

#### "Capacity Building and Strengthening Institutional Arrangement"

#### Workshop: "Best Available Techniques (BAT)

# BAT on Fertilizers Industries (Section 1)

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APAT

Agency for Environmental Protection and Technical Services



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#### **1. Introduction**

#### **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, P2O5, Steam, Water and CO2.
- 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.



#### **1. Introduction**

- Excess thermal energy should be used on-site or offsite 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 NOx concentration emission levels given in the Table:

Diana and a second	NO <sub>x</sub> emission as NO <sub>2</sub>	
Plant concept	mg/Nm <sup>3</sup>	
Advanced conventional reforming processes and processes with reduced primary reforming	90 - 230 <sup>x</sup>	
	a) 80	
Heat exchange autothermal reforming	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 of emission factors of 0.29 – 0.32 kg/tonne NH <sub>3</sub> are seen as a benchmark fo processes and processes with reduced primary reforming. For heat excha emission factor of 0.175 kg/tonne NH <sub>3</sub> is seen as a benchmark.	r conventional reforming	



Techniques such as SNCR at the primary reformer (if the furnace allows the required temperature/retention time windows), low NOx 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.

<u>Techniques</u> to achieve the energy consumption levels

(see table) are:



Plant concent	Net energy consumption <sup>x</sup>	
Plant concept	GJ(LHV)/tonne NH <sub>3</sub>	
Conventional reforming processes, processes with reduced primary reforming or heat exchange autothermal reforming	27.6 - 31.8	

<sup>x</sup> For interpretation of the given energy consumption levels, see Section 2.3.1.1. As a consequence, the levels might vary up to  $\pm$  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.

- a) extended preheating of the hydrocarbon feed, preheating of combustion air;
- b) installation of a second generation gas turbine,
- c) modifications of the furnace burners (to assure an adequate distribution of gas turbine exhaust over the burners),
- d) rearrangement of the convection coils and addition of additional surface,
- e) pre-reforming in combination with a suitable steam saving project.

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Other options are improved CO2 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 washfor 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, <u>sulphur</u> is recovered from flue-gases, e.g. by applying a combination of a <u>Claus unit with tail gas treatment</u> to achieve BAT associated emission levels and efficiencies given in the BREF on Oil and Gas Refineries.

BAT is to remove NH3 from process condensates, e.g. by stripping.

<u>**NH3</u>** is recovered from purge and flash gases in a closed loop.</u>



# **Production of Nitric Acid**

BAT is to use recoverable energy: co-generated steam and/or electrical power. BAT is to reduce emissions of N2O and to achieve the emission factors or emission concentration levels given in the Table:

		N <sub>2</sub> O emission level <sup>x</sup>	
		kg/tonne 100 % HNO <sub>3</sub>	ppmv
M/M, M/H	New plants	0.12 - 0.6	20 - 100
and H/H	Existing plants	0.12 - 1.85	20 - 300
L/M plants No conclusion drawn			
* the levels relate to the average emission levels achieved in a campaign of the oxidation catalyst			



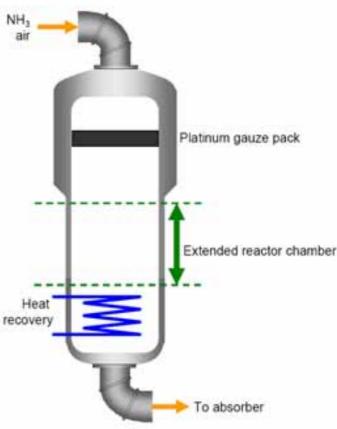
By applying a combination of the following techniques:

- 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 NH3/air ratio
- optimising the pressure and temperature of the oxidation step
- N2O decomposition by extension of the reactor chamber in new plants
- catalytic N2O decomposition in the reactor chamber
- combined NOx and N2O abatement in tail gases.



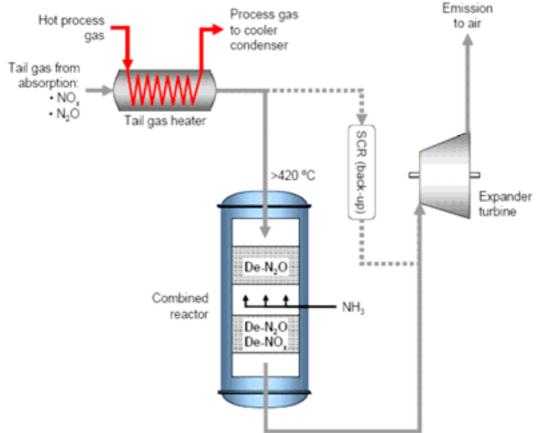
Industry and one Member State do not agree with the N2O emission levels associated with the application of BAT for existing plants due to the limited experience with the **De-N2O techniques**.

Industry and one Member State claim that the BAT range should include 2.5 kg N2O/tonne 100% HNO3 for existing plants.





BAT is to reduce emissions during startup and shutdown conditions. BAT is to reduce emissions of NOx and to achieve the emission levels given in the Table:





		N <sub>2</sub> O emission level <sup>x</sup>	
		kg/tonne 100 % HNO <sub>3</sub>	ppmv
M/M, M/H	New plants	0.12 - 0.6	20 - 100
and H/H	Existing plants	0.12 - 1.85	20 - 300
L/M plants No conclusion drawn			
<sup>x</sup> the levels relate to the average emission levels achieved in a campaign of the oxidation catalyst			

by applying one or a combination of the following techniques: a) optimisation of the absorption stage; b) combined NOx and N2O abatement in tail gases; c) SCR;d) addition of H2O2 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 the Table:

Example plant	Conversion type	SO <sub>2</sub> level in mg/Nm <sup>3</sup>		
		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 5 <sup>th</sup> catalyst bed	250	30	88 %
Newmont Gold, US	Double contact			
CPM, Brazil	Double contact			

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 SO2 levels required to determine the SO2 conversion rate and the SO2 emission level. The options to achieve SO3/H2SO4 mist emission levels (see Table) are:

	Emission level as H <sub>2</sub> SO <sub>4</sub>
All processes	$10-35 \text{ mg/Nm}^3$
Yearly averages	

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 NOx emissions.

BAT is to recycle exhaust gases from product H2SO4stripping 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/Nm3.
- 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 P2O5 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 P2O5 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 P2O5 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 dust emissions from rock grinding, e.g. by application of fabric filters or ceramic filters and to achieve dust emission levels of 2.5 - 10mg/Nm3.



- 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.
- 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/Nm3 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.