Best Available Techniques
for Pollution Prevention and Control
in the European Fertilizer Industry

Booklet No. 5 of 8:

PRODUCTION OF UREA
and
UREA AMMONIUM NITRATE

2000

EFMA
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Best Available Techniques
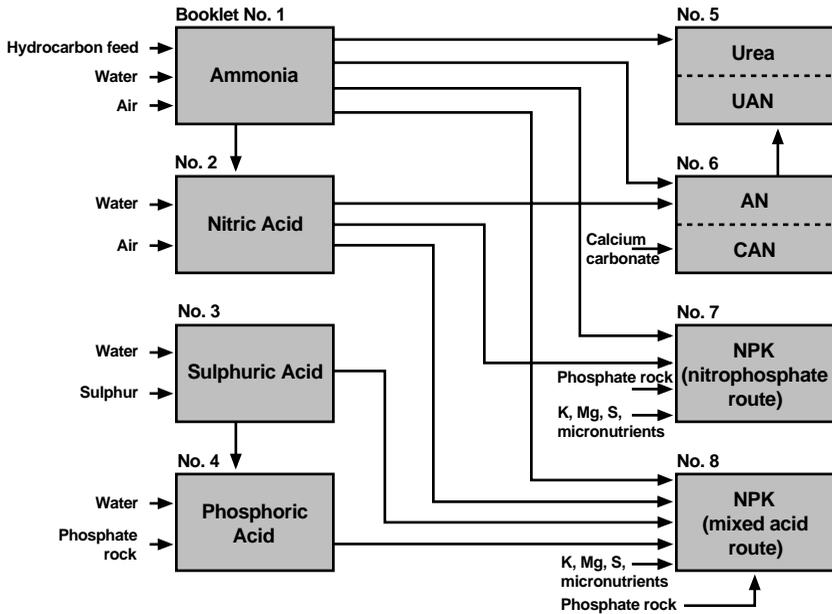for Pollution Prevention and Control
in the European Fertilizer Industry

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PRODUCTION OF UREA
and
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EFMA's BAT Booklets

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PREFACE

In 1995, the European Fertilizer Manufacturers Association (EFMA) prepared eight Booklets on Best Available Techniques (BAT) in response to the proposed EU Directive on integrated pollution prevention and control (IPPC Directive). These booklets were reviewed and updated in 1999 by EFMA experts drawn from member companies. They cover the production processes of the following products:-

No. 1 Ammonia

No. 2 Nitric Acid

No. 3 Sulphuric Acid
       (updated in collaboration with ESA)

No. 4 Phosphoric Acid

No. 5 Urea and Urea Ammonium Nitrate (UAN)

No. 6 Ammonium Nitrate (AN) and Calcium Ammonium Nitrate (CAN)

No. 7 NPK Compound Fertilizers by the Nitrophosphate Route

No. 8 NPK Compound Fertilizers by the Mixed Acid Route

The Booklets reflect industry perceptions of what techniques are generally considered to be feasible and present achievable emission levels associated with the manufacturing of the products listed above. The Booklets do not aim to create an exhaustive list of BAT but they highlight those most widely used and accepted. They have been prepared in order to share knowledge about BAT between the fertilizer manufacturers, as well as with the regulatory authorities.

The Booklets use the same definition of BAT as that given in the IPPC Directive 96/61 EC of 1996. BAT covers both the technology used and the management practices necessary to operate a plant efficiently and safely. The EFMA Booklets focus primarily on the technological processes, since good management is considered to be independent of the process route. The industry recognises, however, that good operational practices are vital for effective environmental management and that the principles of Responsible Care should be adhered to by all companies in the fertilizer business.

The Booklets give two sets of BAT emission levels:-
– For existing production units where pollution prevention is usually obtained by revamps or end-of-pipe solutions
– For new plants where pollution prevention is integrated in the process design

The emission levels refer to emissions during normal operations of typical sized plants. Other levels may be more appropriate for smaller or larger units and higher emissions may occur in start-up and shut-down operations and in emergencies.

Only the more significant types of emissions are covered and the emission levels given in the Booklets do not include fugitive emissions and emissions due to rainwater. Furthermore, the Booklets do not cover noise, heat emissions and visual impacts.

The emission levels are given both in concentration values (ppm, mg.m^{-3} or mg.l^{-1}) and in load values (emission per tonne of product). It should be noted that there is not necessarily a direct link between the concentration values and the load values. EFMA recommends that the given emission levels should be used as reference levels for the establishment of regulatory authorisations. Deviations should be allowed as governed by:-

– **Local environmental requirements**, given that the global and inter-regional environments are not adversely affected
– **Practicalities and costs of achieving BAT**
– **Production constraints** given by product range, energy source and availability of raw materials

If authorisation is given to exceed these BAT emission levels, the reasons for the deviation should be documented locally.

Existing plants should be given ample time to comply with BAT emission levels and care should be taken to reflect the technological differences between new and existing plants when issuing regulatory authorisations, as discussed in these BAT Booklets.

A wide variety of methods exist for monitoring emissions. The Booklets provide examples of methods currently available. The emission levels given in the Booklets are subject to some variance, depending on the method chosen and the precision of the analysis. It is important when issuing regulatory authorisations, to identify the monitoring method(s) to be applied. Differences in national practices may give rise to differing results as the methods are not internationally standardised. The given emission levels should not, therefore, be considered as absolute but as references which are independent of the methods used.

EFMA would also advocate a further development for the authorisation of fertilizer plants. The plants can be complex, with the integration of several production processes and they can be located close to other industries. Thus there should be a shift away from authorisation governed by concentration values of single point emission sources. It would be better to define maximum allowable load values from an entire operation, eg from a total site area. However, this implies that emissions from single units should be allowed to exceed the values in the BAT Booklets, provided that the total load from the whole complex is comparable with that which can be deduced from the BAT Booklets. This approach will enable plant management to find the most cost-effective environmental solutions and would be to the benefit of our common environment.

Finally, it should be emphasised that each individual member company of EFMA is responsible for deciding how to apply the guiding principles of the Booklets.

Brussels, April 2000

DEFINITIONS

The following definitions are taken from Council directive 96/61/EC of 1996 on Integrated Pollution Prevention and Control:-

"Best Available Techniques" mean 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 or, where that is not practicable, generally to reduce emissions and the impact on the environment as a whole:-

"Techniques" include both the technology used and the way in which the installation is designed, built, maintained, operated and decommissioned.

"Available" techniques mean those developed on a scale which allows implementation in the relevant industrial sector under economically 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 for the environment as a whole.
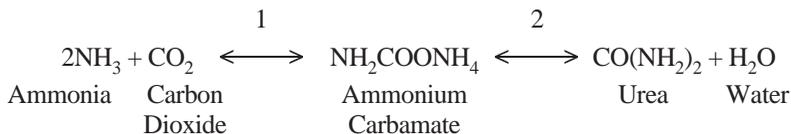
1. INTRODUCTION

The application of the Best Available Techniques (BAT) concept as per the EU Directive on Integrated Pollution Prevention and Control (IPPC) requires emissions into air, water and to land to be prevented. Where this is not practicable the emissions should be minimised by the use of recovery and recycling techniques with due account being given to the efficient use of energy and material resources.

This Booklet describes the production processes for urea and urea ammonium nitrate (UAN) and the associated emissions. The Booklet does not give a detailed description of all the different processes in operation or available from technology suppliers. Any process which can meet the emission figures given in Chapter 8 should be considered as BAT.

2. DESCRIPTION OF UREA PRODUCTION PROCESSES

The commercial synthesis of urea involves the combination of ammonia and carbon dioxide at high pressure to form ammonium carbamate which is subsequently dehydrated by the application of heat to form urea and water.

$$\underset{\substack{\text{Ammonia} \quad \text{Carbon} \\ \text{Dioxide}}}{2NH_3 + CO_2} \xrightarrow{\quad 1 \quad} \underset{\substack{\text{Ammonium} \\ \text{Carbamate}}}{NH_2COONH_4} \xrightarrow{\quad 2 \quad} \underset{\substack{\text{Urea} \quad \text{Water}}}{CO(NH_2)_2 + H_2O}$$

Reaction 1 is fast and exothermic and essentially goes to completion under the reaction conditions used industrially. 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.

The design of commercial processes has involved the consideration of how to separate the urea from the other constituents, how to recover excess NH_3 and decompose the carbamate for recycle. Attention was also devoted to developing materials to withstand the corrosive carbamate solution and to optimise the heat and energy balances.

The simplest way to decompose the carbamate to CO_2 and NH_3 requires the reactor effluent to be depressurised and heated. The earliest urea plants operated on a "Once Through" principle where the off-gases were used as feedstocks for other products. Subsequently "Partial Recycle" techniques were developed to recover and recycle some of the NH_3 and CO_2 to the process. It was essential to recover all of the gases for recycle to the synthesis to optimise raw material utilisation and since recompression was too expensive an alternative method was developed. This involved cooling the gases and re-combining them to form carbamate liquor which was pumped back to the synthesis. A series of loops involving carbamate decomposers at progressively lower pressures and carbamate condensers were used. This was known as the "Total Recycle Process". A basic consequence of recycling the gases was that the NH_3/CO_2 molar ratio in the reactor increased thereby increasing the urea yield.

Significant improvements were subsequently achieved by decomposing the carbamate in the reactor effluent without reducing the system pressure. This "Stripping Process" dominated synthesis technology and provided capital/energy savings. Two commercial stripping systems were developed, one using CO_2 and the other using NH_3 as the stripping gases.

Since the base patents on stripping technology have expired, other processes have emerged which combine the best features of Total Recycle and Stripping Technologies. For convenience total recycle processes were identified as either "conventional" or "stripping" processes.

The urea solution arising from the synthesis/recycle stages of the process is subsequently concentrated to a urea melt for conversion to a solid prilled or granular product.

Improvements in process technology have concentrated on reducing production costs and minimising the environmental impact. These included boosting CO_2 conversion efficiency, increasing heat recovery, reducing utilities consumption and recovering residual NH_3 and urea from plant effluents. Simultaneously the size limitation of prills and concern about the prill tower off-gas effluent were responsible for increased interest in melt granulation processes and prill tower emission abatement. Some or all of these improvements have been used in updating existing plants and some plants have added computerised systems for process control. New urea installations vary in size from 800 to 2,000t.d^{-1} and typically would be 1,500t.d^{-1} units.

Modern processes have very similar energy requirements and nearly 100% material efficiency. There are some differences in the detail of the energy balances but they are deemed to be minor in effect.

Block flow diagrams for CO_2 and NH_3 stripping total recycle processes are shown in Figures 1 and 2.
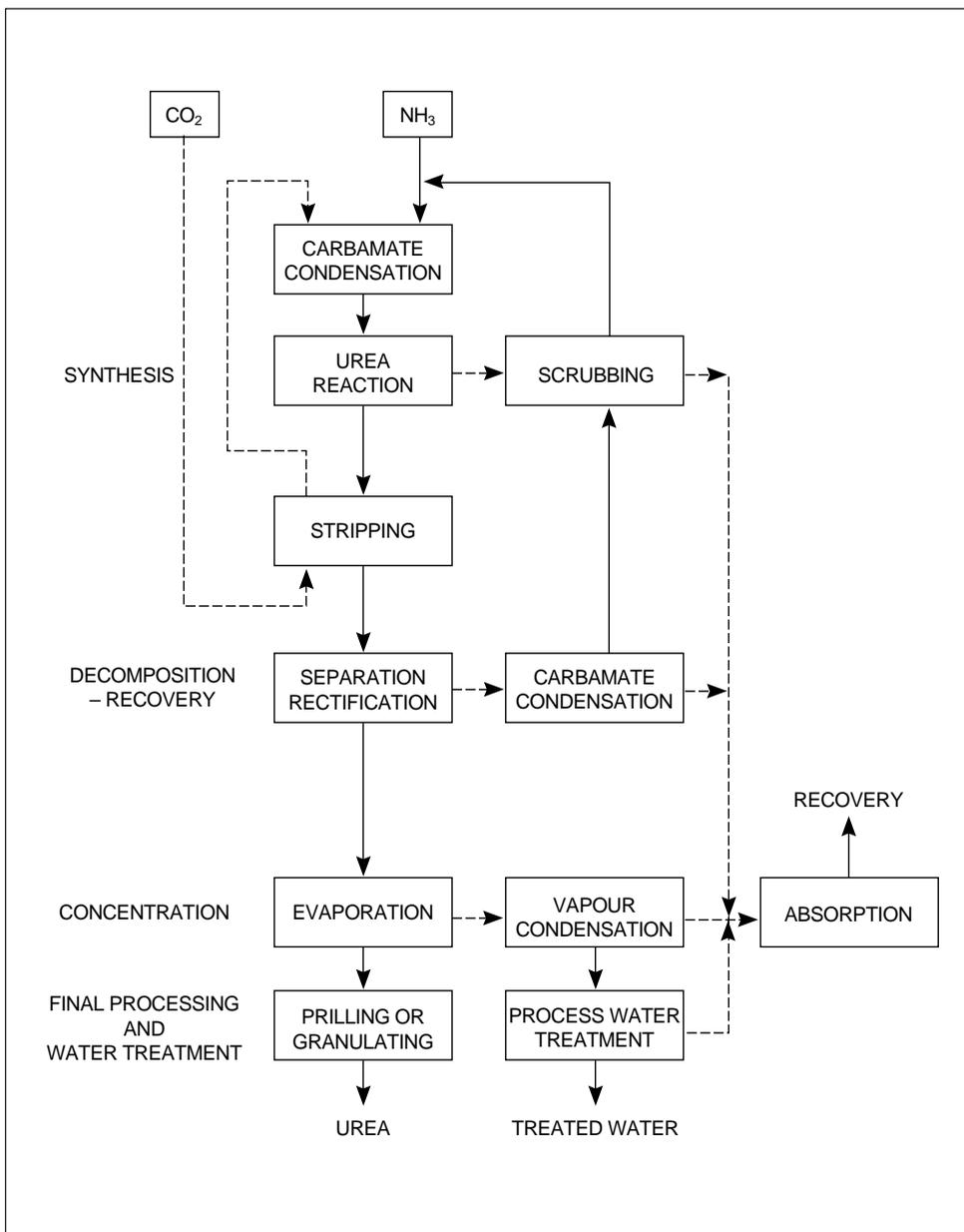
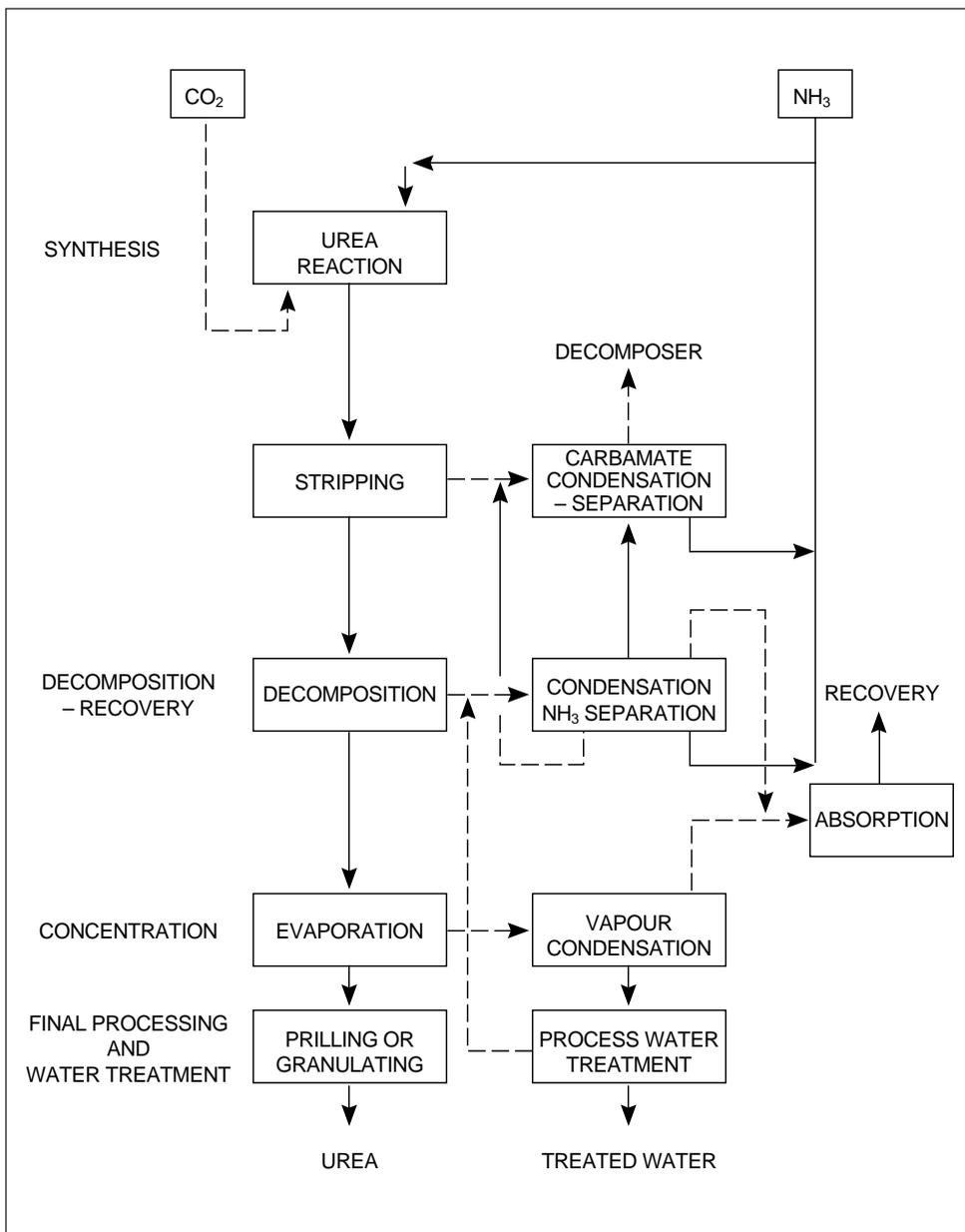*Figure 1 – Block Diagram of a Total Recycle CO$_2$ Stripping Urea Process.*

Figure 2 – Block Diagram of a Total Recycle NH₃ Stripping Urea Process.

2.1 Urea Plant Installations in Europe

62 urea plants are in operation in Western Europe in the year 2000. The total capacity in the fertilizer year 1999/2000 is about 5.8 million tonnes.

2.2 Description of BAT Production Processes

The process water from each process discussed in this section is purified by recovery of dissolved urea, NH_3 and CO_2 which are recycled to the synthesis section via a low pressure carbamate condensation system.

2.2.1 Carbon dioxide stripping process

NH_3 and CO_2 are converted to urea via ammonium carbamate at a pressure of approximately 140bar and a temperature of 180-185°C. The molar NH_3/CO_2 ratio applied in the reactor is 2.95. This results in a CO_2 conversion of about 60% and an NH_3 conversion of 41%. The reactor effluent, containing unconverted NH_3 and CO_2 is subjected to a stripping operation at essentially reactor pressure, using CO_2 as stripping agent. The stripped-off NH_3 and CO_2 are then partially condensed and recycled to the reactor. The heat evolving from this condensation is used to produce 4.5bar steam some of which can be used for heating purposes in the downstream sections of the plant. Surplus 4.5bar steam is sent to the turbine of the CO_2 compressor.

The NH_3 and CO_2 in the stripper effluent are vaporised in a 4bar decomposition stage and subsequently condensed to form a carbamate solution, which is recycled to the 140bar synthesis section. Further concentration of the urea solution leaving the 4bar decomposition stage takes place in the evaporation section, where a 99.7% urea melt is produced.

2.2.2 Ammonia stripping process

NH_3 and CO_2 are converted to urea via ammonium carbamate at a pressure of 150bar and a temperature of 180°C. A molar ratio of 3.5 is used in the reactor giving a CO_2 conversion of 65%. The reactor effluent enters the stripper where a large part of the unconverted carbamate is decomposed by the stripping action of the excess NH_3. Residual carbamate and CO_2 are recovered downstream of the stripper in two successive stages operating at 17 and 3.5bar respectively. NH_3 and CO_2 vapours from the stripper top are mixed with the recovered carbamate solution from the High Pressure (HP)/Low Pressure (LP) sections, condensed in the HP carbamate condenser and fed to the reactor. The heat of condensation is used to produce LP steam.

The urea solution leaving the LP decomposition stage is concentrated in the evaporation section to a urea melt.

2.2.3 Advanced cost & energy saving (ACES) process

In this process the synthesis section operates at 175bar with an NH_3/CO_2 molar ratio of 4 and a temperature of 185 to 190°C.

The reactor effluent is stripped at essentially reactor pressure using CO_2 as the stripping agent. The overhead gas mixture from the stripper is fed to two carbamate condensers in parallel where the gases are condensed and recycled under gravity to the reactor along with absorbent solutions from the HP scrubber and absorber. The heat generated in the first carbamate condenser is used to generate 5bar steam and the heat formed in the second condenser is used to heat the solution leaving the stripper bottom after pressure reduction. The inerts in the synthesis section are purged to the scrubber from the reactor top for recovery and recycle of NH_3 and CO_2. The urea solution leaving the bottom of the stripper is further purified in HP and LP decomposers operating at approx. 17.5bar and 2.5bar respectively. The separated NH_3 and CO_2 are recovered to the synthesis via HP and LP absorbers.

The aqueous urea solution is first concentrated to 88.7%wt in a vacuum concentrator and then to the required concentration for prilling or granulating.

2.2.4 Isobaric double recycle (IDR) process

In this process the urea synthesis takes place at 180-200bar and 185-190°C. The NH_3/CO_2 ratio is approximately 3.5-4, giving about 70% CO_2 conversion per pass.

Most of the unconverted material in the urea solution leaving the reactor is separated by heating and stripping at synthesis pressure using two strippers, heated by 25bar steam, arranged in series. In the first stripper, carbamate is decomposed/stripped by ammonia and the remaining ammonia is removed in the second stripper using carbon dioxides as stripping agent.

Whereas all the carbon dioxide is fed to the plant through the second stripper, only 40% of the ammonia is fed to the first stripper. The remainder goes directly to the reactor for temperature control. The ammonia-rich vapours from the first stripper are fed directly to the urea reactor. The carbon dioxide-rich vapours from the second stripper are recycled to the reactor via the carbamate condenser, irrigated with carbamate solution recycled from the lower-pressure section of the plant.

The heat of condensation is recovered as 7bar steam which is used down-stream in the process. Urea solution leaving the IDR loop contains unconverted ammonia, carbon dioxide and carbamate. These residuals are decomposed and vaporised in two successive distillers, heated with low pressure recovered steam. After this, the vapours are condensed to carbamate solution and recycled to the synthesis loop.

The urea solution leaving the LP decomposition for further concentration, is fed to two vacuum evaporators in series, producing the urea melt for prilling and granulation.

2.3 Process Water Sources and Quantities

A 1,000t.d^{-1} urea plant generates on average approximately 500m^3.d^{-1} process water containing 6% NH_3, 4% CO_2 and 1.0% urea (by weight). The principal source of this water is the synthesis reaction where 0.3tonnes of water is formed per tonne of urea e.g.

$$2NH_3 + CO_2 \longrightarrow CO(NH_2)_2 + H_2O$$
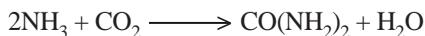
The other sources of water are ejector steam, flush and seal water and steam used in the waste water treatment plant.

The principal sources of urea, NH_3 and CO_2 in the process water are:-

– Evaporator condensate

  The NH_3 and urea in the evaporator condensate are attributable to:-

  – The presence of NH_3 in the urea solution feed to the evaporator

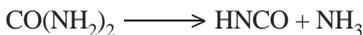 – The formation of biuret and the hydrolysis of urea in the evaporators, both reactions liberating NH_3

  $$2CO(NH_2)_2 \longrightarrow H_2NCONHCONH_2 + NH_3$$

  $$CO(NH_2)_2 + H_2O \longrightarrow 2NH_3 + CO_2$$

  – Direct carry over of urea from the evaporator separators to the condensers (physical entrainment)

  – The formation of NH_3 from the decomposition of urea to isocyanic acid

  $$CO(NH_2)_2 \longrightarrow HNCO + NH_3$$

  The reverse reaction occurs on cooling the products in the condensers

– Off-gases from the recovery/recirculation stage absorbed in the process water

– Off-gases from the synthesis section absorbed in the process water

– Flush and purge water from pumps

– Liquid drains from the recovery section

The purpose of the water treatment is to remove NH_3, CO_2 and urea from the process water and recycle the gases to the synthesis. This ensures raw material utilisation is optimised and effluent is minimised.

2.4 Prilling and Granulation

In urea fertilizer production operations, the final product is in either prilled or granular form. Production of either form from urea melt requires the use of a large volume of cooling air which is subsequently discharged to the atmosphere. A block diagram of the prilling and granulation processes is shown in Figure 3.

2.4.1 Prilling

The concentrated (99.7%) urea melt is fed to the prilling device (e.g. rotating bucket/shower type spray head) located at the top of the prilling tower. Liquid droplets are formed which solidify and cool on free fall through the tower against a forced or natural up-draft of ambient air. The product is removed from the tower base to a conveyor belt using a rotating rake, a fluidised bed or a conical hopper. Cooling to ambient temperature and screening may be used before the product is finally transferred to storage.

The design/operation of the prilling device exerts a major influence on product size. Collision of the molten droplets with the tower wall as well as inter-droplet contact causing

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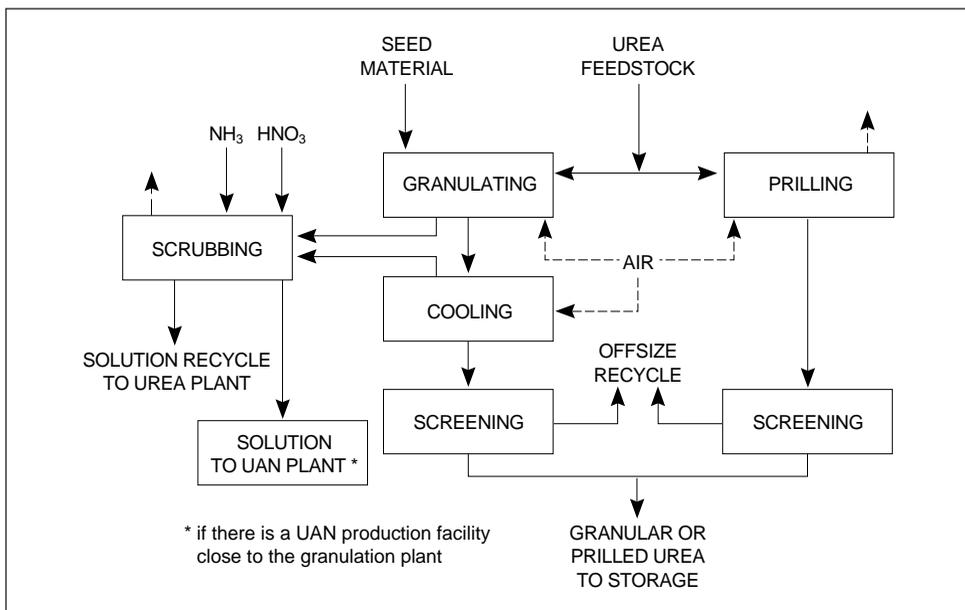
Figure 3 – Block Diagram for Urea Granulation and Prilling Processes.

agglomeration must be prevented. Normally mean prill diameters range from 1.6-2.0mm for prilling operations. Conditioning of the urea melt and "crystal seeding" of the melt, may be used to enhance the anti-caking and mechanical properties of the prilled product during storage/handling.

2.4.2 Granulation

Depending on the process a 95-99.7% urea feedstock is used. The lower feedstock concentration allows the second step of the evaporation process to be omitted and also simplifies the process condensate treatment step. The basic principle of the process involves the spraying of the melt onto recycled seed particles or prills circulating in the granulator. A slow increase in granule size and drying of the product takes place simultaneously. Air passing through the granulator solidifies the melt deposited on the seed material.

Processes using low concentration feedstock require less cooling air since the evaporation of the additional water dissipates part of the heat which is released when the urea crystallises from liquid to solid.

All the commercial processes available are characterised by product recycle, and the ratio of recycled to final product varies between 0.5 and 2.5. Prill granulation or fattening systems have a very small recycle, typically 2 to 4%. Usually the product leaving the granulator is cooled and screened prior to transfer to storage. Conditioning of the urea melt prior to spraying may also be used to enhance the storage/handling characteristics of the granular product.

2.5 Feasible and Available Emission Abatement Techniques

2.5.1 Gaseous emissions

- Scrubbing of off-gases with process condensate prior to venting inerts to atmosphere
- Wet scrubbing of prill tower and granulation plant air to recover urea and NH_3
- Connection of ammonia pump safety relief valves/seals to a flare; connection of tank vents to the plant main stack or other safe location (See 4.6.4)
- Dust reduction by producing granular rather than prilled product
- Bag filtration of dust laden air from transfer points, screens, bagging machines, etc. coupled with a dissolving system for recycle to the process
- Flash melting of solid urea over-size product for recycle to the process
- Collection of solid urea spillages on a dry basis

2.5.2 Liquid emissions

- Treatment of process waste water/condensate for recovery of urea, NH_3 and CO_2
- Improved evaporation heater/separator design to minimise urea entrainment
- Provision of adequate storage capacity for plant inventory to cater for plant upset and shut-down conditions
- Provision of submerged tanks to collect plant washings, etc. from drains for recycle to the waste water treatment section
- Use of mechanical seals instead of gland packing for pumps
- Use of closed circuit gland cooling water system for reciprocating pumps
- Replacement of reciprocating machinery by centrifugal type

2.5.3 General

- Computerisation of process control to provide consistent optimum operating conditions
- Implementation of regular scheduled maintenance programmes and good housekeeping practices

2.6 Description of Process Water BAT Treatment Systems

A block diagram for a waste-water treatment plant is shown in Figure 4.

2.6.1 Desorption hydrolysis system

Heated process water is fed to the top of Desorber 1 where it is stripped of NH_3 and CO_2 by gas streams from Desorber 2 and the hydrolyser. The liquid leaving Desorber 1 bottom is preheated to 190°C and fed at 17bar pressure to the top of the hydrolyser. 25bar steam is introduced to the bottom of the hydrolyser and under these conditions the urea is decomposed and the gases are countercurrently stripped. The vapours go to Desorber 1. The urea free liquid
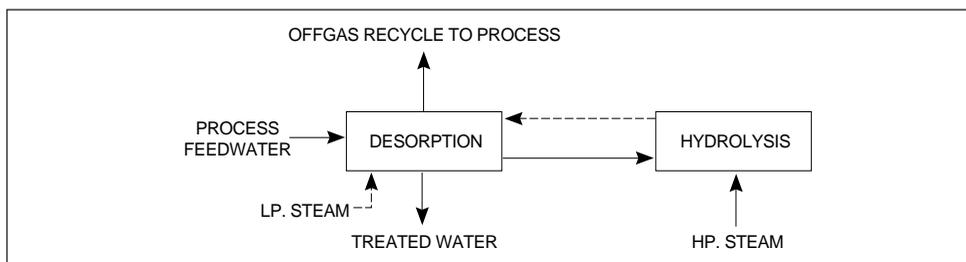
Figure 4 – Block Diagram for Waste Water Treatment Plant.

stream leaving the desorber is used to heat the hydrolyser feed stream and is fed after expansion to Desorber 2 where LP steam countercurrently strips the remaining NH_3 and CO_2 and the off-gases pass to Desorber 1.

The off-gases from Desorber 1 are condensed in a cooled reflux condenser/separator. Part of the separated liquid is pumped back to Desorber 1 and the remainder is returned to the LP recirculation section of the urea plant. Residual NH_3 in the separator off-gas is recovered in an atmospheric absorber and returned to the LP recirculation section also.

The treated water which leaves Desorber 2 is cooled and concentrations of 5mg.l^{-1} free NH_3 and 1mg.l^{-1} urea can be attained.

2.6.2 Distillation-hydrolysis system
Heated process water is fed to the top section of a distillation tower for NH_3 and CO_2 removal. The effluent liquid is pre-heated before entry to the hydrolyser where the urea is decomposed to NH_3 and CO_2. The hydrolyser and distillation tower vapours are mixed with off gases from the LP decomposer separator, cooled and recycled to the process. After effluent treatment, water suitable for boiler feed is stated to be achievable. Treated water containing 5mg.l^{-1} free NH_3 and 1mg.l^{-1} urea is expected.

2.6.3 Stripping-hydrolysis system
Heated process water containing NH_3, CO_2 and urea is fed to the top of a steam stripper operated at 1.5-3bar for separation of NH_3 and CO_2. The water is then fed from the middle section to the hydrolyser operating at 16-30bar. The gaseous overheads are then sent via the LP decomposer/absorber to the synthesis for recovery of NH_3 and CO_2.

Free NH_3 and urea concentrations of 3-5mg.l^{-1} for each component are expected in the treated water.

2.6.4 Existing emissions into water: performance by existing plants
The actual performance of some existing plants may vary considerably from the above with values for emissions into water of 20-230mg.l^{-1} (0.01-0.61kg.t^{-1} of product) of NH_3 and 20-320mg.l^{-1} (0.01-0.84kg.t^{-1}) of urea depending on the treatment system used. Figure 5 shows the emission sources from an existing plant.
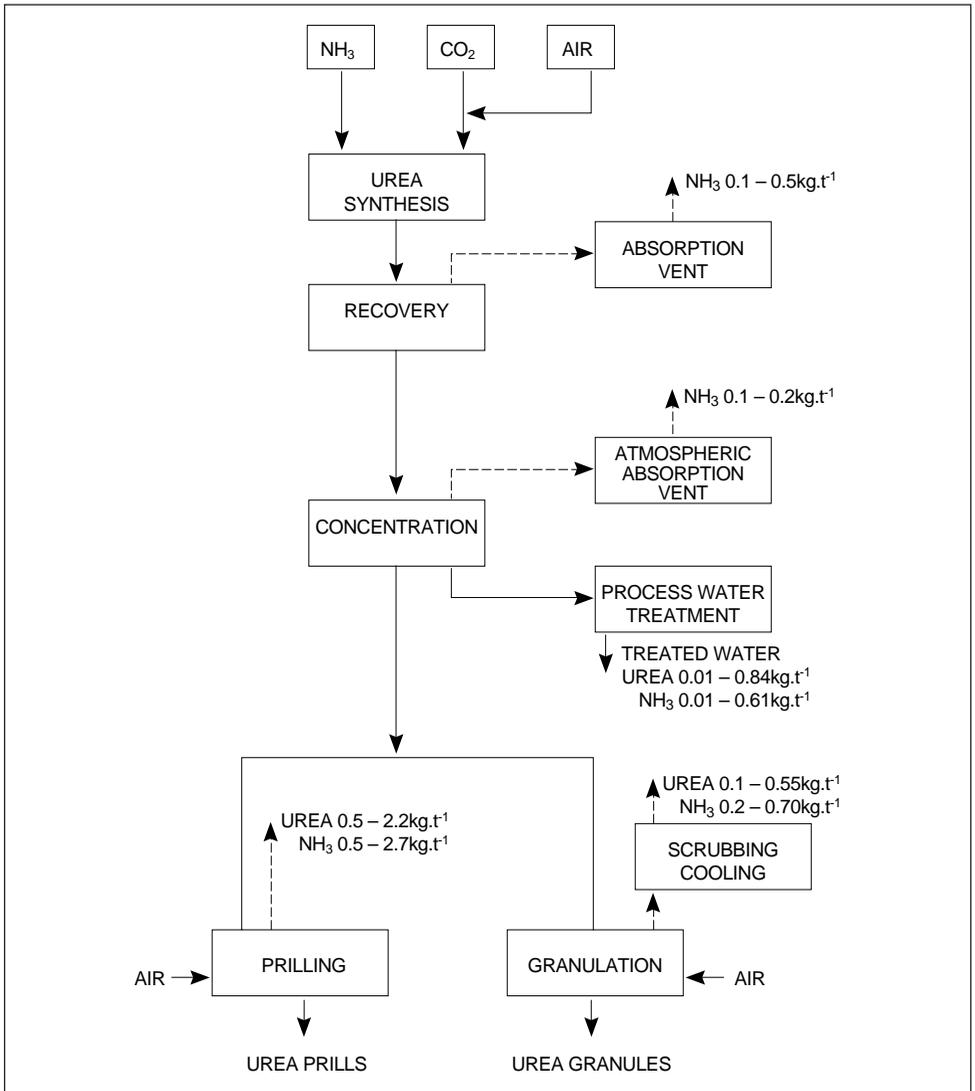
Figure 5 – Block Diagram of Emission Sources and Typical Quantities for Existing Plants.

2.7 Prill Tower Emissions

The prill tower is a major source of emission in urea plants. The large volumes of discharged untreated cooling air contain particulate urea dust ($1\text{-}2\text{kg.t}^{-1}$) as well as NH_3 ($0.7\text{-}1.0\text{kg.t}^{-1}$).

2.7.1 Causes of dust formation

Cause	Particle Size Range	Dust % of Total
Condensation products of urea vapours/aerosols	0.5-2.0μm	50
Reaction product of NH_3 and isocyanic acid (HNCO) to form Urea	0.1-3.0μm	20
Prill satellites and undersize prills	10-100μm	5
Crushing, abrasion and attrition on the tower floor	1-100μm	5
Seeding dust	1-20μm	20

Towers with natural draft cooling are reported to have less dust emission than towers with forced/induced draft air cooling. The lower air velocity and product mass per m³ of tower volume reduces attrition and carryover in the natural draft towers.

2.7.2 Operation and maintenance items significantly affecting dust formation

Fouling of the prilling device causing wider spread in prill granulometry.

High melt feed temperature causing increased evaporation.

High prill temperature at the tower base. The largest prills may not have solidified sufficiently and will fracture on impact.

Dust emission is approximately proportional to prilling tower capacity.

High air velocities and the air velocity distribution cause coarse dust to be entrained.

Weather conditions e.g. relative humidity, temperature can affect the air quality/quantity.

Unequal pressure in the prilling device causing a broad spread of prill size.

2.7.3 Prill tower emission abatement

Selection of the appropriate equipment for existing plants can be a complex issue. Dry dust collectors, irrigated electrostatic precipitators and irrigated dust scrubbers have been considered for dust abatement but few have been commercially proven. Wet scrubbers seem to be more attractive than dry dust collectors. Recovery of the NH_3 from the emission (for example by aqueous scrubbing) is very inefficient due to the low partial pressure of the gas in the discharged air.

2.7.4 Existing prilling plant performance

Figure 5 shows the emission sources from an existing plant

	Urea Dust		NH_3	
	mg.Nm^{-3}	kg.t^{-1}	mg.Nm^{-3}	kg.t^{-1}
Prill Tower (Not Scrubbed)	35-125	0.5-2.2	35-245	0.5-2.7

2.8 Granulator Emissions

A dust emission of 5-40kg.t^{-1} of final product is suggested for granulation process operations (i.e. ex granulator and cooler), which is is considerably higher than for prilling.

2.8.1 Causes of dust formation

The following reflects some speculations about the causes of dust formation in granulation but no quantitative data is available.

– Urea vapour formation during hot spraying of the urea melt and its subsequent condensation/solidification into small (0.5-3.0μm) particles. The vaporisation becomes negligible when the melt concentration is reduced to 95%

– Reaction product of NH_3 with isocyanic acid to form Urea

– Entrainment of fine dust in the air

– Impact of granules with the metal surface of the drum

– Solidification of sprayed molten urea droplets prior to coating due to excessive air flow

– High vapour pressure of sprayed molten urea

– High or low temperature, producing soft or brittle granules

– Inter-granular friction causing surface abrasion

2.8.2 Granulator emission abatement

Air extracted from the plant is normally scrubbed with urea plant process condensate and the resultant urea solution is recycled for reprocessing. With standard wet scrubbers an efficiency of 98% can be achieved for dust removal. The low partial pressure of the NH_3 in the discharged air results in low NH_3 scrubbing/recovery efficiencies which can be increased by acidification but the resultant solution has to be used in other plants.

2.8.3 Existing granulation plant performance

Figure 5 shows the emission sources from an existing plant.

	Urea Dust		NH$_3$	
	mg.Nm^{-3}	kg.t^{-1}	mg.Nm^{-3}	kg.t^{-1}
Granulator (Scrubbed)	30-75	0.1-0.55	60-250	0.2-0.7

3. DESCRIPTION OF STORAGE AND TRANSFER EQUIPMENT

3.1 Ammonia

NH_3 is pumped to the urea plant at 25bar pressure and 27°C. It is then supplied to a high pressure reciprocating pump for discharge to the urea synthesis section of the plant and the flow is regulated by a speed controller at a discharge pressure of 150-200bar depending on the process applied. The storage and transfer of ammonia are described in EFMA BAT Booklet No 1.

3.2 Carbon Dioxide

CO_2 is supplied to the CO_2 compressor and discharged at high pressure to the synthesis section of the urea plant.

3.3 Formaldehyde (if used as a conditioning agent)

An aqueous solution of urea-formaldehyde resin containing 50-60%wt formaldehyde and 20-25%wt urea is supplied by tanker and off-loaded to a buffer storage tank. It is injected by pump into the urea melt prior to prilling or granulation.

In some modern urea granulation plants continuous urea-formaldehyde resin production units are an integral part of the granulation technology.

Feedstocks are aqueous formaldehyde, molten urea and ammonia.

4. ENVIRONMENTAL DATA

4.1 Inputs

Ammonia, carbon dioxide, passivation air, conditioning agent, steam, electricity, cooling water, plant and instrument air.

4.2 Outputs

Urea, inert gases, LP steam, steam condensate, treated waste water.

4.3 Typical Inputs for BAT Synthesis/Prilling Processes

Local conditions have a major influence on optimal consumptions.

Synthesis/ Prilling Process	NH_3 $t.t^{-1}$	CO_2 $t.t^{-1}$	Steam $t.t^{-1}$	Cool. Water $m^3.t^{-1}$	Elec. $MJ.t^{-1}$
CO_2 Stripping	0.57	0.75	0.770(120)ST	70	54
			0.800(24)E	60	396
NH_3 Stripping	0.567	0.735	0.760(108)ST	80	76
IDR	0.57	0.74	0.600(105)ST	75	79
			0.84(24)E	60	425
ACES	0.57	0.74	0.700(98)ST	60	108
			0.570(24.5)E	51	436

Notes

The stoichiometric quantities of NH_3 and CO_2 are 0.567 and 0.733t.t^{-1} respectively.

Values are expressed per tonne of urea product.

Steam pressure in bar is in parenthesis.

Cooling water $\Delta T = 10°C$

CO_2 compressor drive: E = electromotor, ST = steam turbine.

Air to provide O_2 for passivation of stainless steel equipment is necessary.

Conditioning with formaldehyde at 0.01t.t^{-1} and crystal seeding of the melt may be used.

4.4 Typical Inputs for BAT Melt Granulation Process

The consumption of utilities depends to a large extent on local climatic conditions, or requirements for pollution control as well as end product temperature.

Granulation Process	Urea Melt Conc. wt%	Product Temp °C	Elec. MJ.t^{-1}	Steam kg.t^{-1}
Falling Curtain Drum	99.4-99.7	50	93	40 (LP)[1]
Fluid Bed Drum	95-96[3]	40	126	40 (LP)[1]
Spouted bed	98.5	40	70	200
Fluid Drum	99.7	45	40	200 (9bar)[2]

Notes

1 To re-concentrate the recovered urea solution for recycle to the process.

2 To flash-melt the over-size product for recycle to the process.

3 The use of the higher water content in the urea solution provides estimated savings of 90kg.t^{-1} of LP steam in the evaporation section relative to prilling.

4.5 Production Outputs

4.5.1 Urea

Urea production in a new BAT plant is typically 1,500t.d^{-1}.

4.5.2 Process condensate water

The urea synthesis stoichiometric reaction produces process water at 0.3t.t^{-1} urea. Additional water sources as outlined previously may increase the final quantity to about 0.50m^3.t^{-1} urea. The process water can be used as boiler feed water after treatment.

4.5.3 Steam condensate/turbine condensate

Typically both condensates (process and steam condensates) are exported to the battery limits for polishing and re-use as boiler feed water.

4.5.4 Low pressure steam

The LP steam produced in the carbamate condenser is used for heating purposes in the down stream sections of the plant. The excess may be sent to the CO_2 compressor turbine or CO_2 booster or exported for use in other site activities.

4.5.5 General

The actual consumption/outputs of existing plants may differ considerably from the above data.

4.6 Emissions and Waste

Details of the emission sources and quantities are shown in Figure 5.

4.6.1 Emissions into air

The process steps responsible for emissions into air are:-
- Urea solution formation: NH_3, CO_2, inerts in scrubber vent-gas
- Urea solution concentration: NH_3, CO_2, inerts in condenser off-gas
- Urea melt prilling or granulation: NH_3, urea dust in discharged air

4.6.2 Emissions into water

The sources of NH_3, CO_2 and urea are as outlined in 2.3.

Some older plants have been revamped to reduce emissions into air and water, and the recovered gases are recycled to the process. Newer plants have systems integrated in the original design depending on requirements.

4.6.3 Solid waste

No solid waste is produced in the urea production process.

4.6.4 Fugitive emissions

These are discontinuous releases of NH_3, CO_2, urea dust, formaldehyde, oil and steam. Typical sources include: storage tanks, valves including PRVs, flanges, pumps/compressor seals, sewer system vents/drains, waste water treatment units, solid urea transfer points, screens, etc.

4.7 Environmental Hazards Associated with Emissions

4.7.1 Ammonia

The molecular (undissociated) form of ammonia is highly toxic to freshwater fish and the quantity of undissociated NH_3 rises markedly above pH 7.0. With fresh water, the NH_3 should not rise above 25ppb to protect the most sensitive fish. Marine organisms appear far more tolerant of NH_3 and it has been suggested that if the NH_3 content of tidal waters is kept below 5ppm as N there is little cause for concern. However, sea water NH_3 is oxidised by bacteria to nitrate and this may bring about a significant lowering of the dissolved O_2 if it occurs on a large scale in an enclosed estuary or bay.

4.7.2 Carbon dioxide

The more CO_2 in the atmosphere the more effective it is in restricting the flow of radiated energy from the earth's surface, thereby increasing global warming. Urea production plants are extremely effective consumers of the CO_2 by-product from upstream ammonia plants.

4.7.3 Urea

Urea is relatively non toxic to aquatic life. It is a natural excretory product of many marine organisms and like most nitrogenous compounds it is readily assimilated by marine phytoplankton.

4.8 Statutory Emission Limit Values (ELVs)

The statutory emission limit values (ELVs) into air normally refer to specific emissions (e.g. NH_3, urea dust) from specific emission point sources (e.g. prill tower, vent, etc.). ELVs into water usually refer to the combined emissions from a site prior to discharge to the receiving water (sea, estuary or surface). No national statutory ELVs into air or water exist, for urea production units. Frequently, ELVs are negotiated between the plant/site operator and the local licensing authority. The ELVs for existing plants may reflect staged values over a defined period to enable the operator to achieve compliance. In Europe, ELVs for urea dust range from 75 to 150mg.Nm^{-3} and for ammonia, from 100 to 200mg.Nm^{-3}.

4.9 Environmental Quality Standards (EQSs)

Licence conditions may also attempt to control the emissions by means of establishing EQSs which should not be exceeded in the vicinity of the plant.

A time base must be stipulated whenever any limit is set (ELV or EQS) and a measuring method must be clearly defined and in most cases a frequency of monitoring for compliance must be indicated.

5. EMISSION MONITORING

5.1 Parameters and Frequency of Monitoring

The monitoring programme adopted should include measurement of the following parameters at the suggested frequencies.

A description of some of the methods available for monitoring emissions is given in Appendix 1.

5.1.1 Emissions into air

Source discharge flow rates	Monthly
NH_3 concentration in absorber vents	Monthly
NH_3 and urea dust concentration in air from prilling/granulation units	Monthly
Urea dust concentration from bag filter units	Monthly
NH_3 concentration in ambient air beyond/within the site perimeter	Continuous
Meteorological data e.g. wind speed/direction, temperature, etc.	Continuous

5.1.2 Emissions into water

Discharge flow rate to receiving water	Continuous
NH_3, urea or total Kjeldahl N concentration	Twice Daily
BOD or COD, oil and metal corrosion products	Monthly
pH and temperature	Twice Daily

5.2 General

The actual mass emission rates into air and water should be computed from the measured concentrations and flow rates. Standard methods are available for the discontinuous and continuous sampling and measurement of the emissions and should be agreed with the relevant authority. Experience has shown that sampling is the keystone of source analysis. More errors result from poor or incorrect sampling than from any other part of the measurement process. The need for continuous monitoring depends on the consistency of plant performance.

6. MAJOR HAZARDS

In urea production the following major hazards may arise:-

– Equipment/piping failure due to corrosion
– Explosion hazard due to the formation of an explosive gas mixture
– Toxic hazard due to NH_3 release

6.1 Corrosion Protection in Urea Plants

Corrosion protection is achieved by the use of well proven design principles, stringent material and fabrication specifications, complemented by detailed codes of practice for operating, monitoring and inspecting equipment. The corrosiveness at a given point in the plant is determined by the temperature, the process components, the concentration of dissolved oxygen and the presence of contaminants that may accelerate corrosion. The formation on start-up and maintenance of a passive oxide layer on stainless steel surfaces is of the utmost importance. Stainless steel lined carbon steel vessels are usually used in the HP synthesis section for economic reasons, including leak detection units to protect the integrity of the vessels and avoid a potentially hazardous situation.

6.2 Explosive Gas Mixtures

Explosive gas mixtures may form in the inerts scrubber, the off-gas from which consists of O_2, H_2, and N_2 and possibly some non-condensed NH_3 and CO_2. Well controlled operation is a means of keeping these gas mixtures outside the explosion hazardous range. In BAT plants the hydrogen present in the CO_2 feedstock is reduced by catalytic combustion to values below 10ppm, thereby minimising the risk of forming an explosive H_2/O_2 gas mixture in the scrubber.

6.3 Hazard Study

Urea production activities are normally integrated with an NH_3 production/storage facility and are subject to the requirements of EU Directive 96/82/EC. These include the preparation of a Safety Case detailing the procedures which exist to identify and control the major hazards of loading, storage and distribution of liquid NH_3.

7. OCCUPATIONAL HEALTH & SAFETY

In urea plants the main chemicals to be considered for occupational health and safety purposes are ammonia, carbon dioxide, conditioning agents (e.g. Formaldehyde) and urea dust. ACGIH [2] occupational exposure limits are given in the table below. All figures are in ppmv

Component	TLV-TWA (8hr)	TLV-STEL (15min)
NH_3	25	35
CO_2	5,000	30,000
Formaldehyde	-	0.3*

* TLV-C Threshold Limit Value Ceiling that should not be exceeded during any part of the working exposure.

Ammonia is a colourless gas with a characteristic pungent odour under atmospheric conditions.

Carbon Dioxide is a colourless and odourless gas under atmospheric conditions.

Formaldehyde may be incorporated in the final product as a conditioning agent at levels varying from 0.05% to 0.5%. Aqueous formaldehyde is injected into the urea melt and reacts to form polymeric derivatives in the matrix of the urea product. These reaction products do not have any of the hazardous characteristics of free formaldehyde gas. The health hazards (e.g. potential animal carcinogen) associated with aqueous formaldehyde arise mainly from the gaseous formaldehyde released from the solution. Adequate ventilation must be provided to ensure that the OEL is not exceeded. General physical handling of the solution should be kept to the absolute minimum and the recommended precautions in the Safety Data Sheet adhered to.

Urea dust is not regarded as hazardous. However, the general guidance (EH40 UK Health and Safety Executive) is that personal exposure to dust should be controlled to <10mg.m^{-3} (8 hour TWA) for inhalable dust and <5mg.m^{-3} (8 hour TWA) for respirable dust.

Full health and safety information is given in Safety Data Sheets which must be available and updated. General product information on urea is given in Appendix 2.

8. SUMMARY OF BAT EMISSION LEVELS FOR UREA PLANTS

The following emission levels should be achievable for new and existing plants. The levels relate to steady-state production for stand-alone units.

8.1 Achievable Emission Levels for New Plants

8.1.1 Emissions into air

Source	Granulation Unit			Prilling Unit			Vents	
	mg.Nm^{-3}	ppmv	kg.t^{-1}	mg.Nm^{-3}	ppmv	kg.t^{-1}	kg.h^{-1}	kg.t^{-1}
Urea	50	–	0.25	50	–	0.5	0	0
NH_3	50	75	0.25	50	75	0.5	4	0.06

8.1.2 Emissions into water

From Waste Water Treatment Unit

Urea	$1mg.l^{-1}$	$0.0005kg.t^{-1}$ product
NH_3	$5mg.l^{-1}$	$0.0025kg.t^{-1}$ product

8.1.3 Totalised emissions

	Granular Product	Prilled Product
Urea	$0.25kg.t^{-1}$	$0.50kg.t^{-1}$
NH_3	$0.31kg.t^{-1}$	$0.56kg.t^{-1}$

8.2 Achievable Emission Levels for Existing Plants

The setting of these levels can only be dealt with on a site specific basis. The levels achievable are a function of the plant size/design/age, the recovery systems adopted (including retrofits), the product shaping requirements (prilling or granulating) and the degree of integration with other on-site processes. Some existing plants have been/can be upgraded to recover process related effluent for re-use. The main problem is the emission into air of urea dust and NH_3 from the product shaping operation, particularly from prill towers.

8.2.1 Emissions into air

Source	Granulation Unit			Prilling Unit			Vents	
	$mg.Nm^{-3}$	ppmv	$kg.t^{-1}$	$mg.Nm^{-3}$	ppmv	$kg.t^{-1}$	$kg.h^{-1}$	$kg.t^{-1}$
Urea	70-80	-	0.35-0.4	100-150	-	1.0-1.5	0	0
NH_3	130-165	200-250	0.65-0.83	65-100	100-150	0.65-1.0	30	0.75

8.2.2 Emissions into water

From Waste Water Treatment Unit

Urea	$150mg.l^{-1}$	$0.10kg.t^{-1}$ product
NH_3	$150mg.l^{-1}$	$0.10kg.t^{-1}$ product

8.2.3 Totalised emissions

	Granular Product	Prilled Product
Urea	$0.45-0.50kg.t^{-1}$	$1.1-1.6kg.t^{-1}$
NH_3	$1.5-1.7kg.t^{-1}$	$1.5-1.8kg.t^{-1}$

8.3 Solid Wastes

No solid waste should arise from new or existing plants if clean or contaminated spillages are collected for re-use or sale.

8.4 Cost of Pollution Control Measures

The costs of pollution control measures in the fertilizer industry are difficult to generalise as they depend on a number of factors, such as:-

– The emission target or standard to be met

– The type of process, the degree of integration with other processes on site, production volumes, the type of raw materials being used, etc.

– Whether the plant is new so that the design can be optimised with respect to pollution abatement or whether the plant is an existing one requiring revamping or "add-on" pollution abatement equipment

Generally, it is more economical to incorporate the pollution abatement equipment at the process design stage rather than revamping or "adding-on" equipment at a later stage.

The cost of pollution control equipment for an existing plant can be 10-20% of the total cost of the plant. The operational and maintenance costs relating to environmental control can be 10-20% of the total production costs. In new plants, however, the process design would integrate environmental control with the need for high efficiency and productivity, and hence it is difficult to single out the costs of environmental control.

The cost of adding-on equipment to an existing plant must be considered case by case since it is related to the size and type of plant, the type of equipment to be installed, and the pollution control requirements to be met. Hence, the costs shown below are only indicative.

8.4.1 Feasibility of upgrading existing plants to BAT levels

Treating and recovering the nutrients from prill tower effluent would require an investment of at least 6.25 million EUROs.

The reduction of ammonia gas emissions requires investment in gas scrubbing and absorbing systems with additional carbamate condensing capacity for the recycle of the recovered materials to the synthesis section. The cost of these items could be at least 2.5 million EURs.

Other feasible abatement techniques include liquid spillage recovery systems, solids recovery by melting or dissolving, and additional process waste water holding capacity for up to three times the plant inventory. These areas could cost up to 2.5 million EURs.

9. UREA-AMMONIUM NITRATE (UAN) PRODUCTION

9.1 Overview of UAN Process Technology

Ammonium nitrate (AN) and urea are used as feedstocks in the production of urea-ammonium nitrate (UAN) liquid fertilizers. Most UAN solutions typically contain 28, 30 or 32% N but other customised concentrations (including additional nutrients) are produced. Plant capacities for the production of UAN solutions range between 200 and 2,000.t.d^{-1}. Most of the large scale production units are located on complexes where either urea or ammonium nitrate or both are produced.

In some of the European UAN plants, ammonium nitrate is being synthesised directly from nitric acid and ammonia. In some cases carbamate solution from the urea reactor outlet is being used as feedstock for the production of UAN.

In those plants the UAN technology is an integral part of the fertilizer complex. UAN from scrubbing systems, urea from sieving machines, etc. are fed to a central UAN system, where quality adjustments can be done.

The addition of corrosion inhibitors or the use of corrosion resistent coatings allows carbon steel to be used for storage and transportation equipment for the solutions. West European consumption of UAN in 1998/1999 was 3.72 x 10^6 t of solution, 41% of which was imported.

9.1.1 Typical UAN solution analysis

N content 28-32% by weight, pH 7 to 7.5, density 1,280-1,320kg.m^{-3}, salt-out temperature –18 to –2°C, depending on the N content and at its lowest when the Urea N/Ammonium Nitrate N ratio is about 1:1.

9.2 Description of Production Processes

Continuous and batch type processes are used and in both processes concentrated urea and ammonium nitrate solutions are measured, mixed and then cooled. Block diagrams for UAN production are shown in Figures 6 and 7.

In the continuous process the ingredients of the UAN solution are continuously fed to and mixed in a series of appropriately sized static mixers. Raw material flow as well as finished product flow, pH and density are continuously measured and adjusted. The finished product is cooled and transferred to a storage tank for distribution.

In the batch process the raw materials are sequentially fed to a mixing vessel fitted with an agitator and mounted on load-cells. The dissolving of the solid raw material(s) can be enhanced by recirculation and heat exchange as required. The pH of the UAN product is adjusted prior to the addition of the corrosion inhibitor.

A partial recycle CO_2 stripping urea process is also suitable for UAN solution production. Unconverted NH_3 and CO_2 coming from the stripped urea solution, together with the gases from the water treatment unit, are transferred for conversion into UAN solutions.
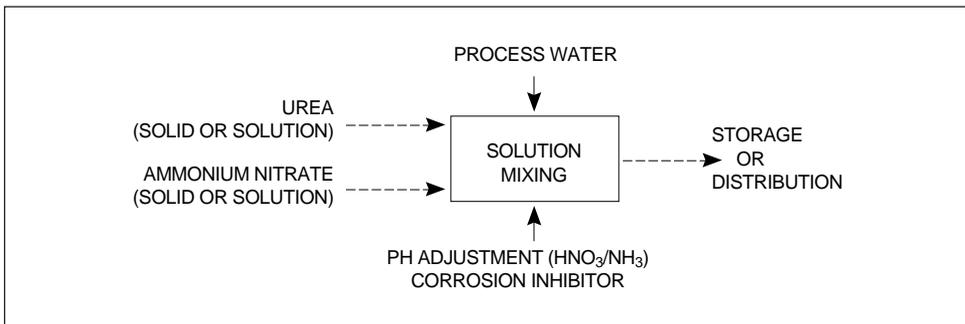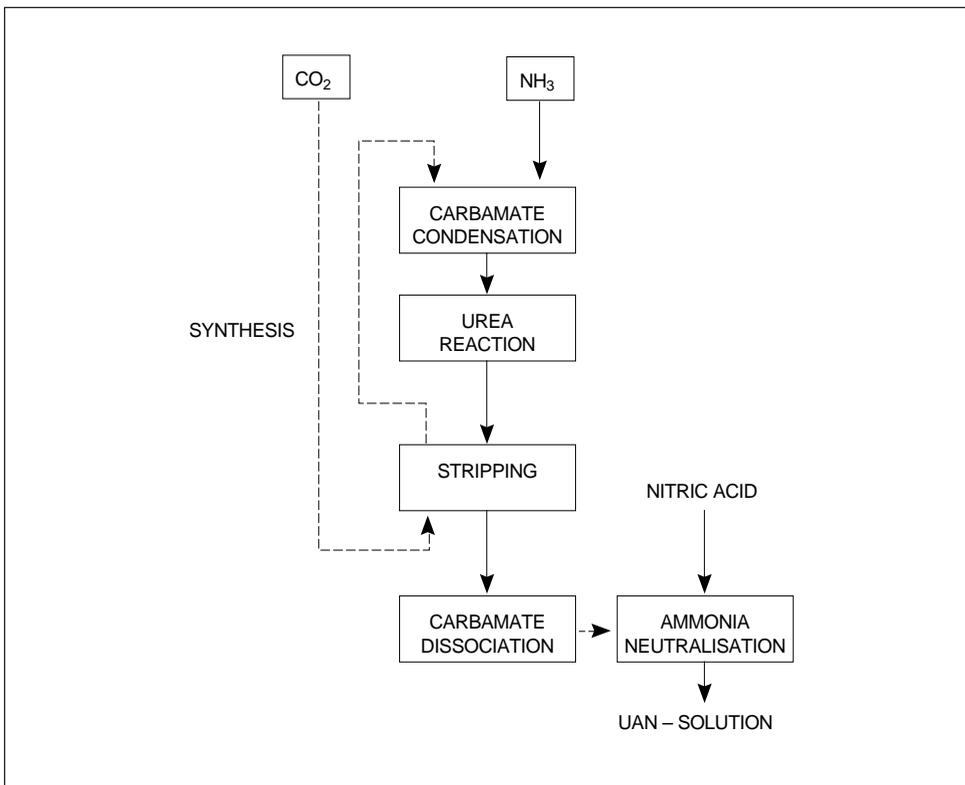
Figure 6 – Block Flow Diagram for UAN Process.

Figure 7 – Block Diagram of a Partial Recycle CO$_2$ Stripping Urea Process for UAN Production.

9.3 Description of Storage and Transfer Equipment

The physical form of the feedstock dictates the handling and storage system requirements. Bunded tank areas and collection pits allow any solution spillages to be collected for recycle. Air ducting and filtration helps the recovery of air-borne dust.

Regulations specific to the storage and handling of solid or solutions of ammonium nitrate must be adhered to. Recommendations for the storage and transfer of ammonia and nitric acid are given in EFMA BAT Booklets Nos 1 and 2 respectively. Recommendations for the storage of solid ammonium nitrate can be found in Reference [1].

9.4 Environmental Data

9.4.1 Raw material and utility inputs

	Solid	Solutions		
	N Content	Conc.	Temperature	pH
Ammon.Nitrate	33-34%	85% min.	Depending on Conc.	4-5
Urea	46%	75% min.	Depending on Conc.	9-10
Process Water	N-containing condensate from AN or urea plants can be used as solvent.			
Nitric Acid or NH_3 gas	For pH adjustment of final solution.			
Corrosion Inhibitor	For protection of carbon steel storage tanks, if necessary.			
Utilities	Cooling water, steam, electric power, instrument air.			

9.4.2 Typical raw materials/utilities consumption

Urea	327.7kg.t^{-1} (30% UAN solution)
Ammonium Nitrate	425.7kg.t^{-1}
Corrosion Inhibitor	1.4kg.t^{-1}
Ammonia	0.3kg.t^{-1}
Water	244.9kg.t^{-1}

Steam and electricity may approximate to 10-11kWh.t^{-1} respectively but are a function of raw material type (solid or solution) and ambient temperature.

9.4.3 Emissions and wastes

No gaseous emissions or waste arise during the non-pressure mixing of the aqueous based components.

Emissions to drain are nil provided solid spillages, washings and leaks are collected in a pit or sump and recycled to the process.

9.5 Emission Monitoring

Emissions do not arise if BAT is employed. Continuous monitoring of process conditions (e.g. flow, pH, density, temperature and level) ensures optimum control and no emissions. Specific national or local requirements for monitoring may exist.

9.6 Major Hazards

The manufacture, use, storage, distribution and possession of ammonium nitrate (solid) are subject to legislation. Recommendations for its handling and storage have been issued [1]. The plant inventory of chemicals for pH adjustment (ammonia/nitric acid) will generally be too small to cause a major hazard.

9.7 Occupational Health & Safety

The materials for consideration include urea and ammonium nitrate (solids and aqueous solutions), pH adjustment chemicals (ammonia and nitric acid) and corrosion inhibitors. Full details and data for urea are given in Chapter 7 of this Booklet. Information covering ammonia, nitric acid and ammonium nitrate can be found in EFMA BAT Booklets Nos 1, 2 and 6 respectively. General product information on UAN is given in Appendix 2.

9.8 Summary of BAT Emission Levels for UAN Solution Technologies

Zero gaseous and liquid emissions are achievable for new as well as for existing UAN solution technologies.

10. REFERENCES

1 Handbook for Safe Storage of Ammonium Nitrate Based Fertilizers. Paris: International Fertiliser Industry Association (IFA) and European Fertilizer Manufacturers Association (EFMA), 1992, 52 p.

2 Threshold Limit Values for Chemical Substances and Physical Agents and Biological Exposure Indices, 1993-1994. American Conference of Governmental Industrial Hygienists (ACGIH). Cincinnati, OH: ACGIH. – ISBN 1–882417–03–8.

GLOSSARY

The following abbreviations occur frequently throughout the series of Booklets but without necessarily appearing in each Booklet:-

ACGIH	American Conference of Governmental Industrial Hygienists
AFNOR	Association Française de Normalisation (France)
AN	Ammonium Nitrate
AQS	Air Quality Standard
AS	Ammonium Sulphate
BAT	Best Available Techniques
BATNEEC	Best Available Technology Not Entailing Excessive Cost
BOD	Biological Oxygen Demand
BPL	Basic Phosphate of Lime (Bone Phosphate of Lime)
BS	British Standard
CAN	Calcium Ammonium Nitrate
CEFIC	Conseil Europeen de l'Industrie Chimique (European Chemical Industry Council)
COD	Chemical Oxygen Demand
DAP	Di-Ammonium Phosphate
DIN	Deutsches Institut für Normung (Germany)
EEC	European Economic Community
EFMA	European Fertilizer Manufacturers Association
ELV	Emission Limit Value
ESA	European Sulphuric Acid Association
EU	European Union (Formerly, European Community, EC)
IFA	International Fertilizer Industry Association
IMDG	International Maritime Dangerous Goods (Code)
IPC	Integrated Pollution Control
IPPC	Integrated Pollution Prevention and Control
ISO	International Standards Organisation (International Organisation for Standardisation)
MAP	Mono-Ammonium Phosphate
MOP	Muriate of Potash (Potassium Chloride)
NK	Compound fertilizer containing Nitrogen and Potash
NP	Compound fertilizer containing Nitrogen and Phosphate
NPK	Compound fertilizer containing Nitrogen, Phosphate and Potash
NS	Fertilizer containing Nitrogen and Sulphur
OEL	Occupational Exposure Limit
SSP	Single Super-Phosphate
STEL	Short Term Exposure Limit
TLV	Threshold Limit Value
TSP	Triple Super-Phosphate
TWA	Time Weighted Average
UAN	Urea Ammonium Nitrate (Solution)

CHEMICAL SYMBOLS

The following chemical symbols may be used where appropriate in the text.

C	Carbon
$CaCO_3$	Calcium Carbonate
Cd	Cadmium
CH_3OH	Methanol
CH_4	Methane
CO	Carbon Monoxide
CO_2	Carbon Dioxide
F	Fluorine
F^-	Fluoride
H (H_2)	Hydrogen
H_2O	Water
H_2S	Hydrogen Sulphide
H_2SiF_6	Hydrofluorosilicic Acid (Hexafluorosilicic Acid)
H_2SO_4	Sulphuric Acid
H_3PO_4	Phosphoric Acid
HNO_3	Nitric Acid
K	Potassium
KCl	Potassium Chloride (Muriate of Potash) ("Potash")
K_2O	Potassium Oxide
N (N_2)	Nitrogen
N_2O	Dinitrogen Monoxide (Nitrous Oxide)
NH_3	Ammonia
NH_4-N	Ammoniacal Nitrogen
NH_4NO_3	Ammonium Nitrate
NO	Nitrogen Monoxide (Nitric Oxide or Nitrogen Oxide)
NO_2	Nitrogen Dioxide
NO_3-N	Nitric Nitrogen
NO_x	Oxides of Nitrogen (Excluding Nitrous Oxide)
O (O_2)	Oxygen
P	Phosphorus
P_2O_5	Phosphorus Pentoxide
S	Sulphur
SO_2	Sulphur Dioxide
SO_3	Sulphur Trioxide

UNITS

Units have been standardised as far as possible and these are abbreviated as follows:-

bar   Unit of pressure (equivalent to one atmosphere)
GJ   Giga Joule
kg   Kilogramme
kg.h^{-1} Kilogrammes per hour
kWh   Kilowatt hour (1,000kWh = 3.6GJ)
l   Litre (liquid volume)
m   Metre
m^3 Cubic Metre (liquid or solid volume)
mg   Milligramme
mg.l^{-1} Milligrammes per litre
MJ   Mega Joule
μm   Micrometre
Nm^3 Normal cubic metre (gas volume)
ppb   Parts per billion
ppm   Parts per million
ppmv   Parts per million by volume
t   Tonnes (Metric Tons)
t.d^{-1} Tonnes per day
t.y^{-1} Tonnes per year
°C   Degree Celsius (Centigrade)
K   Degree Kelvin

APPENDIX 1 EMISSION MONITORING IN UREA/UAN PLANTS

1. Introduction

Monitoring of emissions plays an important part in environmental management. It can be beneficial in some instances to perform continuous monitoring. This can lead to rapid detection and recognition of irregular conditions and can give the operating staff the possibility to correct and restore the optimum standard operating conditions as quickly as possible. Emission monitoring by regular spot checking in other cases will suffice to survey the status and performance of equipment and to record the emission level.

In general, the frequency of monitoring depends on the type of process and the process equipment installed, the stability of the process and the reliability of the analytical method. The frequency will need to be balanced with a reasonable cost of monitoring.

Particulates into air will, on typical processes need to be sampled iso-kinetically. This may be done to provide a routine base-line manual check for any continuous particulate monitoring or as a routine for control purposes where continuous monitoring methods do not exist. It may be possible in some situations, to adapt the sample collection system to provide for continuous monitoring.

Iso-kinetic sampling is subject to a variety of national standards and appropriate methods will generally need to be agreed with regulatory authorities. Typically they consist of combined air flow measurement and extraction sampling equipment that can be controlled to maintain the same velocity in the sampling nozzle as is present at that point in the duct.

The results from checks on dry gas exhausts may then be related to on-line particulate monitoring – although this will not determine changes in aerosols. A separate analysis of the filtered exhaust gas will be necessary to measure aerosols.

Wet gas systems also need to be analysed using essentially a combined iso-kinetic system with the extraction system designed to trap/separate the pollutant components for manual analysis.

National standards for gas sampling systems exist and the appropriate method should be adopted.

Manual methods may be necessary or accepted by the authorities in certain cases and for situations where no continuous method is available.

Vent streams are not normally measured by on-line methods and when measurements are required as base-line checks, manual methods may be more appropriate.

Typical methods for monitoring emissions into water rely on flow-proportioned sample collection or high frequency spot sampling together with analysis and continuous flow measurement.

The employment of trained staff is essential.

Methods available for monitoring the emissions given in Chapter 8 of this Booklet are briefly described next page.

2. Emissions into Air

2.1 NH$_3$ and Urea Dust

Commonly used methods:-

NH$_3$ –   Infra red spectrometry (IR)

Urea dust   –   Transmissometer measurements or iso-kinetic sampling and gravimetric analysis of dust

2.2 On-Line Methods

2.2.1 Infra red spectrometry

In the simplest form of IR spectrometry the equipment consists of an optical filter, the sample cell and a detector. When the wavelength of the radiation is not selected using a prism or diffraction grating the instrument is known as a non-dispersive infra red gas analyser (NDIR), or non-dispersive ultraviolet gas analyser (NDUV), in a UV system. In a single-beam instrument a filter selects the part of the spectral range most characteristic of the substance. In a twin-beam instrument (the most commonly used instrument for on-line analysis) the radiation from the source is split and a comparison is made of the two beams after one has passed through a reference cell and the other through the sample gas.

The two beams are brought together onto a half-silvered mirror or rotating chopper which alternately allows each beam to reach a detector cell which compares the heat received by capacitance or resistance measurements. The twin-beam method is preferred in an on-line system as it overcomes some of the problems associated with drift due to small changes in detector sensitivity and in the optical and spectral properties of the optical filter. However, regular zeroing and calibration are necessary to correct zero and range drift.

2.2.2 Transmissometers

Light from the source passes across the duct and is reflected by a mirror. The light beam is attenuated by the presence of particulate material in the duct and the reduction of light intensity is converted into an electrical signal which can be used to measure the concentration of particulate material in the duct.

2.2.3 Range of Methods Available

Method	Potential Interferences	Comments
Ammonia		
Chemiluminescence	NO_x	
IR	IR absorbing components	
Urea dust		
Double-Pass Transmissometer		Upper limit of 2,000mg.Nm^{-3} with a precision of around 2% of full scale deflection, lower limit of 10mg.Nm^{-3}
Double-Pass Density Monitor		
Beta Attenuation		Range of 2 to 2,000mg.Nm^{-3} depending on sampling rates, frequency and integrating levels
Light Scatter Measurement		Claimed to be accurate at low particulate concentrations down to 1mg.Nm^{-3}

2.3 Manual Methods

2.3.1 Ammonia

A sample of the gas is passed through a series of absorbers containing standard sulphuric acid solution. The ammonium ions in the absorber solution may be determined by using ion chromatography, ion selective electrode or by colormetric methods.

2.3.2 Urea dust

Samples of the gas are drawn into a sampling nozzle attached directly to the inlet of a small cyclone which is inserted bodily into a gas stream at the end of the probe. The particles of grit/dust are centrifuged out of this sample and driven into a hopper.

The cleaned gases are drawn from the cyclone through the probe tube, flexible hose, catch-pot cooler and valve by a suction unit. The system collects substantially all dust and grit particles above 5-10 microns, when operated at sampling above 8.5Nm^3.h^{-1} at STP. The weight of dust is gravimetrically measured in the cyclone.

3. Emissions into Water

NH$_3$, urea or total Kjeldahl N, Biochemical Oxygen Demand (BOD), Chemical Oxygen Demand (COD), oil and metal corrosion products.

3.1 Ammonia/Ammoniacal N

The spectrophotometric method for ammonia relies on the reaction in which mono-chloramine is reacted with phenol to form an indo-phenol blue compound. This method is particularly suitable for the determination of ammonia in cooling waters derived from saline sources (dock, estuarine or sea water) and may be used in continuous flow colorimetry.

Ion selective electrodes may also be used and are suitable for saline applications as well as pure water.

Note that free ammonia exists in equilibrium with NH$_4^+$ as follows:-

$$NH_4^+ + H_2O \longleftrightarrow NH_3 + H_3O^+$$
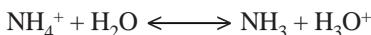
and that the equilibrium depends on pH. The above method determines the NH$_4^+$ ammonia. Free ammonia is particularly toxic to fish and should an incident occur, it may be more important to relate the result to free ammonia. Any suitable pH determination may be used and the free ammonia estimated as given in "Hampson B L, J Cons Int Explor, Mer, 1977,<u>37</u>. 11" and "Whitfield M, J Mar Biol. Ass UK, 1974,<u>54</u>, 562".

Manual laboratory based Kjeldahl methods may be used for spot checks for the determination of organic and ammoniacal nitrogen in a mineralised sample.

3.2 Urea (On-Line Method)

The urea in the sample is chlorinated under very slightly alkaline conditions using sodium hypochlorite, sodium hypobromite and hydrochloric acid/magnesium chloride reagents. The purpose of the sodium hypochlorite is to prevent the interference of ammonia. The presence of magnesium chloride in the acid reagent is to increase the sensitivity of the method and the potassium chloride and hydrogen peroxide are to increase the rate of colour development. The method is strongly pH sensitive and so after the initial mixing of the reagent and sample, the pH of the stream is raised with borate buffer to pH 9.4. The sample, is then allowed to react with an aqueous methanolic solution of phenol to form a yellow compound which is measured spectrophotometrically.

3.3 Oil

A visual inspection of the sample should be sufficient to show that no oil is present.

APPENDIX 2 GENERAL PRODUCT INFORMATION ON UREA

1. Identification

Chemical name	: Carbamide
Commonly used synonyms	: Urea
C.A.S. Registry number	: 57–13–6
EINECS Number	: 200–315–5
EINECS Name	: Urea
Molecular formula	: $CO(NH_2)_2$

2. Hazards to Man and the Environment

To man

Urea is basically harmless when handled correctly.

To the environment

Urea is basically harmless when handled correctly.

3. Physical and Chemical Properties

Appearance	: White solid
Odour	: Odourless
pH water solution (10%)	: 9-10
Melting point	: 133°C (decomposes)
Solubility in water	: 1,080g.l^{-1} at 20°C
Bulk density	: 700-780kg.m^{-3}

**Best Available Techniques Booklets
were first issued by EFMA in 1995
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1. Production of Ammonia

2. Production of Nitric Acid

3. Production of Sulphuric Acid
   (in collaboration with ESA)

4. Production of Phosphoric Acid

5. Production of Urea and Urea-Ammonium Nitrate

6. Production of Ammonium Nitrate and Calcium Ammonium Nitrate

7. Production of NPK Compound Fertilizers by Nitrophosphate Route

8. Production of NPK Compound Fertilizers by Mixed Acid Route