“Capacity Building and Strengthening Institutional Arrangement”

Workshop: “Best Available Techniques (BAT)

BREF on Fertilizers Industries

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1. Introduction

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 super phosphate and ammonium sulphate.

2. Productive Cycles

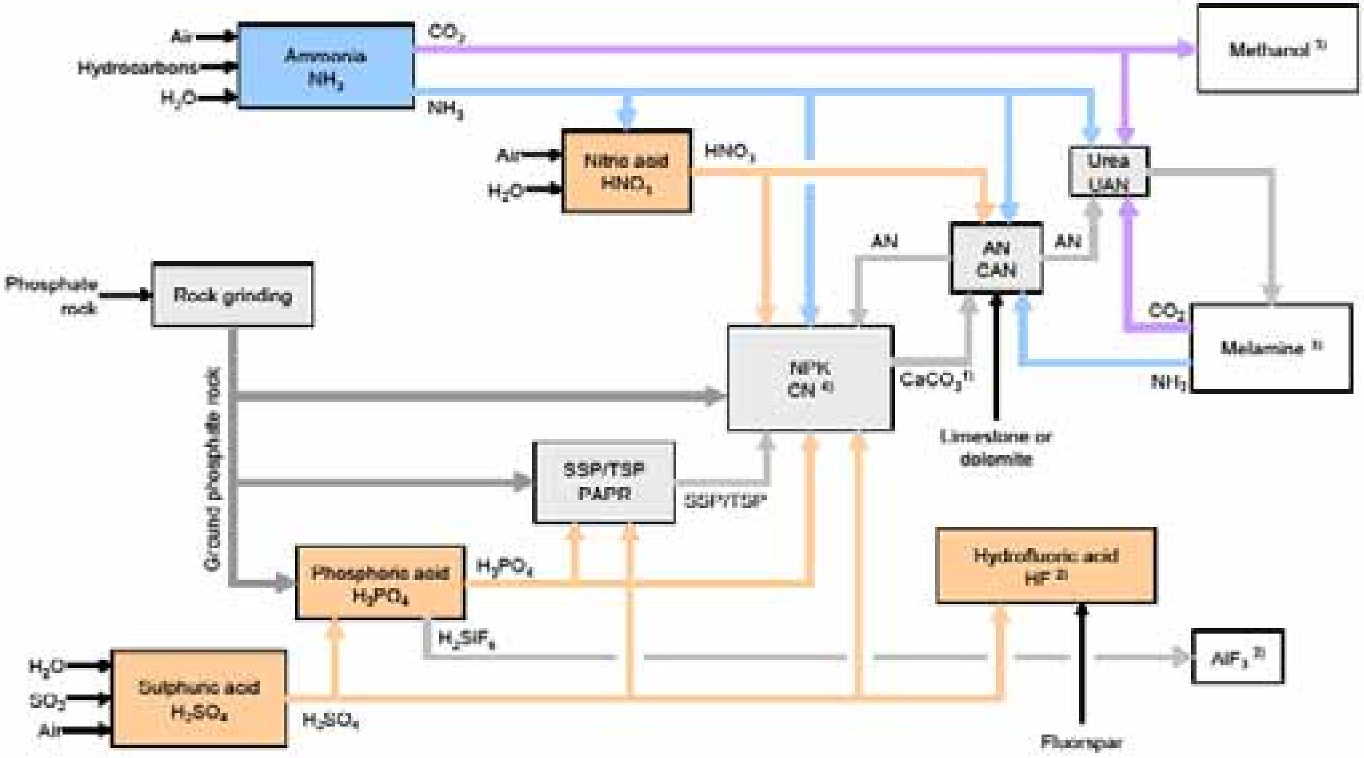


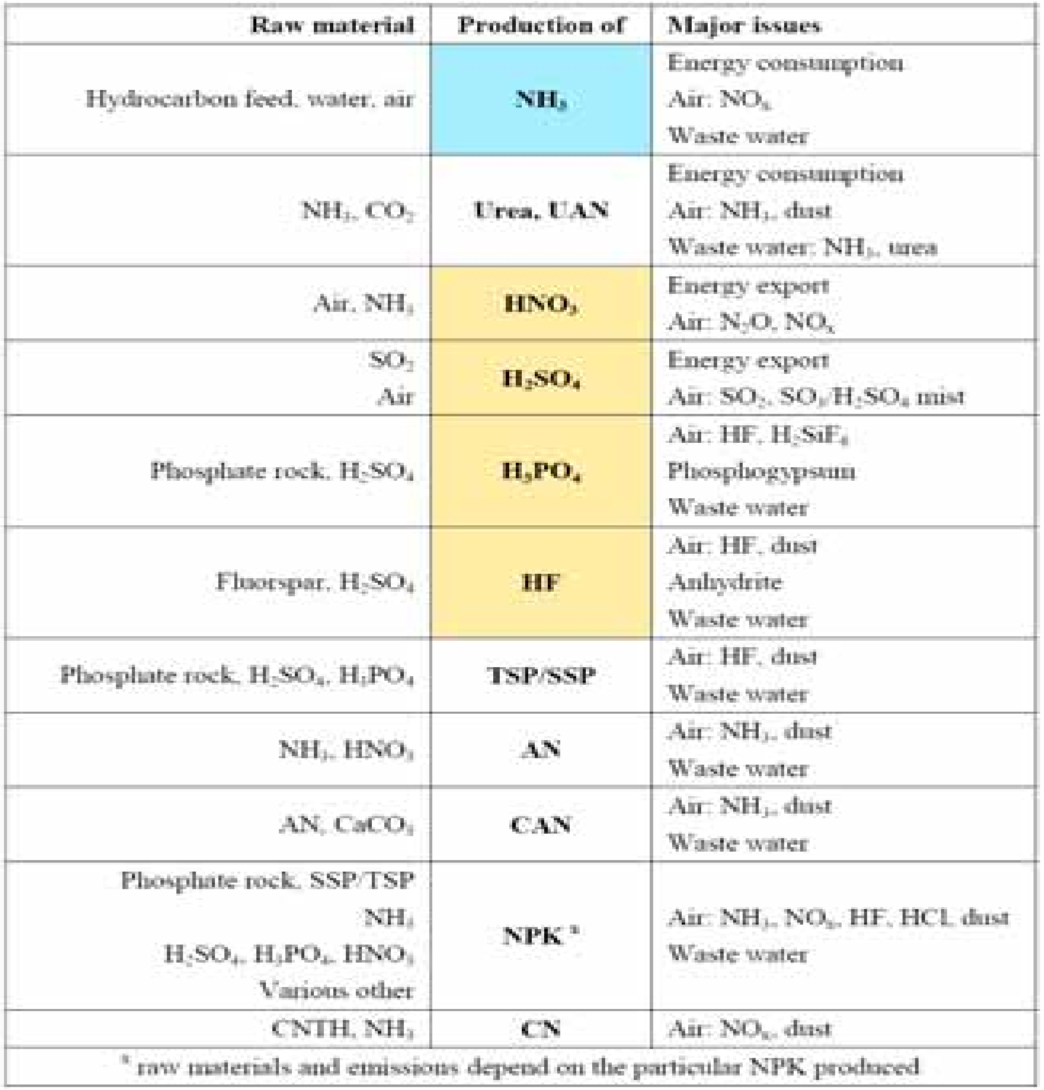
Figure I: Overview of boundaries and links between the LVIC-AAF industries

[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)

2. Productive Cycles

- 97% of N fertilisers are derived from ammonia and 70% of phosphate fertilisers are derived from phosphoric acid. Potash is used as such.
- These three materials: ammonia (NH_3), phosphoric acid (H_3PO_4) and potash (K_2CO_3), give a very good picture of the progression of the fertiliser industry.
- Energy required for N fertiliser production is fairly evenly distributed around the planet (trend towards production in locations where cheap Natural Gas is available: South Asia and China).

2. Productive Cycles



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 [a]	Air: NH_3, NO_x, HF, HCl, dust Waste water
CNTH, NH_3	CN	Air: NO_x, dust

[a] raw materials and emissions depend on the particular NPK produced

2. Productive Cycles

- ***H3PO4*** is obtained by a reaction between phosphate rock and an acid, mostly sulphuric acid. The main producers of phosphate rock and phosphate fertilisers are US, the former USSR, China, Egypt, the Maghreb countries, Senegal, Togo and South Africa, and the Middle East. For several of these countries the phosphate industry makes an important contribution to their economies.
- ***K2CO3*** is produced in the few countries where the ores are located: Russia and Belarus (33%), North America (40%), W.Europe (17%), Israel and Jordan (8%).

3. Main environmental issues

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.

3. Main environmental issues

- The steam is supplied by boiler plants, cogeneration plants or is roduced 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.

- 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 [CO(NH2)2].

3. Main environmental issues

- 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.

3. Main environmental issues

Energy consumption and emission of Greenhouse Gases

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.

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**.

3. Main environmental issues

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.

3. Main environmental issues

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 NH3, compared with 75 GJ/tonne for the processes prevalent in the early 1960s.

3. Main environmental issues

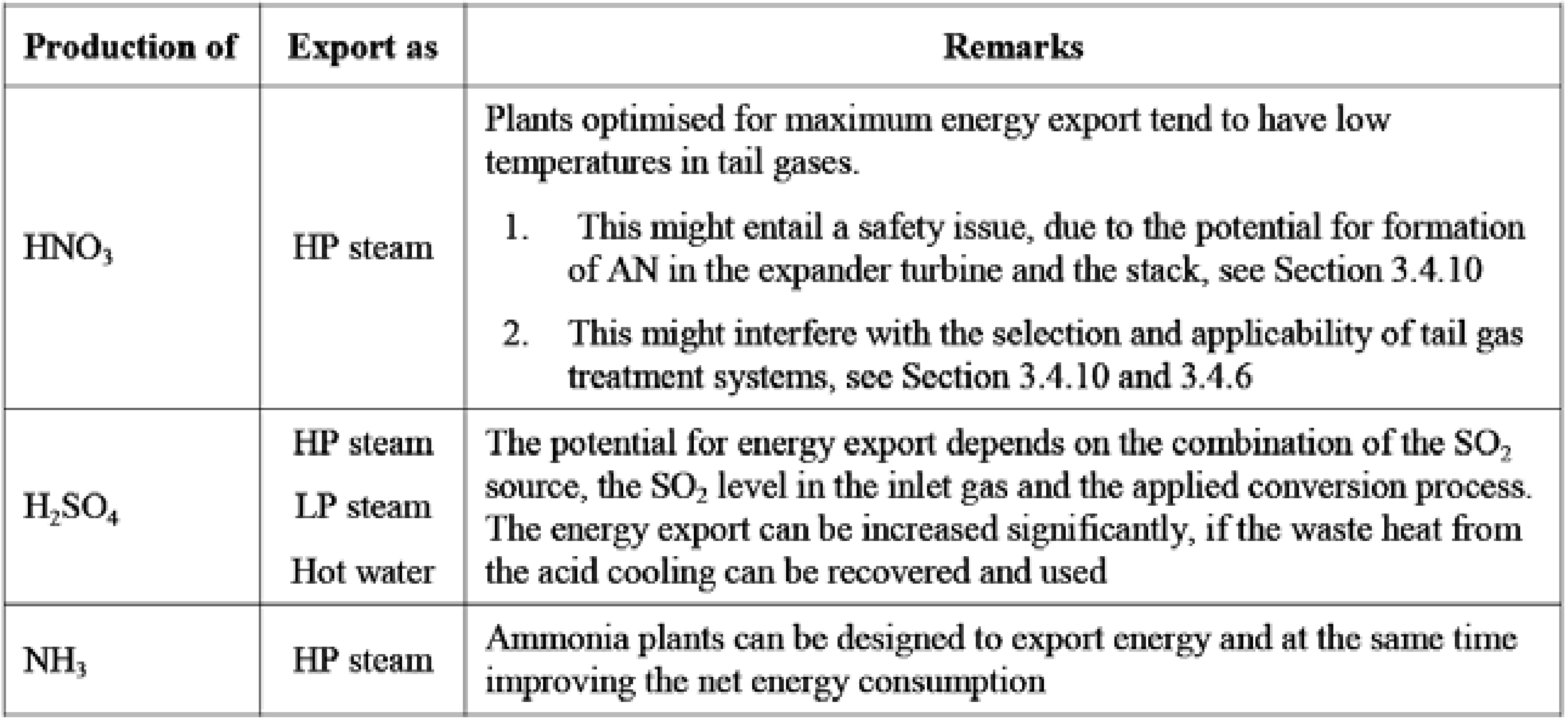
Partial oxidation processes use considerably more energy than reforming processes. In 1995, the average for all plants in the US fertiliser industry was about 40 GJ/tonne

Energy export

Amongst the “Ammonia, Acids and Fertilisers” 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.

3. Main environmental issues

If all thermal energy is converted to electrical power via a steam turbine, the net energy export will be reduced by approximately 65 %.



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

3. Main environmental issues

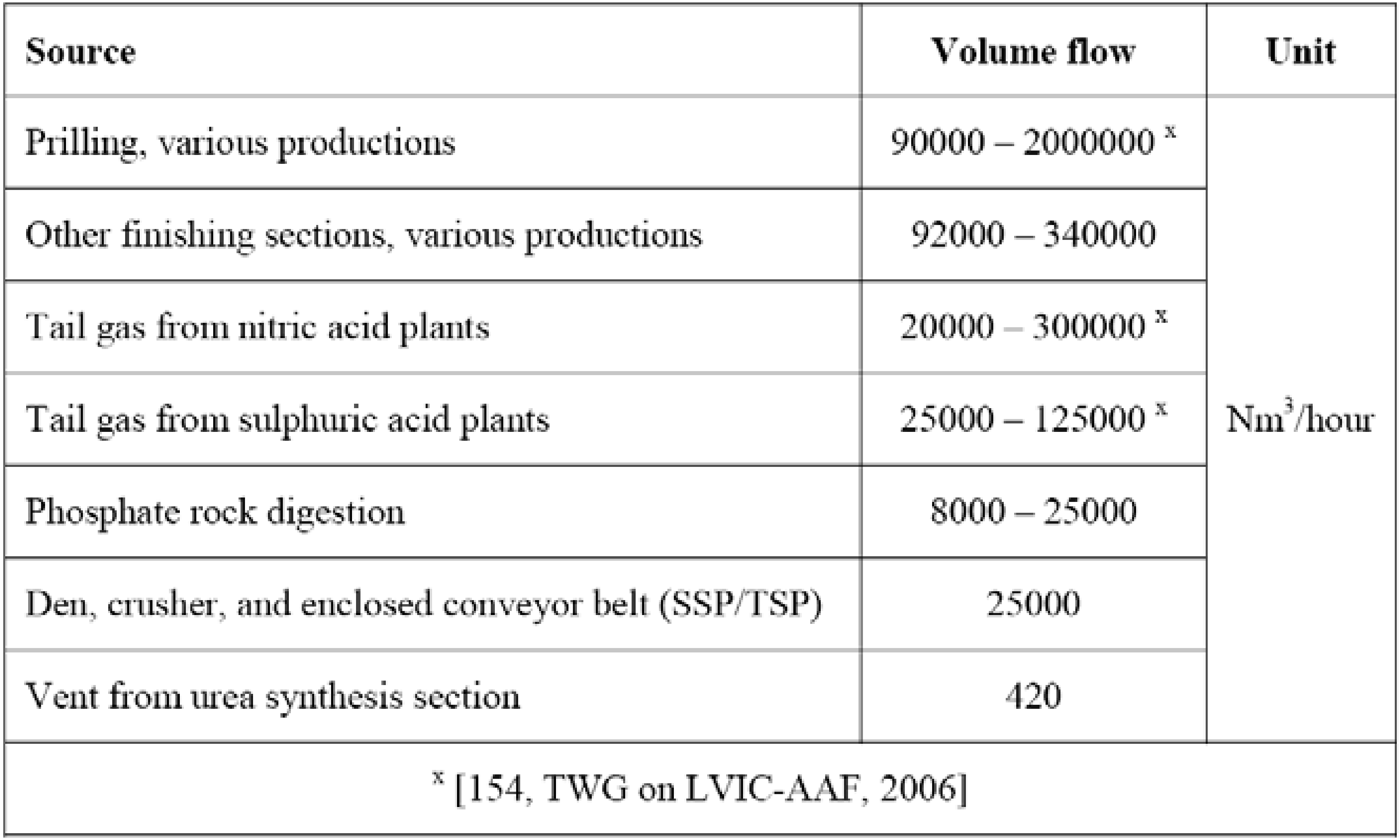
High exhaust gas volume Flows

The main pollutants emitted to air are NOx, SO2, HF and Dust.

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.

Table 1.4 shows some examples for emission volume flows.

3. Main environmental issues



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]

3. Main environmental issues

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.

4–5 tonnes of phosphogypsum are generated per tonne P_2O_5 manufactured in the production of H_3PO_4.

3. Main environmental issues

If Europe’s production capacity (2.25 Mtonnes per year) 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.

3. Main environmental issues

Issues arising from Impurities in raw Materials

Raw materials with the potential for importing undesired compounds into the “Ammonia, Acids and Fertilisers”

Plant are:

-Phosphate rock

-Fluorspar

-H_2SO_4, e.g. technical quality from non-ferrous metal industries, also known as “fatal acid”.

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

3. Main environmental issues

One issue is the radioactivity in different phosphate rocks 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 multi-nutrient fertilisers.

It has a natural radioactivity. However, the radioactivity levels measured are considered to be lower than the background levels.

3. Main environmental issues

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).

3. Main environmental issues

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.

3. Main environmental issues

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.

AN or AN based N/P/K fertilisers

[AN = Ammonium Nitrate (NH_4NO_3)]

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).

3. Main environmental issues

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.

3. Main environmental issues

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 NOx 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, single- and triple- super-phosphates) are still curing. Some of the processes taking place during curing are exothermic (e.g. neutralisation).

Generally, the temperature rises less than 10 ºC.

3. Main environmental issues

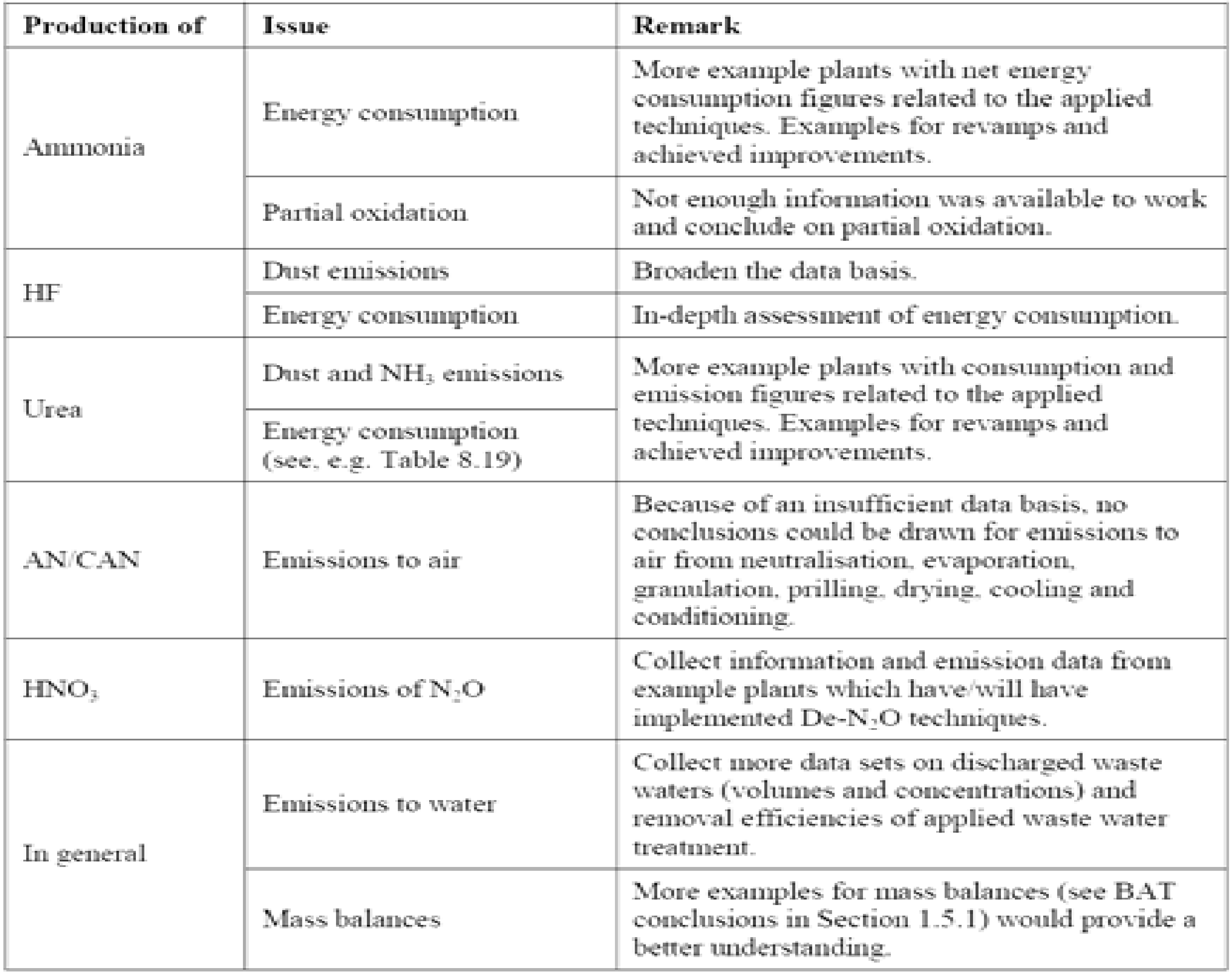
The majority of the information was provided as aggregated data for the production of :

- ***ammonia***
- phosphoric acid
- HF
- ***urea***.

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 N/P/K and AN/CAN.

Next Table gives some *recommendations* for future data collection:

3. Main environmental issues



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.

4. Conclusions

The Techniques and associated Emission and/or consumption Levels, or ranges of Levels, 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;

4. Conclusions

- 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 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.

5. References

Best Available Techniques for the Manufacture of

Large Volume Inorganic Chemicals

- Ammonia, Acids and Fertilisers

http://eippcb.jrc.es/pages/FActivities.htm
(BREF 12.06)