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.

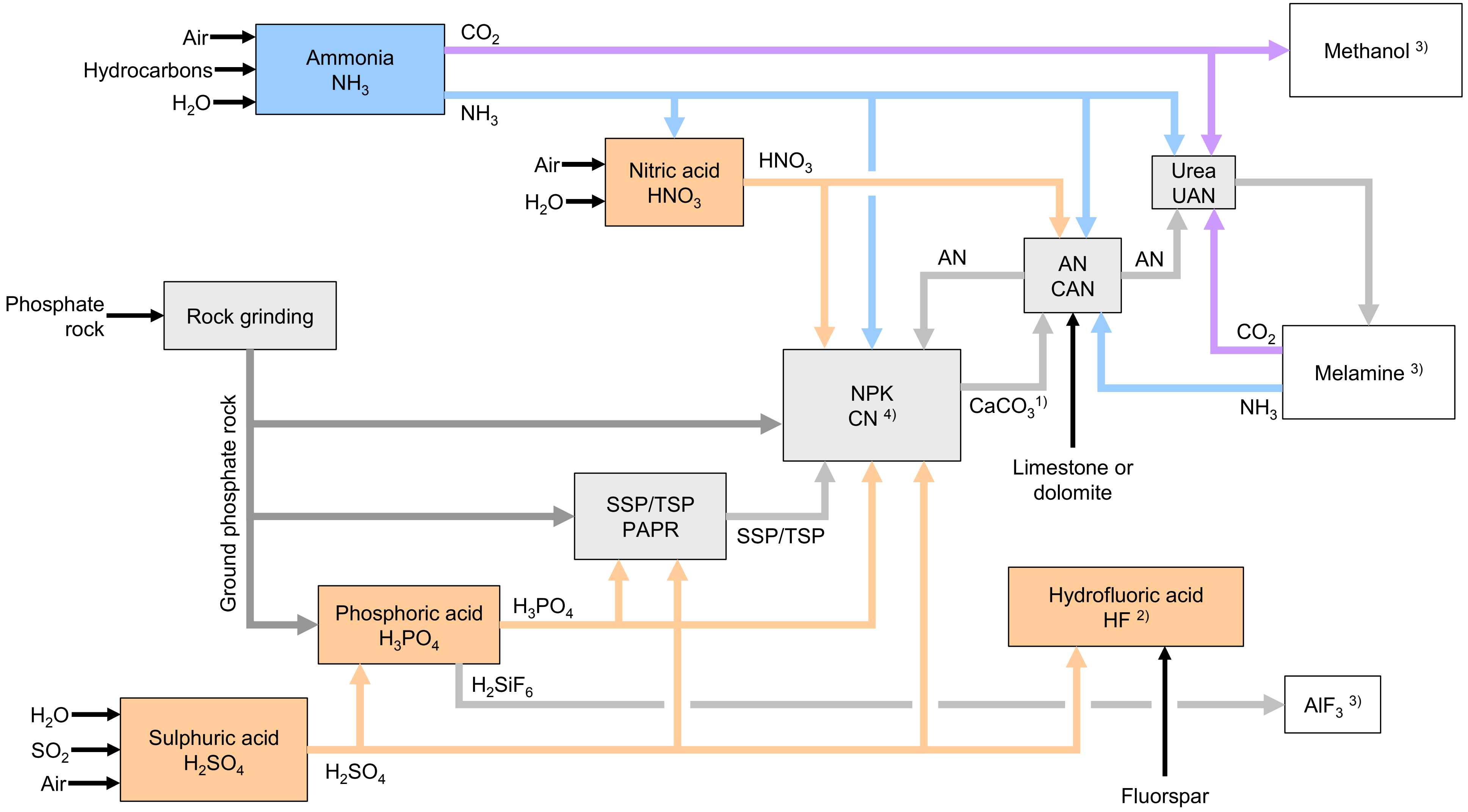

Figure I: Overview of boundaries and links between the LVIC-AAF industries

[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	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 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**	**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 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).