]
	2.6 – 3.3 tonnes	Plant: Nilefos. Levels depend on the rock composition		[33, VITO, 2005]
	3.1 tonnes	Hydro Agri, HDH-2 process		[29, RIZA, 2000] [x]
	2.8 tonnes	Plant: Kemira, HDH-1 process		
H_2SO_4	2.6 tonnes			
	2.4 – 2.9 tonnes	Plant: Nilefos. Levels depend on the rock composition		[33, VITO, 2005]
	2.6 tonnes	Hydro Agri, HDH-2 process		[29, RIZA, 2000] [x]
Process water	51 m^3	Plant: Kemira, HDH-1 process	Including scrubber water	
	52 m^3	Hydro Agri, HDH-2 process	Including scrubber water	
	3.6 – 4 m^3	Plant: Nilefos. Depending on the acid concentration obtained in the filter	Not including scrubber water	[33, VITO, 2005]
	4 – 7 m^3	Depending on the concentration of the weak acid obtained in the filter and whether the condensed water in the evaporation loop is recycled	Not including scrubber water	[31, EFMA, 2000]
Cooling water	100 – 150 m^3	Depending on the process		
	110 – 120 m^3	Plant: Nilefos	Cooler and condenser water	[33, VITO, 2005]
	40 – 50 m^3	Hydro Agri, HDH-2 process	Cooler and condenser water	[29, RIZA, 2000] [x]
	101 m^3	Plant: Kemira, HDH-1 process	Cooler and condenser water	
Electric power	173 kWh			
	167 kWh	Hydro Agri, HDH-2 process		
	170 – 180 kWh	Plant: Nilefos		[33, VITO, 2005]
	120 – 180 kWh	Depends on whether grinding is carried out or not		[31, EFMA, 2000]
Steam	0.5 – 2.2 tonnes	Mainly used for evaporation		
	1.0 tonne	Hydro Agri, HDH-2 process		[29, RIZA, 2000] [x]
	2.2 tonnes	Plant: Kemira, HDH-1 process		
	1.9 – 2.4 tonnes	Plant: Nilefos, depending on the fraction to be concentrated		[33, VITO, 2005]
[x] plants closed because of discharge of the phosphogypsum to sea				

Table 5.5: Reported consumption levels for the production of phosphoric acid

Emission of	mg/Nm^3	g/tonne P_2O_5	Remark	Source
Fluoride	5	40	New plants	[31, EFMA, 2000]
	30		Existing plants	
	<1	6.1	Kemira, HDH-1 process, 1996/97	[29, RIZA, 2000] [x]
		2.8	Hydro Agri, HDH-2 process 1996/97	
	10 – 15	90 – 135	Nilefos	[33, VITO, 2005]
Dust	50		New plants	[31, EFMA, 2000]
	150		Existing plants	
		10 – 15	Nilefos, estimation	[33, VITO, 2005]
	30	12	Kemira, HDH-1 process, 1996/97	[29, RIZA, 2000] [x]
		19	Hydro Agri, HDH-2 process, 1996/97	
	10		Kemira Chemicals Oy	[17, 2nd TWG meeting, 2004]
[x] plants closed because of discharge of the phosphogypsum to sea				

Table 5.6: Reported emissions to air from the production of phosphoric acid

Emission of	mg/l	g/tonne P_2O_5	Remark	Source
Phosphate (P)		1300	Kemira, HDH-1 process, 1996/97	[29, RIZA, 2000] [x]
		700	Hydro Agri, HDH-2 process, 1996/97	
		1000	Nilefos	[33, VITO, 2005]
Fluorine (F)		15000	Kemira, HDH-1 process, 1996/97	[29, RIZA, 2000] [x]
		31000	Hydro Agri, HDH-2 process, 1996/97	
		2000	Nilefos, recuperation of fluosilicic acid	[33, VITO, 2005]
Cadmium		0.03	Kemira, HDH-1 process, 1996/97, estimated value based on input/output calculation	[29, RIZA, 2000] [x]
		0	Hydro Agri, HDH-2 process, 1996/97, all values measured are the detection limit	
		0 – 0.01	Nilefos	[33, VITO, 2005]
Mercury		0	Kemira, HDH-1 process, 1996/97, estimated value based on input/output calculation	[29, RIZA, 2000] [x]
		0.01	Hydro Agri, HDH-2 process, 1996/97	
		<0.002	Nilefos	[33, VITO, 2005]
Arsenic		0.02	Kemira, HDH-1 process, 1996/97, estimated value based on input/output calculation	[29, RIZA, 2000] [x]
		1.9	Hydro Agri, HDH-2 process, 1996/97	
		<0.3	Nilefos	[33, VITO, 2005]
Heavy metals		1.9	Kemira, HDH-1 process, 1996/97, estimated value based on input/output calculation	[29, RIZA, 2000] [x]
		2.8	Hydro Agri, HDH-2 process, 1996/97	
		<3	Nilefos	[33, VITO, 2005]
[x] plants closed because of discharge of the phosphogypsum to sea				

Table 5.7: Reported emissions to water from the production of phosphoric acid

Emission of	Unit	per tonne P_2O_5	Remark	Source
Gypsum	tonnes	4	Kemira, HDH-1 process, 1996/97	[29, RIZA, 2000] [3]
		4.7	Hydro Agri, HDH-2 process, 1996/97	
Phosphate (P)	kg	8.1	Kemira, HDH-1 process, 1996/97	
		5.8	Hydro Agri, HDH-2 process, 1996/97	
Fluorine (F)		33	Kemira, HDH-1 process, 1996/97	
		45	Hydro Agri, HDH-2 process, 1996/97	
Cadmium	g	0.5	Kemira, HDH-1 process, 1996/97	
		1.4	Hydro Agri, HDH-2 process, 1996/97	
Mercury		0.2	Kemira, HDH-1 process, 1996/97	
		0.5	Hydro Agri, HDH-2 process, 1996/97	
Arsenic		0.7	Kemira, HDH-1 process, 1996/97	
		0	Hydro Agri, HDH-2 process, 1996/97, all values measured are the detection limit	
Heavy metals[1]		53	Kemira, HDH-1 process, 1996/97	
		27	Hydro Agri, HDH-2 process, 1996/97	
Rare earth metals[2]		2200	Kemira, HDH-1 process, 1996/97	
		360	Hydro Agri, HDH-2 process, 1996/97	
Radium-226	mBq	1.4	Kemira, HDH-1 process, 1996/97	
		2.3	Hydro Agri, HDH-2 process, 1996/97	
Polonium-210		1.4	Kemira, HDH-1 process, 1996/97	
		2.3	Hydro Agri, HDH-2 process, 1996/97	
Lead-210		1.4	Kemira, HDH-1 process, 1996/97	
		2.1	Hydro Agri, HDH-2 process, 1996/97	

[1] Lead, copper, zinc, nickel and chromium [2] Mainly lanthanum, cerium, praseodymium, neodymium
[3] plants closed because of discharge of the phosphogypsum to sea

Table 5.8: Reported emission levels for the disposal of phosphogypsum to water from the production of phosphoric acid

5.4 Techniques to consider in the determination of BAT

5.4.1 Dihydrate process (DH)

Description

The dihydrate process consists of four stages, namely grinding, reaction, filtration and concentration. Figure 5.3 gives an overview. The dihydrate process offers a wide range of options and the advantages of dihydrate systems are:

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

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.

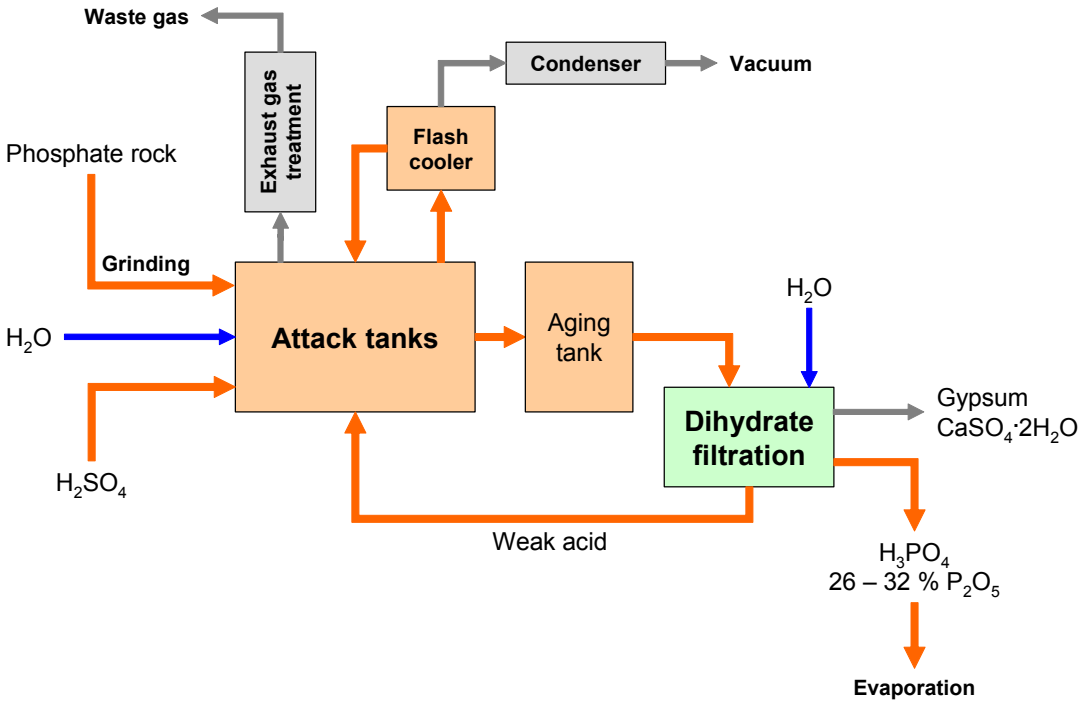

Figure 5.3: Overview of the dihydrate process
[31, EFMA, 2000]

Achieved environmental benefits

- low operating temperatures
- saving of energy for rock drying.

Cross-media effects

- relatively weak product acid (26 – 32 % P_2O_5), hence high energy consumption in the acid concentration stage
- low P_2O_5 efficiency: 94 – 96 %. Losses occur mostly as co-crystallisation with the calcium sulphate
- produces impure dihydrate containing 0.75 % P_2O_5
- may require rock grinding.

Operational data

See Description.

Applicability

Generally applicable.

[33, VITO, 2005] reports a modified DH process with higher yield. The modifications include:

- double attack system (1st step 70 % of the rock, 2nd step 30 % with fresh H_2SO_4)
- prolonged reaction time
- recovery of P_2O_5 washed out of the phosphogypsum during pumping to the stack and from rain water.

The modified DH process achieves an average P_2O_5 efficiency of >97.5 %. The related dihydrate contains 0.58 % P_2O_5. Where waste heat is available on-site that cannot be used elsewhere, the concentration of H_3PO_4 from the DH is not seen as a cross-media issue. For the modification, a significant investment was necessary to increase the residence time. The recycling of water from the stack is common practice in industry.

Economics

No specific information provided.

Driving force for implementation

No phosphate rock limitation, online time is high, wet rock can be used, easy startup and shutdown.

References to literature and example plants

[29, RIZA, 2000, 31, EFMA, 2000, 33, VITO, 2005], Nilefos Chemie

5.4.2 Hemihydrate process (HH)

Description

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 – 46 % P_2O_5 acid directly, enabling valuable savings to be made in energy usage. Figure 5.4 gives an overview of the hemihydrate process.

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

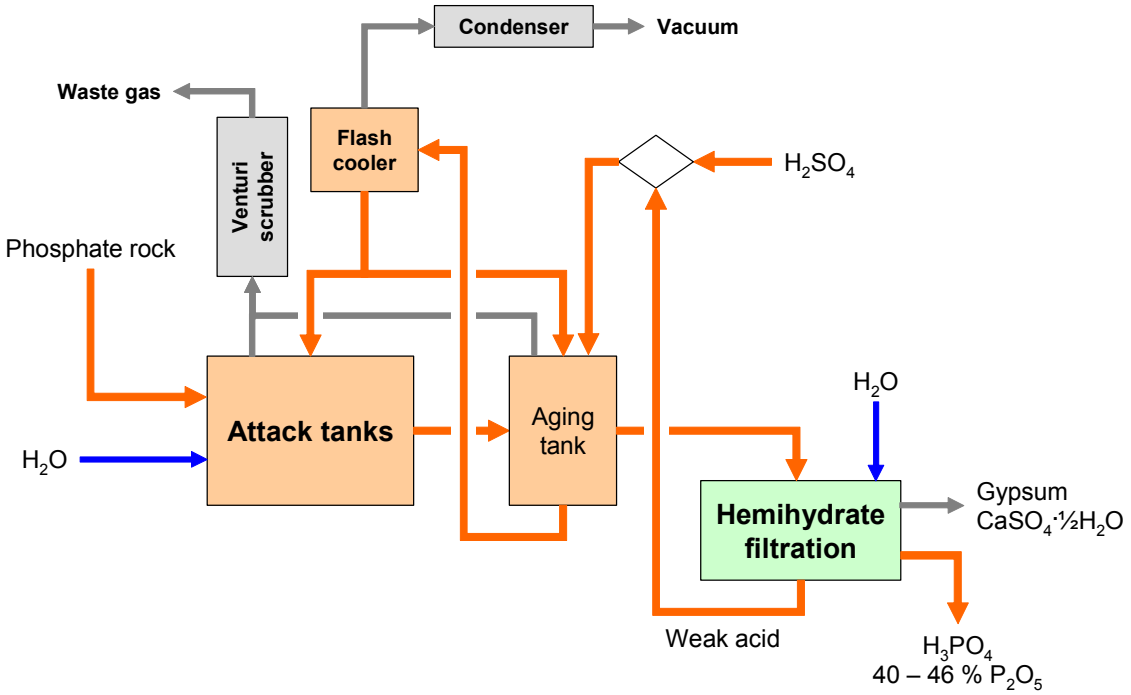

Figure 5.4: Overview of the hemihydrate process
[31, EFMA, 2000]

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 hemihydrate process however, there is no need to use modifiers.

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 hemihydrate plant and the absence of silicofluoride and chukhrovite (a crystallised mineral compound) scaling in the hemihydrate filter may compensate for the higher insoluble P_2O_5 losses through the hemihydrate cake.

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

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

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

Achieved environmental benefits

- energy savings due to reduction or elimination of the need for evaporation
- energy savings due to lower rock grinding requirements (may use coarse rock).

Cross-media effects

- low P_2O_5 efficiency: 90 – 94 %
- produces impure hemihydrate (1.1 % P_2O_5).

Operational data

See description.

Applicability

Generally applicable. Limited number of rocks processed industrially. The overall efficiency depends on the rock type.

Economics

Requires higher grade alloys in comparison to processes with lower temperature.

Driving force for implementation

Cost benefits.

References to literature and example plants

[29, RIZA, 2000, 31, EFMA, 2000], Kemira Chemicals Oy, Finland

5.4.3 Hemi-dihydrate recrystallisation process, single-stage filtration

Description

Figure 5.5 gives an overview of the hemihydrate recrystallisation process (HRC or HDH-1). 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 a similar concentration as that from the dihydrate process but the gypsum is much purer.

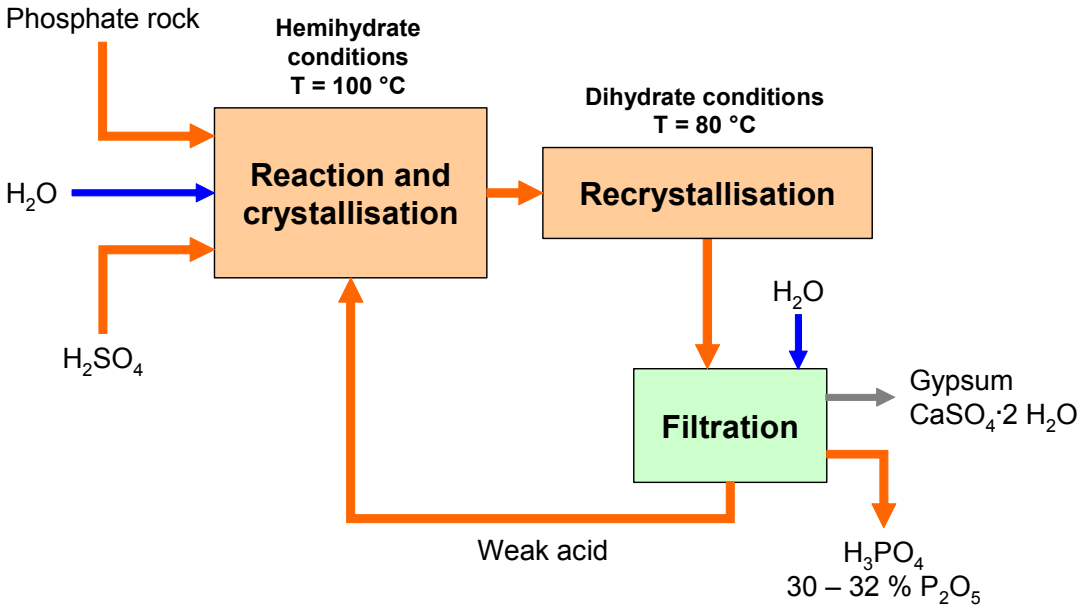

Figure 5.5: Overview of the hemihydrate recrystallisation process [29, RIZA, 2000]

Achieved environmental benefits

- produces relatively pure dihydrate
- high P_2O_5 efficiency: 97 %
- lower sulphuric acid consumption.

Cross-media effects

- requires a fine rock grind
- requires sulphuric acid dilution
- may dissolve more partially soluble impurities
- requires acid evaporation.

Operational data

See description.

Applicability

Applicable for new plants [154, TWG on LVIC-AAF].

Economics

Requires sophisticated materials of construction.

Driving force for implementation

Cost benefits.

References to literature and example plants

[29, RIZA, 2000, 31, EFMA, 2000], Kemira Pernis (the Netherlands, closed), no such plant is in operation in the EU.

5.4.4 Hemi-dihydrate recrystallisation process, double-stage filtration

Description

Figure 5.6 gives an overview of the hemi-dihydrate recrystallisation process with double-stage filtration (HDH-2). 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.

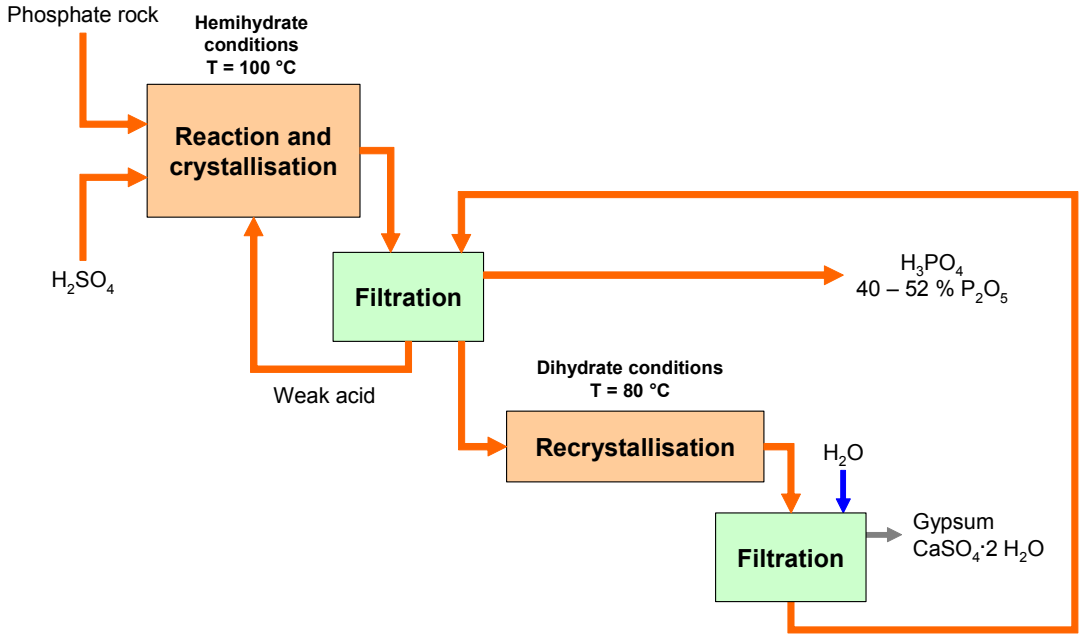

Figure 5.6: Overview of the hemi-dihydrate recrystallisation process with double-stage filtration [29, RIZA, 2000]

Achieved environmental benefits

- energy savings due to reduction or elimination of the need for evaporation equipment if concentrated acid is required for downstream processing
- produces purer acid (low SO_4, Al, F)
- energy savings by elimination of rock grinding (may use coarse rock)
- low sulphuric acid consumption
- highest P_2O_5 efficiency: 98.5 %
- produces relatively pure dihydrate (0.19 % P_2O_5).

Cross-media effects

None believed to be likely.

Operational data

See description.

Applicability

Generally applicable, but limited number of rocks processed industrially.

Economics

- highest P_2O_5 efficiency
- savings on evaporation equipment
- two-stage filtration, lower utilisation
- high recrystallisation volume required
- high capital cost
- requires sophisticated materials of construction.

Driving force for implementation

Cost benefits.

References to literature and example plants

[29, RIZA, 2000, 31, EFMA, 2000], Hydro Agri Rotterdam (the Netherlands, closed), presently, no such process is applied in the EU.

5.4.5 Di-hemihydrate recrystallisation process, double-stage filtration

Description

Figure 5.7 gives an overview of the di-hemihydrate recrystallisation process with double-stage filtration (DH/HH or DHH). 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.

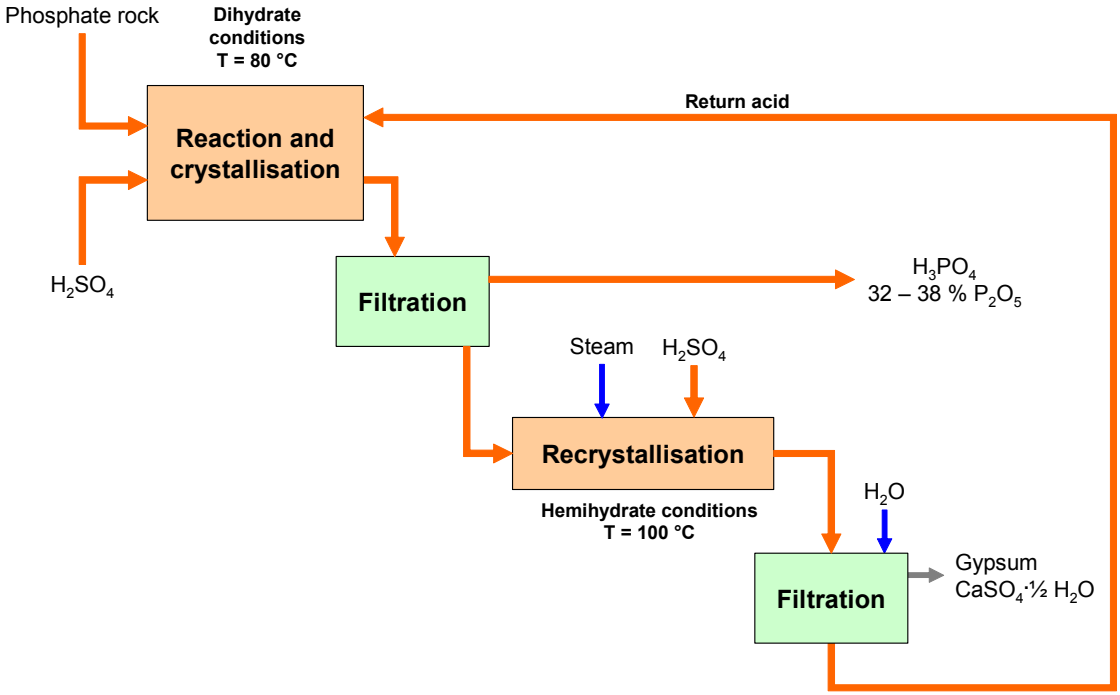

Figure 5.7: Di-hemihydrate recrystallisation process with double-stage filtration [29, RIZA, 2000, 154, TWG on LVIC-AAF]

Achieved environmental benefits

- produces a relatively pure hemihydrate
- 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
- high P_2O_5 efficiency: 98 %.

Cross-media effects

- although higher strength acid is produced, acid evaporation is required
- requires steam for the conversion of dihydrate to hemihydrate
- normally requires rock grinding.

Operational data

See description.

Applicability

Applicable for new plants. Flexible as to rock source. See also Driving force for implementation.

Economics

- two-stage filtration, lower utilisation
- higher capital costs
- requires sophisticated materials of construction.

Driving force for implementation

Cost benefits, mainly due to fact that the process allows marketing of the phosphogypsum.

References to literature and example plants

[29, RIZA, 2000, 31, EFMA, 2000], Prayon S.A.

5.4.6 Repulping

Description

Figure 5.8 gives an overview of the repulping process. This further optimisation of the hemihydrate recrystallisation process (HRC or HDH-1) 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.

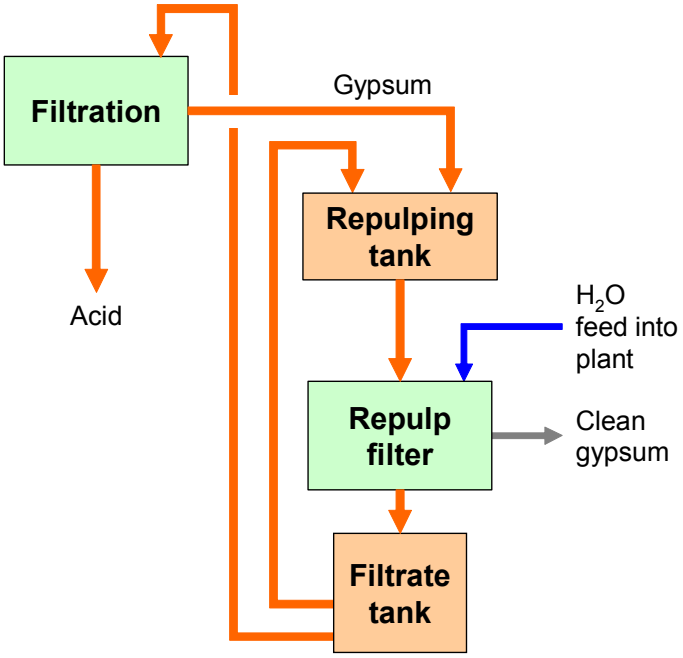

Figure 5.8: Overview of the repulping process
[29, RIZA, 2000, 31, EFMA, 2000]

Achieved environmental benefits

- purer gypsum
- higher efficiency.

Cross-media effects

None believed to be likely.

Operational data

No information provided.

Applicability

Applicable for hemihydrate plants.

Economics

High capital cost.

Driving force for implementation

Cost benefits.

References to literature and example plants

[29, RIZA, 2000, 31, EFMA, 2000], presently no more applied in the EU.

5.4.7 Fluoride recovery and abatement

Description

Fluoride is present in most phosphate rocks at a level of 2 – 4 %, that is 20 – 40 kg/tonne rock or approximately 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 dihydrate (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 hemihydrate (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). 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 condenser water becoming contaminated with fluoride. A typical fluoride distribution in the dihydrate process and hemihydrate process is shown in Table 5.9.

	DH Process (%)	HH Process (%)
Acid	15	12
Gypsum	43	50
Reactor off-gas	5	8
Flash cooler vapour	3	30
Concentrator vapour	35	- [x]
[x] assuming that no concentration is carried out		

Table 5.9: Typical fluoride distribution in DH and HH processes
[31, EFMA, 2000]

Fluoride can be removed by a number of different scrubbing systems (see also Section 6.4.6). 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.

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 (see also Section 6.4.9).

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 fluosilic acid strength, silica deposition is controlled. The silica is then removed by filtration. Usually, a product containing 20 – 25 % fluosilicic acid is recovered in the fluoride recovery system.

Achieved environmental benefits

- with two or more absorbers a recovery efficiency of 99 % or more can be achieved. According to [31, EFMA, 2000], achievable fluoride emission levels for new plants are 5 mg/Nm^3 (40 g/tonne P_2O_5). In the Netherlands, emission levels of 1 – 5 mg/Nm^3 were achieved [29, RIZA, 2000]
- recovery of fluosilicic acid (H_2SiF_6) with potential for valorisation (see Section 6.4.4), for production of HF from fluosilicic acid, see Section 6.4.10.

Cross-media effects

Water, energy and chemicals consumption for scrubbing.

Operational data

No information provided.

Applicability

Generally applicable. Fluosilicic acid can be valorised if there is a market available.

Economics

For cost estimates, see Table 6.10.

Driving force for implementation

Reduced fluoride emission levels.

References to literature and example plants

[29, RIZA, 2000, 31, EFMA, 2000]

5.4.8 Recovery and abatement of dust from rock grinding

Description

Dust emissions begin with the unloading, handling and grinding of phosphate rock. Phosphate rock is normally transported by ship. It is unloaded by cranes and transferred to storage and grinding sections by conveyor belts or trucks. The spread of phosphate rock dust is commonly prevented by using covered conveyor belts and indoor storage. 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. Dust originating from phosphate rock grinding can be recovered by passing the air containing dust through fabric filters. In general, dust emission levels of 2 – 10 mg/Nm^3 can be achieved by using fabric filters [11, European Commission, 2003]. 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 [31, EFMA, 2000] the achievable dust emission level of fabric filters in new phosphoric acid plants is 50 mg/Nm^3. However, by using fabric filters in the Netherlands, dust emission levels of less than 30 mg/Nm^3 were achieved. SSP/TSP plants achieve emissions below 10 mg/m^3 using fabric filters. Dust reduction from grinding operations can be achieved by means of ceramic filters, realising dust emissions of <2.5 – 8 mg/Nm^3.

Achieved environmental benefits

- recovery of raw material
- dust emissions well below 10 mg/m^3 [17, 2nd TWG meeting, 2004].

Cross-media effects

None believed to be likely.

Operational data

No information provided.

Applicability

Generally applicable. The necessity of rock grinding depends on the rock type and the process. [33, VITO, 2005] reports a plant where occasionally phosphate rock is ground. The building has no vent and only diffuse emissions occur.

Economics

See [11, European Commission, 2003].

Driving force for implementation

Reduced dust emission levels.

References to literature and example plants

[11, European Commission, 2003, 17, 2nd TWG meeting, 2004, 29, RIZA, 2000, 31, EFMA, 2000]

5.4.9 Phosphate rock selection (1)

Description

Ideally, the best possible phosphate source rock would consist entirely of tricalcium phosphate $Ca_3(PO_4)_2$. Impurities in phosphate rock are natural but generally undesirable for an assortment of reasons – economic, technical and environmental.

Rock phosphate can be of igneous/volcanic origin or can be sedimentary ores. Whereas igneous rocks (South Africa, Russia) generally show higher P_2O_5 contents, these rocks are generally not available. Sedimentary ores (US, Morocco, Algeria) possess higher amounts of calcium compounds, thus lowering the P_2O_5 content and increasing the CaO/P_2O_5 ratio. In many cases, sedimentary ores are concentrated and beneficiated at the mine in order to increase the phosphate content and to remove impurities like insoluble sand and stones. For beneficiation by floating, usually organic additives are used which remain partially in the rock phosphate. The number of countries supplying rock phosphate is limited. Some countries no longer export rock phosphates (US) or only in limited quantities (Russia). This affects the rock phosphate costs. For selection of the rock phosphate source, not only the availability but also aspects regarding logistics, design of the processing plant, type and amounts of other components (Ca, Fe, Al, C, SiO_2, etc.), and various local factors are taken into account. These are mainly:

- P_2O_5 content determining logistic cost
- CaO/P_2O_5 ratio determining amount of acid and by-products (gypsum, calcium carbonate)
- physical quality of the rock (dust formation through handling)
- presence of organic carbon interfering with the dissolution, interfering with the process, producing, e.g. excessive amounts of NO_x and odour nuisance
- presence of further components like F, Fe, Al, interfering with the process, producing, e.g. excessive amounts of NO_x or fluoride emissions or producing thixotropic slurries (due to Fe and Al compounds) that cannot be easily handled; scaling of equipment, in particular of heat exchangers and off-gas lines, can be promoted by such components; filterability may become impaired; for certain grades the presence of limited amounts of such components can be advantageous
- presence of other components like Si, As, Cd, that may be undesirable for various reasons. Also, certain trace elements serve as micronutrients and their presence is desired
- the ability to process any rock phosphate (or combinations) cannot be assessed from the analyses only: tests on plant scale are required and in all cases, the long time experience is necessary in order to combine and optimise process design, process operating parameters and rock quality.

Achieved environmental benefits

Proper choice of rock phosphate for a given design of plant will:

- minimise the acid required
- optimise the type and amounts of co-products
- minimise emissions into the environment.

Cross-media effects

None believed to be likely.

Operational data

No information provided.

Applicability

Generally applicable, but might be limited by the availability of suitable grade phosphate rock.

Economics

It can be assumed that the prices for low impurity rock will increase with demand [49, ERM, 2001].

Driving force for implementation

Cost benefits if the process efficiency can be increased.

References to literature and example plants

[29, RIZA, 2000, 49, ERM, 2001]

5.4.10 Phosphate rock selection (2)

Description

The production of clean gypsum requires the use of phosphate rock with low levels of impurities. Only limited amounts of gypsum are presently used for purposes such as building construction materials or road pavements. However, regarding size and economy, construction materials, in particular indoor building products, are an area of possible further 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.

Achieved environmental benefits

- facilitation of the valorisation of the phosphogypsum
- less potential contamination for dispersal into the environment.

Cross-media effects

None believed to be likely.

Operational data

No information provided.

Applicability

Generally applicable.

The selection of low impurity phosphate rock is also in discussion in the context with cadmium accumulation in agricultural soils [49, ERM, 2001]. However, the main obstacle for valorisation of phosphogymsum is finding a market for it.

Economics

It can be assumed that the prices for low impurity rock will increase with demand.

Driving force for implementation

Cost benefits if the phosphogypsum can be valorised.

References to literature and example plants

[29, RIZA, 2000, 49, ERM, 2001]

5.4.11 Decadmation of H_3PO_4 by reactive extraction

Description

The decadmation process was installed in the example plant in 1973 and was applied after a wet decomposition of ores with sulphuric acid. An earlier version of this process included several counter stream extraction steps using isopropanol as the solvent and the initial intention was to remove the organic components from the raw phosphoric acid. At the beginning of the 1990s, the quality standards for metal contents, especially cadmium, were increased. Hence the example plant developed a process to be applied prior to the extraction steps already installed.

The decadmation can be described as follows:

- cadmium is removed from the raw phosphoric acid by an extraction step using an organic solvent consisting of a mixture of inert solvent/amines or ammonium compounds with a chlorocomplex as a counterion
- the organic phase is separated
- cadmium is removed from the organic phase by re-extraction with an aqueous phase (containing hydrochloric acid and a chlorocomplex of, e.g. Zn or Fe. The mechanism can be understood as the swapping of the chlorocomplex and cadmium between the two phases
- the phases are separated from each other
- cadmium is removed from the aqueous phase.

The ideal process temperature is between 15 und 25 ºC. The process can be applied in continuous or batch mode. A specific prerequisite condition for the application of the process is that the phosphoric acid is produced by the use of H_2SO_4 from phosphate rock, and not by using HCl or HNO_3. Applied to phosphoric acid with P_2O_5 contents of between 28 to 58 % w/w, cadmium can be reduced by 95 %.

Cadmium is removed from the aqueous phase by precipitation as a final process step after decadmation. This includes the following:

- physical separation of the aqueous phase from the organic phase
- distillation of the dilute hydrochloric acid solution
- cooling of the concentrated solution resulting in precipitation of cadmium compounds in a fine cristalline modification
- decantation of the precipitated cadmium compounds.

The remaining filtrate after removal of hydrochloric acid and cadmium is fed back to the initial raw phosphoric acid and hydrochloric acid is recycled to the extraction step. Hence, the liquids are handled in a closed cycle.

Achieved environmental benefits

- decadmation efficiency of 95 %.

Cross-media effects

- high energy consumption.

Operational data

See description.

Applicability

For specific applications, e.g. for feed- or food phosphates or for pharmaceutical applications, a use of this technique could be possibly recommended [50, German UBA, 2002].

For separation of arsenic, an Na_2S solution is added to the crude acid, and the precipitated arsenic sulphide is removed by filtration.

The separation of cadmium by means of a complexing agent such as alkyldithiophosphoric acid alkyl ester can also be classified as a precipitation reaction because the precipitated cadmium complex is separated in solid form either directly or after addition of a filter aid or absorbent. Such a process is operated on a commercial scale by Tessenderlo Chemie, Belgium.

Further purification of wet phosphoric acid by precipitation of cationic impurities, especially Fe, Al, Mg, and Ca, is possible by neutralising the acid with caustic soda. The precipitated metal phosphates are filtered under pressure from the resulting sodium phosphate solution, which contains 18 – 20 % P_2O_5. In order to decrease P_2O_5 losses in the filter cake from >10 % to <5 %, the filter cake is worked up with more caustic soda to give a trisodium phosphate solution and precipitatable metal hydroxides. Since the phosphoric acid in this neutralisation process is converted to a phosphate salt solution, its uses are limited. For instance, wet phosphoric acid is used for the production of detergent phosphates (pentasodium triphosphate) via this route in the EU [15, Ullmanns, 2001].

Economics

High additional cost.

Driving force for implementation

Quality standards for grades other than fertiliser grade.

References to literature and example plants

[50, German UBA, 2002], Chemische Fabrik Budenheim (CFB), the process is no longer in operation.

5.4.12 Use of entrainment separators

Description

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.

Achieved environmental benefits

Increased P_2O_5 efficiency and reduced phosphate emissions to water.

Cross-media effects

None believed to be likely.

Operational data

No specific information provided.

Applicability

Generally applicable where flash cooling or vacuum evaporation is applied.

A similar effect is achievable by using liquid ring pumps or scrubbing with recycling of the ring or scrubbing liquid.

Economics

No specific information provided. Might be a requirement for the recovery of fluosilicic acid.

Driving force for implementation

Prevention of emissions.

References to literature and example plants

[29, RIZA, 2000, 31, EFMA, 2000]

5.4.13 Disposal and valorisation options for phosphogypsum

Description

Today, all plants in the EU practice land disposal [154, TWG on LVIC-AAF] since disposal to the sea is no longer accepted.

Many of the important considerations in the design and construction of gypsum disposal areas are 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 by acidic and contaminated phosphogypsum leachate and run-off (process water and rainwater), stringent 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 5.10 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 successful, 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 clean pure gypsum.

	Anhydrite $CaSO_4$	**Dihydrate $CaSO_4 \cdot 2\ H_2O$**	**Hemihydrate $CaSO_4 \cdot ½\ H_2O$**
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 sulphur carrier and filler in insecticides and as a filler in the production of fertiliser	Soil conditioner carrier and filler in insecticides, and as a filler in the production of fertiliser	As a source of calcium and sulphur
Industrial uses/other	Filler/pigment in a variety of applications	Filler/pigment in a variety of applications, production of ammonium sulphate and sulphuric acid	Filler/pigment in a variety of applications

Table 5.10: Overview of phosphogypsum applications
[29, RIZA, 2000]

Achieved environmental benefits

- valorisation of the phosphogypsum would be the desirable solution.

Cross-media effects

- disposal into sea: phosphogypsum often contains a wide range of impurities, some of which are considered a potential hazard to the environment and public health.

Operational data

No information provided.

Applicability

Valorisation is generally applicable, if a market is available. Currently in Europe, only phosphogypsum produced by Prayon S.A.(Belgium) is used on a commercial scale (80 % 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 (Kemira), the application of phosphogypsum in a variety of gypsum building products (plaster, building blocks, plasterboard) has been demonstrated on a pilot scale with positive results.

[33, VITO, 2005] reports that the main obstacle when valorising the phosphogypsum is the transportation of a low price product.

Economics

Cost benefits in case of valorisation of the phosphogypsum.

Driving force for implementation

Necessity to dispose or (better) valorise the large volume by-product phosphogypsum.

References to literature and example plants

[29, RIZA, 2000, 31, EFMA, 2000, 33, VITO, 2005]

5.4.14 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 [29, RIZA, 2000]. In this case, only 4 % of the total amount of gypsum was separated as fines. Application of this technique on a commercial scale would not require larger hydrocyclones than those used in the pilot scale, but would require multiple hydrocyclones and therefore scale-up should not be a problem.

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. Hence, 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.

Achieved environmental benefits

- cleaner phosphogypsum for re-use or disposal
- potential for increasing the P_2O_5 efficiency of the production process.

Cross-media effects

- electricity consumption
- the resulting high impurity fraction needs consideration.

Operational data

No information provided.

Applicability

Generally applicable, but not demonstrated on a commercial scale.

Economics

Cost benefits if the phosphogypsum can be valorised.

Driving force for implementation

Environmental and cost benefits.

References to literature and example plants

[29, RIZA, 2000]. Kemira Agro Pernis performed pilot tests before they were closed down. The main target of these tests was to make the gypsum suitable for, e.g. construction works

5.4.15 Thermal process

Description

About the thermal process, see also [155, European Commission, 2006].

The production of thermal phosphoric acid is carried out in two stages. First, elemental phosphorus is produced from phosphate rock. Then the elemental phosphorus is oxidised with air to P_2O_5, which is subsequently hydrated to produce phosphoric acid.

Elemental phosphorus is obtained from phosphate rock. The example plant uses a mixture of sedimentary rock and igneous rock. The process starts with the grinding of the phosphate rock. The ground phosphate rock is mixed with a slurry consisting of water, clay and various waste streams containing phosphorus, to produce pellets in a granulator. The pellets are sintered in a furnace at a temperature of about 800 °C. Phosphorus is released from the sintered pellets by heating the pellets to about 1500 °C in an electric resistance furnace together with cokes (to provide a reducing environment) and gravel (slag formation). The overall reaction can be summarised as follows:

$$2\ Ca_3(PO_4)_2 + 6\ SiO_2 + 10\ C \rightarrow P_4 + 10\ CO + 6\ CaSiO_3$$

The process mainly produces gaseous phosphorus, carbon monoxide and a liquid slag. The gas phase is first passed through an electro filter to remove dust (Cottrell dust). Subsequently gaseous phosphorus is recovered completely through condensation. The remaining gas phase mainly consists of carbon monoxide. This gas is used as fuel gas on-site (e.g. in the sinter furnaces) and is sold to the nearby power plant. The leftover gas, if any, is flared. The liquid slag is tapped from the furnace in batches, and yields a phosphorus slag (the major part) and a ferrophosphorus slag (a minor amount) by-product. After further processing, the former is used as foundation material in large construction works, while the latter is used as a steel additive in the iron and steel industry. The P-recovery efficiency of the phosphorus process is about 94 %. The remaining phosphorus will mainly end up in the furnace slag (as unreacted phosphate). Minor amounts end up in ferrophosphorus (as an alloy) and the Cottrell dust.

To produce phosphoric acid from elemental phosphorus, first the phosphorus is brought into a reaction vessel together with air, after which the phosphorus oxidises to P_2O_5. The heat evolving from this reaction is used for the generation of high pressure steam. Subsequently, the P_2O_5 is contacted with diluted phosphoric acid, and reacts with the water present in the acid to form phosphoric acid. Two configurations for this process are used. In one case, the absorption of P_2O_5 by diluted phosphoric acid is carried out in the same reaction unit as where oxidation of the phosphorus takes place. In the other, preferential, case, the reaction of P_2O_5 to phosphoric acid is carried out in a separate absorption tower, allowing energy recovery as high pressure steam. The production of phosphoric acid from elemental phosphorus is represented by the following reactions:

$$P_4 + 5\ O_2 \rightarrow 2\ P_2O_5$$

$$P_2O_5 + 3\ H_2O \rightarrow 2\ H_3PO_4$$

Achieved environmental benefits

- production of purer acid.

Cross-media effects

Table 5.11 shows an example for emission levels and co-generated output and Table 5.12 typical consumption levels for the production of H_3PO_4 by the thermal process. The main sources of emissions and waste in the production of phosphorus and phosphoric acid from elemental phosphorus are:

1. 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, radio nuclides and SO_2 and NO_x. The off-gas from the ovens is cleaned in two-stage scrubber systems with closed water circuits, before being emitted to the air. To prevent accumulation, pollutants are removed from the recirculating wash-water stream through neutralisation followed by flocculation and separation of the solids. The solids obtained are returned to the process either via the slurry station or via the phosphate rock (after drying).

2. Calcination of Cottrell dust, flaring of fuel gas and drainage of liquid slag from the phosphorus furnace.

   The gas phase produced in the phosphorus furnace contains a considerable amount of dust (so-called Cottrell dust) which is removed through an electrofilter. As a result of closed loops (re-use of waste streams) in the process, the dust is enriched in heavy metals (mainly zinc) and radionuclides (such as 210-Po and 210-Pb). The dust is mixed with water and recycled to the slurry station. However, due to the high zinc content in the dust, part of it is removed to prevent excessive accumulation. The dust is calcined (emission of dust, F and P_2O_5 to the air) and stored. In the near future, storage will by replaced to a special storage facility for all kinds of radioactive waste.
   After the recovery of phosphorus from the gas, the remaining gas mainly consists of carbon monoxide. This gas is used as fuel gas on the site (e.g. in the sinter furnaces) and is sold to the nearby power plant. The leftover gas, if any, is flared, which contributes to SO_2 and NO_x emissions to the air.
   Vapours released while draining of the liquid slags from the phosphorus furnace, are removed, and washed with water in a venturi scrubber before being emitted to the air.
   Process effluents that have been in contact with phosphorus are sent to the waste water station.
   After treatment (sedimentation followed by neutralisation, flocculation and separation of the solids formed), 70 to 90 % of the water is recycled to the process. The remaining water is treated with lime for further P_2O_5 removal and is subsequently treated in an biological waste water treatment plant before being discharged to the sea. All solids are recycled to the process.

3. 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 P_2O_5 and phosphoric acid. To minimise emissions, the off-gas is cooled and washed with recirculating acid and water, and subsequently treated in a venturi scrubber (diluted acid) and a demister. The bleed of the recovery system is re-used either in the wet phosphoric acid purification plant or the slurry station. The emissions of the acid plant are small compared to the emissions of the sinter plant and the phosphorus plant.

   Due to the specific fields of application (e.g. food additive and beverages),, traces of arsenic present in the phosphoric acid have to be removed. To this end, sodium hydrogen sulphide (NaHS) is added to the acid, upon which arsenic is precipitated as arsenic sulphide (As_2S_3). After separation and further processing, the latter is obtained in concentrated form and stored as hazardous chemical waste.

Emission or generation of		Per tonne P_2O_5	
		Level	Unit
To air	Phosphate (P)	0.6	kg
	Fluorine (F)	0.1	
	Dust	0.4	
	Cadmium	1.0	g
	Lead	6.0	
	Zinc	5.9	
	Po-210	3.5	MBq
	Pb-210	0.3	
To water	Phosphate (P)	0.7	kg
	Fluorine (F)	0.7	
	Cadmium	0.2	g
	Mercury	<0.01	
	Arsenic	<0.07	
	Heavy metals	14	
	Po-210	0.05	MBq
	Pb-210	0.06	
Co-product	Fuel gas(1)	1500 – 1600	Nm^3
	Phosphorus furnace slag	3.2	tonnes
Waste	Cottrell dust	3.2	kg
	Arsenic sulphide filter cake	0.1	
(1) In 1998 about 20 % of this gas was flared			

Table 5.11: Emission levels and co-generated output for the production of thermal H_3PO_4 [29, RIZA, 2000]

Operational data

Table 5.12 gives typical consumption levels for the production of thermal H_3PO_4.

Consumption of	Per tonne P_2O_5	
	Level	Unit
Phosphate rock	3.0 – 3.4	tonnes
Clay	0.2 – 0.3	
Cokes	0.5 – 0.6	
Process water	40	m^3
Cooling	120	
Electric power	5700 – 6000	kWh
Natural gas	n.a.	
Steam	n.a.	
n.a. = not available		

Table 5.12: Typical consumption levels for the production of thermal H_3PO_4 [29, RIZA, 2000]

Applicability

At present, only about 20 % of the phosphorus produced is converted into phosphoric acid. In the past, a considerable amount of thermal phosphoric acid was used for the production of sodium phosphate salts. More and more however, thermal phosphoric acid is being replaced (on the basis of economics) by purified wet phosphoric acid. Thermal phosphoric acid is almost exclusively produced for specific applications which require a very pure acid such as metal surface treatment in the micro-electronics industry and the acidulation of beverages.

Economics

Higher production costs per tonne H_3PO_4 in comparison with wet processes.

Driving force for implementation

Product purity requirements.

References to literature and example plants

[29, RIZA, 2000], Thermphos International, Vlissingen

5.5 BAT for phosphoric acid

BAT is to apply the common BAT given in Section 1.5.

BAT for storage is to apply BAT given in [5, European Commission, 2005].

BAT for existing installations using a wet process is to achieve P_2O_5 efficiencies of 94.0 – 98.5 %, e.g. by applying one or a combination of the following techniques:

- dihydrate process or improved dihydrate process (see Section 5.4.1)
- increasing the residence time (see Section 5.4.1)
- recrystallisation process (see Sections 5.4.3, 5.4.4 and 5.4.5)
- repulping (see Section 5.4.6)
- double-stage filtration (see Section 5.4.4 and 5.4.5)
- recycling the water from the phosphogypsum pile (see Section 5.4.1)
- selection of phosphate rock (see Sections 5.4.9 and 5.4.10).

BAT for new installations is to achieve P_2O_5 efficiencies of 98.0 % or higher, e.g. by applying a recrystallisation process with double-stage filtration (see Sections 5.4.4 and 5.4.5).

BAT for the wet process is to minimise the emissions of P_2O_5 by applying one or a combination of the following techniques (see Section 5.4.12):

- entrainment separators, where vacuum flash coolers and/or vacuum evaporators are used
- liquid ring pumps with recycling of the ring liquid to the process
- scrubbing with recycling of the scrubbing liquid.

BAT is to reduce dust emissions from rock grinding, e.g. by application of fabric filters or ceramic filters and to achieve dust emission levels of 2.5 – 10 mg/Nm^3 (see Section 5.4.8).

BAT is to prevent dispersion of phosphate rock dust by using covered conveyor belts, indoor storage, and frequently cleaning/sweeping the plant grounds and the quay (see Section 5.4.8).

BAT is to reduce fluoride emissions by application of scrubbers with suitable scrubbing liquids and to achieve fluoride emission levels of 1 – 5 mg/Nm^3 expressed as HF (see Section 5.4.7).

BAT for wet processes is to market the generated phosphogypsum and fluosilicic acid, and, if there is no market, to dispose of it. For precautionary measures concerning phosphogypsum pile and recycling water from these piles (see Section 5.4.13).

BAT for wet processes is to prevent fluoride emissions to water, e.g. by application of indirect condensation system or by a scrubbing with recycling or marketing the scrubbing liquid (see Section 5.4.7).

BAT is to treat waste water by applying a combination of the following techniques (see Section 5.4.7)

- neutralisation with lime
- filtration and optionally sedimentation
- recycling of solids to the phosphogypsum pile.

6 HYDROFLUORIC ACID

6.1 General information

Production capacity in the EU is around 300000 tonnes 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 in alkylation processes in industry. 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 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.

The EU plants are located in the Czech Republic, UK, Germany, France, Italy, Spain and Greece. Table 6.1 shows the production plants in Europe. The majority of the plants were built between 1917 and 1989, but all have undergone major refurbishment during the last twelve years. The plant size varies from below 5000 to above 40000 tonnes/year. In Europe, approximately 400 people in total are employed directly in the manufacturing of HF.

Company
Arkema SA, (formerly Atofina SA), Pierre-Bénite
Lanxess, (formerly Bayer AG), Leverkusen
Derivados del Fluor SA, Ontón
Fluorchemie Dohna GmbH, Dohna
Fluorchemie Stulln GmbH, Stulln
Honeywell Specialty Chemicals Seelze GmbH
INEOS Fluor Limited, Runcorn
Chemical Works Lubon S.A., Lubon
Phosphoric Fertilizers Industry SA, Thessaloniki
Solvay Fluor GmbH, Bad Wimpfen
Solvay Fluor Italy, Porto Marghera
Spolchemie AS, Ústi nad Labem

Table 6.1: HF production plants in Europe
[6, German UBA, 2000, 22, CEFIC, 2000, 24, Dreveton, 2000]

6.2 Applied processes and techniques

6.2.1 Overview

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:

$$CaF_2 + H_2SO_4 \rightarrow 2HF + CaSO_4 \qquad \Delta H_R = 59 \text{ kJ/mol} \qquad (1)$$

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:

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

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

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

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

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

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

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

H_2S formed by reaction (7) is 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.

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

As an alternative, HF can be produced starting from H_2SiF_6 (see Section 6.4.10).

6.2.2 Fluorspar

[22, CEFIC, 2000]

The raw material for the production of HF 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 physical flotation at the mining site. The flotation chemicals in current use are mainly saturated and unsaturated vegetable fatty acids. They remain in the fluorspar, which should ideally contain at least 97 % CaF_2 for use as "acid spar".

Table 6.2 shows the components in acid spar. Acid spar should not contain any fraction above 0.2 mm in diameter. It is transported to the user as a bulk material with a water content of approximately 10 % to minimise dust generation.

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

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 6.2: Components in acid spar
[22, CEFIC, 2000]

6.2.3 Reaction stage and options for increasing the capacity

Figure 6.1 gives an overview of the production of HF. 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 approximately 450 °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 [22, CEFIC, 2000].

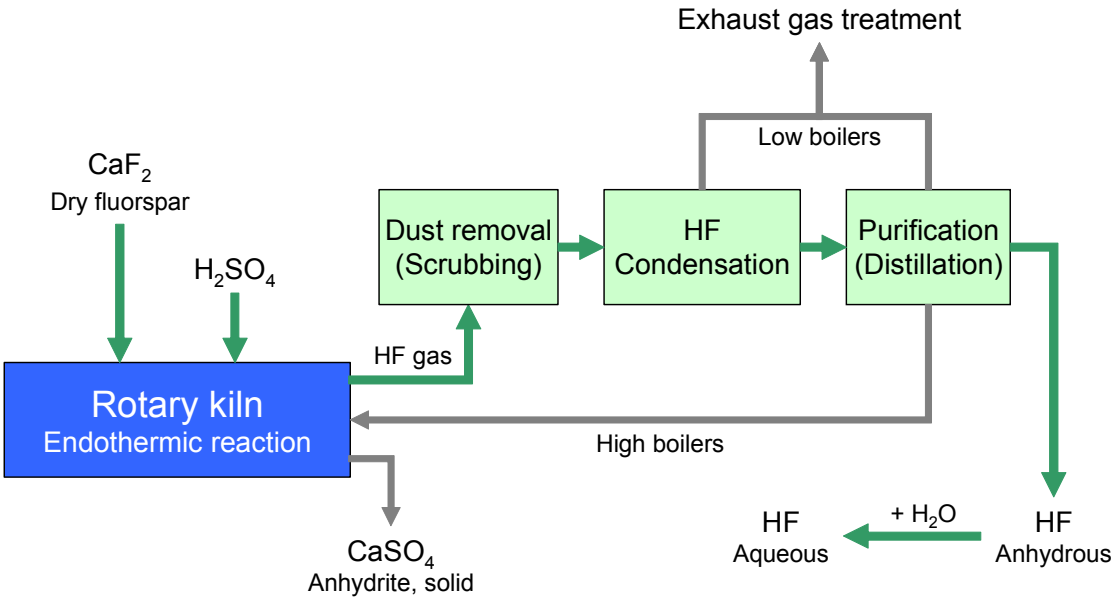

Figure 6.1: Overview of the production of HF
The figure is based on [22, CEFIC, 2000] and [20, Eurofluor, 2005].

The heated kiln surface area needed to produce 1 tonne HF/d is approximately 5 to 10 m^2 with this arrangement. Dried fluorspar is not easily mixed with the sulphuric acid due to the flotation chemicals. Table 6.3 shows the options to achieve a higher HF production capacity for a given kiln and Figure 6.2 illustrates the different option including energy supply and heat recovery. 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 flue-gas as a heat source. The production of HF solution causes higher fuel consumption, because of the higher level of H_2O present in the kiln.

Preheating H_2SO_4	
Pre-reactor (kneader)	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 %
Calcination	Calcination of the dried fluorspar, by heating it directly with flue-gases containing oxygen 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 tonne HF/day is only 2.5 – 3 m^2

Table 6.3: Options to achieve a higher production capacity for a given kiln

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 approximately 150 °C and approximately 220 °C in the second case where the temperature of the anhydrite is in the range of 200 – 220 °C.

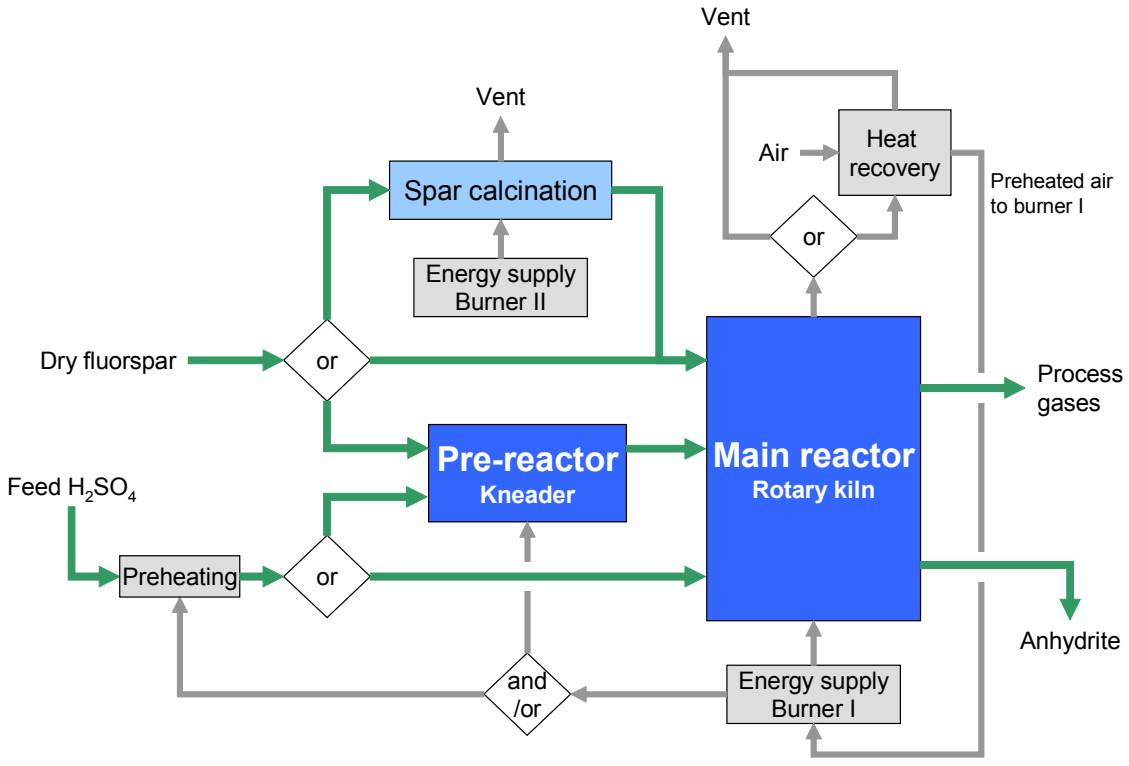

Figure 6.2: Increasing the production capacity for a given kiln and energy supply/recovery [22, CEFIC, 2000]

6.2.4 Process gas treatment

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

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

There are different possibilities available to achieve these objectives as shown in Figure 6.3.

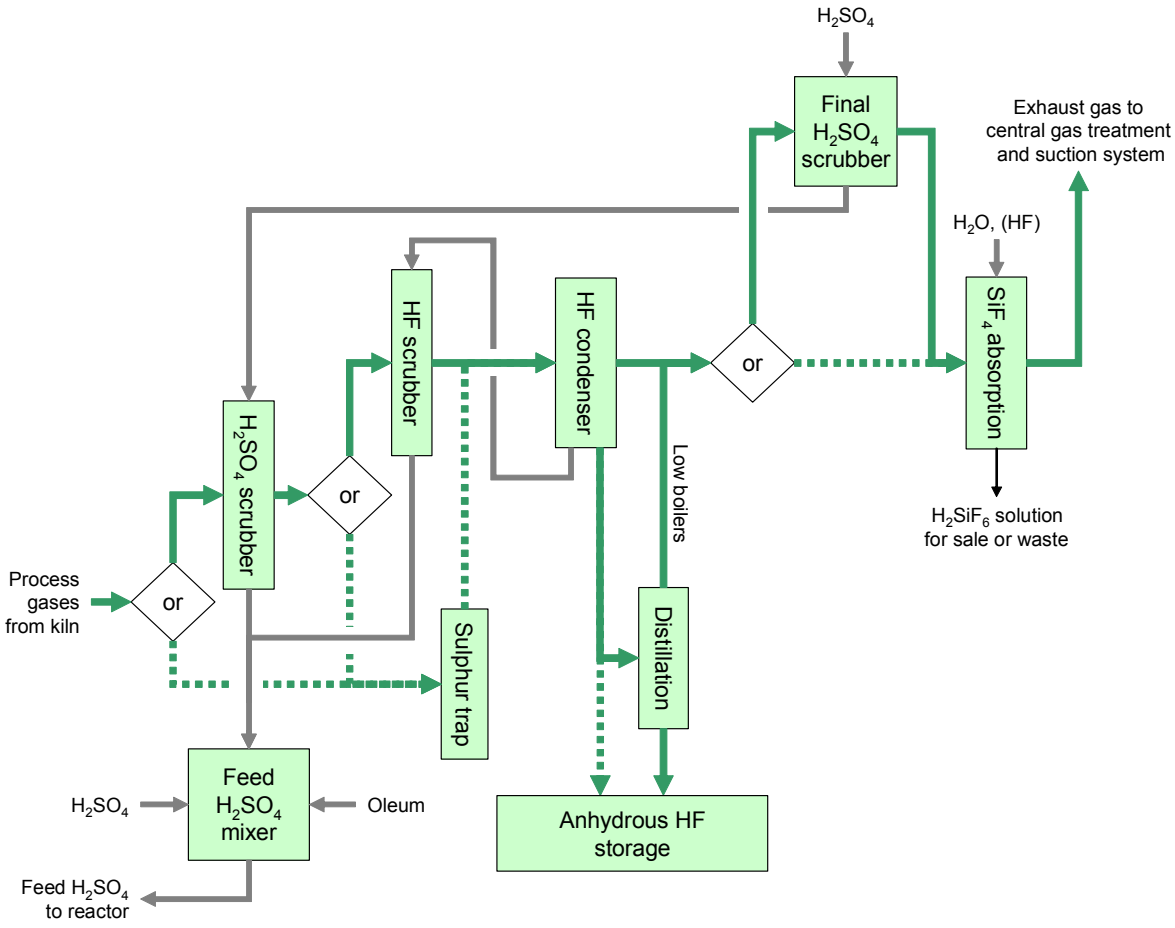

Figure 6.3: Process gas treatment options
[22, CEFIC, 2000]

In most HF plants, process gases are first scrubbed in a pre-purification column with concentrated H_2SO_4 to remove dust and water and to cool the gas below 100 ºC. Secondary scrubbing and quenching is carried out with liquid HF to remove any remaining dust, H_2SO_4 and water and to cool the gas to approximately 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 through a cooled sulphur trap instead. The HF scrubber and the sulphur trap have to be 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 H_2SO_4 scrubber, where most of the HF is recovered. Thereafter residual gases pass through the SiF_4 absorber, where H_2SiF_6 is produced as an aqueous solution. In plants without a final H_2SO_4 scrubber, H_2SiF_6 acid with a relatively high HF content is produced.

Cold H_2SO_4 from the final H_2SO_4 scrubber, which contains dissolved HF, passes to the first H_2SO_4 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 H_2SO_4 and oleum to yield the feed H_2SO_4 for the reaction process.

Depending on the quality of the HF after the low boilers distillation and on the end-use, a second distillation may be required to remove any high boilers, mainly H_2O and H_2SO_4. As all the HF has to be evaporated, this distillation requires a significant amount of energy, estimated at 350 kg steam per tonne of HF (0.6 GJ/tonne HF). The corresponding amount of refrigeration energy required to condense the HF also needs to be taken into account. The liquid HF leaving the head condenser is pure HF. Part of the HF is mixed with water to produce HF 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.

6.2.5 Tail gas treatment

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. In order to reduce SO_4^{2-} and F^- concentrations, precipitation with calcium compounds and solid/liquid separation techniques are applied. This results in a solid waste ($CaSO_4$, CaF_2) which may be combined with the main flow of anhydrite co-product. 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.

6.2.6 Co-product anhydrite

The process generates anhydrite, $CaSO_4$. This can, after further treatment of varying complexity and cross-media effects (i.e. after neutralisation), be further used as a market product in cement industries or as binders for floor screed. This reduces the amount of waste for disposal [6, German UBA, 2000]. If not marketable, anhydrite is disposed of.

6.2.7 Product storage and handling

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

6.3 Current emission and consumption levels

6.3.1 Consumption levels

Table 6.4 shows the reported consumption levels for the production of HF.

Consumption of		per tonne HF	Remark	Reference
Raw materials	Fluorspar (CaF_2)	2100 – 2200 kg	Of CaF_2	[22, CEFIC, 2000]
	H_2SO_4	2600 – 2700 kg	Of equivalent 100 % H_2SO_4	
Auxiliary chemicals	NaOH		For alkaline scrubbing	
	$Ca(OH)_2$, CaO		For neutralisation	
Utilities	Steam	150 – 800 kg	For distillation, kiln heating, cooling/condensation of HF. Concerning the fuel consumption, a data set gathered in 1999 from 11 companies shows: - 7 plants with levels between 4.5 and 6.5 GJ/tonne HF - 2 plants with levels <4.5 GJ/tonne HF - 2 plants with levels >7 GJ/tonne HF	
	Process water	0.5 – 25 m^3		
	Cooling water	30 – 100 m^3		
	Electric power	150 – 300 kWh		
	Refrigeration	2 – 3 GJ		
	Fuel	4 – 10 GJ		

Table 6.4: Reported consumption levels for the production of HF

6.3.2 Emission levels to air

Table 6.5 shows the reported dust emission levels for the production of HF. Table 6.6 shows the reported SO_2 and HF emission levels.

Emission of		kg/tonne HF	Remark	Reference
Dust	CaF_2	0.05 – 0.1	Average emissions from the flue-gases of directly heated driers and/or from pneumatic conveying gases, abated using cyclones and filters. The maximum average values are 0.50 kg/tonne HF, depending on the extent of pneumatic conveying and the number of storage silos (yearly average concentrations of 24 – 45 mg/Nm^3)	[22, CEFIC, 2000]
		0.01 – 0.05	Plant without drying section, i.e. the fluorspar has been pre-dried. The maximum value is 0.15 kg/tonne HF (yearly average concentrations of 10 – 20 mg/Nm^3)	
			An increase in dust emissions (typically 0.005 kg/t HF) and emissions of organic carbon compounds (approximately 0.1 kg/tonne HF) occurs in spar calcination, where an additional vent is needed	
		<0.07	Filtration of CaF_2 dust	[6, German UBA, 2000]
	$CaSO_4$	0.05 – 0.1	From an anhydrite neutralisation process and additional treatments, which is not avoided when landfilling or discharging to rivers or seawater. The abatement includes cyclones, filters and/or wet scrubbers. Maximum: 0.25 kg/tonne HF, depending on different types of treatment	[22, CEFIC, 2000]
	CaO and/or $Ca(OH)_2$	<0.001	Filtration equipment is used to reduce dust emissions which are generated during the handling of the CaO and/or $Ca(OH)_2$ needed in anhydrite neutralisation	
	CaF_2		25.6 mg/Nm^3 (2000), 13 mg/Nm^3 (2004), average values. 3.4 – 4.2 mg/Nm^3 were achieved (official sampling in 2004)	Solvay, Bad Wimpfen
			35 mg/Nm^3 (2001), 15 mg/Nm^3 (2004), average values	Fluorchemie, Stulln
			15.9 mg/Nm^3 (2000), 18.8 mg/Nm^3 (2003), average values	Fluorchemie, Dohna

Table 6.5: Reported dust emission levels for the production of HF

Emission of	kg/tonne HF	Remark	Reference
SO_2	0.010	Yearly average, alkaline scrubbing, concentration <20 mg/m^3, other parameters from this plant: (per tonne HF) NO: 0.325 kg, NO_2: 0.056 kg, CO: 0.054 kg	[6, German UBA, 2000] [28, Comments on D2, 2004]
	0.007	Yearly averages, alkaline scrubbing, concentration <20 mg/m^3 Newer data: <0.020 kg SO_2/tonne HF at concentrations <10 mg/m^3	
	0.017		
	0.3 – 0.5	Water scrubbing, maximum: 1 kg/tonne HF	[22, CEFIC, 2000]
	0.001 – 0.01	Alkaline scrubbing, maximum: 0.065 kg/tonne HF	
Fluorides as HF	0.002	Yearly averages, alkaline scrubbing, concentration <5 mg/m^3 Newer data: <0.002 kg HF/tonne HF at concentrations of <0.6 mg/m^3	[6, German UBA, 2000] [28, Comments on D2, 2004]
	0.005		
	0.002		
	0.005 – 0.015	Maximum: 0.1 kg/tonne HF. The release levels depend on absorption and anhydrite treatment effectiveness and complexity	[22, CEFIC, 2000]

Table 6.6: Reported emissions of SO_2 and fluorides

6.3.3 Liquid effluents and solid wastes

Table 6.7 shows the reported emission levels in liquid effluents from the production of HF. Table 6.8 shows the reported levels of solid waste.

Parameter	kg/tonne HF	Remark	Reference
SO_4^{2-}	0.7 – 20	The quantity of tail gases needing treatment depends on the composition of the fluorspar.	[22, CEFIC, 2000]
Fluoride	0.07 – 1	A water and/or caustic absorption treatment of tail gases produces a neutralised aqueous effluent.	
SS	0.1 – 1	Neutralisation with lime, addition of coagulation agents, sedimentation, filtration [6, German UBA, 2000]	

Table 6.7: Reported emission levels in liquid effluents from the production of HF

Parameter	kg/tonne HF	Remark	Reference
$CaSO_4$	about 3700	If not marketable as co-product disposal. The $CaSO_4$ contains unreacted H_2SO_4	[22, CEFIC, 2000]
	5 – 50	Solids from precipitation of SO_4^{2-} and F^- from scrubber effluents. This amount may be combined with the main flow of anhydrite co-product	
CaF_2	6 – 70		

Table 6.8: Reported emission levels for solid waste from the production of HF

6.4 Techniques to consider in the determination of BAT

6.4.1 Heat transfer design

Description

One of the main heat transfer problems in HF manufacturing comes from the limitation for supplying enough energy for the main reaction. 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 temperature limitations resulting from the corrosion and mechanical resistance of the equipment.

Table 6.9 shows four options to improve the energy transfer. See also Figure 6.2.

	Process	Description
0	**Basic process**	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 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.
1	**Double jackets and optimised temperature profile control**	The first improvement of this basic process involves the installation of several double jackets around the rotary kiln and feeding the heating gases in at decreasing temperatures 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.
2	**Preheating the H_2SO_4**	The second improvement is achieved by the preheating of H_2SO_4 before it is fed into the kiln. Preheating the sulphuric acid feed is generally easy, but special construction materials are needed if it contains some HF.
3	**Preheating the fluorspar**	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 gases containing oxygen to approximately 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.
4	**Pre-reactor**	Another improvement involves feeding the raw materials into a pre-reactor before feeding them to the kiln. This rotary equipment, which is designed to mix and heat the reactants to give a conversion rate of CaF_2 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 pre-reactor has two important beneficial consequences: it lowers the kiln workload and it suppresses the pasty and sticky state in the kiln almost completely, which gives better heat transfer and avoids many scaling problems. Using a pre-reactor leads to lower heating gas temperatures, and consequently to lower corrosion risks in the kiln itself, and to a more stable reaction.

Table 6.9: Options for improving the energy transfer to the main reaction

Achieved environmental benefits

Higher efficiency.

Cross-media effects

The following numbering refers to the numbering in Table 6.9.

3) the downside of this process is the emission to air of about 2 – 5 % of the flotation chemicals as organic carbon in the form of cracked products.

Operational data

No information provided.

Applicability

The following list refers to the numbering in Table 6.9.

1) applicable for new and existing plants
2) generally applicable
3) generally applicable
4) generally applicable.

Economics

The following list refers to the numbering in Table 6.9.

1) very high investment costs for existing plants
2) relatively low investment costs
3) high investment costs
4) significant investment, high maintenance costs.

Driving force for implementation

Process optimisation and increasing the plant capacity for a given kiln. Lower corrosion risks and more stable reaction.

References to literature and example plants

[22, CEFIC, 2000], Lanxess (fluorspar preheating), Arkema (kneading for one kiln), Derivados del Fluor SA (H_2SO_4 preheating).

6.4.2 Energy recovery from kiln heating

Description

The kiln shell exit gas temperature goes up to about 400 °C, depending on the HF production rate (expressed as tonne HF/m^2 of kiln shell surface area). 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 preheat reactant feeds, the combustion air, or by other fluids in the production unit.

Achieved environmental benefits

Energy savings. The recovered energy for the whole installation is estimated to be around 20 % of the total energy used.

Cross-media effects

None believed likely.

Operational data

No information provided.

Applicability

Generally applicable for new installations.

The installation of a recovery system for an existing plant might encounter technical limitations in specific cases. When it is possible to install a recovery system, the associated cost and modifications are usually disproportionate compared with the actual energy savings.

Economics

No specific information provided.

Driving force for implementation

Energy and cost savings.

References to literature and example plants

[22, CEFIC, 2000]

6.4.3 Valorisation of anhydrite

Description

A substantial amount of calcium sulphate is co-produced with hydrogen fluoride in the anhydrite form ($CaSO_4$ without the crystallisation of water). The preferred 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, landfilling is the most common disposal option and three plants in Europe apply 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

None believed likely.

Operational data

No information provided.

Applicability

Generally applicable. Still, calcium sulphate co-products have to compete in open markets with natural and synthetic anhydrite and cement, hence, recovery is of course eased in countries in which natural anhydrite or gypsum availability is limited. Anhydrite is sometimes not of an equivalent quality to other products. 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, increasing the cost. 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.

Economics

Cost benefits.

Driving force for implementation

Cost benefits.

References to literature and example plants

[22, CEFIC, 2000]

6.4.4 Valorisation of fluosilicic acid

Description

The absorption of SiF_4 in hydrofluoric acid solutions yields a 25 to 35 % fluosilicic 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 kryolite (sodium hexafluoroaluminate), potassium hexafluoroaluminate, and aluminum fluoride, for aluminum production
- depending on the intended scale, production of HF.

Achieved environmental benefits

Disposal of the by-product into the environment is avoided.

Cross-media effects

None believed likely.

Operational data

No information provided.

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 is neutralised with lime to CaF_2 and SiO_2, before landfilling.

For production of HF from fluosilicic acid, see Section 6.4.10.

Economics

Cost benefits.

Driving force for implementation

Cost benefits.

References to literature and example plants

[22, CEFIC, 2000, 24, Dreveton, 2000, 25, Davy, 2005]

6.4.5 Spar calcination

Description

25 % of the total fuel is used in a separate burner for the fluorspar feed calcination process. The spar is heated to approximately 400 °C by countercurrent contact with flue-gases at a temperature of approximately 900 ºC. The gases exit the calcinator at approximately 110 °C. Relatively small kiln dimensions are needed because of the high energy input into the feed to the rotary kiln.

Achieved environmental benefits

No SO_2 is produced by the reaction of the flotation chemicals with sulphuric acid.

Cross-media effects

Emission of approximately 2 to 5 % of the flotation chemicals as organic carbon in the form of cracked products.

Operational data

No specific information provided.

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 concentrations, which may in turn cause heavy kiln scaling.

Economics

The investment cost for spar calcination is approximately 50 to 100 % higher than for the pre-reactor. This may be partially compensated for by lower fuel consumption and lower maintenance costs in comparison to the pre-reactor.

Driving force for implementation

Increasing plant capacity for an existing kiln.

References to literature and example plants

[22, CEFIC, 2000]

6.4.6 Scrubbing of tail gases: fluorides

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 a vent gas containing HF can be carried out by a once-through water countercurrent contact absorber. 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 or entrainment of liquid acidic droplets with the gas flow. The latter problems normally do not occur if an alkaline solution is used for absorption but the recovery of the absorbed gas is not 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

For achievable emission levels for the different scrubber setups, see Table 6.10.
Alkaline scrubbing also reduces the emission of SO_2 drastically [6, German UBA, 2000].

Scrubber setup	Fluoride emission level as HF in mg/Nm^3	Cost estimate
Single-stage, once through absorption with copious amounts of water make up or multistep water sprayers	5 – 10	The equipment is very simple (neither recirculation nor temperature control is needed). Investment costs are also limited
Water, single-stage, closed loop with HF solution production	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	The resulting acid is purged and may be re-used for other purposes, with concentrations of up to 20 %. It may be necessary to control the temperature by cooling the recirculated solution
Double-stage water absorption	Low emissions values	
Liquid phase alkaline absorption (single-stage)	Typically 1 – 5	
Combination of water and alkaline absorption	Typically 1 – 5	Investment is high (more than twice as expensive as in water absorption due to the necessary control instrumentation)
Solid alkaline absorption	<5 mg	For small effluent streams, an economic possibility

Table 6.10: Achievable fluoride emission levels for different scrubber setups [22, CEFIC, 2000]

Cross-media effects

Energy, water and, in the case of alkaline scrubbing, chemicals consumption.

Operational data

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).

Applicability

Generally applicable. Scrubbing with water or alkaline solution is a well established and proven technique.

Liquid phase alkaline absorption (single-stage) is sufficient for limited or intermittent 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 alkaline absorption is preferred.

Solid alkaline absorption in a fixed bed is an economic possibility for small effluent streams of moist gases containing HF.

Economics

See also Table 6.10.

The investment for a 100 m^3/hour gas flow in a single-stage, once-through absorption is in the range of EUR 50000 – 80000 (data valid for new plants).

For a double-stage gas treatment, the investment cost is in the range of EUR 150000 – 200000 (new plants), or EUR 2000 – 4000 per 1000 m^3/hour.

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 solution 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.

References to literature and example plants

[22, CEFIC, 2000], [6, German UBA, 2000] three example plants listed in this reference.

6.4.7 Scrubbing of tail gases: fluorides along with SO_2 and CO_2

Description

SO_2 absorption in water is limited, and at low pH 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 (with oxygen, hydrogen peroxide). For absorption of HF, see Section 6.4.6.

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. Table 6.11 shows the achievable emission levels.

SO_2 levels <20 mg/Nm^3 are achievable with the combination of water and alkaline scrubbing [6, German UBA, 2000].

SO_2 levels <40 mg/Nm^3 are achievable [11, European Commission, 2003], depending on variant and scrubber liquid, 1- or 2-stage.

[28, Comments on D2, 2004] reports the levels given in Table 6.12 for a German reference plant.

Scrubber setup	SO_2 emission level	Cost estimate
Single-stage, once through absorption with copious amounts of water make up or multistep water sprayers	SO_2 removal efficiency of 20 – nearly 100 %, depending on the amount and alkalinity of the water used	The equipment is very simple (neither recirculation nor temperature control is needed). Investment costs are also limited
Water, single-stage, closed loop with HF solution production	SO_2 is virtually not absorbed (low pH value)	The resulting acid is purged and may be re-used for other purposes, with concentrations of up to 20 %. It may be necessary to control the temperature by cooling the recirculated solution
Double-stage water absorption		
Liquid phase alkaline absorption (single-stage)	SO_2 concentration is typically in the range of 5 –100 mg/m^3	
Combination of water and alkaline absorption	1 – 100 mg/m^3, depending on pH and the design	Investment is high (more than twice as expensive as in water absorption due to the necessary control instrumentation)
Solid alkaline absorption		

Table 6.11: Achievable SO_2 emission levels for different scrubber setups [22, CEFIC, 2000]

	kg/tonne HF	mg/m^3
SO_2	0.02	<10
HF	0.002	<0.6

Table 6.12: Achieved HF and SO_2 emission levels [28, Comments on D2, 2004]

Cross-media effects

Additional water and chemicals consumption.

Operational data

Alkaline absorption: pH 7 – 9.

Applicability

Generally applicable. Scrubbing with water or alkaline solution is a well established and proven technique.

Economics

See Section 6.4.6.

Driving force for implementation

Emission reduction.

References to literature and example plants

[22, CEFIC, 2000], [6, German UBA, 2000] and three example plants listed in this reference.

6.4.8 Abatement of dust emissions from drying, transfer and storage

Description

In the production of HF, the main sources for dust emissions are:

- CaF_2 dust emission, from fluorspar drying (directly heated dryers), transfer (pneumatic conveying) and storage
- $CaSO_4$ dust emission, from anhydrite treatment
- CaO and/or $Ca(OH)_2$ dust emission from transfer and storage.

The abatement techniques include cyclones, filters and wet scrubbers.

Achieved environmental benefits

Reduction of dust emissions.

The BAT associated emission levels given in [11, European Commission, 2003] are presented in Table 6.13.

Technique	Emission level	Removal rate
	mg/Nm^3	%
Fabric filter	2 – 10	99 – 99.9
Dry or wet cyclone		20 – 99
Wet scrubber		50 – 99

Table 6.13: Selected abatement techniques and corresponding achievable dust emission levels [11, European Commission, 2003]

Cross-media effects

Wet scrubbing creates an additional waste water stream.

Operational data

No specific information provided, see also [11, European Commission, 2003].

Applicability

Generally applicable.

Economics

No information provided.

Driving force for implementation

Reduction of dust emissions.

References to literature and example plants

[6, German UBA, 2000, 11, European Commission, 2003, 22, CEFIC, 2000].

6.4.9 Waste water treatment

Description

Waste water is generated in the different stages of waste gas treatment (wet scrubbing). The waste water contains inorganic components and are treated usually by

- neutralisation with lime
- addition of coagulation agents
- sedimentation
- filtration.

Achieved environmental benefits

Reduction of emissions to water.

Cross-media effects

Consumption of auxiliary chemicals.

Operational data

No specific information provided.

Applicability

Generally applicable.

Economics

No information provided.

Driving force for implementation

Reduction of emissions to water.

References to literature and example plants

[6, German UBA, 2000, 28, Comments on D2, 2004].

6.4.10 Fluosilicic acid process

Description

Hydrogen fluoride is produced by the decomposition of an aqueous solution of H_2SiF_6 in the presence of strong sulphuric acid in a reactor. Products of decomposition are SiF_4 and HF. The HF leaves the reactor in the sulphuric acid solution and the HF is evaporated and purified to obtain the desired product quality. Next, the SiF_4 gas leaving the reactor is absorbed in the H_2SiF_6 feed solution to generate additional H_2SiF_6 and silica. For an overview, see Figure 6.4.

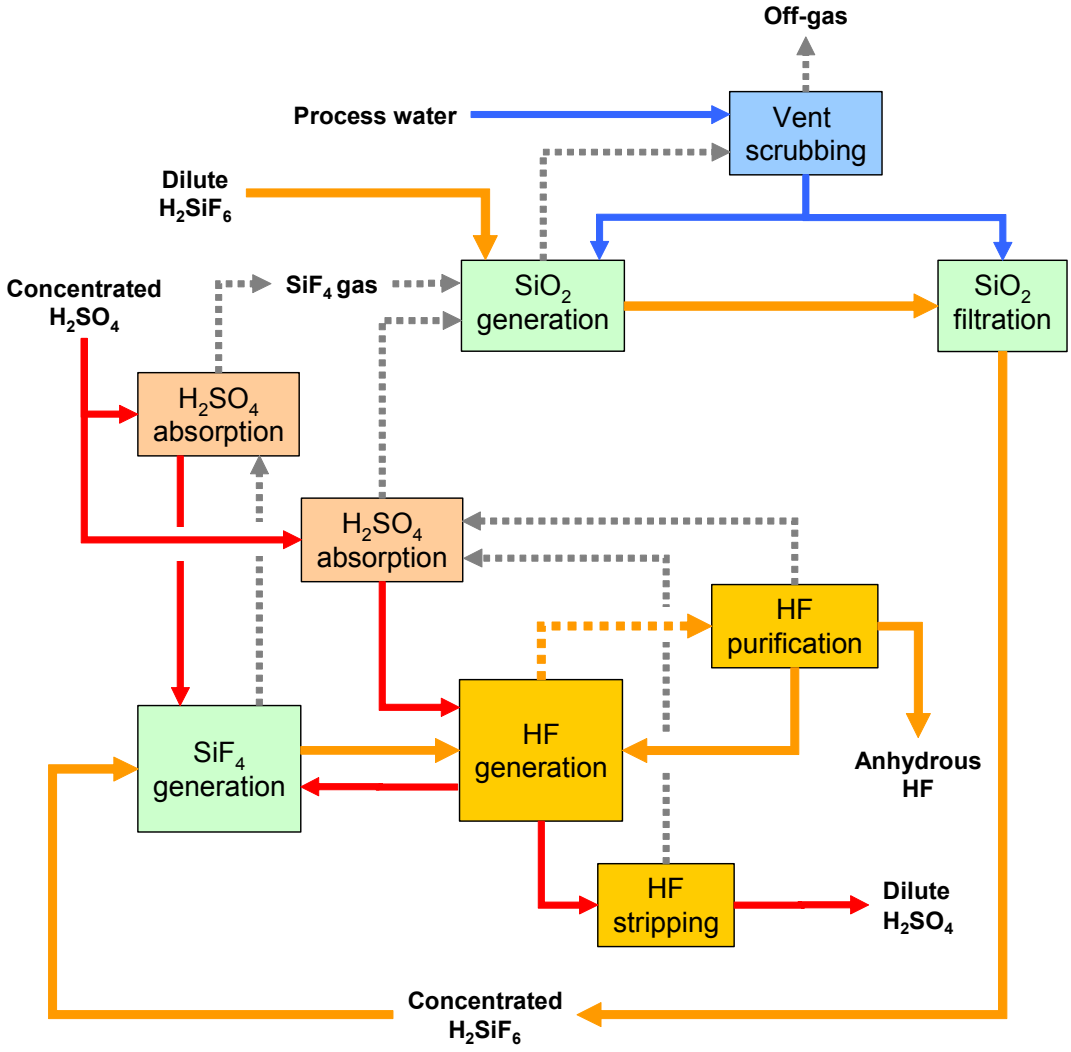

Figure 6.4: Overview of the fluosilicic acid process
[25, Davy, 2005]

Achieved environmental benefits

- recycling of the large scale by-product H_2SiF_6 instead of natural resource consumption
- if carried out on an integrated site with the production of phosphoric acid, the dilute H_2SO_4 can be recycled.

Cross-media effects

- 5 – 6 times higher direct energy consumption in comparison to fluorspar process.

Operational data

Input specifications:

• fluosilicic acid, F as H_2SiF_6	18 – 25 % wt
• sulphuric acid	96 – 98 %.

Output specifications:

• H_2SiF_6	99.98 %
• sulphuric acid	70 – 75 %
• silica	1.35 – 1.8 tonnes/tonne HF (recycled to the phosphoric acid plant).

Consumption per tonne anhydrous HF:

• H_2SiF_6	1.5 tonnes
• sulphuric acid	28 – 30 tonnes (recycled to phosphoric acid plant)
• steam HP	5.5 tonnes
• steam LP	0.43 tonnes
• process water	4.5 tonnes
• electric power	220 kWh.

Applicability

Applicable only on integrated production sites in combination with the production of phosphoric acid.

Economics

No specific information provided.

Driving force for implementation

Cost benefits.

References to literature and example plants

[24, Dreveton, 2000, 25, Davy, 2005], Chemical Works Lubon S.A., Oswal (in planning)

6.5 BAT for hydrofluoric acid

BAT is to apply the common BAT given in Section 1.5.

BAT for storage is to apply BAT given in [5, European Commission, 2005].

BAT for the fluorspar process is to apply a combination of the following techniques and to achieve fuel consumption levels within the ranges given in Table 6.14:

- preheating the feed H_2SO_4 (see Figure 6.2 and Section 6.4.1)
- optimised kiln design and optimised temperature profile control for the rotary kiln (see Section 6.4.1)
- using a pre-reactor system (see Figure 6.2 and Section 6.4.1)
- energy recovery from kiln heating (see Section 6.4.2)
- spar calcination (see Figure 6.2 and Sections 6.4.1and 6.4.5).

	GJ/tonne HF	Remark
Fuel for kiln heating	4 – 6.8	Existing installations
	4 – 5	New installations, production of anhydrous HF
	4.5 – 6	New installations, production of anhydrous HF and HF solutions

Table 6.14: Achievable consumption levels associated with BAT for the production of HF

BAT for the treatment of tail gases from the fluorspar process is to apply e.g. water scrubbing and/or alkaline scrubbing and to achieve the emission levels given in Table 6.15 (see Sections 6.4.6 and 6.4.7).

	kg/tonne HF	mg/Nm^3	Remark
SO_2	0.001 – 0.01		Yearly averages
Fluorides as HF		0.6 – 5	

Table 6.15: Achievable emission levels associated with BAT for the production of HF

BAT is to reduce dust emissions from fluorspar drying, transfer and storage and to achieve dust emission levels of 3 – 19 mg/Nm^3 (see Section 6.4.8).

Split view: Part of industry claims that the dust emission levels are not achievable, because changing the bags in the applied fabric filters more than once a year would not be economically viable.

BAT is to treat waste water from wet scrubbing by applying a combination of the following techniques (see Section 6.4.9):

- neutralisation with lime
- addition of coagulation agents
- filtration and optionally sedimentation.

BAT for the fluorspar process is to market the generated anhydrite and fluosilicic acid, and, if there is no market, to dispose of it, e.g. by landfilling.

7 NPK AND CN

7.1 General information

[154, TWG on LVIC-AAF, 2006]

When defining compound fertilisers, the large number of N/P/K – ratios and the numerous processes applied in their production must be taken into account. Product types are PK, NP (e.g. DAP), NK and NPK. These products might contain:

- nitrogen, expressed as % of N, in ureic, ammoniacal and/or nitrate forms
- phosphorus, usually expressed as % of P_2O_5, in forms soluble in water and/or neutral ammonia citrate and/or mineral acids
- potassium, usually expressed as % of K_2O, in forms soluble in water
- secondary nutrients, as calcium (CaO), magnesium (MgO), sodium (Na_2O) and/or sulphur (SO_3)
- microelements (zinc, copper, boron, etc.)
- other elements.

For example, NPK(Mg-S) with boron 20-6-12(3-20) 0.1B indicates that this particular grade contains 20 % nitrogen (N), 6 % phosphorous (P_2O_5), 12 % potassium (K_2O), 3 % magnesium (MgO), 20 % sulphur (SO_3) and 0.1 % boron (B). The typical content of nutrients (N + P_2O_5 + K_2O) will normally be in the range of 30 – 60 %. Table 7.1 shows consumption levels for the most frequently used compound fertilisers.

The demand for NPK fertilisers in various compositions results basically in two plant types: production by the mixed acid route and production by the nitrophosphate route. Although the nitrophosphate route requires higher investment and integration with other fertiliser production, it offers the option to increase the P component in the product without using phosphoric acid. Five plants operate this process in Europe (BASF, Antwerp, AMI, Linz, Lovochemie, Lovosice, YARA, Porsgrunn, YARA, Glomfjord).

The plant size varies from some hundred to up to more than 3000 tonnes per day. A plant of typical size produces about 50 tonnes per hour (1200 tonnes per day or 350000 tonnes per year).

	Expressed as 1000 tonnes nutrient		
	N	**P_2O_5**	**K_2O**
NPK	2171	1739	2253
NP	461	807	0
PK	0	498	525

Table 7.1: Consumption of the most frequently used compound fertiliser types in Western Europe [9, Austrian UBA, 2002]

Country	Company	Place	Approx. ktonnes of product
Austria	AMI	Linz	400
	Donauchemie	Pischelsdorf	150
Belgium	BASF	Antwerp	1200
	Rosier	Moustier	300
Czech Rep.	Lovochemie	Lovosice	160
Finland	Kemira GrowHow	Siilinjärvi	500
		Uusikaupunki	525
			425
France	Roullier Group	CFPR St Malo	250
		CFPR Tonnay-Charente	200
	Grande Paroisse	Grand-Quevilly/Rouen	400
			200
	CEDEST	Mont Notre Dame	150
	Yara France	Montoir	500
	Pec-Rhin	Ottmarsheim	200
	S.Engrais Chim.Orga.	Seco Ribecourt	300
	Roullier Group	Sète	200
Germany	Compo	Krefeld	250
Greece	PFI	Kavala	270
Hungary	Kemira GrowHow Kft	Veszprem	200
Italy	Yara Italy	Ravenna	480
	Roullier Group	Ripalta	200
Lithuania	Kemira GrowHow/Lifosa	Kedainiai	240
	Eurochem/Lifosa	Kedainiai	800
	Arvi & CO JSC	Marijampole	160
Netherlands	Amfert	Amsterdam	200
	DSM Agro	IJmuiden	230
	Zuid Chemie	Sas van Gent	260
			200
Poland	Fabryka Nawozow Fosforow	Gdansk	150
	Zaklady Police	Police	580
			550
Portugal	Adubos	Setúbal/Lisbon	250
			200
Slovakia	Duslo	Sala Nad Vahom	290
Spain	Fertiberia	Avilés	200
		Huelva	200
	Roullier Group	Lodosa	270
	Sader	Luchana	150
	Mirat SA	Salamanca	150
	Agrimartin	Teruel	200
Sweden	Yara Sweden	Koeping	330
UK	Kemira Grow How	Ince	630

Table 7.2: Overview of major NPK plants in the EU-25 with a capacity bigger than 150000 tonnes per year as of February 2006

7.2 Applied processes and techniques

7.2.1 Overview

Figure 7.1 gives an overview of the production of NPK fertilisers. Compound fertilisers can be produced in four, basically different, ways:

- production by the mixed acid route, without phosphate rock digestion
- production by the mixed acid route, with phosphate rock digestion
- production by the nitrophosphate route (ODDA process)
- mechanical blending or compactation of single or multi-nutrient components (not included in the figure).

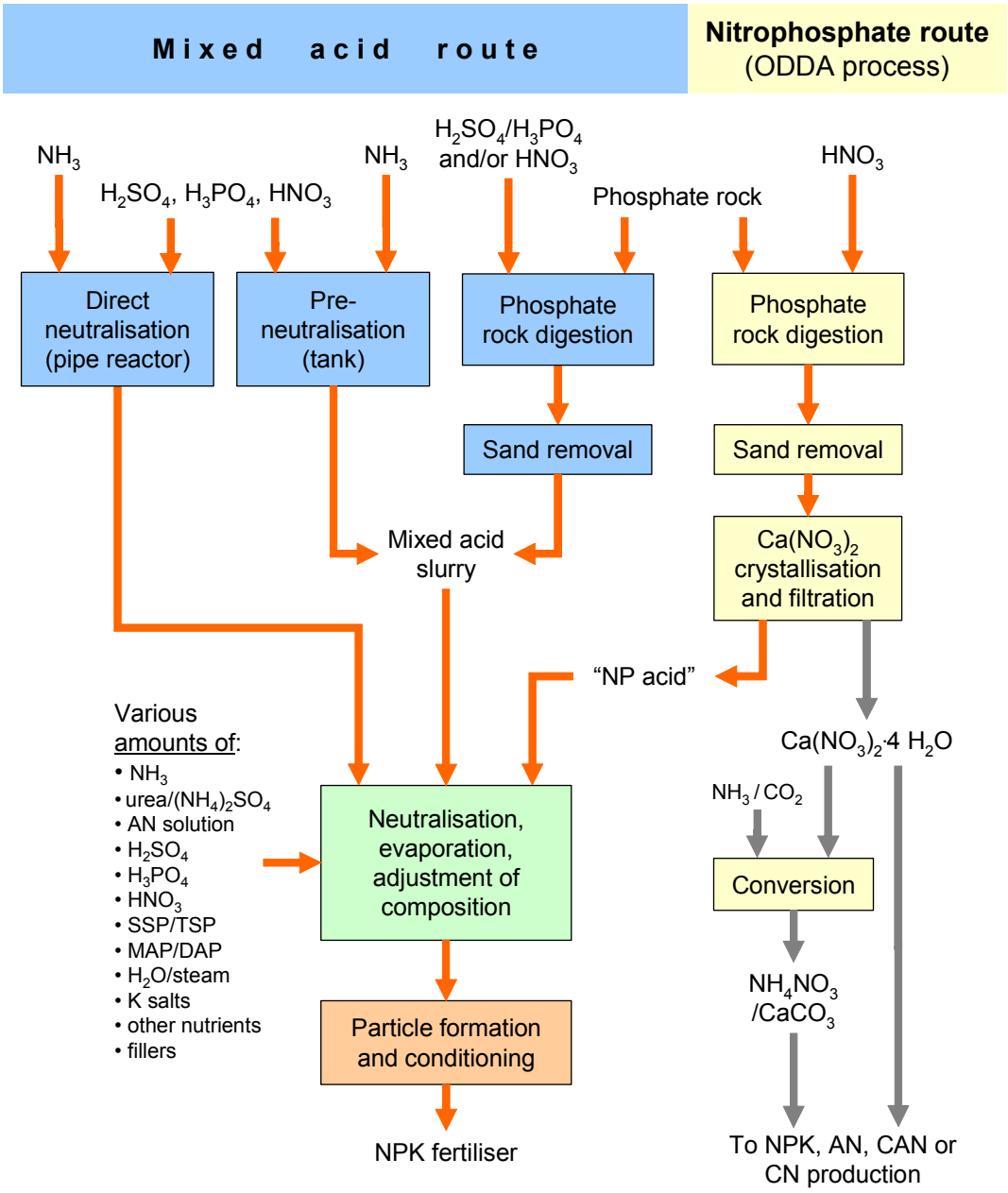

Figure 7.1: Overview of the production of NPK fertilisers from phosphate rock or SSP/TSP [154, TWG on LVIC-AAF, 2006]

7.2.2 Phosphate rock digestion

Phosphate rock digestion is carried out with nitric acid (nitrophosphate route) or with a combination of nitric, sulphuric and/or phosphoric acids (mixed acid route).

For digestion of phosphate rock, see

- production of phosphoric acid, Section 5.2.2 “Wet process”
- Section 7.2.2.1 “Nitrophosphate route”
- production of SSP/TSP, Section 10.2 ”Applied processes and techniques”.

Because of the required starting materials and the creation of co-products, the nitrophosphate route (also called the “ODDA” process) is usually realised integrated with ammonia, HNO_3 and CAN production. Additionally, liquid ammonia can be economically used to cool the nitrophoshporic acid section (crystallisation of CNTH).

7.2.2.1 Nitrophosphate route

For an overview of the nitrophosphate route, see Figure 7.2. The nitrophosphate process for producing NPK grades is characterised by the use of nitric acid for rock phosphate digestion and the subsequent cooling of the digestion solution in order to separate out most of the calcium ions from the solution as calcium nitrate crystals. The main difference to processes based on sulphuric acid is that it avoids the formation of gypsum. After filtration of the calcium nitrate crystals, the resultant NP solution is used for neutralisation and particulation as in other NPK processes. The final cooling temperature affects the range of NPK formulations possible with this process. The by-product calcium nitrate is converted into ammonium nitrate and calcium carbonate for CAN production or, after purification, marketed as CN fertiliser. Because of the required starting materials, the nitrophosphate route is usually realised integrated with ammonia, nitric acid and CAN production.

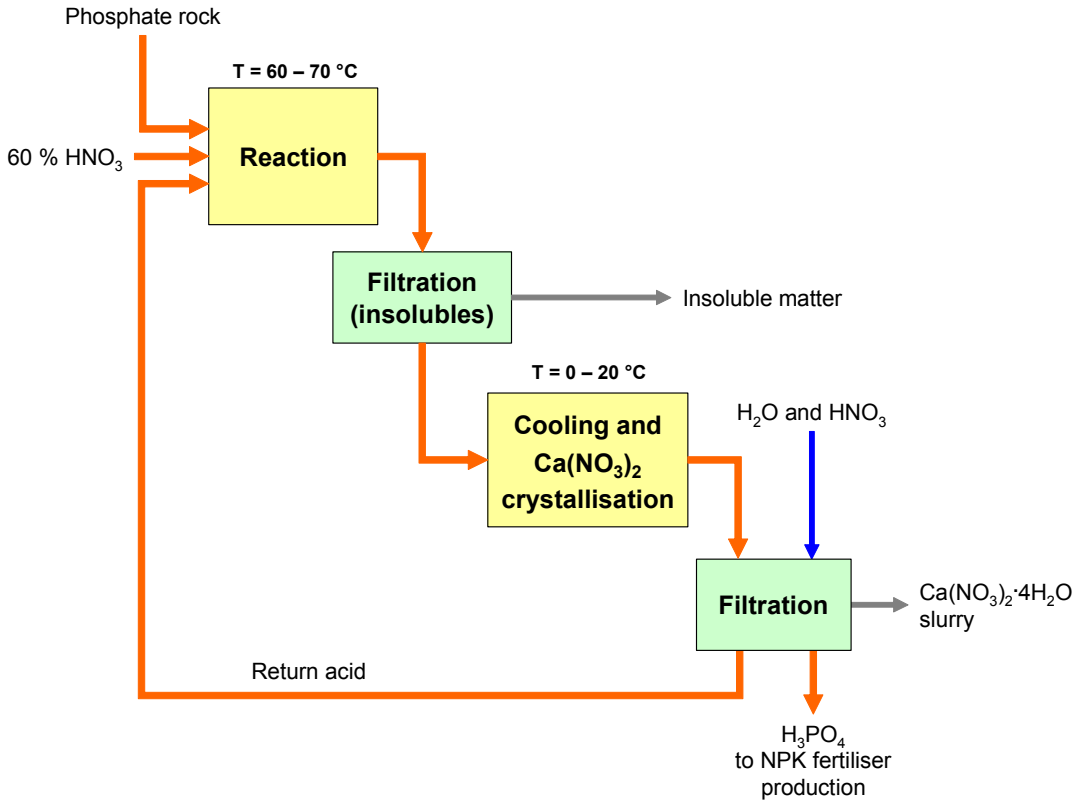

Figure 7.2: Overview of the nitrophosphoric acid process
Based on [29, RIZA, 2000].

7.2.3 Direct neutralisation (pipe reactor)

Various amounts of H_3PO_4, H_2SO_4 and HNO_3 are neutralised in pipe reactors with gaseous or liquid NH_3. The pipe reactor is usually fitted in the granulation drum. Another pipe reactor may be used in the dryer.

A wide range of grades can be produced, including ammonium phosphates (DAP/MAP). The heat of the reaction is used to evaporate the water contained in the phosphoric acid so the process can be operated at low recycle ratios and thus with low utilities consumption.

7.2.4 Pre-neutralisation

The conventional slurry process is carried out in a series of tanks/reactors, using a pre-neutraliser. Various amounts of H_3PO_4, H_2SO_4 and HNO_3 are neutralised with NH_3 and the resulting slurry can be partly evaporated to achieve the water content necessary for the subsequent particle formation. This process can produce NPKs and ammonium phosphates (DAP/MAP) with a good final product quality but yields a slurry with a high water content and hence, a high recycle ratio and increased energy consumption.

7.2.5 Drum granulation with ammoniation

This process uses mainly solid raw materials. Some NH_3 is reacted with $H_2SO_4/H_3PO_4/HNO_3$ within the bed of solid raw and recycle material in the granulation drum. The process is very flexible and can produce a broad range of grades, including products with a low nitrogen content.

7.2.6 Particle formation and conditioning

The options for particle formation include:

- spherodiser, see Section 7.4.2
- granulation drum, see Section 7.4.3
- prill tower, see Section 7.4.4
- pugmill (also called blunger) granulation
- pan granulation (for use in CN production, see Section 7.4.8)
- compaction.

The required temperatures for particle formation and drying with spherodiser or drum granulation depend also on the composition of the NPK product. For example, for NPK 15-15-15 dryer inlet temperatures of about 320 ºC and for NPK 20-8-8 dryer inlet temperatures <200 ºC are usually applied. These temperatures are influenced by the type of product (e.g. products with high AN contents tend to melt at higher temperatures). Also, such lower temperatures of the air may be required, even though the total heat input may be similar, implying quite different daily production rates in the same plant.

After particle formation, the product is dried and then screened. Fines and crushed oversize material are recycled back into the process. The commercial product is then cooled and coated before storage in order to minimise the subsequent caking of the material. See also:

- for product cooling, see Section 7.4.5
- for recycling of warm air, see Sections 7.4.6 and 7.4.2
- concerning granulation recycle, see Section 7.4.7.

7.2.7 Conversion of $Ca(NO_3)_2 \cdot 4\ H_2O$ into AN and lime

The production of NPK fertilisers by digestion of phosphate rock with HNO_3 in the ODDA process produces calcium nitrate tetra hydrate (CNTH, $Ca(NO_3)_2 \cdot 4\ H_2O$) as a by-product. The conversion of CNTH with NH_3 and CO_2 results in the production of ammonium nitrate and lime, which can both be used for the production of CAN (see also Section 9.2.1).

For the conversion, NH_3 and CO_2 are dissolved in an NH_4NO_3 solution, which is circulated in a carbonising column, and forms ammonium carbonate according to:

$$2\ NH_3 + CO_2 + H_2O \rightarrow (NH_4)_2CO_3$$

The reaction is exothermic and the heat is removed by cooling. Also CNTH is dissolved in a NH_4NO_3 solution and both solutions react according to:

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

On completion, excess $(NH_4)_2CO_3$ is neutralised with HNO_3 and the approx. 65 % NH_4NO_3 (AN) solution is separated (belt filter) from the $CaCO_3$ (lime) and concentrated in a two stage evaporator (e.g. falling film type) using steam.

Alternatively, the CNTH may be converted into commercial calcium nitrate fertiliser.

7.2.8 Ammonium phosphates production

Ammonium phosphates, DAP/MAP, are a special case within the mixed acid route (ammonium phosphates can not be produced by the nitrophosphate route). Production is usually carried out in a big, dedicated unit. Large quantities of diluted phosphoric acid are neutralised with ammonia in a pre-neutraliser, or a pipe reactor, or a combination of both. The resulting slurry is later granulated, dried and conditioned in a conventional granulation loop. Exhaust gas treatment is made by a combination of high performance cyclones and intensive wet scrubbing with phosphoric acid liquors and acidic water.

7.2.9 Emission sources into air and exhaust gas treatment

Exhaust gases arise from various sources. The main pollutants are:

NO_x (mainly NO and NO_2) with some nitric acid. The main source of NO_x is the dissolution of phosphate rock in nitric acid. The amount of NO_x formed during particulate formation depends on the grade produced (reaction temperature, drying rate, etc.) and the production process (amount of HNO_3 used). The nature of the rock, for example organic matter and iron contents and the reaction temperature, also affect the amount of NO_x.

NH_3 originating from the neutralisation process (pipe reactor, pre-neutralisation tank, granulation drum ammoniation or ammoniation tanks). The amount depends basically on the grade produced (amount of ammonia to be reacted, pH, temperature and slurry viscosity, drying rate) and the production process (again the amount of ammonia to be reacted, availability of acidic scrubbing liquors, etc.). Some ammonia also evaporates in the spherodiser (when used) or in the drying drum, because of the applied temperatures.

In the nitrophosphate route, there are also ammonia emissions originating from the CNTH conversion section and the AN evaporation section.

Fluorine compounds originating from the phosphate rock. In practice, the main part of the fluorine compounds goes through the process into the fertiliser and the remaining part is released into the gaseous phase.

The main sources for **fertiliser dust** are the drying and granulation drums, spherodiser and/or prilling towers, with dust also coming from the cooling drum, screens, crushers and conveyors.

The optimum exhaust gas treatment to be used depends strongly on the source of the emissions, the inlet concentration of the pollutants, the availability of optimum scrubbing liquors and at the end, on the production process being used and on the grade produced.

Exhaust gas treatment might include:

- wet scrubbing of exhaust gases from phosphate rock digestion, see Section 7.4.9
- condensation of neutralisation/evaporation vapours
- combined scrubbing of exhaust gases from neutralisation/evaporation and particle formation and conditioning, see Section 7.4.10
- cyclones and fabric filters for dry dedusting.

7.3 Current emission and consumption levels

Table 7.3 shows the reported energy consumption levels for the production of NPK fertilisers, Table 7.4 shows the reported water consumption levels, Table 7.5 the reported emissions to air, and Table 7.6 shows the reported emission levels to water.

	Per tonne product			Remark		Reference
	kWh	Nm^3	kg			
Total energy for drying	89			At a production level of 50 tonnes/hour (1200 tonnes/day or 350000 tonnes/year)	Granulation with a pipe reactor	[77, EFMA, 2000]
	125				Mixed acid route with rock digestion	
	83				Drum granulation with ammoniation	
Electricity	34			NPK types	Mixed acid route, starting from SSP/TSP	Donauchemie
	28			PK types		
	109			NP and NPK	Nitrophosphate route	AMI, Linz
	25 – 80			NPK	Mixed acid route	Compo, Krefeld
	30			Steam / water granulation	Mixed acid route	[52, infoMil, 2001]
	50			Chemical granulation	Nitrophosphate route	
	33			At a production level of 50 tonnes/hour (1200 tonnes/day or 350000 tonnes/year)	Drum granulation with ammoniation	[77, EFMA, 2000]
	50				Mixed acid route with rock digestion	
	30				Granulation with a pipe reactor	

	Per tonne product			Remark		Reference
	kWh	Nm^3	kg			
Natural gas	80.7	8		NPK types, drying	Mixed acid route, starting from SSP/TSP	Donauchemie
	100.8	10		PK types, drying		
		23		NP and NPK	Nitrophosphate route	AMI, Linz
	209			Steam / water granulation	Mixed acid route	[52, infoMil, 2001]
	116			Chemical granulation	Nitrophosphate route	
Heavy fuel oil			10 – 35	For spherodiser heating	50 % of the S content (1.8 %) remain in the product, the rest is emitted	Compo, Krefeld
Steam			80	NPK types, granulation	Mixed acid route, starting from SSP/TSP	Donauchemie
			60	PK types, granulation		
			170	NP and NPK	Nitrophosphate route	AMI, Linz
				20000 tonnes/year	Mixed acid route	BASF, Ludwigshafen
			60	Steam / water granulation	Mixed acid route	[52, infoMil, 2001]
			310	Chemical granulation	Nitrophosphate route	
Compressed air		38		NP and NPK	Nitrophosphate route	AMI, Linz

Table 7.3: Energy consumption levels for the production of NPK fertilisers

	m^3/tonne product	Remark		
Cooling water	17		Nitrophosphate route	AMI, Linz
Granulation and exhaust gas scrubbing	1.4	NPK	Pipe reactor, mixed acid route starting from SSP/TSP	Donauchemie
	0.9	PK		

Table 7.4: Water consumption levels for the production of NPK fertilisers [9, Austrian UBA, 2002]

	Emission level			Remark	Reference
	mg/Nm^3	ppm	kg/hour		
NO_x as NO_2	100		0.8 – 1.2	8000 – 12000 m^3/hour, exhaust gases from wet process part (phosphate rock digestion), wet scrubbers	Compo, Krefeld
	<100		1.9	19000 m^3/hour, exhaust gas from digestion of Kola phosphate rock, wet scrubber	BASF, Ludwigshafen
	425		8.1	19000 m^3/hour, exhaust gas from digestion of Florida phosphate rock, wet scrubber	BASF, Ludwigshafen
	50		4.5	90000 m^3/hour, exhaust gases from dry process part, cyclones only	Compo, Krefeld
	206		5.15	25000 m^3/hour, levels from 2001, digestion of phosphate rock, multistage scrubbing (see Section 7.4.9)	AMI, Linz
	245		6.12	25000 m^3/hour, levels from 2000, digestion of phosphate rock, multistage scrubbing (see Section 7.4.9)	AMI, Linz
	22		5.6	250000 m^3/hour, combined scrubbing of exhaust gas from neutralisation/evaporation and granulation (see Section 7.4.10)	AMI, Linz
	500	250		Mixed acid route, indicative levels	[77, EFMA, 2000]
	500			Nitrophosphate route	[77, EFMA, 2000]
NH_3	16		1.4	90000 m^3/hour, exhaust gases from dry process part, cyclones only	Compo, Krefeld
	6		0.05	8000 – 12000 m^3/hour, exhaust gases from wet process part (phosphate rock digestion), wet scrubbers	Compo, Krefeld
		21 – 34		Mixed acid route, pipe reactor, 3-stage scrubbing	CFL, India [79, Carillo, 2002]
	0 – 10		0 – 3.4	340000 m^3/hour, exhaust gases from neutralisation, granulation, drying, cyclones and scrubber	BASF, Ludwigshafen
	4.6		0.74	160000 m^3/hour, exhaust gas from granulation/pipe reactor, drying, cooling and screening, cyclones and 3-stage scrubbing	Donauchemie
	7.4		1.9	250000 m^3/hour, combined scrubbing of exhaust gas from neutralisation/evaporation and granulation (see Section 7.4.10)	AMI, Linz
	60	100		Mixed acid route, indicative levels	[77, EFMA, 2000]

	Emission level			Remark	Reference
	mg/Nm^3	ppm	kg/hour		
	60			Nitrophosphate route, including conversion units	[76, EFMA, 2000]
Fluoride as HF	6		0.05 – 0.07	8000 – 12000 m^3/hour, exhaust gases from wet process part (phosphate rock digestion), wet scrubbers	Compo, Krefeld
	1 – 3		0.02 – 0.06	19000 m^3/hour, exhaust gas from digestion of Florida phosphate rock, wet scrubber	BASF, Ludwigshafen
	1 – 2.7		0.34 – 0.92	340000 m^3/hour, exhaust gases from neutralisation, granulation, drying, conditioning , cyclones and scrubber	BASF, Ludwigshafen
	3.2		0.51	160000 m^3/hour, exhaust gas from granulation/pipe reactor, drying, cooling and screening, cyclones and 3-stage scrubbing	Donauchemie
	1.65		0.4	250000 m^3/hour, combined scrubbing of exhaust gas from neutralisation/evaporation and granulation (see Section 7.4.10)	AMI, Linz
	0.34		0.008	25000 m^3/hour, levels from 2001, digestion of phosphate rock, multistage scrubbing (see Section 7.4.9)	AMI, Linz
	0.30		0.008	25000 m^3/hour, levels from 2000, digestion of phosphate rock, multistage scrubbing (see Section 7.4.9)	AMI, Linz
		1.4 – 2.0		Mixed acid route, pipe reactor, 3-stage scrubbing	CFL, India [79, Carillo, 2002]
	5	6		Mixed acid route, indicative levels	[77, EFMA, 2000]
	5			Nitrophosphate route and conversion units	[76, EFMA, 2000]
Dust	40 – 75		3.6 – 6.8	90000 m^3/hour, exhaust gases from dry process part, cyclones only	Compo, Krefeld
	16.8			Drum granulator, drying drum, cyclones and scrubber	AMFERT, Amsterdam
	10 – 35		3.4 – 11.9	340000 m^3/hour, exhaust gases from neutralisation, granulation, drying, conditioning , cyclones and scrubber	BASF, Ludwigshafen
	26.6		6.7	250000 m^3/hour, combined scrubbing of exhaust gas from neutralisation/evaporation and granulation (see Section 7.4.10)	AMI, Linz
	70		11.2	160000 m^3/hour, exhaust gas from granulation/pipe reactor, drying, cooling and screening, cyclones and 3-stage scrubbing	Donauchemie

	Emission level			Remark	Reference
	mg/Nm^3	ppm	kg/hour		
		30 – 40		Mixed acid route, pipe reactor, 3-stage scrubbing	CFL, India [79, Carillo, 2002]
	5		2.5	500000 m^3/hour, nitrophosphate route, emission from prill tower, no abatement	[76, EFMA, 2000]
	20		7.4	370000 m^3/hour, CN production, emission from prill tower, no abatement	
	50			Wet dust expressed as dry matter, mixed acid route	
HCl	23		3.7	160000 m^3/hour, exhaust gas from granulation/pipe reactor, drying, cooling and screening, cyclones and 3-stage scrubbing	Donauchemie
	3.7			Exhaust gas from drying drum, cyclones and scrubber	AMFERT
	15			Exhaust gas from drum granulator and drying	Zuid-Chemie
	<30			Dedusting shop floor, transportation, sieves, two fabric filters	
	<30			Exhaust gas from drum granulator, cyclones, two scrubbers	
	19.1			PK production, scrubber	Amfert Ludwigshafen

Table 7.5: Emissions to air from the production of NPK fertilisers

m^3/day	Parameter	kg/day	kg/tonne P	kg/tonne P_2O_5	Remark	Reference
2400 – 4000	P	237		1.12	Waste water from exhaust gas scrubbing (rock digestion with HNO_3), sand washing, cleaning and rinsing, production of about 210 tonnes P_2O_5/day. Biological waste water treatment	BASF, Ludwigshafen [78, German UBA, 2001]
	F	282		1.33		
	NO_3-N = N_{total}	901		4.26		
3450	pH = 6.8	--	--	--	Waste water from the ODDA plant, based on a production capacity of 1200 tonnes NPK fertiliser, discharge after neutralisation, including waste water from CNTH conversion	AMI, Linz [9, Austrian UBA, 2002]
	FS	215	1.47			
	PO_4	77	0.53			
	NH_4-N	100	0.68			
	NO_3-N	124	0.85			
	NO_2-N	2	0.01			
	Fluoride	43	0.29			
	Cd	0.0014	0.00001			
	N_{total}			1.2	Nitrophosphate route, rock digestion and CNTH conversion	[76, EFMA, 2000]
	P_2O_5			0.4		
	Fluoride			0.7		
	N_{total}			0.2 [x]	Nitrophosphate route, neutralisation, granulation, drying, coating	[76, EFMA, 2000]
	Fluoride			0.03 [x]		
	N_{total}			0.2 [x]	Mixed acid route	[77, EFMA, 2000]
	Fluoride			0.03 [x]		
[x] kg/tonne NPK						

Table 7.6: Emissions to water from the production of NPK fertilisers

7.4 Techniques to consider in the determination of BAT

7.4.1 Minimisation of NO_x formation

Description

NO_x loads in exhaust gases from the digestion of phosphate rock can be minimised by a selection of proper operating conditions, e.g. temperature control and correct ratio of rock phosphate/acid. If the digestion temperature is too high, NO_x is formed excessively. NO_x formation can also be reduced by using phosphate rock with low contents of organic compounds and ferrous salts.

Achieved environmental benefits

Minimisation of NO_x formation. An example is reported by [78, German UBA, 2001]:

NO_x emission using Florida rock (IMC): about 425 mg/m^3
NO_x emission using Russian rock (Kola): <100 mg/m^3.

Cross-media effects

None believed likely.

Operational data

No specific information provided.

Applicability

Generally applicable, but might be limited by the availability of high grade phosphate rock. However, Florida rock is actually of minor relevance on the European market.

[52, infoMil, 2001]: The organic content in phosphate rock can also create odour problems.

See also Sections 5.4.9 and 5.4.10 on the selection of phosphate rock.

Economics

It can be assumed that the prices for low impurity rock would increase.

Driving force for implementation

No specific information provided.

References to literature and example plants

[9, Austrian UBA, 2002, 78, German UBA, 2001]

7.4.2 Particle formation (1): spherodiser

Description

Granulation of slurries produced by phosphate rock digestion is often carried out in spherodisers. The spherodiser process combines granulation and drying in a single process step. It consists of an inclined rotary drum, divided into a granulation and a drying zone.

Undersized and crushed oversize material particles are recycled to the granulation zone (granulation loop). The recycled particles generate a moving bed in the drum, into which the slurry containing 10 – 20 % water is sprayed. Air is preheated with gas burners up to 400 ºC and flows co-currently through the spherodiser evaporating the water and building up dry granules with a water content of <1.5 %.

A part of the granulation air can be taken from warm exhaust gas of the subsequent cooling step ("recycling of warm air", see also Section 7.4.6) and from dedusting processes (volume flows from conveyors and elevators).

Achieved environmental benefits

Table 7.7 shows the raw gas properties for a spherodiser.

	Raw gas			
	mg/Nm^3	**kg/hour**	**Nm^3/hour**	
Dust	150	37	About 245000	NPK production via the nitrophosphate route, the raw gas is treated together with the exhaust gases from neutralisation/evaporation (see Section 7.4.10)
NH_3	150	37		
NO_x	25	6		

Table 7.7: Properties of raw gas leaving a spherodiser
[9, Austrian UBA, 2002]

Cross-media effects

None believed likely.

Operational data

No specific information provided.

Applicability

Generally applicable.

Economics

No information provided.

Driving force for implementation

No specific information provided.

References to literature and example plants

[9, Austrian UBA, 2002], AMI, Linz (nitrophosphate route), Kompo, Krefeld (mixed acid route)

7.4.3 Particle formation (2): drum granulation

Description

The NP liquor obtained from neutralisation at approximately 135°C and with a water content of 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 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 100000 Nm^3/hour for the production of 55 tonnes per hour of NPK 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 (<50 mg/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. The NPK product, after drying, is screened and the hot product sized material is sent to the conditioning section. The oversized granules after crushing and the undersized granules are returned to the granulator. Screens, crushers and conveyor discharge points are de-dusted in one mode of operation using the air going to the drums.

Achieved environmental benefits

- low exhaust gas dust levels after treatment in cyclones: <50 mg/Nm^3, but also up to 75 mg/Nm^3 (nitrophosphate route)
- average ammonia content in exhaust gases at pH 5 of <150 mg/Nm^3 (nitrophosphate route)
- AMFERT Amsterdam achieves dust levels of 16.8 mg/Nm^3 by treatment of exhaust gases from drum granulation and the drying drum with cyclones and scrubbing. AMFERT is a multi purpose plant (mixed acid route)
- Zuid Chemie achieves NH_3 emissions <100 mg/Nm^3 by treating exhaust gases from their multi purpose line 1 with a cyclone and two scrubbers in series (acidic/water)
- Zuid Chemie achieves NH_3 emissions <30 mg/Nm^3 by treating exhaust gases from their multi purpose line 2 with a cyclone and two scrubbers in series (acidic/water).

Cross-media effects

None believed likely.

Operational data

The exhaust gas volume flow for production of 55 tonnes per hour of NPK 15-15-15 is about 100000 Nm^3/hour (nitrophosphate route).

Applicability

Generally applicable.

Economics

No information provided.

Driving force for implementation

No specific information provided.

References to literature and example plants

[76, EFMA, 2000]

7.4.4 Particle formation (3): prill tower

Description

Evaporated NP liquor from neutralisation is mixed with the required salts and recycled product. The final water content is approximately 0.5 %. The mixer overflows into a rotating prill bucket from which the slurry is sprayed into the prill tower. Fans at the bottom of the tower cause ambient air to flow countercurrently 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 NPK product is sent to the conditioning section.

Achieved environmental benefits

Table 7.8 shows the emission levels from prill towers in the production of NPK and CN.

	Emission			
	mg/m^3	**kg/hour**	**m^3/hour**	
Dust	5	2.5	500000	NPK production via the nitrophosphate route, levels without abatement system (the dust emission depends on the AN content, the NH_3 emission is related to pH, temperature and the NH_3/P_2O_5 ratio of the NP acid)
NH_3	10 – 15	5 – 7.5		
CN dust	20	7.4	370000	CN production, levels relate to a 40 tonnes/hour plant

Table 7.8: Emission levels from prill towers in the production of NPK and CN [76, EFMA, 2000]

Cross-media effects

None believed likely.

Operational data

No specific information provided.

Applicability

Generally applicable. Nowadays in Western Europe, only one NPK prilling tower is in operation. For NPK prilling, if not carried out in a favourable climatic environment, high investment costs can be expected.

Economics

No information provided.

Driving force for implementation

No specific information provided.

References to literature and example plants

[76, EFMA, 2000], YARA, Porsgrunn

7.4.5 Plate bank product cooler

Description

After drying and screening, most fertiliser products need additional cooling to avoid potential caking in storage. The primary types of coolers that are typically considered are as follows:

- rotary drum
- fluidised bed
- plate bank (or bulk flow) heat exchanger.

The rotary drum relies on ambient or chilled air as the cooling medium and is probably the most common unit used in the industry. Although it is fairly expensive from both a capital and operating perspective, it has proven to be reliable. Fluid bed coolers also use air as the cooling medium and are commonly used overseas. They are smaller units than rotary drums and have a lower capital cost. However, the operating cost is significantly increased due to the need for more airflow at a higher pressure drop.

The plate bank exchanger is an additional option that has significant capital and operating cost advantages and has been successfully used in several recent applications. The concept of using a plate bank exchanger to cool a solid product is very simple. The unit consists of a vertical bank of hollow, stainless steel plates. The bulk solids pass through a feed hopper and pass slowly between the plates while cooling water is passed countercurrently through the hollow plates. Plate spacing is critical to achieve efficient cooling without causing bridging of the solid material. The cooled material is discharged by a gate mechanism located on the bottom of the cooler. The cooler is designed to run full with the gate opening being controlled by the level in the feed hopper. A small amount of dry air is used to purge the unit of moisture and prevent caking. Figure 7.3 gives an impression.

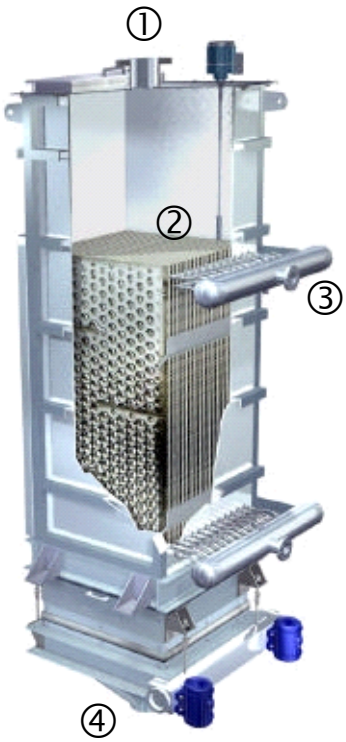

Figure 7.3: Example for a plate bank cooler
① warm granules inlet, ② plate bank, ③ cooling water manifold, ④ cooled granules outlet
[55, Piché and Eng, 2005]

Achieved environmental benefits

- reduced emissions to air. The purge air flow is a tiny fraction (in the order of 1 %) of the airflow typically required for a rotary or fluid bed cooler
- for energy savings, see Table 7.9.

	per tonne product	
Rotary cooler	3 kWh	The rotary cooler requires fairly large motors for the cooler drive, the exhaust fan, and the scrubber circulation pump
Fluid bed cooler	5 kWh	The fluid bed cooler requires even larger motors for the exhaust fan and the scrubber circulation pump
Plate bank cooler	0.6 kWh	The only motors needed are for a small cooling water pump, blower, and conveyor

Table 7.9: Comparison of energy requirements for different product cooling systems [54, Snyder, 2003]

Cross-media effects

Cooling water: 280 – 4200 litre/minute [52, infoMil, 2001]
200 – 300 m^3/hour (BASF, Antwerp)
150 m^3/hour (AMI, Linz).

The energy saving will be partially offset by the energy requirements for the internal cooling system and purge air drying/compression. For example, BASF (Antwerp) applies 10000 m^3/hour, AMI (Linz) applies 300 m^3/hour dried purge air [154, TWG on LVIC-AAF, 2006].

The fines contained in the product are not removed in a plate bank cooler in contrast to the fines removal in the drying drum and fluid bed cooler [154, TWG on LVIC-AAF, 2006].

Operational data

[52, infoMil, 2001]:

Typical throughput: 5 – 60 tonnes/hour
Approximate heat capacity: 209300 – 3140000 kJ/hour
Instrument air: 10 litre/minute.

The cooling water inlet should have a 10 ºC lower temperature than the targeted temperature of the material to be cooled.

Applicability

Generally applicable. The plate bank cooler shows a compact design; the requirement for a 100 tonne per hour unit was approximately 1.8 m square by 9 m high. The tall elevation was due to two stages of plate banks with one immediately above the other. In addition, this type of cooler does not require nearly the same amount of ancillary equipment. The product is handled gently

– the product drops slowly through the unit with no measurable creation of dust or product degradation. [52, infoMil, 2001] describes the technique for urea, but names example plants also for other fertilisers.

Plate bank coolers have been used to cool the full range of fertilisers: urea granules and prills, ammonium nitrate and CAN, NPKs, MAP, DAP, TSP, ammonium sulphate [55, Piché and Eng, 2005].

Plate bank coolers may not be applicable for urea-based NPK fertilisers and AN/CAN fertilisers as the primary cooler. Plate bank coolers may not be applicable for SSP/TSP fertilisers [154, TWG on LVIC-AAF, 2006].

Economics

Cost benefits in operation.

Low installed cost – the total items required for a bulk flow cooler system are as follows [54, Snyder, 2003]:

- plate coil cooler
- cooling water pump
- purge air package (blower and air drying)
- internal cooling, e.g. small cooling tower package (may not be required)
- an additional elevator system might be required [154, TWG on LVIC-AAF, 2006]

- the total installed cost for a 100 tonnes per hour system is estimated to be approximately USD 1400000 – 1800000. This is estimated to be slightly less than for a fluid bed cooler system and considerably less than for a rotary cooler system, even without considering the cost of the scrubber system required by these types of coolers. The pricing comparison for a bulk flow cooler becomes more pronounced at smaller sizes

- low operating cost – a bulk flow cooler system uses considerably less electrical energy than a rotary or fluid bed cooler system. The net cost savings for using a plate coil cooler (compared to the other types) is in the range of USD 0.12 – 0.22 per tonne.

The economic justification for this option increases significantly if cooler (and/or scrubber) repair, upgrade, or replacement is already needed. As noted earlier, in one case study where a bulk flow cooler was used, the reduced airflow allowed an improvement in emissions that, in turn, eliminated the need for a scrubber upgrade.

Where increased volumes of dried purge air have to be applied, higher costs can be expected [154, TWG on LVIC-AAF, 2006], see also under Cross-media effects.

Driving force for implementation

Cost benefits.

References to literature and example plants

[52, infoMil, 2001, 54, Snyder, 2003], BASF Antwerp, AMI Linz, Yara, Porsgrunn, P.F.i., Kavala

7.4.6 Recycling warm air

Description

The traditional practice for handling exhaust air from the product cooler (and equipment vents) was to send it through a scrubber system. However, it is not necessary or efficient to use a wet recovery system. The preferred option is to first take this warm air (about 60 – 65 ºC, and about 40000 m^3/hour) and use a fabric filter or high efficiency cyclones to recover the dust. After dust removal, the warm air is then recycled as dilution air to the dryer combustion system, replacing ambient air. Good experience has been reported in a number of plants that have switched to this type of system. This system has proven feasible in both dry (Western US) and humid (US Gulf Coast) climates, however, the moisture content of the recycled air is a sensitive factor that must be carefully evaluated.

Figure 7.4 gives an overview of the change over from the conventional setup to the optimised setup. Primary components of this revised configuration are as follows:

- removal of old equipment and ductwork
- new fabric filter (or high efficiency cyclones)
- new "recycle air" fan (if the existing unit is not available or not sufficient)
- revised ductwork.

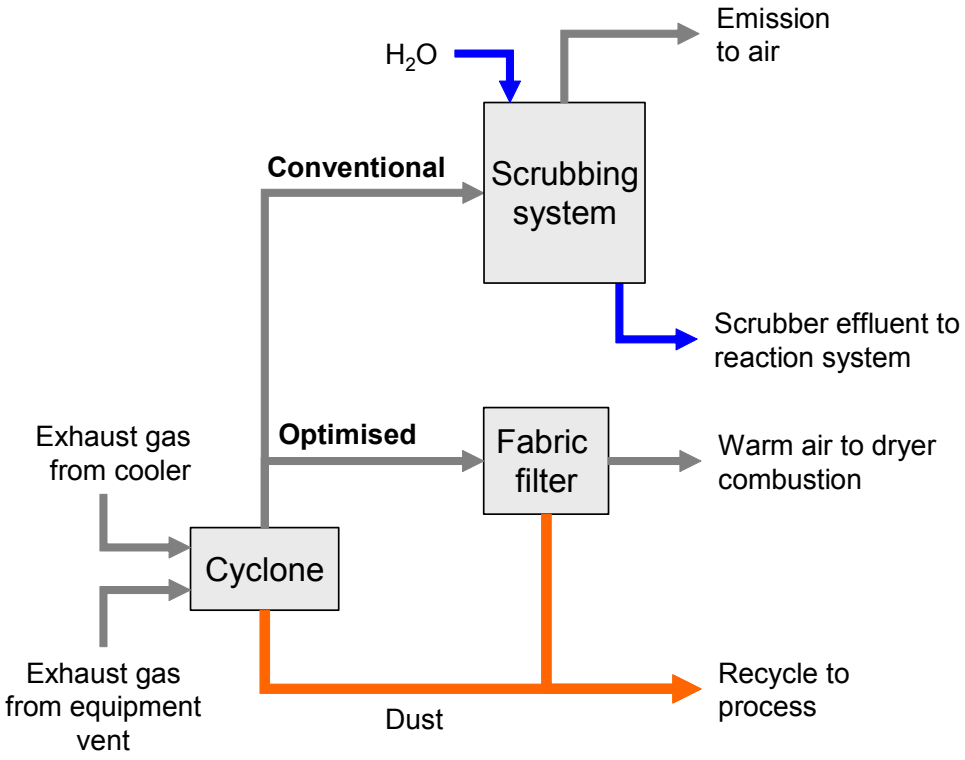

Figure 7.4: Overview of the recycling of warm air
[54, Snyder, 2003]

Achieved environmental benefits

In general, a dry recovery system is expected to be a simplified, more efficient operation with reduced pluggage, corrosion, and resultant maintenance. Specific benefits from a warm air recycle system are as follows:

- recovered heat from warm air results in fuel savings at the dryer
- various benefits due to reduced volume flow in the scrubber system, e.g. as follows:

  - ❖ reduced fan power (lower pressure drop associated with fabric filter or cyclones)
  - ❖ reduced scrubber circulation pump power
  - ❖ reduced make-up water requirement (and resultant evaporation required)
  - ❖ reduced fluoride emissions associated with reduced wet gas flow to atmosphere.

The total dryer fuel savings are estimated to be in the range of 6 – 12 % which translates to approximately USD 0.1 – 0.2 per tonne. The total power savings are estimated to be approximately 2 kWh per tonne or USD 0.1 per tonne.

Cross-media effects

The technique requires a specific burner design, and higher NO_x emissions can be expected (still below 200 mg/Nm^3 NO_x at 3 % O_2 [52, infoMil, 2001].

Operational data

No specific data provided.

Applicability

Generally applicable to all kinds of fertilisers. The problems with implementation/use of this technique have resulted in changing back to the original configuration in the plants of Fertiberia (Huelva) and BASF (Ludwigshafen). The main reasons for this were increased clogging in the equipment and increased maintenance cost [154, TWG on LVIC-AAF, 2006].

When recycling warm air within AN/CAN production, safety issues should be taken into consideration [154, TWG on LVIC-AAF, 2006].

Economics

The total installed cost for a warm air recycle system for a 100 tonnes per hour plant is estimated to be USD 600000 – 1000000. The economic justification for this option increases significantly if scrubber repair, upgrade, or replacement is already needed.

The example plant achieves fuel savings of about EUR 61000 per year (based on a price of EUR 0.14/m^3 of natural gas).

Driving force for implementation

Cost benefits through fuel savings.

References to literature and example plants

[52, infoMil, 2001, 54, Snyder, 2003], AMFERT, Amsterdam, AMI, Linz

7.4.7 Optimising the recycle ratio to granulation

Description

Another method of maximising plant efficiency is to control and minimise the amount of material being recycled from the screens and mills back through the granulator and dryer. Several approaches can be used to achieve this:

- select proper combination of screens and mills
- online product size distribution management
- mills, e.g. roller or chain mills
- surge hoppers.

Achieved environmental benefits

The primary benefit is a reduced recycle rate which can increase plant capacity and power consumption efficiency.

Cross-media effects

None believed likely.

Operational data

No specific information provided.

Applicability

Generally applicable.

Economics

No specific information provided, but cost benefits can be assumed.

Driving force for implementation

Cost benefits.

References to literature and example plants

[54, Snyder, 2003, 154, TWG on LVIC-AAF, 2006]

7.4.8 Conversion of $Ca(NO_3)_2 \cdot 4\ H_2O$ into CN

Description

For an overview of the conversion of CNTH into CN, see Table 7.10.

Process	Description
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 tank reactor system for neutralisation with gaseous ammonia. The reaction between ammonia and the remaining acids in the CNTH melt is exothermic. The ventilation gases from the two reactors are scrubbed with water before being discharged to atmosphere. The total discharge from the scrubbers is <0.3 kg/hour (NO_3-N and NH_4-N) for a 100 tonnes/hour plant and the concentration is <35mg N/Nm^3 off-gas. 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 pan 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 100 tonnes/hour CN plant is around 30 kg/hour, 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 fluid bed. The cooled product is screened in two stages and the on-size product is transferred to a coating drum and finally to storage. The oversized material is crushed, mixed with the fines and recycled to the granulator. The ventilation gases from the granulation and dry part of the process are scrubbed with water and process condensate from the wet part of the process, in a lamella separator before being discharged to atmosphere. The emission of aerosols containing CN to air is normally <4 mg NO_3-N/Nm^3 off-gas. The volume of ventilation air from a pan granulator producing 50 tonnes/hour CN fertiliser is 170000 Nm^3/hour. 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	For prilling, see Section 7.4.4.

Table 7.10: Conversion of CNTH into CN

Achieved environmental benefits

For achievable emission levels, see Table 7.10.

Cross-media effects

None believed likely.

Operational data

The volume of ventilation air from a pan granulator producing 50 tonnes/hour CN fertiliser is 170000 Nm^3/hour.

Applicability

Generally applicable. Applicable to production via the nitrophosphate route.

Economics

No information provided.

Driving force for implementation

No specific information provided.

References to literature and example plants

[76, EFMA, 2000]

7.4.9 Multistage scrubbing of exhaust gas containing NO_x

Description

For multistage scrubbing in NPK production, exhaust gases are collected from the following sources:

- phosphate rock digestion
- separation/washing of sand
- filtration/washing of $Ca(NO_3)_2 \cdot 4\ H_2O$ (CNTH).

A 10 % AN solution is used as the scrubbing medium and is recycled to NPK production at a sufficient concentration level. The sequence of feeding the exhaust gases to the scrubber ensures that the higher loaded gases pass through the greater number of scrubbing stages.

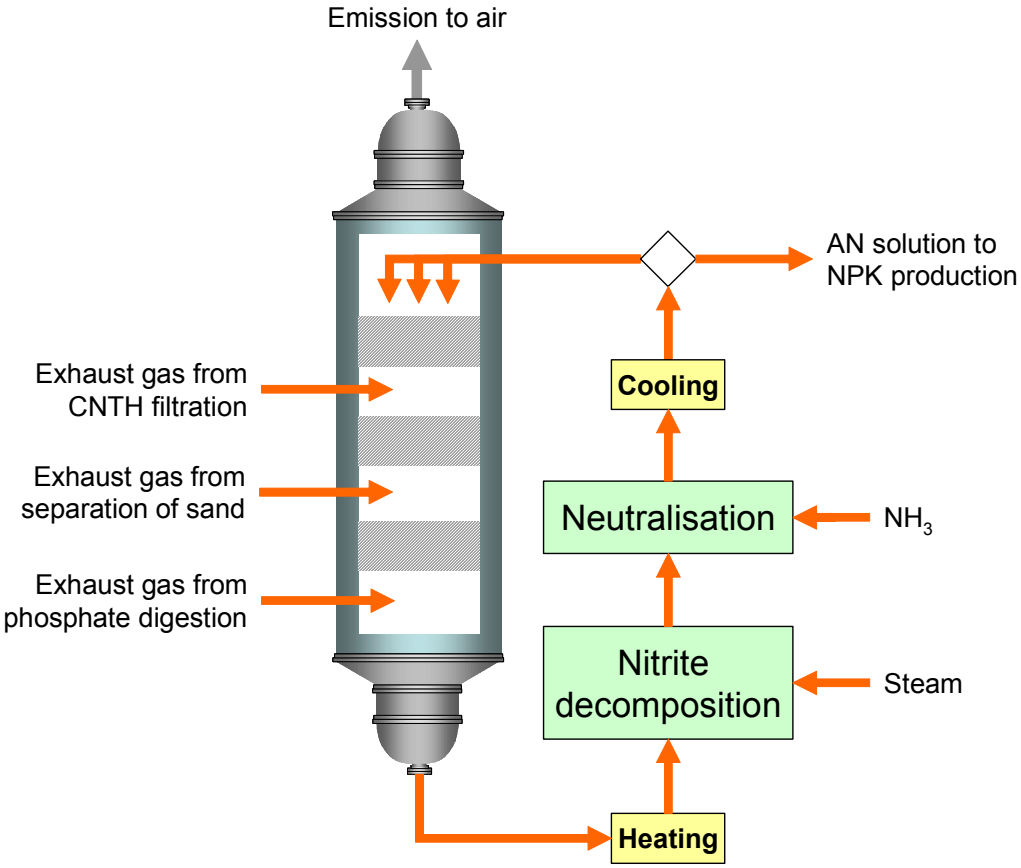

Figure 7.5: Multistage scrubbing of exhaust gases containing NO_x
Figure based on [9, Austrian UBA, 2002]

Achieved environmental benefits

The technique provides multistage scrubbing with thev recycling of nutrients. Table 7.11 shows the achieved emission levels.

	Raw gas		Emission level		Efficiency	Reference
	mg/Nm^3	Nm^3/hour	mg/Nm^3	kg/hour	%	
NO_x		25000	160 – 288 [x]	5.2 – 6.1		AMI, Linz
HF			0.30 – 1.40	0.035		
[x] using Moroccan phosphate rock, the higher levels result from operation at full capacity						

Table 7.11: Achieved average emission levels and efficiencies for multistage scrubbing [9, Austrian UBA, 2002]

Cross-media effects

Energy and chemicals consumption.

Operational data

No specific information provided.

Applicability

Applicable for AN-based NPK production.

Economics

No information provided.

Driving force for implementation

Reduction of NO_x emissions.

References to literature and example plants

[9, Austrian UBA, 2002], AMI, Linz

7.4.10 Combined treatment of exhaust gases from neutralisation/ evaporation and granulation

Description

The example plant renewed its NPK fertiliser production and a new combined waste gas scrubber was installed for treating exhaust gases/vapours from neutralisation/evaporation and exhaust gases from two spherodisers. The former setup (venturi scrubber and co-condensation of the neutralisation/evaporation exhaust vapours, scrubbing of NH_3 loaded gases) was replaced. Figure 7.6 illustrates the combined treatment.

Instead of condensing the vapours from neutralisation/evaporation, they are combined with the hot exhaust gas from the spherodiser (about 100 ºC, not saturated with H_2O) and the added heat leads to additional evaporation of H_2O in the scrubber. The additional H_2O removal enables the recycling of all scrubber liquids (and the contained nutrients) to the production process.

In the example, the total gas volume flow is about 250000 Nm^3/hour and about 1800 m^3/hour scrubbing liquor is circulated. An amount of about 1 m^3/hour scrubbing liquor is drawn off for recycling to the NPK production and contains about 25 % w/w AN. The scrubber is fed with liquid effluents from NPK production. The scrubber is equipped with a demister located above the scrubber packing and requires periodic cleaning, because insoluble compounds in the exhaust gases, e.g. dolomite, $CaSO_4$ and $Ca_3(PO_4)_2$ can cause clogging.

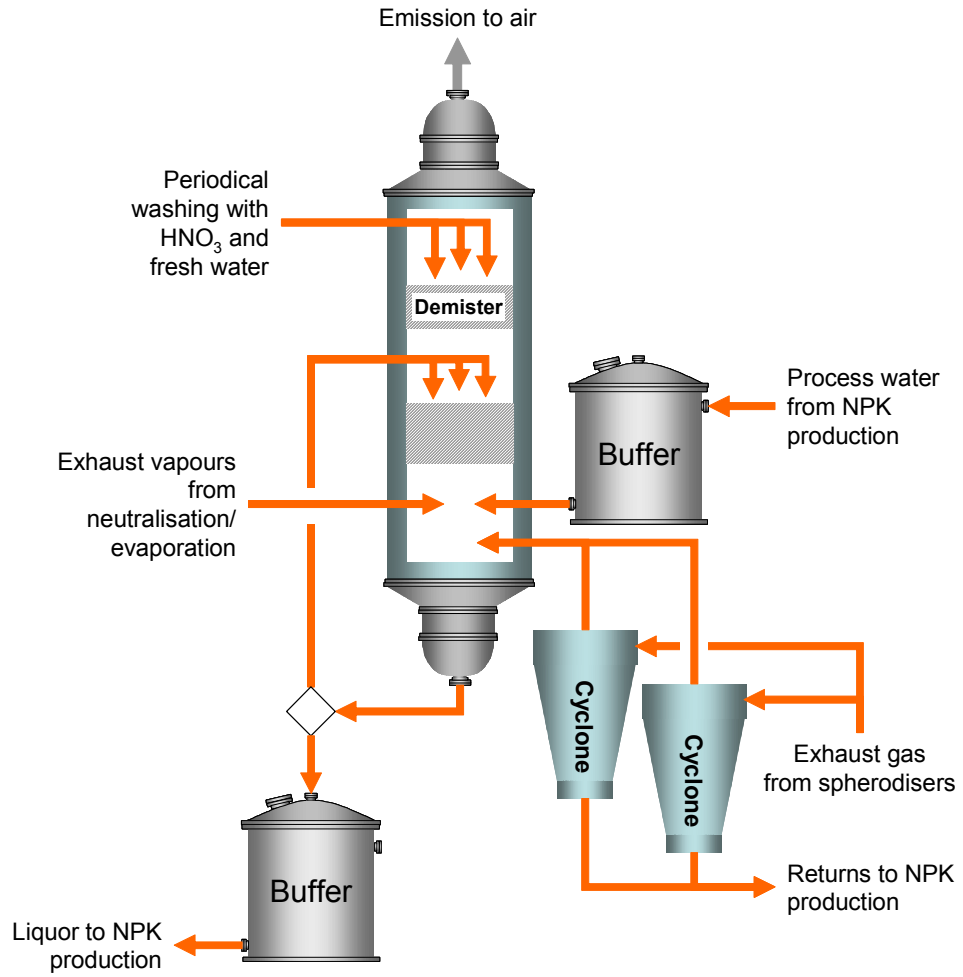

Figure 7.6: Combined treatment of exhaust gases from NPK production
Figure based on [9, Austrian UBA, 2002]

Achieved environmental benefits

With the combined treatment, a considerable amount of waste water from the scrubbing of exhaust gases from neutralisation/evaporation and the spherodisers is avoided and the AN solution can be recycled to the process.

Table 7.12 shows the achieved emission levels for the combined treatment of neutralisation/evaporation and spherodiser exhaust vapours/gases.

	Raw gas		Emission level		Efficiency	Reference
	mg/Nm^3	**Nm^3/hour**	**mg/Nm^3**	**kg/hour**	**%**	
Dust	150	About 250000	11.1 – 26.6	6.7	82	AMI, Linz (nitrophosphate route)
NH_3	200		7.4 – 11.2	1.9	96	
NO_x	25.3		4 – 22.4	5.6	12	
HF			0.2 – 1.7	0.4		
Dust		About 340000	20	6.8		BASF, Ludwigshafen (mixed acid route with HNO_3)
NH_3			0 – 10	0 – 3.4		
HF			1.4	0.5		

Table 7.12: Achieved average emission levels and efficiencies for combined scrubbing [9, Austrian UBA, 2002, 78, German UBA, 2001]

[154, TWG on LVIC-AAF, 2006]: in the case of DAP production with multistage scrubbing with H_3PO_4, HF levels of up to 10 mg/Nm^3 might be expected.

Cross-media effects

Energy consumption.

Operational data

No specific information provided.

Applicability

Only applicable for AN-based NPK production.

Economics

[9, Austrian UBA, 2002] lists the following costs:

- investment: EUR 5600000
- maintenance (4 % of investment) EUR 225000 per year.

Driving force for implementation

Plant revamp.

References to literature and example plants

[9, Austrian UBA, 2002], AMI, Linz (nitrophosphate route), BASF, Ludwigshafen (mixed acid route)

7.4.11 Recycling of scrubbing and washing liquors

Description

The following measures result in a considerable reduction of waste water volumes from NPK production:

- recycling of NO_x loaded scrubber liquors from treatment of exhaust gases from phosphate rock digestion
- recycling of washing liquor from sand washing
- avoid co-condensation of vapours from the evaporation
- recycling of scrubbing liquors from scrubbing of exhaust gases from neutralisation
- combined scrubbing of exhaust gases from neutralisation/evaporation and granulation units (see Section 7.4.10)
- using effluents as the scrubber medium.

Achieved environmental benefits

Table 7.13 shows achievable emission reductions.

	Recycling		
	without	**with**	
Recycling of NO_x scrubbing liquors	1.2	0.6	kg N/tonne P_2O_5
	0.7	0.02	kg F/tonne P_2O_5
Recycling of sand washing liquor	0.4	0.02	kg P_2O_5/tonne P_2O_5

Table 7.13: Achievable emissions from the recycling of scrubbing/washing liquors

Cross-media effects

None believed likely.

Operational data

No specific information provided.

Applicability

Generally applicable. However, the degree of recycling water into the process will depend on the water balance of the specific NPK production. For an example of a water balance, see [9, Austrian UBA, 2002].

On the Kompo, Krefeld site, all wash and scrubbing waters are recycled and no waste water is generated [78, German UBA, 2001].

On the Donauchemie site, no waste water is generated in NPK production. All scrubbing liquor is recycled into the process. Usually, rinsing and cleaning waters are collected and used as scrubbing liquid in the following production campaign if the production is carried out alternately under acidic (PK) and alkaline (NPK) conditions. Waste water is only released if the same fertiliser type is produced within two following campaigns [9, Austrian UBA, 2002].

[79, Carillo, 2002] describes techniques using favourable atmospheric conditions for improving the water balance of NPK production by evaporation. Variants use wind and sun only or are supported by ventilation or use residual heat from other processes.

Economics

No information provided.

Driving force for implementation

Reduction of emissions to water.

References to literature and example plants

[9, Austrian UBA, 2002, 76, EFMA, 2000, 77, EFMA, 2000, 78, German UBA, 2001], Compo, Krefeld, AMI, Linz

7.4.12 Waste water treatment

Description

Waste water that cannot be avoided is discharged after adequate treatment, e.g. biological waste water treatment with nitrification/denitrification and precipitation of phosphorous compounds.

Achieved environmental benefits

Lower emission levels to water.

Cross-media effects

Energy and chemicals consumption.

Operational data

No specific information provided.

Applicability

Generally applicable.

Economics

No information provided.

Driving force for implementation

Lower emission levels to water.

References to literature and example plants

[9, Austrian UBA, 2002], AMI, Linz, BASF, Ludwigshafen

7.5 BAT for NPK fertilisers

BAT is to apply the common BAT given in Section 1.5.

BAT for storage is to apply BAT given in [5, European Commission, 2005].

BAT is to reduce dust emissions from rock grinding, e.g. by application of fabric filters or ceramic filters and to achieve dust emission levels of 2.5 – 10 mg/Nm^3 (see Section 10.4.2).

BAT is to prevent dispersion of phosphate rock dust by using covered conveyor belts, indoor storage, and frequently cleaning/sweeping the plant grounds and the quay (see Section 5.4.8).

BAT is to improve environmental performance of the finishing section by one or a combination of the following techniques:

- apply plate bank product cooling (see Section 7.4.5)
- recycling of warm air (see Section 7.4.6)
- select proper size of screens and mills, e.g. roller or chain mills (see Section 7.4.7)
- apply surge hoppers for granulation recycle control (see Section 7.4.7)
- apply online product size distribution measurements for granulation recycle control (see Section 7.4.7).

BAT is to minimise the NO_x load in exhaust gases from phosphate rock digestion, by one or a combination of:

- accurate temperature control (see Sections 7.4.1)
- proper rock/acid ratio (see Sections 7.4.1)
- phosphate rock selection (see Sections 5.4.9 and 5.4.10)
- or by controlling other relevant process parameters.

BAT is to reduce emissions to air from phosphate rock digestion, sand washing and CNTH filtration by applying, e.g. multistage scrubbing, and to achieve emission levels given in Table 7.14 (see Section 7.4.9).

BAT is to reduce emission levels to air from neutralisation, granulation, drying, coating and cooling by applying the following techniques and to achieve the emission levels or removal efficiencies given in Table 7.14:

- dust removal, such as cyclones and/or fabric filters (see Sections 7.4.6 and 7.4.10)
- wet scrubbing, e.g. combined scrubbing (see Section 7.4.10).

BAT is to minimise waste water volumes by recycling washing and rinsing waters and scrubbing liquors into the process, e.g. by using residual heat for waste water evaporation (see Sections 7.4.10 and 7.4.11).

BAT is to treat the remaining waste water volumes according to Section 7.4.12.

	Parameter	Level	Removal efficiency in %
		mg/Nm^3	
Phosphate rock digestion, sand washing, CNTH filtration	NO_x as NO_2	100 – 425	
	Fluoride as HF	0.3 – 5	
Neutralisation, granulation, drying, coating, cooling	NH_3	5 – 30 [x]	
	Fluoride as HF	1 – 5 [xx]	
	Dust	10 – 25	>80
	HCl	4 – 23	

[x] the lower part of the range is achieved with nitric acid as the scrubbing medium, the upper part of the range is achieved with other acids as the scrubbing medium. Depending on the actual NPK grade produced (e.g. DAP), even by applying multistage scrubbing, higher emission levels might be expected

[xx] in the case of DAP production with multistage scrubbing with H_3PO_4, levels of up to 10 mg/Nm^3 might be expected

Table 7.14: Emission levels to air associated with the application of BAT

8 UREA AND UAN

8.1 General information

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. 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 nitrogen for the build-up of protein. Another application of urea is the $DeNO_x$ treatment of waste gases (SCR and SNCR). The annual global production has increased by approximately 30 Mtonnes in the last 10 years. Current world output amounts to more than 100 Mtonnes/year. 16 urea plants were in operation in Western Europe in the year 2000. The total capacity was 5.141 Mtonnes in 1999/2000. New urea installations vary in size of up to 3500 tonnes/day and are typically 2000 tonnes/day units.

Urea ammonium sulphate compounds are produced in some facilities by adding ammonium sulphate to the urea melt before granulation.

Urea ammonium nitrate (UAN)

UAN solutions typically contain 28 to 32 % N but other customised concentrations (including additional nutrients) are produced. Plant capacities for the production of UAN solutions range between 200 and 2000 tonnes/day. Most of the large scale production units are located within integrated plants where either urea or ammonium nitrate or both are produced. Western European consumption of UAN in 1998/99 was 3.72 Mtonnes of solution, 41 % of which was imported.

Country	Company	Location	Year startup	Capacity in kt/y	Comment
Austria	Agrolinz	Linz	1977	380	Captive use
Czech Republic	Chemopetrol	Litvinov	1973	204	
Estonia	Nitrofert	Kothla Jarve	1968	90	
			1969	90	
France	Grande Paroisse	Oissel	1969	120	
	Yara	Le Havre	1970	300	
Germany	BASF	Ludwigshafen	1968	545	Captive use
	SKW	Piesteritz	1974	1221	Three plants after revamp 2004
			1975		
			1976		
	Yara	Brunsbüttel	1979	530	
Hungary	Nitrogenmuvek	Petfuerdoe	1975	198	
Italy	Yara	Ferrara	1977	500	
Lithuania	Achema	Jonava	1970	445	Status unknown
Netherlands	DSM	Geleen	1998	525	Captive use melamine
	Yara	Sluiskil	1971	425	
			1979	325	
Poland	Zaklady Azotowe ZAK	Kedzierzyn	1957	167	
	Zaklady Azotowe ZAP	Pulawy	1998	561	
			1998	214	
	Zaklady Chemiczne	Police	1986	400	
Portugal	Adubos	Lavradio	1963	80	
Slovakia	Duslo	Sala Nad Vahom	1973	204	
Spain	Fertiberia	Palos	1976	250	Revamped 1988
		Puertollano	1970	135	

Table 8.1: Urea production plants in the European Union as of July 2006 [154, TWG on LVIC-AAF, 2006]

8.2 Applied processes and techniques

8.2.1 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:

$$2\ NH_3 + CO_2 \leftrightarrow \underset{\text{Ammonium carbamate}}{NH_2COONH_4} \leftrightarrow \underset{\text{Urea}}{CO(NH_2)_2} + H_2O$$

Both reactions take place in the liquid phase in the same reactor and are in equilibrium. The yield depends on various operating parameters. The most typical production conditions are summarised in Table 8.2. 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.

Parameter		Unit
Pressure	140 – 250	bar
Temperature	180 – 210	ºC
NH_3/CO_2 ratio	2.8:1 – 4:1	molar ratio
Retention time	20 – 30	minutes

Table 8.2: Typical urea production parameters
[121, German UBA, 2001]

Several side reactions may occur in urea synthesis. The most relevant equilibrium reactions are

- hydrolysis of urea: $CO(NH_2)_2 + H_2O \leftrightarrow NH_2COONH_4 \leftrightarrow 2\ NH_3 + CO_2$
- formation of biuret: $2\ CO(NH_2)_2 \leftrightarrow NH_2CONHCONH_2 + NH_3$
- formation of isocyanic acid: $CO(NH_2)_2 \leftrightarrow NH_4NCO \leftrightarrow NH_3 + HNCO$.

The hydrolysis reaction is the reverse reaction of the urea formation and only takes place in the presence of water. Acids or alkaline solutions can also accelerate the rate of hydrolysis. In practice, residence times of urea solutions with low NH_3 content at high temperatures must be minimised. Biuret must be limited in fertiliser urea (preferably maximum of 1.2 % EC), since biuret might cause crop damage, notably during foliage spraying. In technical urea (e.g. used in the production of synthetic resins), the biuret content is generally up to 0.3 – 0.4 % 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 equilibrium forming isocyanic acid is shifted to the right.

At an economical conversion rate of NH_3 and CO_2 to urea, the process design intends nowadays to efficiently separate product urea from the other reaction components, to recover excess NH_3, and to decompose residual ammonium carbamate to NH_3 and CO_2 for recycling into the process ("total recycling processes"). This is usually realised by stripping (still at high pressure) and subsequent depressurisation/heating of the urea solution or combinations of both.

Various strategies have been developed to realise "total recycling processes", these include:

- conventional processes without stripping (older plants, provided by various suppliers, see Section 8.4.1)
- CO_2 stripping processes, e.g. by Stamicarbon or Toyo's ACES process (see Section 8.4.2)
- NH_3 stripping processes, e.g. by Snamprogetti (see Section 8.4.3)
- the Isobaric Double Recycling process (IDR), applying stripping with NH_3 and CO_2, by Montedison (see Section 8.4.4).

Finally, the urea solution from the synthesis/recycling stages of the process is concentrated via evaporation or crystallisation to a urea melt for conversion to a solid prilled or granular product for use as a fertiliser or technical grade. In some cases, urea is produced solely for melamine production.

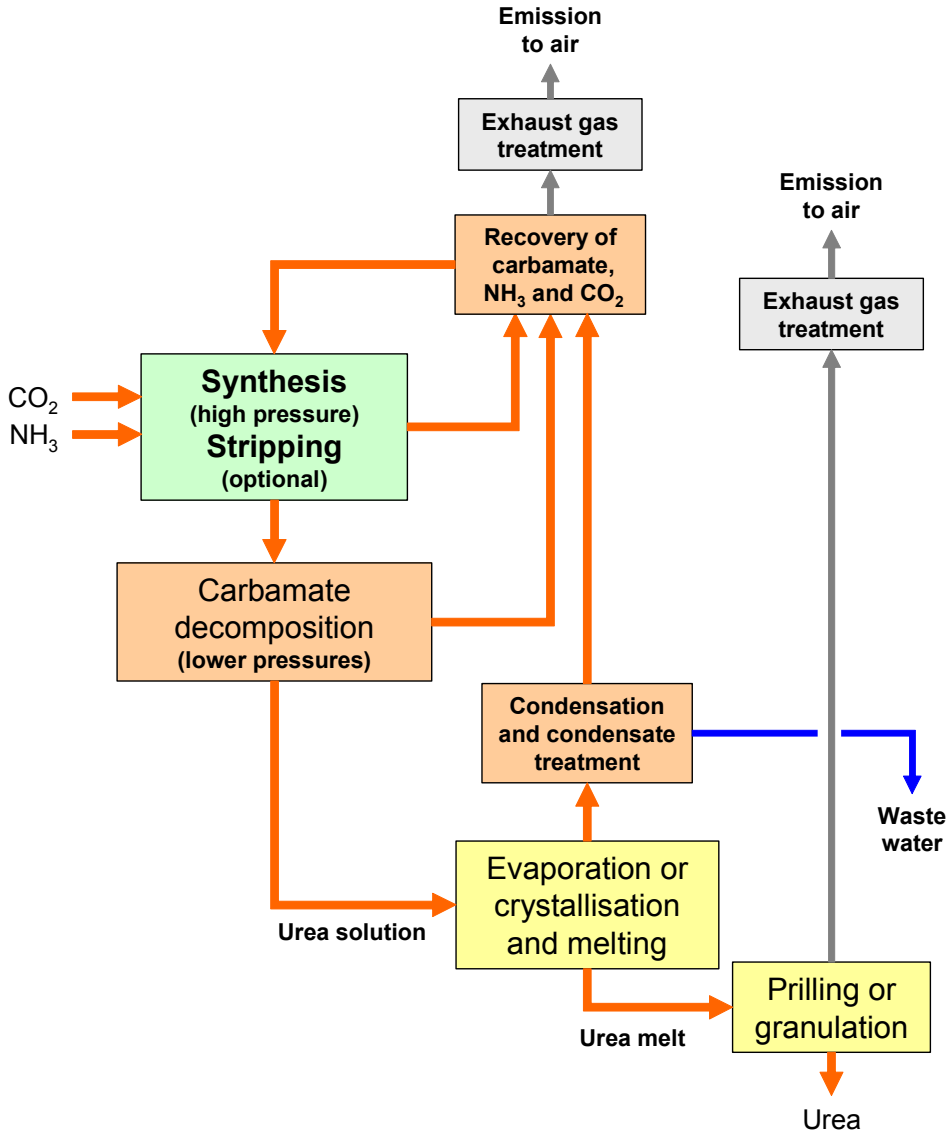

Figure 8.1: Overview of the production of urea by total recycling processes
Figure based on [52, infoMil, 2001]

8.2.1.1 Particle formation

Prilling

Concentrated urea melt is sprayed through a spinning bucket or prill head located at the top of a tower. The liquid droplets ("prills") that are formed fall through the tower and are cooled against a countercurrent flow of air which allows the prills to solidify. Further cooling is usually required. With some plant designs, the cooler is incorporated into the base of the prill tower; in others, a cooling takes place after the prills have been removed from the tower.

Granulation

Various types of granulation equipment are available, including drum granulators, pan granulators and fluidised bed granulators. The basic principle of the process involves the spraying of concentrated melt onto recycled seed particles circulating in the granulator. An increase in granule size and drying of the product take place simultaneously. Air passing through the granulator solidifies the melt deposited on the seed material. All commercial processes are characterised by product recycling. After the formation of the granules, it may be necessary to dry and/or to cool the product.

8.2.2 UAN

For production of UAN using the partial recycle CO_2 stripping process, see Section 8.4.14.

Continuous and batch type processes are used for the production of UAN. In both processes concentrated urea and ammonium nitrate solutions are measured, mixed and then cooled. Figure 8.2 gives an overview.

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.

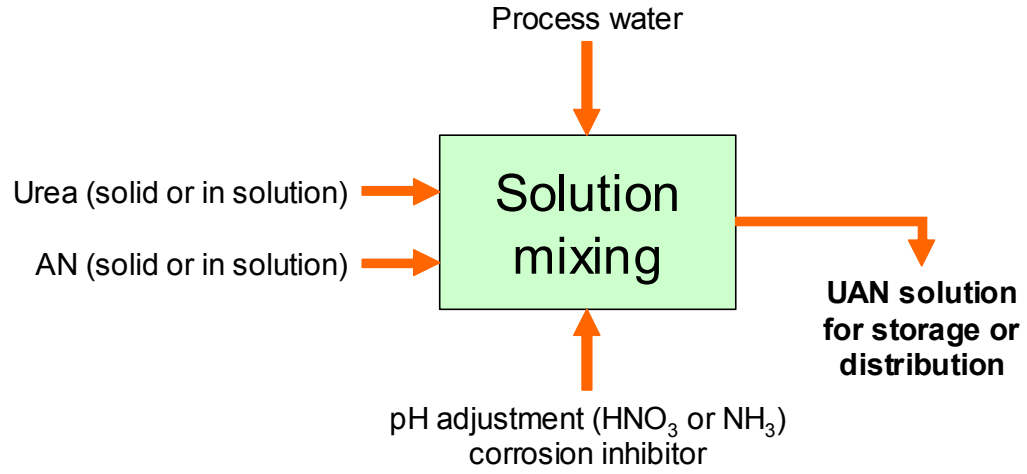

Figure 8.2: Overview of the production of UAN solution
[128, EFMA, 2000]

8.3 Current emission and consumption levels

Consumption of	Per tonne urea	Unit	Remarks		Reference
NH_3	567	kg	Snamprogetti NH_3 stripping		[9, Austrian UBA, 2002]
	570		Other stripping processes		
	567		CO_2 stripping		[52, infoMil, 2001]
	567		NH_3 stripping		
	570		IDR process		
	570		ACES process		
	564		Specification for new plants		[130, Uhde, 2004]
	580 – 600		Typical figures for conventional processes		[124, Stamicarbon, 2004]
CO_2	735	kg	Snamprogetti NH_3 stripping		[9, Austrian UBA, 2002]
	740 – 750		Other stripping processes		
	730		Specification for new plants		[130, Uhde, 2004]
	733		CO_2 stripping		[52, infoMil, 2001]
	735		NH_3 stripping		
	740		ACES process		
	740		IDR process		

Table 8.3: Reported raw material consumption levels for the production of urea

Consumption of	Per tonne urea	Unit	Remarks		Reference
Cooling water	80	m^3	Snamprogetti NH_3 stripping		[9, Austrian UBA, 2002]
	60 – 70	m^3	CO_2 stripping process		
	75 – 80	m^3	NH_3 stripping process, CO_2 compression with steam turbine		[52, infoMil, 2001]
	60	m^3	CO_2 stripping process, CO_2 compression with electromotor		
	70	m^3	CO_2 stripping process, CO_2 compression with steam turbine		
	60 – 80	m^3	ACES process, CO_2 compression with steam turbine		
	51	m^3	ACES process, CO_2 compression with electromotor		
	60	m^3	IDR process, CO_2 compression with electromotor		
	75	m^3	IDR process, CO_2 compression with steam turbine		
	70	m^3	Stamicarbon CO_2 stripping process		SKW Piesteritz [121, German UBA, 2001]
	75	m^3	Snamprogetti NH_3 stripping process		Yara, Brunsbüttel [121, German UBA, 2001]
	100	m^3	Typical figures for conventional processes		[124, Stamicarbon, 2004]

Table 8.4: Reported cooling water consumption levels for the production of urea

Consumption of	Per tonne urea	Unit	Remarks		Reference
Steam	0.76	tonne	Snamprogetti NH_3 stripping	At 108 bar	[9, Austrian UBA, 2002]
	0.77 – 0.92	tonne	CO_2 stripping process, CO_2 compression with steam turbine	At 120 bar	[52, infoMil, 2001]
	0.77	tonne	CO_2 stripping process, CO_2 compression with steam turbine	At 120 bar	[9, Austrian UBA, 2002]
	0.8	tonne	CO_2 stripping process, CO_2 compression with electromotor	At 24 bar	[9, Austrian UBA, 2002]
	0.8	tonne	CO_2 stripping process, CO_2 compression with electromotor	At 24 bar	[52, infoMil, 2001]
	1.3	tonne	Conventional total recycle process (Toyo)		BASF, Ludwigshafen [121, German UBA, 2001]
	1.6 – 1.8	tonne	Typical figures for conventional processes	At 13 bar	[124, Stamicarbon, 2004]
	0.92	tonne	Stamicarbon CO_2 stripping process	At 20 – 25 bar	SKW Piesteritz [121, German UBA, 2001]
	0.85	tonne	Snamprogetti NH_3 stripping process		Yara, Brunsbüttel [121, German UBA, 2001]
	0.76 – 0.95	tonne	NH_3 stripping process, CO_2 compression with steam turbine	At 108 bar	[52, infoMil, 2001]
	0.7 – 0.8	tonne	ACES process, CO_2 compression with steam turbine	At 98 bar	
	0.57	tonne	ACES process, CO_2 compression with electromotor	At 24.5 bar	
	0.84	tonne	IDR process, CO_2 compression with electromotor	At 24 bar	
	0.6	tonne	IDR process, CO_2 compression with steam turbine	At 105 bar	

Table 8.5: Reported steam consumption levels for the production of urea

Per tonne urea	Unit	Remarks	Reference
21.1	kWh	Snamprogetti NH_3 stripping	[9, Austrian UBA, 2002]
21 – 23		Snamprogetti NH_3 stripping, excluding CO_2 compression	Yara, Brunsbüttel [121, German UBA, 2001]
115		Snamprogetti NH_3 stripping, including CO_2 compression	
21.1		CO_2 stripping process, CO_2 compression with steam turbine	[9, Austrian UBA, 2002]
110		CO_2 stripping process, CO_2 compression with electromotor	[9, Austrian UBA, 2002]
70		Conventional total recycle process (Toyo), the figure does not include electricity for CO_2 compression	BASF, Ludwigshafen [121, German UBA, 2001]
43		Stamicarbon CO_2 stripping process. The figure does not include electricity for CO_2 compression. The figure includes 23 kWh/tonne for the granulation	SKW Piesteritz [121, German UBA, 2001]
76 – 82	MJ	NH_3 stripping process, CO_2 compression with steam turbine	[52, infoMil, 2001]
54		CO_2 stripping process, CO_2 compression with steam turbine	
396		CO_2 stripping process, CO_2 compression with electromotor	
54 – 108		ACES process, CO_2 compression with steam turbine	
436		ACES process, CO_2 compression with electromotor	
425		IDR process, CO_2 compression with electromotor	
79		IDR process, CO_2 compression with steam turbine	

Table 8.6: Reported electrical power consumption levels for the production of urea

Per tonne urea in GJ	Remarks	Reference
2.7	Conventional total recycle process (Toyo), electricity for CO_2 compression not included	[121, German UBA, 2001]
1.9	Stamicarbon CO_2 stripping process, electricity for CO_2 compression not included	
1.7	Snamprogetti NH_3 stripping, electricity for CO_2 compression not included	
3.3	Modern total recycling stripping process, conversion of ammonia to solid urea	[107, Kongshaug, 1998]
4.1	Average requirements for European plants	
4.6	Best plants 30 years ago	
3.1	Specification for new plants (steam + electricity), including CO_2 compression	[130, Uhde, 2004]
2.7	Stamicarbon CO_2 stripping process (steam + electricity)	SKW Piesteritz
2.9	NH_3 stripping, prilling, CO_2 compression with steam turbine, prilling	[126, Snamprogetti, 1999]
2.0	NH_3 stripping, prilling, CO_2 compression with electromotor, prilling	[126, Snamprogetti, 1999]
3.1	NH_3 stripping, prilling, CO_2 compression with steam turbine, granulation	[126, Snamprogetti, 1999]
1.9	NH_3 stripping, prilling, CO_2 compression with electromotor, granulation	[126, Snamprogetti, 1999]
5.5	Existing installation, conventional total recycling, crystallisation, natural draft prilling, compression with steam turbine	[122, Toyo, 2002]
3.8	Revamp study, CO_2 stripping, vacuum evaporation, prilling with fan, process condensate treatment	
3.9	Revamp study, CO_2 stripping, vacuum evaporation, granulation, process condensate treatment	
3.0	CO_2 stripping (ACES21), spout fluid bed granulation, CO_2/NH_3/carbamate pumps driven by steam turbine	[123, Toyo, 2003]
2.7	CO_2 stripping (ACES21), spout fluid bed granulation, only the CO_2 pump driven by steam turbine	

Table 8.7: Reported total energy consumption levels for the production of urea (sum of steam and electricity import and exports)

Waste water per tonne urea						Remark		Reference
m^3	COD	Urea-N	NO_3-N	NH_3-N	N_{total}			
	g							
						No waste water discharge	Conventional total recycle process. Process water remains in product urea solution for downstream glue production, waste water from vacuum processes are used in a cooling tower	BASF, Ludwigshafen [121, German UBA, 2001]
0.46	50				100	To biological waste water treatment	Stamicarbon CO_2 stripping process. The volume includes 0.3 tonne process water (loaded with 6 % NH_3, 4 % CO_2 and 1 % urea) from the reaction, and additionally rinsing/cleaning water and steam	SKW Piesteritz [121, German UBA, 2001]
0.65	48					To process water treatment plant	Snamprogetti NH_3 stripping. The process water contains about 0.08 kg NH_3/tonne urea and 0.06 kg urea/tonne urea	Yara, Brunsbüttel [121, German UBA, 2001]
		75	341	120		To process water treatment plant	Part of the process water is used as cooling water, the remainder and the cooling water is forwarded to waste water treatment. Levels include cooling and scrubbing water	DSM Geleen [52, infoMil, 2001]
		3.7 – 5.2	51 – 102	6 – 8.4		After treatment		
			95.7		96.4 [x]	To biological treatment	Levels include cooling and scrubbing water.	Yara Sluiskil 5 + 6 [52, infoMil, 2001]
			<500		338 [x]		Levels include cooling and scrubbing water.	Kemira Rozenburg [52, infoMil, 2001]
	12			51	131 [x]	Direct discharge	Total volume of 40000 m^3/day, including cooling water. Scrubbing solution is partially recycled to other fertiliser production. Levels converted from kg/tonne N by division with 4.29	AMI, Linz [9, Austrian UBA, 2002]
[x] Kjeldahl-N								

Table 8.8: Reported specific waste water levels expressed per tonne of urea

Process water after treatment ppm w/w		Utilisation	Remark	Reference
Urea	**NH_3**			
		Boiler feed-water	The reaction produces 0.3 tonnes process water per tonne urea. Additional sources may increase the level to a final quantity of about 0.5 m^3/tonne urea	[128, EFMA, 2000]
1	1		Typical effluent values achieved with 1st desorber/hydroliser/2nd desorber/reflux condenser	[125, Stamicarbon, 2003]
<5	<5	None	Performance figures in recent plants, achieved with 1st desorber/hydroliser/2nd desorber/reflux condenser	[125, Stamicarbon, 2003]
<1	1.2	Cooling water		
<1	<1	Boiler feed-water		
<1	<1	Boiler feed-water		
<1	<1	Boiler feed-water		
1	1	E.g. boiler feed-water		[126, Snamprogetti, 1999]
1	1		Achievable with condensate stripper/urea hydroliser system	[127, Toyo, 2006]
	66	None	Ammonia recovery by distillation, level before treatment: 37000 ppm w/w	AMI, Linz [9, Austrian UBA, 2002]
<10	<10	Partially for cooling	Desorption/hydrolisation. The water is forwarded to biological treatment	SKW Piesteritz
3 – 5	3 – 5	E.g. as boiler feed-water	Achievable with a stripping/hydrolysis system	[128, EFMA, 2000]
1	5		Achievable with a distillation/hydrolysis system	
1	5		Achievable with desorber/hydrolysis/desorber system	
1	1		Specification for new plants	[130, Uhde, 2004]

Table 8.9: Reported concentration levels in treated process condensates

Pollutant	Source	g/tonne urea	mg/m^3	Remarks	Reference
Dust	Prilling	270	15 – 23	Wet scrubbing, 300000 – 350000 Nm^3/hour. Raw gas concentrations of 60 – 130 mg/Nm^3	AMI, Linz [9, Austrian UBA, 2002]
	Central dedusting unit		18.8 – 20		
	Prilling	500 – 2200	35 – 125	No treatment	[128, EFMA, 2000]
	Granulation	100 – 550	30 – 75	Scrubbing	
	Prilling or granulation		30	Packed bed scrubber	[127, Toyo, 2006]
	Prilling		25 – 30	Scrubber	[129, Stamicarbon, 2006]
	Urea drying	<20	<20	Except from prilling, all exhaust gases are treated in a scrubber (slightly acidic)	SKW Piesteritz
	Prilling	1500/1250	50/75		
	Granulation	200	up to 30		
	Urea drying (1+2)	30	20	Cyclone	BASF, Ludwigshafen [121, German UBA, 2001]
	Urea drying 3	30	20	Cyclone and scrubbers	
	Prilling	1000 – 1300	55	Scrubber	
	Prilling	510	40	No treatment	Yara, Brunsbüttel [121, German UBA, 2001]
	Granulation		30	Specification for new plants	[130, Uhde, 2004]

* Table continues on the next page.

Pollutant	Source	g/tonne urea	mg/m^3	Remarks	Reference
NH_3	Prilling	500 – 2700	35 – 245	No treatment	[128, EFMA, 2000]
	Granulation	200 – 700	60 – 250	Scrubbing	
	Granulation		30	Specification for new plants, including acidic scrubbing	[130, Uhde, 2004]
	Process vent	2.5	<700	Scrubbing with water, 420 m^3/hour	DSM Geleen [52, infoMil, 2001]
	Prilling	60	3 – 9	Wet scrubbing, 300000 – 350000 Nm^3/hour. Raw gas concentrations of 70 – 140 mg/Nm^3	AMI, Linz [9, Austrian UBA, 2002]
	Central dedusting unit		6.8 – 19.2		
	Synthesis section		1.5 – 1.73	Snamprogetti NH_3 stripping process, scrubbing. CH_4: 22.9 mg/Nm^3, CO: 2.5 mg/Nm^3	
	Emergency valve system		1.7 – 3.7		
	Synthesis section	70	2000	Stamicarbon CO_2 stripping, low pressure scrubber	SKW Piesteritz
	Urea drying	<20	<20	Except from prilling, all exhaust gases are treated in a scrubber (slightly acidic)	
	Prilling	1600	60		
	Granulation	300	10 – 20		
	Urea drying (1+2)	90	60	Cyclone	BASF, Ludwigshafen [121, German UBA, 2001]
	Urea drying 3	55	35	Cyclone and scrubbers	
	Prilling	600 – 700	30	Scrubber	
	Carbamate decomposition	180	16700	Snamprogetti NH_3 stripping process, scrubber	Yara, Brunsbüttel [121, German UBA, 2001]
	Concentration	150	29300	Snamprogetti NH_3 stripping process, no treatment	
	Prilling	400	30	No treatment	

Table 8.10: Reported emission levels to air for the production of urea

Plant	Emission	Amount (tonne/year)	Measurement/estimation
DSM, Geleen	NH_3	<11	Estimation
YARA Sluiskil 5	NH_3	12.4	Estimation
	CO_2	15.2	Estimation
YARA Sluiskil 6	NH_3	11.6	Estimation
	CO_2	12.9	Estimation
Kemira Rozenburg	NH_3	10	Estimation

Table 8.11: Diffuse emissions to atmosphere from Dutch plants
[52, infoMil, 2001]

Raw material	Per tonne 30 % UAN solution
Urea	327.7 kg
AN	425.7 kg
NH_3	0.3 kg
Corrosion inhibitor	1.4 kg
Water	244.9 kg
Steam and electricity	10 – 11 kWh
The urea used has a nitrogen content of 46 %, a minimum concentration of 75 % and a pH of 9 – 10. The AN has a nitrogen content of 33 – 34 %, a minimum concentration of 85 % and a pH of 4 – 5. The corrosion inhibitor is used for the protection of carbon steel storage tanks, if necessary. HNO_3 or NH_3 gas can be needed for pH adjustment of the final solution. The condensate containing nitrogen from AN or urea plants can be used as solvent in this process. Steam and electricity use are a function of the type of the raw material (solid or solution) and the ambient temperature	

Table 8.12: Raw material and utility consumption for the production of UAN
[128, EFMA, 2000]

8.4 Techniques to consider in the determination of BAT

- for product cooling, see Section 7.4.5
- concerning granulation recycle, see Sections 7.4.7.

8.4.1 Conventional total recycling process

Description

Table 8.13 gives an overview of a conventional total recycling process. A key feature of this process is the separation of NH_3 and CO_2 from the reaction solution by stepwise pressure reduction (decomposers) and recycling into the reactor (as carbamate or NH_3).

In order to minimise effluent volumes, aqueous NH_3 solutions of various origins are recycled into the reactor. This decreases the conversion to urea in the reactor due to the higher water content. To keep the overall yield, carbamate and NH_3 recycling are extended, requiring additional energy.

Process sequence	Steps and conditions	
Reactor	NH_3/CO_2 ratio	4:1
	Conversion	65 – 67 % of CO_2 input
	Pressure	200 bar
Carbamate decomposition (heat distillation)	Decomposer 1	at 16 – 20 bar
	Decomposer 2	at 3 bar
	Decomposer 3	at 1 bar
Carbamate recycling	Absorption/rectification	
NH_3 recycling	Condensation, NH_3 buffer	
Purge gas treatment (from decomposition)	Scrubbing with H_2O, the liquor (NH_3 solution) is recycled to the process	
Solidification and finishing	Vacuum crystallisation, condensate treatment (stripping)	
	Centrifugation	
	Drying, (wet) cyclones, scrubbing for exhaust gas treatment	
	Melting	
	Prilling, scrubber for exhaust gas treatment	

Table 8.13: Example for a conventional total recycling process [121, German UBA, 2001], BASF, Ludwigshafen

Achieved environmental benefits

- enables almost complete raw material recovery.

Cross-media effects

Higher energy consumption in comparison with newer (stripping) processes (see also Table 8.5).

Operational data

See Table 8.13.

Applicability

Generally applicable. Conventional total recycling plants were built until the early 1990s. Modern plants are designed with stripping technology and show a more favourable performance.

Economics

No information provided.

Driving force for implementation

Most economic setup at that time.

References to literature and example plants

[9, Austrian UBA, 2002, 52, infoMil, 2001, 121, German UBA, 2001, 122, Toyo, 2002, 123, Toyo, 2003, 128, EFMA, 2000], BASF, Ludwigshafen (first commissioned in 1968, extended 1979), Achema, Lithuania

8.4.2 CO_2 stripping process

Description

Table 8.14 gives an overview of a total recycling CO_2 stripping process. A key feature of this technology is the removal of most of the residual carbamate and NH_3 from the reaction solution by stripping with CO_2 at high pressure. In comparison with conventional processes, this saves considerable amounts of energy for decomposition at low pressures and recompression for recycling to the process.

Process sequence	Steps and conditions	
Reactor	NH_3/CO_2 ratio	2.8, CO_2 is fed via the HP stripper
	Temperature	180 ºC
	Pressure	140 bar
Stripping with CO_2 and recycling at high pressure	HP stripper	
	HP condenser	
Purge gas (from reactor)	treated in HP scrubber, LP scrubber (4 bar), NH_3 solutions are recycled	
Carbamate decomposer (rectification)	Pressure	3 bar
Carbamate recycling	Condensation, exhaust gas treated with scrubbing	
NH_3 recycling	Condensation, NH_3 buffer, NH_3 solution is recycled	
Solidification and finishing	Vacuum cystallisation, condensate treatment (desorber/hydroliser/desorber)	
	Centrifugation	
	Drying, cyclone, acidic scrubbing for exhaust gas treatment	
	Melting	
	Prilling or granulation	

Table 8.14: Example for a total recycling CO_2 stripping process
[121, German UBA, 2001]

Achieved environmental benefits

- enables almost complete raw material recovery
- energy savings in comparison with conventional processes.

Cross-media effects

None believed likely in comparison with other urea production processes.

Operational data

See Table 8.14.

Applicability

Generally applicable. CO_2 stripping technology is nowadays the most frequent plant type for urea production.

Economics

No information provided.

Driving force for implementation

Improved performance in comparison to conventional total recycling processes.

References to literature and example plants

[9, Austrian UBA, 2002, 52, infoMil, 2001, 121, German UBA, 2001, 124, Stamicarbon, 2004, 125, Stamicarbon, 2003, 128, EFMA, 2000], SKW, Piesteritz

8.4.3 NH_3 stripping process

Description

Table 8.15 gives an overview of a total recycling NH_3 stripping process. Key feature of this technology is the removal of most of the residual carbamate from the reaction solution by self stripping with NH_3 at high pressure. In comparison with conventional processes, this saves considerable amounts of energy for decomposition at low pressures and recompression for recycling to the process.

Process sequence	Steps and conditions	
Reactor	NH_3/CO_2 ratio	3.5
	Temperature	170 ºC
	Pressure	150 bar
Stripping with NH_3 and recycle at high pressure	HP stripper (NH_3 feed via the stripper or self stripping)	
	HP condenser	
Carbamate decomposition	Pre-decomposer	
	Decomposer 1	17 bar
	Decomposer 2	4.5 bar
Carbamate recycling	Condensation	
NH_3 recycling	Condensation	
Purge gas (from decomposition)	treated in 2 stage scrubber, NH_3 solutions are recycled	
Solidification	Vacuum decomposer	Condensate treatment (desorption, hydrolisation with 25 bar steam, hydrolisation with 70 bar steam)
	Evaporation	
	Prilling	

Table 8.15: Example for a total recycling NH_3 stripping process
[121, German UBA, 2001]

Achieved environmental benefits

- enables almost complete raw material recovery
- energy savings in comparison with conventional processes.

Cross-media effects

None believed likely in comparison with other urea production processes.

Operational data

See Table 8.14.

Applicability

Generally applicable. NH_3 stripping technology is a frequent plant type for urea production.

Economics

No information provided.

Driving force for implementation

Improved performance in comparison to conventional total recycling processes.

References to literature and example plants

[9, Austrian UBA, 2002, 52, infoMil, 2001, 121, German UBA, 2001, 126, Snamprogetti, 1999, 128, EFMA, 2000], Yara, Brunsbüttel; AMI, Linz

8.4.4 Isobaric double recycling process (IDR)

Description

In this process, the urea synthesis takes place at 180 – 200 bar and 185 – 190 °C. The NH_3:CO_2 ratio is approximately 3.5 – 4, giving approximately 70 % CO_2 conversion per pass.

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 in the first stripper, with the remaining NH_3 being removed in the second stripper using CO_2 as the 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 carbamate condenser. The remainder goes directly to the reactor to control the temperature. 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 medium 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 three successive distillers and heated with medium pressure steam and low pressure recovered steam. After this, the vapours are condensed to carbamate solution and recycled back into 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.

Achieved environmental benefits

- enables almost complete raw material recovery
- energy savings in comparison with conventional processes.

Cross-media effects

None believed likely in comparison with other urea production processes.

Operational data

See description.

Applicability

Generally applicable.

Economics

No information provided.

Driving force for implementation

Improved performance in comparison to conventional total recycling processes.

References to literature and example plants

[52, infoMil, 2001, 128, EFMA, 2000], Yara, Ferrara, Zaklady Azotowe Pulawy, Pulawy.

8.4.5 Safe NH_3 washing from inerts

Description

A special washing method was developed in order to remove NH_3 from the inert purge gas stream arising from the urea synthesis section of the plant under safe conditions. This process consists of washing the inerts with water after the addition of a quantity of flammable gas, e.g. natural gas, in such an amount, that the composition is kept safely beyond the explosion limits. The washed inerts are sent to a burner together with the natural gas.

Achieved environmental benefits

- reduction of NH_3 emissions
- recovery of NH_3
- recovery of heat from H_2.

Cross-media effects

None believed likely.

Operational data

No specific information provided.

Applicability

The applicability depends on:

- the availability on site of flammable gas at the right pressure
- the availability of the NH_3 recovery system
- the possibility of using the resulting gas stream as a fuel, e.g. for a boiler.

Economics

Cost benefits can be assumed.

Driving force for implementation

Reduction of NH_3 emission and energy recovery from the inert gas.

References to literature and example plants

YARA, Ferrara.

8.4.6 Redirecting fines to the concentrated urea solution

Description

When granulation is applied as a finishing technique, oversized and undersized products are recycled to the granulator and form the nuclei of the granules. Dust is often separated after the granulator and also redirected to the installation, where it is taken along with the fluidisation air to the scrubber and ends up in a dilute solution. This solution is concentrated due to evaporation. However, it is also possible to *redirect the dust to concentrated solution instead* to the granulator [52, infoMil, 2001].

Achieved environmental benefits

Energy savings.

Cross-media effects

None believed likely.

Operational data

No specific information provided.

Applicability

Applicable to all urea plants where a solidification process is applied.

YARA Sluiskil, applied this technique in 1999, and saves about 32000 tonnes of steam per year [52, infoMil, 2001].

Economics

The project cost was EUR 143000, implemented in 1999.

Driving force for implementation

Cost benefits

References to literature and example plants

[52, infoMil, 2001],YARA, Sluiskil

8.4.7 Revamping conventional plants with stripping technology

Description

Revamping a conventional plant with stripping technology usually includes one or more of the following changes:

- increasing front end production capacity
- reducing utility consumption
- potential for reducing pollution
- reducing maintenance costs
- increasing the onstream factor.

Table 8.16 shows examples for revamping conventional plants with stripping technology and Table 8.17 shows study cases for a revamp project.

	Example 1	**Example 2**	
Capacity before / after revamp	1620 / 2460	1065 / 1750	tonnes/day
Energy saving	30 %		per tonne urea
Steam consumption before / after revamp		1.6 / 1	tonne/tonne urea
Cooling water consumption before / after revamp		100 / 73	m^3/tonne urea
CO_2 compression	New centrifugal compressor		
Installed HP stripper	Improved ACES	Stamicarbon	
Installed condenser	VSCC [x]	Pool condenser [x]	
HP NH_3 pumps	NH_3 recycling omitted, lower pumping requirements despite of increased capacity		
Synthesis reactor	Relined with 25Cr-22Ni-2Mo steel		
	Installation of baffles	Installation of trays	
	Continuous monitoring of the N/C ratio		
[x] see also Section 8.4.9			

Table 8.16: Examples for revamping conventional plants with stripping technology [123, Toyo, 2003, 124, Stamicarbon, 2004]

	Existing plant	Case 2 Revamp option	Case 3 Revamp option
Some features	Conventional, crystallisation, natural draft prilling	CO_2 stripping, vacuum evaporation, prilling with fan, process condensate treatment	CO_2 stripping, vacuum evaporation, granulation, process condensate treatment
Energy consumption in GJ/tonne urea			
Steam	4.6	3.1	3.1
Electricity	0.9	0.7	0.8
Total	5.5	3.8	3.9

Table 8.17: Studies on steam and electricity consumption for a revamp project [122, Toyo, 2002]

Achieved environmental benefits

- particular potential for reduction of steam consumption (see also Table 8.5)
- considerable potential for reduction of electrical energy consumption
- considerable potential for reduction of cooling water consumption.

Cross-media effects

None believed likely.

Operational data

No specific information provided.

Applicability

Generally applicable to existing conventional total recycling plants. Various technology suppliers claim compatibility of their stripping equipment with various existing systems.

Economics

High investment costs are paid back by considerable savings through

- increased capacity, assuming that this requires additional CO_2 compression capacity and additional capacity for product finishing
- lower utility requirements
- lower maintenance costs
- increased onstream factor.

Driving force for implementation

Increase production capacity.

References to literature and example plants

[52, infoMil, 2001, 123, Toyo, 2003, 124, Stamicarbon, 2004, 126, Snamprogetti, 1999]

- Sichuan Chemical Works Ltd revamped a Toyo TR-Ci to an improved ACES system in 2004
- PIC Kuwait revamped a conventional 1065 tonnes/day plant to a capacity of 1750 tonnes/day with CO_2 stripping technology and a pool condenser in 2004.

8.4.8 Heat integration in stripping plants

Description

Heat integration between the synthesis section and downstream sections reduces the energy requirement. MP steam is supplied to the synthesis to decompose and separate excess NH_3 and carbamate in the stripper. The stripped CO_2 and NH_3 gas mixture is sent to the carbamate condenser and the condensation heat is recovered as LP steam or by process to process heat exchange in the MP and LP decomposition sections, and the evaporation stage(s). Depending on the degree of integration, the urea plant exports LP steam.

See also Section 8.4.7 "Revamping conventional plants with stripping technology".

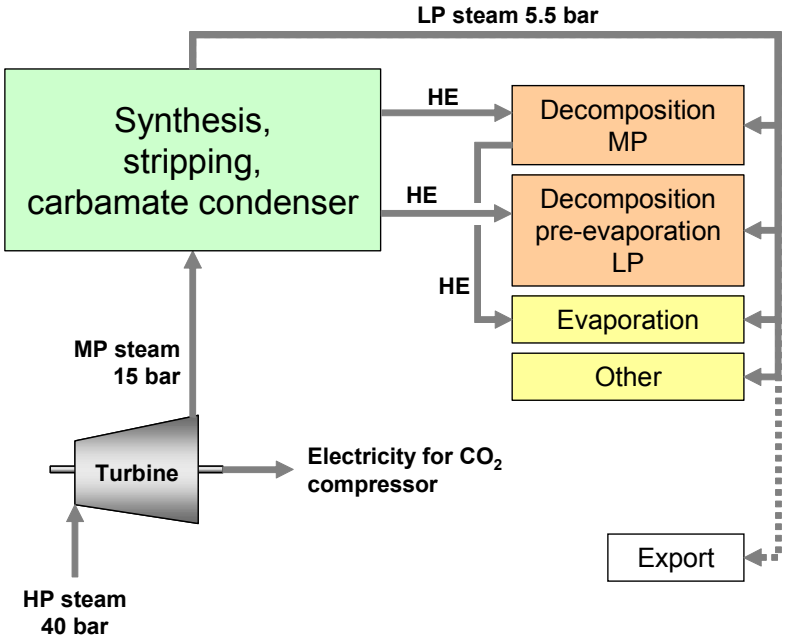

Figure 8.3: Example for the heat integration on a total recycling stripping plant
HE: process to process heat exchange
Based on [124, Stamicarbon, 2004]. Similar: [122, Toyo, 2002, 126, Snamprogetti, 1999]

Achieved environmental benefits

- reduced energy requirements.

In a modern total recycling process, conversion of ammonia to a solid urea requires 3.3 GJ/tonne urea. It is assumed that the average requirement for European plants is 4.1 GJ/tonne urea [107, Kongshaug, 1998].

Cross-media effects

None believed likely.

Operational data

No specific information provided.

Applicability

Generally applicable.

Economics

No specific information provided, but considerable savings are assumed.

Driving force for implementation

Reduces energy costs.

References to literature and example plants

[122, Toyo, 2002, 124, Stamicarbon, 2004, 126, Snamprogetti, 1999]

8.4.9 Combined condensation and reaction in one vessel

Description

Basically, with combined condensation and reaction in one vessel, two configurations are possible:

- stripper + combined condenser/pre-reactor + reactor (rather as revamp option)
- stripper + combined condenser/reactor (rather for new plants).

Pool reactor. 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 recycled 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 [52, infoMil, 2001, 124, Stamicarbon, 2004].

Pool condenser. 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 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 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 [52, infoMil, 2001, 124, Stamicarbon, 2004].

Vertical submerged carbamate condenser (VSCC/ACES21). The stripped gases from the stripper are led to a vertical submerged carbamate condenser, where NH_3 and CO_2 condense to form ammonium carbamate and urea on its shell side. The condensation heat is recovered to generate low pressure steam on the tube side. A packed bed for scrubbing is provided at the top of the carbamate condenser to absorb uncondensed NH_3 and CO_2 into recycled carbamate solution (coming from the medium pressure section). Urea is partly formed in the carbamate condenser and the reaction is completed in the reactor [122, Toyo, 2002, 123, Toyo, 2003].

Technical advantages of the combined condenser/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 combined condenser/pre-reactor are:

- the urea reactor volume is reduced, or the capacity of the reactor is increased accordingly
- less heat exchange area
- the horizontal arrangement offers a structural alternative
- less stress corrosion
- higher operational flexibility.

Achieved environmental benefits

- when a pool reactor is used, an ammonia emission in the synthesis phase of 2.5 g/tonne product (<700 mg/m^3) is achievable
- some potential for energy saving.

Operational data

No specific information provided.

Applicability

The combined condenser/reactor is applicable mainly for new plants. The installation of this type of reactor in an existing urea plant might not be economically viable. Combined condenser/pre-reactor systems are generally applicable.

Economics

No specific information provided, the installation of a combined condenser/reactor in an existing urea plant might not be economically viable. Generally, savings are expected through increased efficiency and lower utility consumption.

Driving force for implementation

Capacity increase of the reactor.

References to literature and example plants

[132, Stamicarbon, 2001], [52, infoMil, 2001], [122, Toyo, 2002], [123, Toyo, 2003], [124, Stamicarbon, 2004], [125, Stamicarbon, 2003], [127, Toyo, 2006], [129, Stamicarbon, 2006], [130, Uhde, 2004], [131, Toyo, 2002].

DSM Geleen (1998, 525 ktonnes/year): pool reactor
Karnaphulli Fertilisers Company, Bangladesh: pool condenser
P.T. Pupuk Kujang, Indonesia: ACES21
Sichuan Chemical Works, China: ACES21

8.4.10 Minimisation of NH_3 emissions from granulation

Description

The liquid urea feedstock to the solidification section, either as a melt or as a concentrated solution, contains some dissolved NH_3. This arises from residual traces of ammonium carbonates, urea decomposition products and the dimerisation to biuret. This residual NH_3 is stripped/flashed during the solidification process and is released along with cooling air to the air.

Gaseous formaldehyde, vaporised from a fine liquid mist injected into the hot air stream at the granulator vent, reacts preferentially with the stripped NH_3 to form HMTA (hexamethylene tetramine). 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 (in this example, process water condensate) and is recycled to the vacuum concentration section, where HMTA decomposes to NH_3 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. By absorption in the process water condensate, NH_3 is recycled to the urea synthesis section. The formaldehyde finally ends up in the product urea, where it is anyway used as a standard additive.

Achieved environmental benefits

- 50 % reduction in NH_3 emission.

Cross-media effects

None believed likely, if it is assumed that formaldehyde would have been used as a standard additive anyway.

Operational data

See description.

Applicability

Generally applicable.

Economics

No information provided.

Driving force for implementation

Reduced emission levels.

References to literature and example plants

[133, Hydro Fertilizer Technology, 2000], YARA, Sluiskil and Incitec, Brisbane

8.4.11 Treatment of exhaust gas from prilling/granulation

Description

In modern urea plants, the main pollution to the environment originates from the finishing section, prilling or granulation. In both cases, the load of pollutants (0.4 – 0.6 % of the total feed to the plant) outweighs the load from the wet section of the plant by at least one order of magnitude (about 0.005 – 0.05 % of the total feed). In finishing (be it prilling or granulation) a huge amount of air comes into contact with hot urea solution and solid urea, hence the exhaust gases are loaded with NH_3 and dust. With respect to exhaust gas treatment, a comparison of granulation and prilling yields the following results:

- for particular industrial downstream applications, urea prills might be preferred
- expensive treatment outweighs the main prilling advantage: low cost
- granulation requires less air
- dust from granulation is coarser, making dust removal easier.

The efficiencies for NH_3 removal depend mainly on the applied scrubbing medium (acidic or water scrubbing) and the number of absorption stages. The scrubbing liquor containing NH_3 and urea dust can be recycled to the urea process in the case of water scrubbing.

Source	Treatment	Achievable levels in mg/Nm^3		Reference
		Dust	NH_3	
Prilling	(no treatment)	60 – 130	70 – 140	b
	Acidic scrubbing, up to 350000 Nm^3/hour	15 – 23	3 – 9	b
	Scrubbing, 1 kWh/1000 Nm^3	25 – 30 [x]		a
		15	20 [xx]	f
	Water scrubbing	55	30	e
	Packed bed scrubber	30		d
Granulation		30	30 [xx]	c
	Packed bed scrubber	30		d
	Water scrubber, slightly acidic	up to 30	10 – 20	g
		15	20 [xx]	f

[x] lower levels are achievable, but connected with a rapid rise in pressure drop and power consumption
[xx] including acidic scrubbing
a [129, Stamicarbon, 2006]
b [9, Austrian UBA, 2002], average levels, the permit level for both is 30 mg/Nm^3, acidic scrubber
c [130, Uhde, 2004], process specifications
d [127, Toyo, 2006]
e [121, German UBA, 2001]
f [126, Snamprogetti, 1999]
g SKW Piesteritz

Table 8.18: Overview of the treatment of exhaust gases from urea finishing

Achieved environmental benefits

Reduced emissions to air. For achievable levels, see Table 8.18.

Cross-media effects

- water consumption
- recycling of more water to the urea synthesis section might negatively effect the conversion rate per pass, in consequence, energy consumption in subsequent decomposition and recompression might increase. This is relevant especially in conventional total recycling plants [121, German UBA, 2001]
- additional electrical power consumption.

Operational data

See description.

Applicability

Generally applicable.

The formation of urea nitrate has to be considered as a safety issue when using HNO_3 as a scrubbing medium [154, TWG on LVIC-AAF, 2006].

Available space or structural foundation limitations may inhibit the installation of a scrubbing facility of sufficient capacity on top of a urea prilling tower. A scrubber at ground level is usually excessively expensive.

Economics

Economics for the installation of a scrubbing system for prilling in 1994 [9, Austrian UBA, 2002]:

- investment: EUR 2900000 (on top of the prilling tower)
- total operating cost: EUR 110000 per year.

Driving force for implementation

Reduced emission levels.

References to literature and example plants

[9, Austrian UBA, 2002, 52, infoMil, 2001, 121, German UBA, 2001, 127, Toyo, 2006, 129, Stamicarbon, 2006]

BASF, Ludwigshafen; SKW Piesteritz, AMI, Linz

8.4.12 Process water treatment

Description

A 1000 tonnes/day urea plant generates approximately 500 m^3 process water per 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.

Figure 8.4 shows an example for a process water treatment. Heated process water is fed to the top of desorber 1, where NH_3 and CO_2 are removed by the gas flow from desorber 2 and the hydrolyser. The liquid leaving the bottom of desorber 1 is preheated and fed under pressure to the top of the hydrolyser. Steam 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 hydrolyser 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. A part of the separated liquid is pumped back to desorber 1 and the remainder is returned to the the urea process plant. Residual NH_3 in the separator off-gas is recovered in an atmospheric absorber and is also returned to the process.

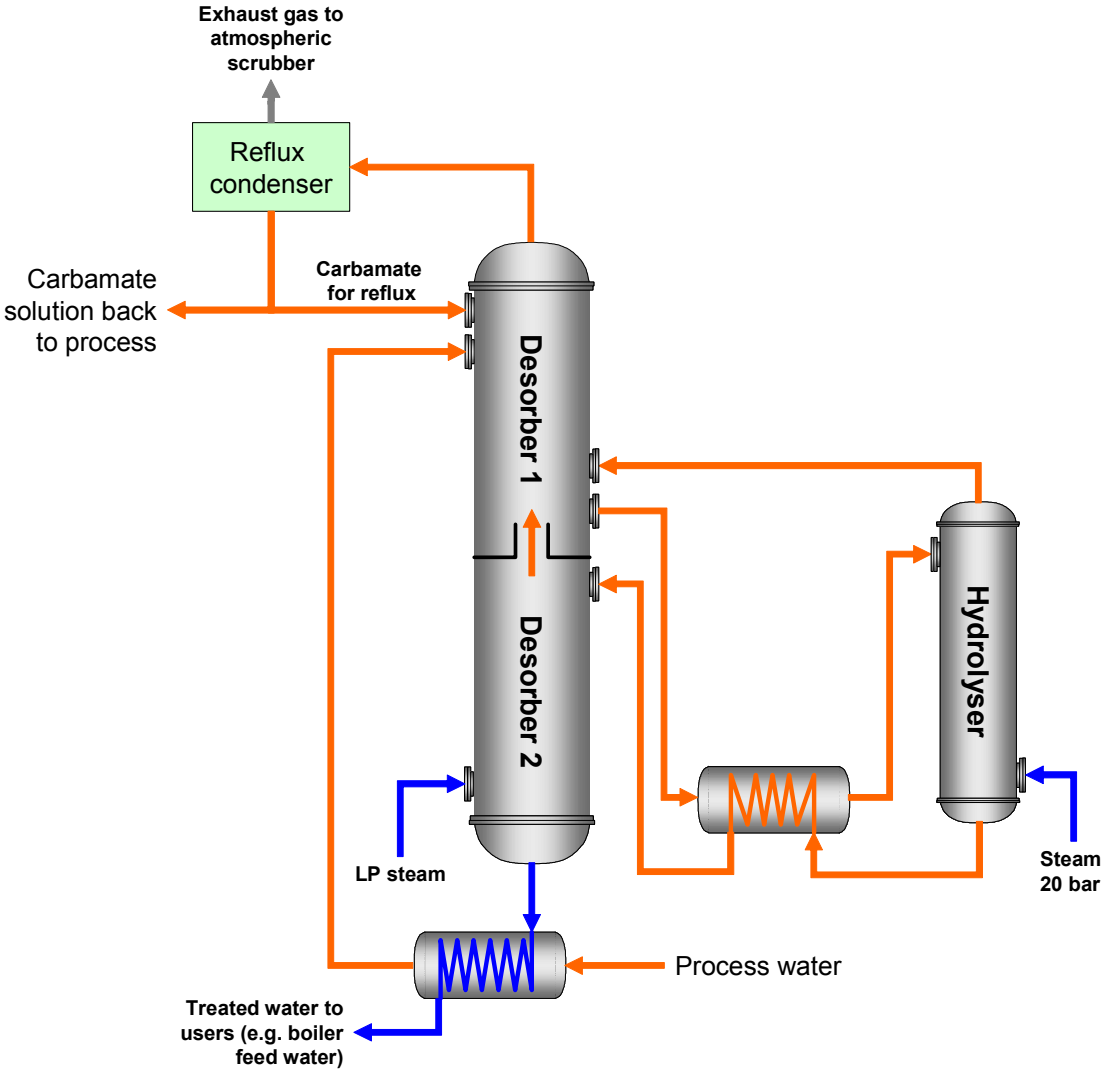

Figure 8.4: Example for a process water treatment
[52, infoMil, 2001, 125, Stamicarbon, 2003]

Other approaches to process water treatment include:

- distillation and hydrolysis [52, infoMil, 2001]
- stripping and hydrolysis [52, infoMil, 2001]
- CO_2/NH_3 removal (distillation, stripping) and subsequent biological waste water treatment [52, infoMil, 2001, 121, German UBA, 2001].

Achieved environmental benefits

- lower water consumption, if re-use of treated process water is possible
- lower emission levels to water (for achievable levels, see Table 8.9)
- recycling of NH_3 and CO_2 to the process.

Cross-media effects

- energy consumption.

Operational data

See description.

Applicability

Generally applicable. The combination with biological treatment is only applicable if the required C-source and neutralisation equivalents are available, e.g. in the case of joint treatment in a municipal waste water treatment plant [52, infoMil, 2001].

Economics

No specific information provided.

Driving force for implementation

Environmental benefits.

References to literature and example plants

[52, infoMil, 2001, 121, German UBA, 2001, 125, Stamicarbon, 2003, 126, Snamprogetti, 1999, 127, Toyo, 2006]

- [125, Stamicarbon, 2003] references 36 plants using countercurrent hydrolysation
- all urea plants in the Netherlands treat their process water and partially re-use the treated water
- Sichuan Chemical Works Ltd retrofitted a hydrolisation/desorption system
- SKW Piesteritz applies CO_2/NH_3 removal and biological waste water treatment
- BASF applies stripping and re-uses the treated water for the cooling tower.

8.4.13 Monitoring of key performance parameters

Description

Monitoring of key performance parameters creates the basis for improvement strategies and allows benchmarking. For an overview of the key performance parameters in urea production, see Table 8.19.

			Level	
Feedstocks	NH_3	Total		tonnes/day
		Pressure		bar
		Phase		liquid or gas
	CO_2	Total		tonnes/day
		Pressure		bar
		Phase		liquid or gas
	Other	Total		tonnes/day
		Specify		e.g. passivation air
		Conditions		e.g. pressure
Utilities consumed	Power			MWh/day
	Steam 1	Temperature		ºC
		Pressure		bar
		Amount		tonne/day
		Cond. return		%
	Steam 2	Temperature		ºC
		Pressure		bar
		Amount		tonne/day
		Cond. return		%
Utilities generated	Power			MWh/day
	Steam 4	Temperature		ºC
		Pressure		bar
		Amount		tonne/day
	Steam 5	Temperature		ºC
		Pressure		bar
		Amount		tonne/day
	Condensate	Temperature		ºC
		Amount		tonne/day
Products	Urea	Total		tonne/day
		Content		% w/w
		Temperature		ºC
	Water	Total		tonne/day
		NH_3		% w/w
		Temperature		ºC
	Other	Total		tonne/day
		Specify		% w/w
				ºC
Notes: The energy consumption figures do not include prilling and/or granulation				

Table 8.19: Example of a set of key performance parameters for the production of urea Benchmark questionnaire (Process Design Center)

Achieved environmental benefits

Key performance parameters creates the basis for improvement strategies.

Cross-media effects

None believed likely.

Operational data

None.

Applicability

Generally applicable.

Economics

No information provided.

Driving force for implementation

Benchmarking.

References to literature and example plants

AMI, Linz

8.4.14 UAN: partial recycle CO_2 stripping

Description

In the partial recycling CO_2 stripping process, 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.

In these plants, UAN production is an integral part of the fertiliser complex. UAN from scrubbing systems, sieving machines, etc. are fed to a central UAN system, where quality adjustments can be made.

Achieved environmental benefits

- considerable saving of utility consumption by omitting various urea finishing steps.

Cross-media effects

None believed likely.

Operational data

No specific information provided.

Applicability

Generally applicable.

Economics

No specific information provided, but cost savings can be assumed.

Driving force for implementation

Cost benefits from omitting various urea finishing steps.

References to literature and example plants

[9, Austrian UBA, 2002, 128, EFMA, 2000]

8.5 BAT for Urea and UAN

BAT is to apply the common BAT given in Section 1.5.

BAT for storage is to apply BAT given in [5, European Commission, 2005].

BAT is to improve environmental performance of the finishing section by one or a combination of the following techniques:

- apply plate bank product cooling (see Section 7.4.5)
- redirecting urea fines to the concentrated urea solution
- select proper size of screens and mills, e.g. roller or chain mills
- apply surge hoppers for granulation recycle control
- apply product size distribution measurement and control.

BAT is to optimise the total energy consumption for urea production by applying one or a combination of the following techniques:

- for existing stripping installations, continue applying stripping technology
- for new installations, applying total recycling stripping processes (see Sections 8.4.2, 8.4.3 and 8.4.4)
- for existing conventional total recycling installations, only in the case of a substantial urea plant capacity increase, upgrading to stripping technology (see Section 8.4.7)
- increase heat integration of stripping plants (see Section 8.4.8)
- applying combined condensation and reaction technology (see Section 8.4.9).

BAT is to treat all exhaust gases from the wet sections by scrubbing, taking into account the lower explosion limit and to recycle the resulting ammonia solutions to the process (e.g. see Section 8.4.5).

BAT is to reduce ammonia and dust emissions from prilling or granulation and to achieve ammonia emission levels of 3 – 35 mg/Nm^3, e.g. by scrubbing or optimising the operation conditions of prilling towers, and to re-use scrubber liquids on-site (see Section 7.4.11). If the scrubbing liquid can be re-used, then preferably by acidic scrubbing, if not, by water scrubbing. In optimising the emission levels to the values mentioned above, it is assumed that dust emission levels of 15 – 55 mg/Nm^3 are achieved, even, with water scrubbing.

Where process water with or without treatment is not re-used, BAT is to treat process water, e.g. by desorption and hydrolysation and to achieve the levels given in Table 8.20 (see Section 8.4.12). If in existing plants the levels cannot be achieved, it is BAT to apply subsequent biological waste water treatment.

		NH_3	**Urea**	
After process water treatment	New plants	1	1	ppm w/w
	Existing plants	<10	<5	

Table 8.20: BAT levels for the treatment of process water from urea production

BAT for production of urea is to monitor key performance parameters according to Section 8.4.13.

9 AN AND CAN

9.1 General information

Ammonium nitrate (AN) is used extensively as a nitrogenous fertiliser. The main marketable products are: hot solution of ammonium nitrate, ammonium nitrate containing 33.5 – 34.5 % nitrogen and calcium ammonium nitrate containing less than 28 % nitrogen. The world production of AN solution (ANS) is estimated to be 40 – 45 Mtonnes per year.

Calcium ammonium nitrate (CAN) is obtained from AN solution by mixing with dolomite, limestone or calcium carbonate and represents Western Europe's most applied fertiliser product. Plants for the production of AN and CAN generally produce from a few hundred tonnes per day up to 3600 tonnes per day.

Other products, similarly obtained by mixing are **magnesium ammonium nitrate, MAN** (addition of relatively large quantities of dolomite)**, ammonium sulphate nitrate, ASN** (addition of $(NH_4)_2SO_4$ or H_2SO_4) and NS fertilisers (generally based on gypsum).

Fertiliser products must comply with EU regulation 2003/2003/EC. AN and CAN fertilisers containing an excess of the specified thresholds of ammonium nitrate are classified as oxidising substances under the UN Transport Regulations.

Country	Company	Location	Year startup	Capacity in kt/yr	Comment
Austria	Agrolinz	Linz	1989	630	
Belgium	BASF	Antwerp	1990	650	
Czech Republic	Lovochemie	Lovosice	1991	415	
France	Grande Paroisse	Mazingarbe	1971	250	
Germany	Yara	Rostock	1985	633	Line 1
		Rostock	1985	633	Line 2
Lithuania	Achema	Jonava	2003	415	Status unknown
The Netherlands	DSM	Geleen	1979	1150	
			1993		
Poland	Anwil	Wloclawek	2000	500	
	Zaklady Azotowe	Kedzierzyn	1987	616	
	Zaklady Azotowe	Tarnow	1965	360	
Portugal	Adubos	Alverca	1961	290	
Slovakia	Chemko Strazske	Straske	1997	75	
	Duslo	Sala Nad Vahom	1976	500	
Spain	Fertiberia	Avilés	1970	250	
Switzerland	Lonza	Visp	1982	120	Number of plants and status unknown

Table 9.1: CAN production plants in the European Union as of July 2006 [154, TWG on LVIC-AAF, 2006]

Country	Company	Location	Year startup	Capacity in kt/y	Comment
Belgium	BASF	Antwerp	1980	300	
	Kemira GrowHow	Tertre	1990	900	
France	Grande Paroisse	Grandpuits	1970	300	
		Rouen	1989	550	
		Mazingarbe		150	Technical
	PEC RHIN	Ottmarsheim	1970	330	
	Yara	Ambès	1990	500	
		Montoir	1972	260	
		Pardies	1990	120	Technical
Germany	Yara	Rostock	1985	65	Technical
Greece	PFI	Kavala	1982	300	
Hungary	Nitrogenmuvek	Petfuerdoe	1975	479	
			1991	200	
Italy	Yara	Ravenna	1970	500	
Lithuania	Achema	Jonava	1972	550	Status unknown
The Netherlands	DSM	IJmuiden	1948	550	
			1997		
	Yara	Sluiskil	1983	550	
			1989	1100	
Poland	Anwil	Wloclawek	2000	353	
	Zaklady Azotowe	Pulawy	1968	1100	
Spain	Fertiberia	Luchana	1974	300	Shutdown June 2006
		Puertollano	1959	215	Revamped 1980
		Sagunto	1988	500	
Sweden	Dyno	Ljungaverk		44	Technical
	Yara	Koeping	1991	170	Technical
UK	Kemira GrowHow	Ince	1971	400	Prilling
	Terra	Billingham	1979	500	
		Severnside	1965	500	

Table 9.2: AN/CAN production plants in the European Union as of July 2006 [154, TWG on LVIC-AAF, 2006]

9.2 Applied processes and techniques

9.2.1 Overview

AN (NH_4NO_3) is produced by neutralising 50 – 70 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 three main operations: neutralisation, evaporation and solidification (prilling or granulation).

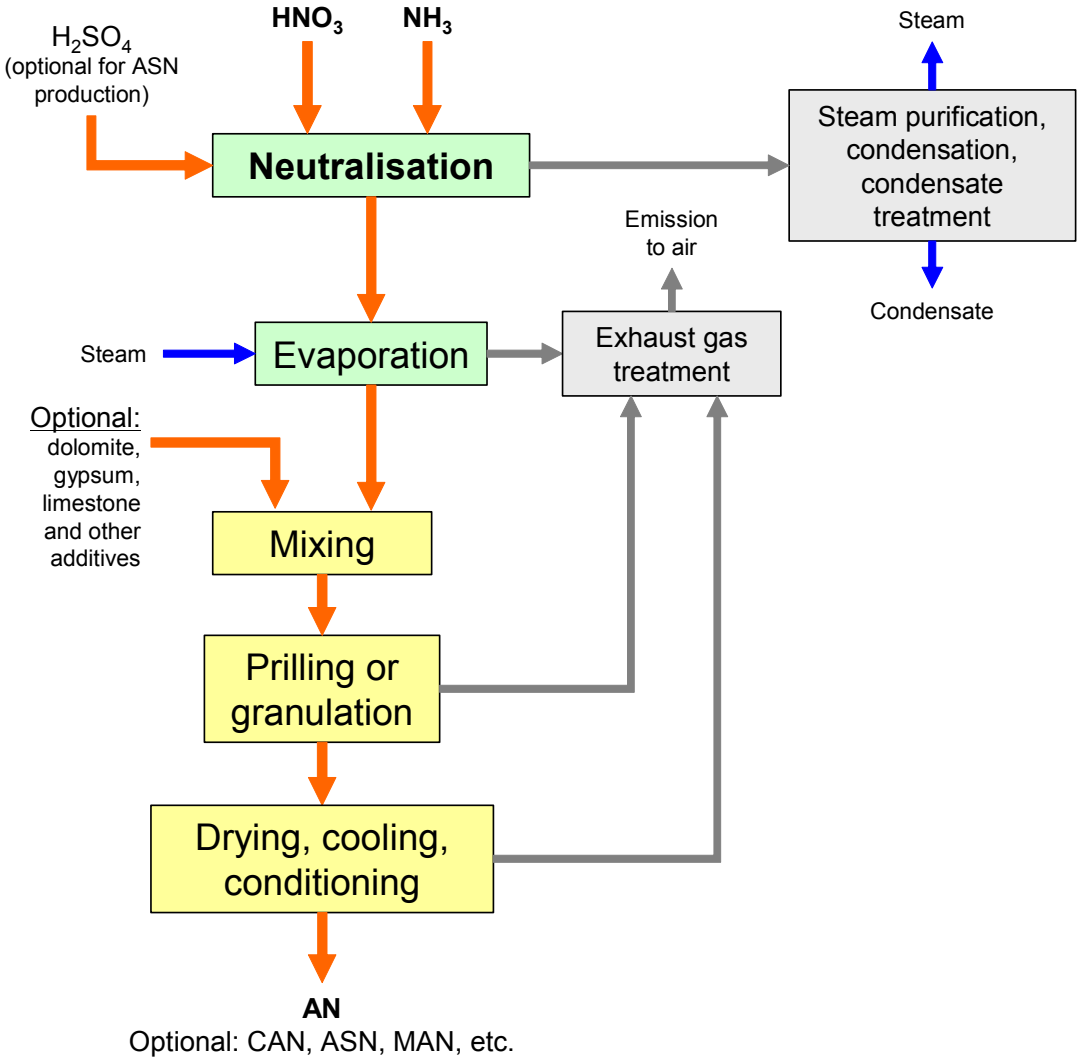

Figure 9.1: Overview of the production of AN and related products
This figure is based on [52, infoMil, 2001] and descriptions in [148, EFMA, 2000]

9.2.2 Neutralisation

The exothermic neutralisation of HNO_3 with NH_3 gas produces ANS (ammonium nitrate solution) and steam. The HNO_3 is normally preheated in corrosion-resistant equipment, particularly if the concentration of nitric acid is at the lower end of the 50 – 70 % range. Preheating using steam or hot condensate from the AN 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 HNO_3 and the concentration of AN 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. Pressure, temperature and concentrations in most neutralisers are linked by the boiling point characteristics of the AN solutions, with only two of these variables being independent. As an example, when operating a neutraliser at 4 bar and controlling the ANS at 76 % w/w, the temperature is 180 ºC.

For safety reasons, the temperature in the neutraliser has to be limited. To achieve this, a part of the condensed steam may be recycled back to the neutraliser. Alternatively this may be achieved by limiting the acid strength led to the neutraliser. The same temperature would be achieved by feeding the neutraliser with a 55 % HNO_3. Hence, in a conventional process, it is not possible to take full advantage of using a high concentrated HNO_3 for reduction of the water content.

NH_3 gas may contain small quantities of unreacted H_2 and inert N_2. These are vented from the neutraliser system at a suitable point, depending on the characteristics of the particular process. 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 AN 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 ANS is more unstable than an alkaline solution.

The selection of neutraliser pressure involves, amongst other things, a trade off between inherent safety and energy efficiency.

Neutralisers may be free boiling vessels, circulating systems, or pipe reactors. The factors which influence the choice of neutraliser are:

- a two-stage neutraliser produces most of the boil-off steam in the first stage and most of the NH_3 emission in the second stage. This reduces the total NH_3 emission
- a single-stage neutraliser is simpler and cheaper
- neutralisation at an elevated pressure will produce steam at a higher temperature. 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.

An example of a neutraliser is the pipe reactor. The neutralisation reaction is carried out in a pipe. The design allows an efficient mixing of HNO_3 and NH_3, which in turn allows minimisation of the residence time. Both, NH_3 and HNO_3 are preheated using a part of the process steam generated in the reaction. Raw material dosing is optimised by flowrate measurement. Because of the mixing and the reaction, the pressure decreases within the pipe from about 4 – 7 bar at the reactor head to about 1 bar in the following separator tank, where the outlet of the pipe reactor is located. In the separator, the ANS flows down to the bottom and the generated process steam flows up. The ANS overflows by gravity to a buffer, where the pH is

automatically adjusted by a small flow of gaseous NH_3. The pipe reactor process can be operated with 63 % HNO_3 (preheated to 60 ºC) and can yield a 97 % w/w ANS without further concentration/evaporation.

ANS 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 AN, CAN or NPK fertiliser, it is normally concentrated by evaporation.

The starting materials AN and calcium carbonate may be derived from a nitrophosphate process, see Section 7.4.8.

9.2.3 Evaporation

The ANS is normally concentrated in an evaporator to the water content required for the particular product finishing. The water concentration is normally below 1 % for a prilled product and up to 8 % for some granulation processes.

Steam from the neutraliser or from a steam raising facility on the site is used as the heat source for evaporation. Saturated steam at a controlled temperature must be used to avoid the decomposition of AN. 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.

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 with ammonia, along with droplets of ammonium nitrate. 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.

9.2.4 Process steam purification

The process steam leaving the neutraliser can be used directly or is purified, or it can be condensed and then purified. The steam may be used in the evaporator or it may be used to preheat and evaporate ammonia, and also to preheat the nitric acid. The following techniques have been used for the purification of the steam:

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.

AN 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 to process heat exchange is preferred where practicable for condensation of the steam. Alternatively, water or air cooled exchanger(s) are required.

9.2.5 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 AN and in some plants for CAN. The granulation of AN 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.

9.2.5.1 Prilling

The AN from a prilling tower needs to be virtually anhydrous. To achieve this, the slurry 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 filler material (limestone and/or dolomite) is added before the slurry is prilled. Sometimes prills from the prilling tower may be increased in size by processing in a fattening drum.

NH_3 and AN (and filler material in CAN production) become entrained in the air discharged at the top of the prilling tower. A lower melt temperature can reduce emissions. 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. AN fume is also lost from the surface of the prills, which are submicron in size and more difficult to remove.

9.2.5.2 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. The granular product can also be made in a wide range of particle sizes, which are larger than prills. Some granulation processes can use AN containing up to 8 % water but this water still has to be removed in the process. However, as the temperature needed is lower, a better 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 is normally added in the process before the granulator if CAN is to be produced, with the AN being added to the granulator as a spray of hot concentrated solution. No further drying of the granules will normally be required. 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 AN solution before granulation or in the granulator itself. Granules from this process will normally require drying in a fluidised bed or rotary drier. 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.

9.2.6 Cooling

Both granulators and prill towers normally produce a product which needs further cooling in rotary or fluidised bed coolers, with the air cleaned. Air cleaned in a dry system can generally be re-used as secondary air to the drier, after dedusting.

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.

Sometimes two-stage cooling is used where the bulk flow heat exchanger normally works as the second stage [28, Comments on D2, 2004].

9.2.7 Conditioning

AN and CAN tend to cake during storage and are therefore conditioned. 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.

9.3 Current emission and consumption levels

Product	Steam	Electricity	Cooling water	Total	
	kg/tonne product	kWh/tonne product	m^3/day	GJ/tonne product	
CAN	13	13.2	24500 [x]		AMI, Linz
	150 – 200	10 – 50			[148, EFMA, 2000] / [52, infoMil, 2001]
Solid AN		25 – 60			New AN facility [148, EFMA, 2000]
	0 – 50				[148, EFMA, 2000]
				0.7	European average [52, infoMil, 2001]
				0.09 – 0.22	Modern AN plants [52, infoMil, 2001]
ANS	- 170 [xx]	5			[148, EFMA, 2000]

[x] with a ΔT of 10 ºC, production of 663000 tonnes CAN in 2000

[xx] steam export

Table 9.3: Energy and cooling water consumption for the production of CAN/AN

Pollutant	mg/Nm^3	g/tonne product	Remark	Reference
Dust	14.5 – 14.8	17.4	Central waste gas scrubber (waste gas volume 92250 Nm^3/hour)	AMI, Linz [9, Austrian UBA, 2002]
	5 – 6.5	13.5	From cooling drum, cyclones (waste gas volume 107750 Nm^3/hour)	AMI, Linz [9, Austrian UBA, 2002]
	5		From cooling drum, cyclones (waste gas volume 91500 Nm^3/hour)	AMI, Linz [9, Austrian UBA, 2002]
	5	20.5	From prilling tower producing technical grade AN, about 100000 Nm^3/hour, scrubbing in a packed column, emission volume flow of 10000 Nm^3 treated with candle filters	AMI, Linz [9, Austrian UBA, 2002]
	15		From prill tower of new plants, no insoluble solids	[148, EFMA, 2000]
	30		New plants, other point sources than prilling, no insoluble solids	[148, EFMA, 2000]
	50		New plants, with insoluble solids present, including CAN	[148, EFMA, 2000]
	72	12	Concentration, high efficiency scrubber	DSM Geleen [52, infoMil, 2001]
	1	1	Granulation, rotary drum dryer 1, fabric filter	DSM Geleen [52, infoMil, 2001]
	1	2	Granulation, rotary drum dryer 2, fabric filter	DSM Geleen [52, infoMil, 2001]
	1	2	Granulation, rotary drum dryer 3, fabric filter	DSM Geleen [52, infoMil, 2001]
	37	86	Fluid bed cooling 1	DSM Geleen [52, infoMil, 2001]
	44	99	Fluid bed cooling 2	DSM Geleen [52, infoMil, 2001]
	26	70	Fluid bed cooling 3	DSM Geleen [52, infoMil, 2001]
	25	17	Dedusting system granulation	DSM IJmuiden, [52, infoMil, 2001]
		400	From prill towers and coolers, CFCA shroud abatement	Terra, Billingham [28, Comments on D2, 2004]
		30	From prilling tower (“with state-of-the-art abatement”)	Terra, Severnside [28, Comments on D2, 2004]

Pollutant	mg/Nm^3	g/tonne product	Remark	Reference
NH_3	2	4	Fluid bed cooling 1	DSM Geleen [52, infoMil, 2001]
	2	4	Fluid bed cooling 2	DSM Geleen [52, infoMil, 2001]
	2	4	Fluid bed cooling 3	DSM Geleen [52, infoMil, 2001]
	36	47	Rotary drum dryer 1, fabric filter	DSM Geleen [52, infoMil, 2001]
	38	47	Rotary drum dryer 2, fabric filter	DSM Geleen [52, infoMil, 2001]
	41	49	Rotary drum dryer 3, fabric filter	DSM Geleen [52, infoMil, 2001]
	0	0	Concentration, high efficiency scrubber	DSM Geleen [52, infoMil, 2001]
	1.30 – 5.07	1.6	Central waste gas scrubber (waste gas volume 92250 Nm^3/hour)	AMI, Linz [9, Austrian UBA, 2002]
	2.75 – 3.65	6.7	From cooling drum, cyclones (waste gas volume 107750 Nm^3/hour)	AMI, Linz [9, Austrian UBA, 2002]
	3.2 – 3.05		From cooling drum, cyclones (waste gas volume 91500 Nm^3/hour)	AMI, Linz [9, Austrian UBA, 2002]
	4.25 – 6.55	13.7	From prilling tower producing technical grade AN, about 100000 Nm^3/hour, scrubbing in a packed column, emission volume flow 10000 Nm^3 treated with candle filters	AMI, Linz [9, Austrian UBA, 2002]
	10		From prill tower of new plants, no insoluble solids	[148, EFMA, 2000]
	50		New plants, other point sources than prilling, no insoluble solids	[148, EFMA, 2000]
	50		New plants, with insoluble solids present, including CAN	[148, EFMA, 2000]
F as HF	0.40 – 0.44	0.5	Central waste gas scrubber (waste gas volume 92250 Nm^3/hour). CAN plant uses raw materials obtained from an ODDA plant	AMI, Linz [9, Austrian UBA, 2002]

Table 9.4: Emissions to air from the production of CAN fertilisers

Parameter	Waste water emission levels	
Waste water volume	6 m^3/hour	0.24 m^3/t N [x]
Total N (NH_3-N + NO_3-N)	16 kg/d	0.026 kg/t N [x]
[x] calculation based on the production capacity of 612 tonnes N/day (corresponding to the production capacity of 1800 tonnes/day of AN and an N content of 34 % in the AN		

Table 9.5: Waste water emission levels from the AN pressure neutralisation at AMI, Linz [9, Austrian UBA, 2002]

Plant	Amount (m^3/hour)	Specific emission (1)		
		N-emission	g/m^3	g/tonne CAN
DSM Geleen (3)	37 (5)	Kj-N	8.4 – 11.7 (167)	2.5 – 3.4 (49)
		NO_3^- as N	33.8 – 67.5 (225)	9.9 – 19.8 (66)
	10 (4)	Kj-N	1 – 1.4 (20)	0.08 – 0.11 (1.6)
		NO_3^- as N	16.5 – 33 (110)	1.3 – 2.6 (8.8)
Kemira Rozenburg	20 (2)	Kj-N		
		NO_3^- as N		
Figures in brackets are levels before treatment (1) Calculations based on a continuous process (± 8640 hours/year) (2) Including cooling water (3) Discharge to WWTP (4) Waste water discharged from the cooling water system (5) Process condensate + scrubber water				

Table 9.6: Emissions to water of DSM Geleen and Kemira Rozenburg for the production of AN-based fertilisers [52, infoMil, 2001]

9.4 Techniques to consider in the determination of BAT

- for product cooling, see Section 7.4.5
- for recycling of warm air, see Sections 7.4.6
- concerning granulation recycle, see Sections 7.4.7.

9.4.1 Optimisation of the neutralisation section

Description

The neutralisation section has a significant effect on the environmental performance of the system. Various neutralisation processes are used and several parameters can affect the neutralisation section environmental performance. Table 9.7 gives an overview.

Parameter	Description
Preheating	AN formation is an exothermic reaction. The heat produced is frequently used to preheat the HNO_3 or to concentrate the ANS
pH control	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 NH_3 emission in the second. A two-stage neutraliser reduces the overall NH_3 emission compared to a single-stage neutraliser, but it is more expensive
Water content	The decomposition of AN proceeds slower at higher water contents
Temperature	Higher temperatures lead 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
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, most modern processes at elevated pressures are net producers of energy (excluding product finishing). Most older plants working at atmospheric pressure need to import steam. 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. Building pressure might cause physical explosions, however in all cases it should be possible to relieve pressure
Impurities	Many substances have a significant catalytic effect on AN decomposition. 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. Organic materials, chloride, heavy metals and nitrite will give particularly hazardous mixtures. 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.

Table 9.7: Parameters affecting the environmental performance of the neutralisation section [52, infoMil, 2001]. Note that all conditions quoted are plant specific. Actual values may vary considerably from plant to plant.

Achieved environmental benefits

- reduced concentration of NH_3 and AN in the steam
- neutralisation at an elevated pressure will produce steam at a higher temperature and AN of a higher concentration.

Cross-media effects

Process using increased pressure might require energy for NH_3 compression.

Operational data

No specific information provided.

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 an 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.

Driving force for implementation

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.

References to literature and example plants

[52, infoMil, 2001], AMI, Linz

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), which is now closed, used a two-stage neutraliser. The first step of the neutralisation took place at a pH value of 2 to prevent ammonia losses. In the second step, the solution was neutralised to pH 6.

Lovochemie (Czech Republic) uses a single-stage neutraliser pressurised to 3.5 bar and the concentration of resulting AN is 72 – 75 % at a temperature of 168 – 171 ºC.

9.4.2 Recovery of residual heat for chilling process water

Description

Large volumes of contaminated low temperature (125 – 130 ºC) steam are generated during the manufacture of AN. Some of this steam is discharged into the air.

However, residual low temperature heat can be used to chill water, using a $LiBr/H_2O$ absorption cooler. In the example plant, the chilled water was used to cool down air for product cooling.

Achieved environmental benefits

- reduction of energy consumption.

Cross-media effects

Energy consumption for the pumps.

Operational data

- heat source: process steam
- process steam pressure: 180 kPa
- process steam flow: 2.77 kg/kWh
- concentrator, number of 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.

Applicability

Absorption cooling processes are widely used in industry. The application in the fertiliser industry is particularly interesting, where there is no consumer of low pressure NH_3 available. It is more profitable than a conventional ammonia compression refrigeration system.

Economics

Investment: approximately EUR 900000.

Driving force for implementation

Plant modernisation and cost benefits.

References to literature and example plants

[52, infoMil, 2001, 152, Galindo and Cortón, 1998]

Fertiberia S.A. in Cartagena (Spain) operated two granulation units for the production of AN/CAN and NPK fertilisers, with a capacity of up to 900 tonnes/day, each. This plant shut down in 2003. The units have been in operation since 1969. The production was based on an 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 factory originally had problems with the concentration of AN liquor, energy consumption, pollution, quality and its production capacity. To overcome these problems, the company decided to install the absorption cooling system in the AN plant.

9.4.3 Energy considerations and steam export

Description

The formation of AN is strongly exothermic. The produced heat is often used to generate steam, which is often used to preheat the nitric acid or to concentrate the obtained AN solution. The concentration of the HNO_3 used represents an important factor, since it influences the amount of water that has to be removed. Product finishing requires energy, but due to the amount of energy introduced to the finishing section by the warm ANS, additional energy requirement for drying is zero or very low (see also Section 9.4.5).

Average energy consumption in Europe is 0.7 GJ/tonne AN produced, but modern AN plants require only 0.09 – 0.22 GJ/tonne AN. The energy consumption of a CAN production plant is somewhat higher, due to the fact that the grinding of raw materials (e.g. dolomite) also requires energy. The process requires 150 – 200 kg steam/tonne CAN and 10 – 50 kWh/tonne CAN (about 36 – 180 MJ/tonne CAN) [52, infoMil, 2001].

Steam is needed to evaporate the ANS but the amount needed will depend on the HNO_3 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 ANS, steam can be exported at a rate of up to 170 kg/tonne of AN and some plants can export hot water. The production of an ANS with approximately 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 [148, EFMA, 2000]. Table 9.8 shows a comparison of expected consumption levels for new plants.

	Vacuum neutralisation	**Pressure neutralisation**	
		At 2 bar with direct heat recovery	At 4 bar with clean steam production
Steam import, kg/tonne AN	130 (10 bar)	10	52 (10 bar)
Steam export, kg/tonne AN	None	None	240 (5 bar)
Cooling water, m^3/tonne AN	31.0	22.5	3.8
Electricity, kWh/tonne AN	2.0	3.8	4.8
Ammonia, kg/tonne AN	213	213	213
Nitric acid, kg/tonne AN	789	789	789
Figures for 60 % w/w HNO_3 and 96 % w/w AN product, a cooling water ΔT of 10 ºC			

Table 9.8: Comparison of expected consumptions for new plants [101, Uhde, 2003]

Achieved environmental benefits

If the plant only makes ANS, steam can be exported at a rate of up to 170 kg/tonne of AN and some plants can export hot water. The production of an ANS with approximately 95 % AN is achievable without an additional energy demand for evaporation by carrying out a pressure neutralisation.

Cross-media effects

None believed to be likely.

Operational data

No specific information provided.

Applicability

Generally applicable.

Economics

No specific information provided, but cost benefits can be assumed.

Driving force for implementation

Cost benefits.

References to literature and example plants

[17, 2nd TWG meeting, 2004, 52, infoMil, 2001, 101, Uhde, 2003, 148, EFMA, 2000]

9.4.4 Steam purification and treatment/recycling of condensates

Description

Whatever the process, some water is fed along with HNO_3 and, as only a part of this water can end up in the ANS, there is an important remaining quantity to be removed from the process as process steam or from the evaporation section. Depending on the process conditions and the treatment of the process steam, the resulting condensate can be polluted by various amounts of AN, HNO_3 or NH_3.

Table 9.9 shows an example for a combination of steam purification and condensate treatment. According to [148, EFMA, 2000], 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.

Options for discharging the condensate, arising from the steam leaving the neutraliser, include the following ways [148, EFMA, 2000]:

- to biological treatment (on-site or joint treatment with municipal waste water)
- 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.

Input	Process steam from neutraliser
Venturi scrubber	Acidic scrubbing with ANS to neutralise NH_3
Cyclonic column	
Filter candles	Removal of remaining AN droplets
Evaporator	In a shell and tube, a part of the process steam is used to produce a “clean” steam and a concentrated condensate, by heating the tubes and evaporation in the shell
Condenser	Condensation of the “clean” steam
Output	Concentrated condensate for recycling as scrubbing liquid in the ANS plant, to HNO_3 plant absorption tower, or elsewhere
	“Clean” condensate with a AN content of <50 mg/l

Table 9.9: Example for a process steam purification and condensate treatment [140, Peudpièce, 2006]

Achieved environmental benefits

- reduced emissions to water
- recycling of N compounds into production.

Cross-media effects

None believed to be likely.

Operational data

No specific information provided.

Applicability

Generally applicable.

Economics

No specific information provided, but cost benefits can be assumed.

Driving force for implementation

Cost benefits.

References to literature and example plants

[9, Austrian UBA, 2002, 52, infoMil, 2001, 148, EFMA, 2000], [140, Peudpièce, 2006]

Grande Paroisse, Mazingarbe:	See Table 9.9
DSM Geleen:	The "dirty" steam is cleaned by means of a venturi scrubber and a candle filter and is used to vaporise and heat ammonia to 90 ºC. Used steam is condensed (25 m^3/hour condensate): 20 – 25 % is recycled as scrubber water, the remainder is sent to the plant waste water treatment.
DSM IJmuiden:	The "dirty" 2 bar steam is used to vaporise and heat ammonia, to heat nitric acid and to produce 1.5 bar "clean" steam. The remainder of the "dirty" steam is condensed and partly re-used, the rest is emitted to the surface water. Water vapour from the concentration section is condensed, cleaned by scrubbing with a circulating sour AN solution and emitted to the surface water.
Kemira Rozenburg:	The "dirty" steam is condensed and collected with the condensate from the evaporation section. Half of this water is re-used as absorption water in the nitric acid plant, while 3 % is re-used as dilution water in the UAN plant. The remainder is emitted to the surface water.
Yara Sluiskil:	The "dirty" steam is condensed and collected by means of closed sewage system in a basin. All water from the basin is re-used as scrubber water, as process water in the urea plant or the nitric acid plant and/or is demineralised before re-use.
AB ACHEMA	The company uses ion-exchange to treat process condensates. The regenerate, containing up to 180 g/litre AN and up to 70 g/l HNO_3, is used in the HNO_3 plant.

9.4.5 Autothermal granulation

Description

Off-gas from fluid bed coolers can be used for drying the product in the drying drum. This a significant energy saving feature and enables the plant to run autothermally for nearly all CAN grades.

See also Section 7.4.6.

Achieved environmental benefits

- significant energy savings
- exhaust gas volume flow reduced by approximately 50 %.

Cross-media effects

None believed to be likely.

Operational data

No specific information provided.

Applicability

Generally applicable to CAN production.

Economics

No specific information provided, but cost benefits can be assumed.

Driving force for implementation

Cost benefits.

References to literature and example plants

[147, Uhde, 2006, 148, EFMA, 2000]

9.4.6 Exhaust gas treatment

Description

Table 9.10 gives an overview of the exhaust gas treatment in the example plants.

Source	Treatment	Reference
Prill tower	Wet scrubber, packed column for recycled flows, irrigated candle filters for the released volume flow	a
Non condensable off gases from neutralisation/evaporation	Steam purification, condensation, central scrubber	a
Evaporation	High efficiency scrubber	b
Granulation, drying	Cyclones, central scrubber	a
Granulation	Fabric filter	c
Drying	Fabric filter	b
Cooling drums	Cyclones	a
Filler material grinding	Fabric filters, cyclones	b, c, d, f
Prilling tower + evaporated effluent	Irrigated candle filters	e
Fluid bed cooler	Cyclones	e
	Scrubbers	f
a) AMI, Linz b) DSM, Geleen c) DSM, IJmuiden d) Kemira, Rozenburg e) Terra, Severnside f) Yara, Sluiskil		

Table 9.10: Overview of exhaust gas treatment in the example plants
[9, Austrian UBA, 2002, 52, infoMil, 2001, 154, TWG on LVIC-AAF, 2006]

Achieved environmental benefits

- reduced emission levels to air.

With fabric filters, dust levels of <10 mg/Nm^3 are achievable.

Cross-media effects

None believed likely, if the scrubber liquids are recycled.

Operational data

No specific information provided.

Applicability

Irrigated candle filters are not applicable for finishing products containing insoluble material. Recycling of scrubbing solutions, in particular from CAN production may influence the product quality.

Available space or structural foundation limitations may inhibit the installation of a scrubbing facility of sufficient capacity on top of an AN prilling tower. A scrubber at ground level is usually excessively expensive.

Economics

Additional cost for recovery/abatement systems.

Driving force for implementation

Reduced emissions to air.

References to literature and example plants

AMI, Linz
DSM, Geleen
DSM, IJmuiden

9.5 BAT for AN/CAN

BAT is to apply the common BAT given in Section 1.5.

BAT for storage is to apply BAT given in [5, European Commission, 2005].

BAT is to optimise the neutralisation/evaporation stage by a combination of the following techniques:

- using the heat of reaction to preheat the HNO_3 and/or to vapourise NH_3 (see Section 9.4.1)
- operating the neutralisation at an elevated pressure and exporting steam (see Sections 9.4.1)
- using the generated steam for evaporation of water from ANS (see Section 9.4.3)
- recovering residual heat for chilling process water (see Section 9.4.2)
- using the generated steam for the treatment of process condensates
- using the heat of the reaction for additional water evaporation.

BAT is to effectively and reliably control pH, flow and temperature.

BAT is to improve environmental performance of the finishing section by one or a combination of the following techniques:

- apply plate bank product cooling (see Section 7.4.5)
- recycling of warm air (see Sections 7.4.6 and 9.4.5)
- select proper size of screens and mills, e.g. roller or chain mills (see Section 7.4.7)
- apply surge hoppers for granulation recycle control (see Section 7.4.7)
- apply product size distribution measurement and control (see Section 7.4.7).

BAT is to reduce dust emissions from dolomite grinding to levels <10 mg/Nm^3 by applying, e.g. fabric filters.

Because of an insufficient data basis, no conclusions could be drawn for emissions to air from neutralisation, evaporation, granulation, prilling, drying, cooling and conditioning.

BAT is to recycle process water on-site or offsite and to treat the remaining waste water in a biological treatment plant or using any other technique achieving an equivalent removal efficiency.

10 SUPERPHOSPHATES

10.1 General information

Superphosphates, i.e. single superphosphate (SSP) and triple superphosphate (TSP), account for one quarter of the world's phosphate fertiliser production. Superphosphates are defined by the percentage of phosphorus as P_2O_5 and are used as straight fertilisers (marketable products), but are also a feedstock for multinutrient fertilisers. Table 10.1 provides a general overview of superphosphates. SSP and TSP are mainly used for downstream production of PK and NPK fertiliser.

	Content %		World consumption 1999/2000	Raw materials
	P_2O_5	**$CaSO_4$**	**Mtonnes P_2O_5**	**Phosphate rock and …..**
Normal SSP	16 [x] – 24	50 – 38	6.1	H_2SO_4
Concentrated SSP	25 – 37	37 – 15		H_2SO_4 and H_3PO_4
TSP	38 [x] – 48	15 – 5	2.2	H_3PO_4
[x] According to EC Directive 2003/2003, SSP must contain at least 16 % soluble P_2O_5 in neutral ammonium citrate, of which at least 93 % is soluble in water. TSP must contain at least 38 % soluble P_2O_5 in neutral ammonium citrate, of which at least 85 % is soluble in water				

Table 10.1: Overview of superphosphates
[154, TWG on LVIC-AAF, 2006]

		Capacity in 2006 ktonnes P_2O_5
Austria	Donauchemie (Roullier Group)	16
Belgium	Ste Chimique Prayon Ruppel [x]	60
	Rosier SA	27
France	Roullier Group [x]	101
Germany	Amfert	54
Hungary	Tiszamenti Vegyimuvek	211
Italy	Roullier Group	41
	Puccioni	15
The Netherlands	Amfert [x]	110
	Zuid Chemie [x]	40
Poland	Zaklady Chemiczne Siarkopol	110
	Zaklady Chemiczne Lubon	100
	Fabrija Nawozow Fosforowych Ubozcz	50
	Szczecinskie Zaklady Nawozow Fosforowych	80
Portugal	Adubos	56
Romania	SA Continatul de Ingrasaminte	15
Spain	Asturiana de Fertilizantes	90
	Roullier Group	23
	Mirat	9
[x] also TSP producers		

Table 10.2: Overview of the European superphosphate plants as of July 2006
[154, TWG on LVIC-AAF, 2006]

10.2 Applied processes and techniques

10.2.1 Overview

For an overview, see Figure 10.1.

SSP and TSP are manufactured as follows: phosphate rock is ground very finely and mixed with acid (SSP: 65 – 75 % H_2SO_4; TSP: a H_3PO_4 with a P_2O_5 content of 50 – 55 %), giving the following overall reactions:

(SSP) $Ca_{10}F_2(PO_4)_6 + 7\ H_2SO_4 + H_2O \rightarrow 3\ Ca(H_2PO_4)_2{\cdot}H_2O + 7\ CaSO_4 + 2\ HF$

(TSP) $Ca_{10}F_2(PO_4)_6 + 14\ H_3PO_4 + 10\ H_2O \rightarrow 10\ Ca(H_2PO_4)_2{\cdot}H_2O + 2\ HF$

In the SSP process, H_3PO_4 is formed only as an intermediate. The reactions are rapid (more than 96 % yield) but can continue for several days as the remaining free acid continues reacting with the excess phosphate rock. The SSP process retains the calcium sulphate ($CaSO_4$) in the product unlike the similar reaction producing phosphoric acid.

Ground phosphate rock and acid are mixed in a reaction vessel. The reaction begins in the reactor, and is exothermic, reaching temperatures of 90 – 100 ºC. The slurry is fed on to a slow moving conveyor belt (the so-called "den") or to a holding vessel and held for a period from 10 to up to 40 minutes. The superphosphate is crushed and afterwards fed to a granulation line (direct granulation) or to storage (pile) for "curing" from one to up to six weeks. The superphosphate can be fed to the granulation line (indirect granulation) or sold without further processing from the storage facility.

As well as SSP or TSP, partially acidulated phosphate rock (PAPR) can also be produced. PAPR is a mixture of superphosphate and phosphate rock. This product can be made in an SSP or TSP plant using a lower proportion of H_2SO_4 or H_3PO_4 to phosphate rock.

From the storage pile, the cured superphosphate is ground and granulated. Steam, water or acid may be added to help granulation. Direct granulation has some advantages in comparison to granulation after storage (pile) for curing; production costs are usually lower and the granules are denser and stronger [52, infoMil, 2001]. Some disadvantages of direct granulation are the need to use reactive phosphate rock and the possibility of greater losses of soluble P_2O_5 due to the incomplete reactions.

Phosphate rock can contain small amounts of organic compounds. During the reaction with the acid, these organic compounds are released. Compounds, such as mercaptanes can cause odour nuisance. For phosphate rock selection, see also Section 5.4.9.

10.2.2 Raw materials

An important factor in the production of SSP and TSP is the amount of aluminium (as Al_2O_3), iron (as Fe_2O_3) and magnesium compounds in the phosphate rock; the presence of these elements reduces the water solubility of the phosphate. Two sources of H_2SO_4 used in superphosphate production are virgin acid and spent acid of sufficient quality. Virgin acid is produced from SO_2 derived from burning elemental sulphur (sulphur-H_2SO_4), 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 H_2SO_4. For more information on phosphate rock and sulphuric acid, see Sections 5.2.2.1.1 and 5.2.2.1.2.

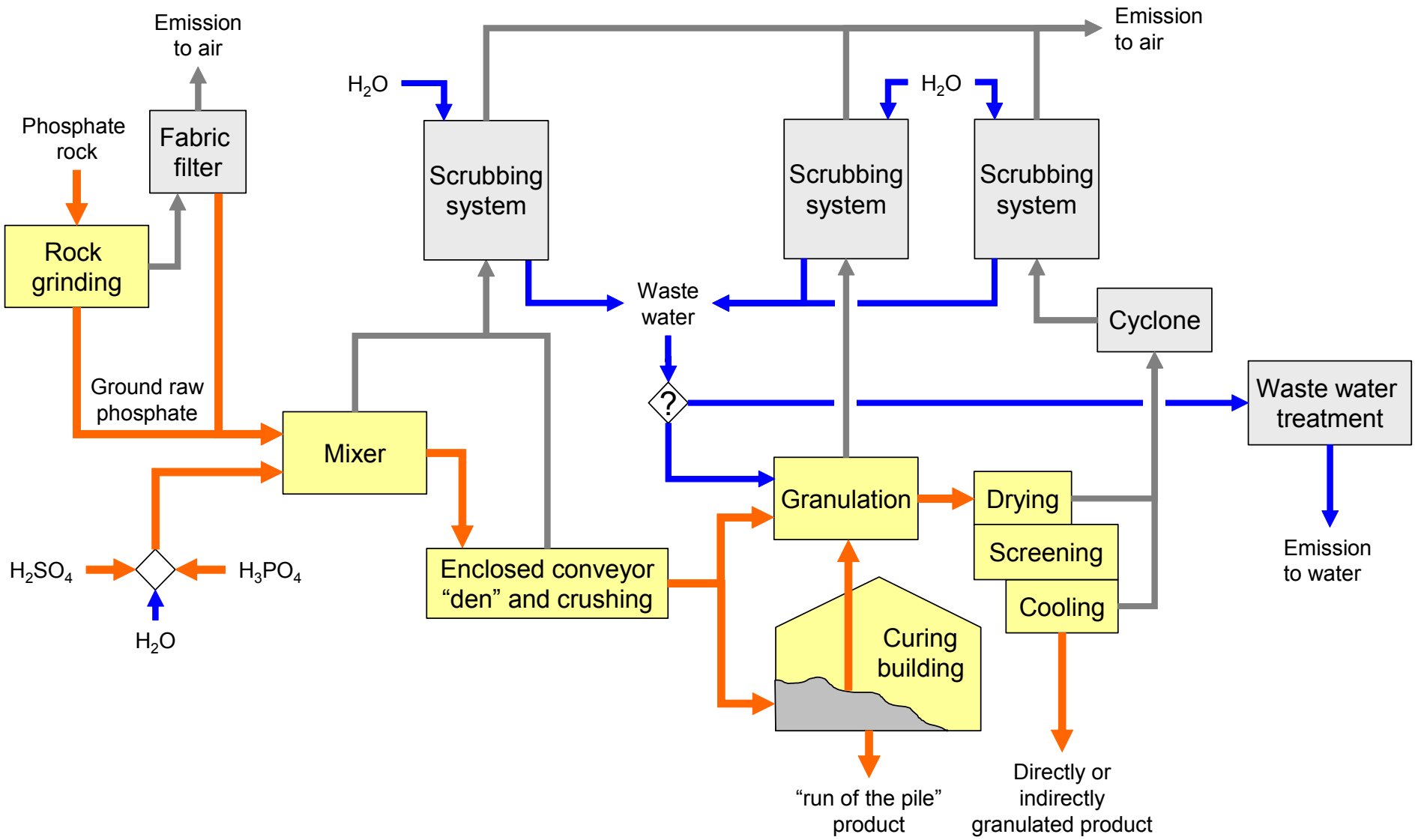

Figure 10.1: Overview of the production of superphosphates including an example for an exhaust gas abatement system
This figure is based on [9, Austrian UBA, 2002, 52, infoMil, 2001, 53, German UBA, 2002]

10.3 Current emission and consumption levels

Table 10.3 gives an overview of the consumption levels for the production of superphosphate. For comparison of direct and indirect TSP granulation, see Table 10.4. Table 10.5 gives an overview of emissions to air, Table 10.6 shows an example for water emission levels.

		Per tonne product		
Power	Grinding		Depends on the type of phosphate rock: about 15 – 18 kWh per tonne phosphate rock	[9, Austrian UBA, 2002]
	Scrubbing		Three stage scrubbing: 20 kWh/tonne product due to high pressure drop in the Venturi scrubbers	
Water		1.2 m^3	This includes 0.8 m^3 H_2O/tonne product for scrubbing	
Power	Run of the pile (powdery product, SSP 18 % P_2O_5)	19 kWh		[53, German UBA, 2002]
Water		0.1 m^3	Most scrubber liquids are recycled back into the process	
Steam/fuel			No steam and no fuel consumption	
Power	Granulate (SSP 18 % P_2O_5)	34 kWh		
Water		2.0 m^3		
Steam		55 kg		
Fuel		0.75 GJ	For air heating	
Energy	Directly granulated SSP	1.4 GJ	This includes 0.4 GJ for powder production and 1.0 GJ for granulation	[52, infoMil, 2001]
Power	Powdered SSP	19 kWh		
Energy	Directly granulated TSP	2.0 GJ	This includes 0.3 GJ for powder production, 1.0 for granulation, 0.7 for evaporation	

Table 10.3: Consumption levels for the production of superphosphates

Input	Indirect granulation	Direct granulation
H_3PO_4	Based on 52 % P_2O_5	> 50 % P_2O_5
	per tonne granulated TSP	
Ratio of recycle		1.0 – 1.25
Cured TSP	1.02 tonnes	-
Steam	75 kg	50 – 60 kg
Cooling water	250 kg	250 kg
Water consumption		60 – 65 kg
Fuel	0.67 GJ	
Electrical power	29 kWh	36 kWh
Operation labour	0.3 work hours	0.25 work hours

Table 10.4: Comparison of some input requirements of direct and indirect granulation of TSP
The table is based on [52, infoMil, 2001, 154, TWG on LVIC-AAF, 2006]

		mg/Nm^3	kg/hour		
Dust	AMFERT, Rock grinding, different mills	<7 – 8	<0.05	Cyclones, fabric filters	[52, infoMil, 2001]
		<9.3	<0.05	Cyclones, fabric filters	
	AMFERT, dedusting shop floor mill house	<10	<0.05	Fabric filters	
	AMFERT, drum granulator, drying drum	16.8		Cyclones, scrubber	
	Zuid-Chemie, rock grinding, different mills, volume flows of 1x 3600 and 2 x 4900 Nm^3/hour	2.5 – 3.8	0.04	Cyclones/ceramic filters	
		2.5 – 3.8	0.04	Cyclones/ceramic filters	
		2.5 – 3.8	0.05	Cyclones/ceramic filters	
Dust	Donauchemie, rock grinding	4.2		Fabric filters	[9, Austrian UBA, 2002]
Dust	Donauchemie (from den, crusher, and enclosed conveyor belt)	46		Sequence of three scrubbers, 25000 Nm^3/hour, removal efficiency >99 % for HF	
Fluorides as HF		4.9			
Fluorides as HF	AMFERT, various origins	0.2 [x] – 5		Scrubber, cyclones and scrubber	[52, infoMil, 2001]
	Zuid-Chemie	<5		Scrubber	
Fluorides as HF	Amsterdam Fertilizers, exhaust gases from acidulation, granulation and drying	0.5 – 4		Scrubbers, cyclone	[53, German UBA, 2002]
Chlorides [xx]		19.1			
Dust		30 – 50			

[x] later information indicates that this level is related to the production of NPK products

[xx] in the case of downstream NPK production

Table 10.5: Emissions to air from the production of superphosphates

From scrubbing	Volume	5 – 10 m^3/hour	Donauchemie, [9, Austrian UBA, 2002]
	Temperature	29 ºC	
	pH	6 – 7.5	
	Filterable substances	0.36 kg/tonne P_2O_5	
	Total P	0.59 kg/tonne P_2O_5	
	NH_4-N	1.7 kg/tonne P_2O_5	
	Fluoride as F	1.17 kg/tonne P_2O_5	
	Cd	<0.01 g/tonne P_2O_5	
	Hg	<0.01 g/tonne P_2O_5	
	Zn	n.a.	
	COD	0.6 kg/tonne P_2O_5	

Table 10.6: Example for emissions to water from the production of superphosphates with downstream production of NP/NPK
On the Donauchemie site, no waste water is generated in the NPK production. All scrubbing liquor is recycled back into the process. Usually, rinsing and cleaning waters are collected and used as scrubbing liquid in the following production campaign if the production is carried out alternately under acidic (PK) and alkaline (NPK) conditions. Waste water is only released if the same fertiliser type is produced within two following campaigns [9, Austrian UBA, 2002].

10.4 Techniques to consider in the determination of BAT

- for product cooling, see Section 7.4.5
- for recycling of warm air, see Sections 7.4.6
- concerning granulation recycle, see Sections 7.4.7.

10.4.1 Avoiding diffuse emissions from curing

Description

In direct granulation, the product is not stored for curing, hence less diffuse emissions occur. However, direct granulation requires reactive phosphate rock and might cause losses of plant available P_2O_5 due to the incomplete reaction.

Achieved environmental benefits

- direct granulation is a measure to reduce the potential for diffuse emissions from curing.

Cross-media effects

Direct granulation might cause losses of plant available P_2O_5.

Operational data

No information provided.

Applicability

Direct granulation requires reactive phosphate rock to reduce the amount of not plant available P_2O_5. In the case of indirect granulation, the curing section can be designed as an indoor system and the vent from the curing can be connected to a scrubber system or to the granulation section.

Economics

No specific information provided.

Driving force for implementation

Cost savings.

References to literature and example plants

[52, infoMil, 2001, 154, TWG on LVIC-AAF, 2006], Donauchemie

10.4.2 Recovery and abatement of dust from rock grinding

Description

For a description, see Section 5.4.8.

Achieved environmental benefits

- recovery of raw material
- dust emissions well below 10 mg/m^3 [17, 2nd TWG meeting, 2004].

Cross-media effects

None believed to be likely.

Operational data

See Table 10.5.

Applicability

Generally applicable. The prevention of dust by wetting is not applicable if the product is water soluble.

Economics

Cost for applying a ceramic filter [52, infoMil, 2001]:

- investment per 1000 m^3/hour: EUR 30000 – 55000 (approximately linear with the volume flow, as the filter material mainly determines the investment)
- operational costs per 1000 m^3/hour: >EUR 650 per year.

See also [11, European Commission, 2003].

Driving force for implementation

Cost benefits.

References to literature and example plants

[11, European Commission, 2003, 17, 2nd TWG meeting, 2004, 29, RIZA, 2000, 31, EFMA, 2000]

10.4.3 Fluoride recovery and abatement

Description

For a description, see Section 5.4.7.

Achieved environmental benefits

- in the Netherlands, emission levels of 0.2 [x] – 5 mg/Nm^3 were achieved [52, infoMil, 2001]
- in a German example, emission levels of 0.5 – 4 mg/Nm^3 were achieved [53, German UBA, 2002].

([x] late information indicates that this level is related to the production of NPK).

Cross-media effects

Water, energy and chemicals consumption for scrubbing.

Operational data

No information provided.

Applicability

Abatement of fluorides is generally applicable. However, the recovery of a H_2SiF_6 pure enough for valorisation is not considered viable.

Economics

For cost estimates, see Table 6.10.

Driving force for implementation

Reduced fluoride emission levels.

References to literature and example plants

[29, RIZA, 2000, 31, EFMA, 2000]

10.4.4 Recycling of scrubbing liquids back into the process

Description

The scrubbing of exhaust gases from superphosphates manufacture generates waste water. Where, besides the manufacture of SSP or TSP, acidulated phosphate rock (PAPR) is also produced, the water balance allows the reduction of waste water volumes drastically by recycling of scrubbing liquids back into the process.

Achieved environmental benefits

- reduced waste water volumes.

Cross-media effects

None believed likely.

Operational data

No information provided.

Applicability

Applicable to the production of PAPR besides the manufacture of SSP/TSP.

Economics

No specific information provided.

Driving force for implementation

Reduced waste water volume.

References to literature and example plants

[53, German UBA, 2002]

10.5 BAT for superphosphates

BAT is to apply the common BAT given in Section 1.5.

BAT for storage is to apply BAT given in [5, European Commission, 2005].

BAT for waste water treatment is to apply BAT given in [11, European Commission, 2003].

BAT is to reduce dust emissions from rock grinding by application of, e.g. fabric filters or ceramic filters and to achieve dust emission levels of 2.5 – 10 mg/Nm^3 (see Section 10.4.2).

BAT is to prevent dispersion of phosphate rock dust by using covered conveyor belts, indoor storage, and frequently cleaning/sweeping the plant grounds and the quay (see Section 5.4.8).

BAT is to improve environmental performance of the finishing section by one or a combination of the following techniques:

- apply plate bank product cooling (see Section 7.4.5)
- recycling of warm air (see Section 7.4.6)
- select proper size of screens and mills, e.g. roller or chain mills
- apply surge hoppers for granulation recycle control
- apply online product size distribution measurement for granulation recycle control.

BAT is to reduce fluoride emissions by application of scrubbers with suitable scrubbing liquids and to achieve fluoride emission levels of 0.5 – 5 mg/Nm^3 expressed as HF (see Section 10.4.3).

BAT is to reduce waste water volumes by recycling of scrubbing liquids, where, besides the manufacture of SSP or TSP, acidulated phosphate rock (PAPR) is also produced.

BAT for production of SSP/TSP and multipurpose production is to reduce emissions to air from neutralisation, granulation, drying, coating, cooling by applying the following techniques and to achieve the emission levels or removal efficiencies given in Table 10.7.

- cyclones and/or fabric filters (see Sections 7.4.6 and 7.4.10)
- wet scrubbing, e.g. combined scrubbing (see Section 7.4.10).

	Parameter	Level	Removal efficiency in %
		mg/Nm^3	
Neutralisation, granulation, drying, coating, cooling	NH_3	5 – 30 [x]	
	Fluoride as HF	1 – 5 [xx]	
	Dust	10 – 25	> 80
	HCl	4 – 23	

[x] the lower part of the range is achieved with nitric acid as the scrubbing medium, the upper part of the range is achieved with other acids as the scrubbing medium. Depending on the actual NPK grade produced (e.g. DAP), even by applying multistage scrubbing, higher emission levels might be expected

[xx] in the case of DAP production with multistage scrubbing with H_3PO_4, levels of up to 10 mg/Nm^3 might be expected

Table 10.7: Emission levels to air associated with the application of BAT

11 CONCLUDING REMARKS

11.1 Quality of the information exchange

Timing of the work

The information exchange on Best Available Techniques for the Manufacture of Large Volume Inorganic Chemicals – Ammonia, Acids and Fertilisers was carried out from 2001 to 2006. Table 11.1 shows the milestones of the work.

Kick-off meeting		29 – 31 October 2001
First draft		March 2003
Second draft		August 2004
Final Technical Working Group meeting		6 – 10 September 2004
Follow-up meeting of final meeting		07 October 2004
Meetings to finalise the work	on ammonia, HF	18 – 19 January 2006
	on H_3PO_4, SSP/TSP, NPK, H_2SO_4	02 – 05 May 2006
	on AN/CAN, urea, HNO_3	12 – 14 June 2006

Table 11.1: Timing of the work on the BREF LVIC-AAF

Sources of information and development of this document

Some reports were elaborated on purpose to provide targeted information for the development of this document. EFMA's booklets "Best Available Techniques for Pollution Prevention and Control in the European Fertilizer Industry" and the reports submitted by Austria, Germany, the Netherlands, ESA and Eurofluor can be considered building blocks for this document.

This document was developed based on about 600 comments to the first draft and about 1100 comments to the second draft.

Level of consensus

The information exchange process did not yield a second draft document developed enough to enable the finalisation of the work based on the TWG's comments and the final TWG meeting on a sufficient quality level. For this reason, a series of additional meetings was necessary in order to successfully establish a final draft. Finally, a high degree of consensus was reached. Two split views were recorded (see Sections 3.5 and 6.5).

11.2 Recommendations for future work

Data collection

A lot of information was provided to develop this document. However, for the determination of BAT, it would have been desirable to be able to rely on more data from individual example plants, addressing particular techniques more specifically in the context with the achieved performance levels (loads, concentrations, volume flows; full monitoring reports would have been even better). In the following cases, the majority of the information was provided as aggregated data:

- for the production of ammonia
- for the production of phosphoric acid
- for the production of HF
- for the production of urea.

Similarly, the determination of BAT was hindered in cases where the number of example plants was low in comparison to the diversity of the production to be assessed. This applies especially to the manufacture of NPK and AN/CAN. Table 11.2 gives some recommendations for future data collection.

Production of	Issue	Remark
Ammonia	Energy consumption	More example plants with net energy consumption figures related to the applied techniques. Examples for revamps and achieved improvements.
	Partial oxidation	Not enough information was available to work and conclude on partial oxidation.
HF	Dust emissions	Broaden the data basis.
	Energy consumption	In-depth assessment of energy consumption.
Urea	Dust and NH_3 emissions	More example plants with consumption and emission figures related to the applied techniques. Examples for revamps and achieved improvements.
	Energy consumption (see, e.g. Table 8.19)	
AN/CAN	Emissions to air	Because of an insufficient data basis, no conclusions could be drawn for emissions to air from neutralisation, evaporation, granulation, prilling, drying, cooling and conditioning.
HNO_3	Emissions of N_2O	Collect information and emission data from example plants which have/will have implemented De-N_2O techniques.
In general	Emissions to water	Collect more data sets on discharged waste waters (volumes and concentrations) and removal efficiencies of applied waste water treatment.
	Mass balances	More examples for mass balances (see BAT conclusions in Section 1.5.1) would provide a better understanding.

Table 11.2: Some recommendations for future data collection

Production of HNO_3: De-N_2O catalysts and techniques

Two approaches have been realised in *existing* plants to reduce the N_2O emissions from nitric acid production:

1. catalytic decomposition of N_2O in the reactor chamber (see Section 3.4.6) and
2. combined catalytic abatement of N_2O and NO_x applied to the tail gas (see Section 3.4.7).

A modified combined catalytic treatment applied to the tail gas is shown in Section 3.6.1 as an emerging technique. However, no *new* plant has been yet equipped with any of these catalytic De-N_2O technologies. Future work could present and build on the experience gained from the implementation of these techniques in current projects, projects triggered by the conclusions in Section 3.5, CDM or JI projects.

Improved SCR catalyst

The technique shown in Section 3.4.7 also offers selective catalytic reduction of NO_x to very low NO_x levels and with practically zero NH_3 slip. Future work could assess to which extent this performance can be transferred to other SCR systems. This would represent a major achievement.

Abatement/recovery of NO_x if SNCR or SCR are not applicable

As an example, Section 1.4.7 presents a technique to recover NO_x from exhaust gases based on scrubbing. Future work could assess the technical and economic viability of recovering NO_x from exhaust gas, e.g. from strong NO_x sources, such as the digestion of phosphate rock with HNO_3 (see, e.g. Section 7.4.9 and the related BAT in Section 7.5).

RTD programmes launched by the EC

The EC is launching and supporting, through its RTD programmes, a series of projects dealing with clean technologies, emerging effluent treatment and recycling technologies and management strategies. Potentially these projects could provide a useful contribution to future BREF reviews. Readers are therefore invited to inform the EIPPCB of any research results which are relevant to the scope of this document (see also the preface of this document).

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13 GLOSSARY

Molecular weights of some compounds used in this document

Compound	Weight	Multiply by	To convert to
P_2O_5	142	1.38	H_3PO_4
H_3PO_4	98	0.725	P_2O_5
$Ca_3(PO_4)_2$	310		
$CaSO_4$	136		
$CaSO_4 \cdot 2\ H_2O$	172		
NH_3	17	0.823	N_2
CO_2	44		
F_2	38		
HF	20		
HCl	36.5		
HNO_3	63	0.222	N_2
H_2SiF_6	144	0.792	F_2
H_2SO_4	98		

Conversion of energy units

Input		Output	
1	GJ	0.2388	Gcal
		0.2778	MWh
		0.9478	MBtu[(1)]
1	Gcal	4.1868	GJ
		1.1630	MWh
		3.9683	MBtu
1	MWh	3.6	GJ
		0.86	Gcal
		3.4121	MBtu
[(1)] Mega British thermal unit			

For online conversion of energy levels, see http://www.eva.ac.at/enz/converter.htm.

Conversion of other units

For online conversion of other units, such as pressure, volume, temperature and mass, see http://www.chemicool.com/cgi-bin/unit.pl.

Calculation of steam properties

For online calculation of steam properties, see:

http://www.higgins.ucdavis.edu/webMathematica/MSP/Examples/SteamTable

or

http://www.thexcel.de/HtmlDocs/Frame_funkt.html.

Abbreviations and explanations

A	
ACES	Advanced Process for Cost and Energy Saving
ADEME	Agence de l'Environnement et de la Maîtrise de l'Energie
AG	Aktiengesellschaft
aMDEA	Activated Methyl Diethanolamine
AN	Ammonium Nitrate (NH_4NO_3)
ANS	Ammonium Nitrate Solution
APC	Advanced Process Control
ASN	Ammonium Sulphate Nitrate

B	
BAT	Best Available Techniques
BFW	Boiler Feed-water
BOD	Biochemical Oxygen Demand
BPL	Bone Phosphate of Lime
BREF	BAT Reference Document

C	
CAN	Calcium Ammonium Nitrate
CEFIC	European Chemical Industry Council
CDM	Clean Development Mechanism – emission reduction projects, where an industrialised country invests in an emission reduction project in a developing country
CHF	Swiss francs
CIS	Commonwealth of Independent States – Armenia, Azerbaijan, Belarus, Georgia, Kazakhstan, Kyrgyzstan, Moldova, Russia, Tajikistan, Ukraine, and Uzbekistan
CN	Calcium Nitrate $Ca(NO_3)_2$
CNTH	Calcium Nitrate Tetra Hydrate $Ca(NO_3)_2.4H_2O$
COD	Chemical Oxygen Demand
Conversion rate	The SO_2 conversion rate for the production of H_2SO_4 is defined as follows: $$\text{Conversion rate} = \frac{(SO_2 \text{ in} - SO_2 \text{ out}) \times 100\ (\%)}{SO_2 \text{ in}}$$ See also Section 4.2.1
Combination of	At least two

D	
DAP	Diammonium Phosphate $(NH_4)_2HPO_4$
$DeNO_x$	Abatement system to remove nitrogen oxides (NO_x)
DeN_2O	Abatement system to remove nitrous oxide (N_2O)
DH	Dihydrate process
DHH or DH/HH	Di-hemihydrate recrystallisation process with double-stage filtration

E	
EFMA	European Fertilizer Manufacturers Association
EGTEI	Expert Group of Techno Economic Issues – this group is working under the umbrella of United Nations/Economic Commission for Europe
EIPPCB	European IPPC Bureau
EMAS	Eco-Management and Audit Scheme
EMS	Environmental Management System
EA	Environment Agency
EPER	European Pollutant Emission Register
ERM	Environmental Resources Management
ESP	Electrostatic Precipitator
EU	European Union
EU-15	Austria, Belgium, Denmark, Finland, France, Germany, Greece, Ireland, Italy, Luxembourg, the Netherlands, Portugal, Spain, Sweden, United Kingdom
EU-25	Austria, Belgium, Cyprus, the Czech Republic, Denmark, Estonia, Finland, France, Germany, Greece, Hungary, Ireland, Italy, Latvia, Lithuania, Luxembourg, Malta, the Netherlands, Poland, Portugal, Slovakia, Slovenia, Spain, Sweden, United Kingdom
EUR	Euro

H	
H/H	Dual high/high pressure nitric acid plants, see Table 3.1
HDH-1	Hemi-dihydrate recrystallisation process single-stage filtration
HDH-2	Hemi-dihydrate recrystallisation process double-stage filtration
HDS	Hydrodesulphurisation unit
HEA	High Efficiency Absorption
HH	Hemihydrate
HHV	High Heating Value – amount of heat released by a specified quantity (initially at 25 °C) once it is combusted and the products have returned to a temperature of 25 °C.
HMTA	Hexamethylene Tetramine
HP	High Pressure steam
HRC	Hemihydrate Recrystallisation process

I	
IDR	Isobaric Double Recycling process
IRMA	Institut Régional des Materiaux Avancés
IEF	Information Exchange Forum
IFA	International Fertiliser Industry Association
InfoMil	Dutch information centre for environmental licensing and enforcement

IPCC	Intergovernmental Panel on Climate Change
IPPC	Integrated Pollution Prevention Control
ISO 14001	International Standards Organization – environmental management

J

JI	Joint Implementation – emission reduction projects, where an industrialised country invests in another industrialised country. Both countries must be Kyoto protocol signatory states

L

L/M	Dual Low/Medium pressure nitric acid plants, see Table 3.1
LEL	Low Explosion Limit
LHV	Low Heating Value – amount of heat released by combusting a specified quantity (initially at 25 °C or another reference state) and returning the temperature of the combustion products to 150 °C.
Low NO_x burner	Technology to reduce NO_x emissions from combustion, by modifying the introduction of air and fuel, to retard their mixture, reduce the oxygen availability and the peak flame temperature. It delays the conversion of fuel-bound nitrogen to NO_x and the formation of thermal NO_x, while maintaining the high combustion efficiency
LP	Low Pressure steam
LPG	Liquefied Petroleum Gas

M

M/H	Dual Medium/High pressure nitric acid plants, see Table 3.1
M/M	Dual Medium/Medium pressure nitric acid plants, see Table 3.1
MAN	Magnesium Ammonium Nitrate
MAP	Monoammonium Phosphate $NH_4.H_2PO_4$
MEA	Mono Ethanolamine
MP	Medium Pressure
Multipurpose plant	Installation for production of NPK, AN/CAN and phosphate fertilisers, using the same line of equipment and abatement system

N

New installation	As opposed to an existing installation or a substantial change of an existing installation
NLG	Dutch Guilders
NG	Natural Gas
NPK	Compound/multinutrient fertiliser
NSCR	Non Selective Catalytic Reduction

O

ODDA	See Section 7.2.2

P

PAPR	Partially Acidulated Phosphate Rock
PRDS	Pressure Reduction and De-superheating

PSA	Pressure Swing Adsorption – gas separation process in which the adsorbent is regenerated by rapidly reducing the partial pressure of the adsorbed component, either by lowering the total pressure or by using a purge gas
PTFE	Polytetrafluoroethylene

R

R & D	Research and Development
RIZA	Dutch Institute for Inland Water Management and Waste Water Treatment
RTD	Research and Technology Development

S

S. A.	Sociedad Anónima
SCR	Selective Catalytic Reduction
SNCR	Selective Non-Catalytic Reduction
SSD	Self-Sustaining Decomposition
SSP	Single Superphosphates
Substantial change	According to the IPPC Directive, a substantial change in operation shall mean a change in operation which, in the opinion of the competent authority, may have significant negative effects on human beings or the environment

T

TAK-S	Technischer Arbeitskreis Schwefel
TSP	Triplesuperphosphates
TWG	Technical Working Group

U

UAN	Urea Ammonium Nitrate
UBA	Umweltbundesamt Federal Environmental Agency
UNEP	United Nations Environment Programme
UNFCCC	United Nations Framework Convention on Climate Change
Urea	$CO(NH_2)_2$
USD	US dollar

V

VITO	Flemish Institute for Technological Research
VSCC	Vertical Submerged Carbamate Condenser
VOC	Volatile Organic Compounds

W

WESP	Wet Electrostatic Precipitator
WSA	Wet gas Sulphuric Acid (Topsøe)

Chemical formulas

Al_2O_3	Aluminium oxide (alumina)
$Ca(OH)_2$	Calcium hydroxide
$Ca_{10}(PO_4)_6(F,OH)_2$	Fluorapatite
$Ca_3(PO_4)_2$	Tricalcium phosphate
$CaCO_3$	Calcium carbonate (lime)
CaF_2	Fluorite
CaO	Calcium oxide
$CaSO_4$	Calcium sulphate (gypsum)
CH_3OH	Methanol
CH_4	Methane
CO	Carbon monoxide
CO_2	Carbon dioxide
Co_3O_4	Tricobalt tetraoxide
CoO	Cobalt oxide
CS_2	Carbon disulfide
CuO	Copper oxide
CuS	Copper (II) sulphide
C_xH_y	Hydrocarbons
Fe_2O_3	Hematite, Iron (III) oxide
H_2	Hydrogen
H_2O_2	Hydrogen peroxide
H_2S	Hydrogen sulphide
H_2SiF_6	Fluosilicic acid, hydrofluorosilicic acid
H_2SO_4	Sulphuric acid
H_2SO_5	Peroxomonosulphuric acid
HCl	Hydrochloric acid
HF	Hydrofluoric acid
$HNCO$	Isocyanic acid
HNO_3	Nitric acid
K_2SO_4	Potassium sulphate
KCl	Potassium chloride
$LiBr$	Lithium bromide
$Mg(NO_3)_2$	Magnesium nitrate
$MgCO_3$	Magnesium carbonate
$MgSiF_6$	Magnesium hexafluorosilicate
$MgSO_4$	Magnesium sulphate

MoS_2	Molybdenite
N_2	Nitrogen
N_2O	Dinitrogen oxide, nitrous oxide
$NH_2CONHCONH_2$	Biuret
NH_2COONH_4	Ammonium carbamate
NH_3	Ammonia
$(NH_4)_2SO_4$	Ammonium sulphate
NO	Nitric oxide
NO_2	Nitrogen dioxide
NO_x	Nitrogen oxides
P_2O_5	Phosphorus pentoxide
SiF_4	Tetrafluorosilane
SiO_2	Silicon dioxide
SO_2	Sulphur dioxide
SO_3	Sulphur trioxide
TiO2	Titanium dioxide
V_2O_5	Vanadium pentoxide
ZnO	Zinc oxide
ZnS	Zinc sulphide

14 ANNEXES

14.1 Cost calculations for retrofitting H_2SO_4 plants

Table 14.1 shows cost calculations for retrofitting H_2SO_4 plants. The calculation is based on the following assumptions:

SO_2 content:	with 5 – 7 % SO_2, calculated with 5 %
	with 9 – 12 % SO_2, calculated with 10 %
O_2 content:	5 – 7 % SO_2 corresponds to 6 – 9 % O_2
	9 – 12 % SO_2, corresponds to 8 – 11 % O_2
Conversion rate in %:	accuracy of 0.1 %

Fixed: lifetime for all installations of 10 years
operation costs of 3 %
interest rate of 4 %
price of H_2SO_4: EUR 20/tonne ex works
labour costs: EUR 37000/man/year
utilities for Peracidox and alkaline scrubbing: +30 % capital investment costs
warranted SO_2 content after scrubbing: <200 mg SO_2/Nm^3 (<70 ppm SO_2)
a steam price of EUR 10/tonne.

Abbreviations: SC single contact
SA single aborption
DC double contact
DA double absorption.

	Capacity	Inlet SO_2	Process		Average SO_2 conversion %		Costs	
							EUR/tonne SO_2	EUR/tonne H_2SO_4
	tonnes H_2SO_4/day	%	before retrofit	after retrofit	before	after	abated	additional
1	250	5 – 7	4 bed SC/SA	4 bed DC/DA	98.00	99.60	1.317	13.76
2			4 bed SC/SA	4 bed DC/DA + Cs in bed 4	98.00	99.70	1.159	12.87
3			4 bed SC/SA	+ Cs in bed 4	98.00	99.10	3	0.02
4			4 bed SC/SA	+ TGS Peracidox	98.00	99.87	1.048	12.80
5			4 bed SC/SA	+ TGS (alkaline)	98.00	99.87	1.286	15.70
6		9 – 12	4 bed DC/DA	+ Cs in bed 4	99.60	99.70	367	0.24
7			4 bed DC/DA	5 bed DC/DA + Cs in bed 5	99.60	99.80	3.100	4.03
8			4 bed DC/DA	+ TGS Peracidox	99.60	99.94	3.910	8.68
9			4 bed DC/DA	+ TGS (alkaline)	99.60	99.94	6.636	14.73
10	500	5 – 7	4 bed SC/SA	4 bed DC/DA	98.00	99.60	867	9.06
11			4 bed SC/SA	4 bed DC/DA + Cs in bed 4	98.00	99.70	835	9.27
12			4 bed SC/SA	+ Cs in bed 4	98.00	99.10	5	0.04
13			4 bed SC/SA	+ TGS Peracidox	98.00	99.87	718	8.77
14			4 bed SC/SA	+ TGS (alkaline)	98.00	99.87	883	10.78
15		9 – 12	4 bed DC/DA	+ Cs in bed 4	99.60	99.70	363	0.24
16			4 bed DC/DA	5 bed DC/DA + Cs in bed 5	99.60	99.80	1.559	2.03
17			4 bed DC/DA	+ TGS Peracidox	99.60	99.94	2.209	4.90
18			4 bed DC/DA	+ TGS (alkaline)	99.60	99.94	4.591	10.19
19	1000	9 – 12	4 bed DC/DA	+ Cs in bed 4	99.60	99.70	356	0.23
20			4 bed DC/DA	5 bed DC/DA + Cs in bed 5	99.60	99.80	1.020	1.33
21			4 bed DC/DA	+ TGS Peracidox	99.60	99.94	1.359	3.02
22			4 bed DC/DA	+ TGS (alkaline)	99.60	99.94	3.432	7.62

Table 14.1: Cost calculation for retrofitting H_2SO_4 plants
[154, TWG on LVIC-AAF, 2006], developed by an ESA group for EGTEI