



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

Booklet No. 6 of 8: PRODUCTION OF AMMONIUM NITRATE and CALCIUM AMMONIUM NITRATE

2000 Edition



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for Pollution Prevention and Control
in the European Fertilizer Industry

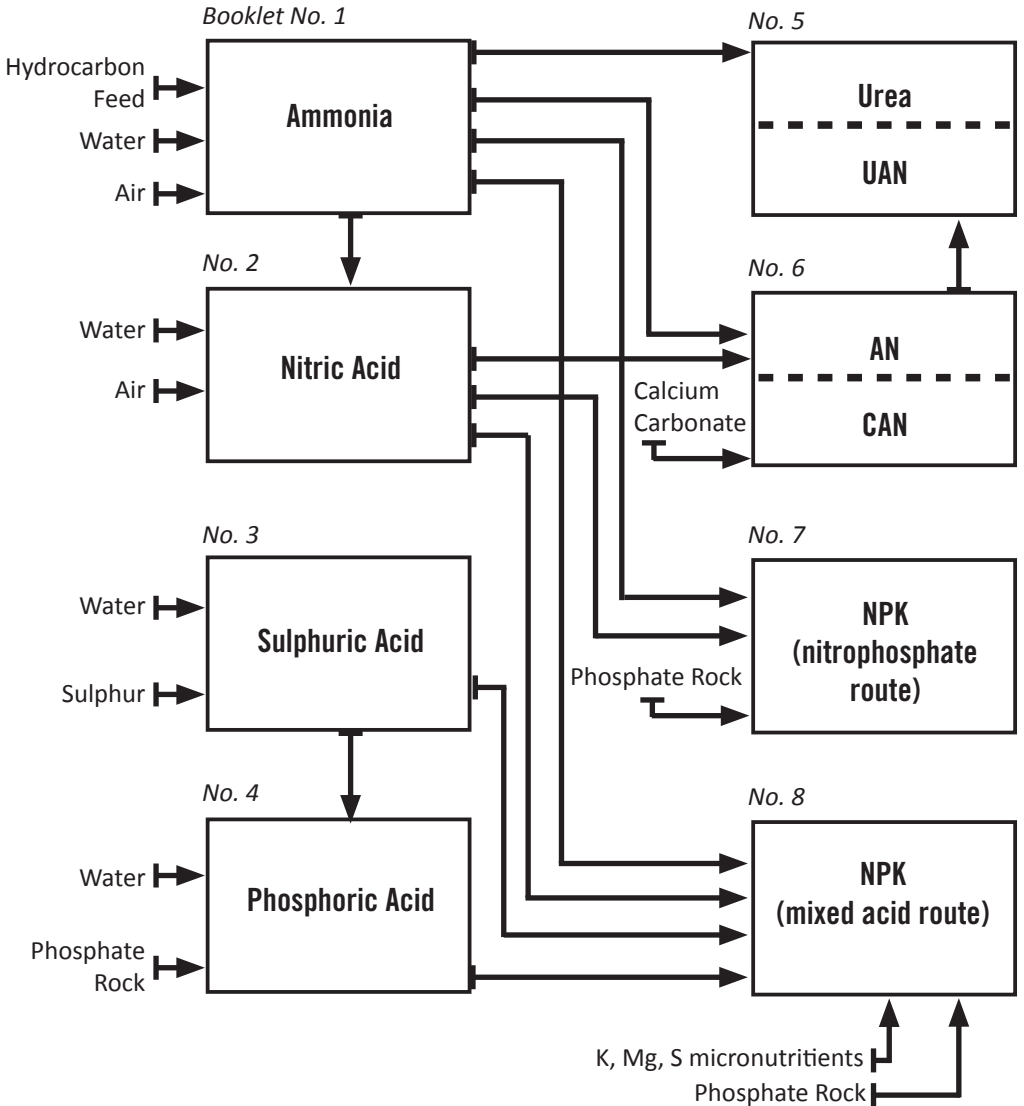
Booklet No. 6 of 8:

**PRODUCTION OF AMMONIUM
NITRATE AND
CALCIUM AMMONIUM NITRATE**

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Fertilizers Europe BAT Booklets



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PREFACE

In 1995, Fertilizers Europe 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 Fertilizers Europe 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 Fertilizers Europe 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. Fertilizers Europe 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.

Fertilizers Europe 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 Fertilizers Europe 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

Ammonium nitrate is used extensively as a nitrogenous fertilizer. It is made exclusively by the reaction between gaseous ammonia and aqueous nitric acid, the production of which are covered in the Fertilizers Europe BAT Booklets 1 and 2 respectively.

The resultant ammonium nitrate solution may be used in various ways:-

- It can be stored as a solution and then used in down-stream plants or sold as such
- It can be formed into solid ammonium nitrate by prilling or granulation
- It can be mixed with a solid filler. The most common filler is calcium carbonate in the form of ground limestone, dolomite or byproduct calcium carbonate from, for example, a nitrophosphate process, to make a product which is known in the industry as "Calcium Ammonium Nitrate" (CAN) and then prilled or granulated. Granular products containing ammonium nitrate and either ammonium or calcium sulphate are also manufactured

Gaseous ammonia may be produced on site from the vaporisation of liquid ammonia, this is mentioned in this Booklet but the relevant technical information is contained in the Fertilizers Europe BAT Booklet No 1. Waste heat must be used, as far as is practicable, to supply the latent heat of evaporation if liquid ammonia is to be vaporised.

One of the important parameters in the production of ammonium nitrate is the strength of the nitric acid feedstock which can vary from 50 to 70%. Normally the ammonium nitrate is made from the nitric acid which is available from the production facility. It may also be made from purchased nitric acid.

The final solid fertilizer product may leave the production site either as loose bulk or in a variety of pack sizes.

Plants for the production of ammonium nitrate and CAN generally produce from a few hundred up to 3,600t.d⁻¹. In summary, the scope of this Booklet is therefore:-

- The manufacture and storage of ammonium nitrate solution made from gaseous ammonia and aqueous nitric acid
- The conversion of ammonium nitrate solution into solid ammonium nitrate or CAN

Fertilizer regulations in the European Union (EU) place requirements on the quality of ammonium nitrate which is to be labelled as an EC Fertilizer. Product must conform to these specifications if the plant is to qualify for BAT, which include:-

- No addition of substances which increase the sensitivity of the ammonium nitrate to heat or detonation
- The oil retention must pass a specified test
- The combustible material must be less than 0.2% for product containing more than 31.5% N and less than 0.4% for product between 28 and 31.5% N
- The pH of a 10% solution must be greater than 4.5
- Less than 5% of product must be smaller than 1mm and less than 3% smaller than 0.5mm

- Chlorine content less than 0.02% by weight
- Heavy metals should not be added and traces incidental to the process should not exceed the limit fixed by the Committee
- Product must pass a specified detonation test (optional)

AN and CAN fertilizers containing in excess of specified thresholds of ammonium nitrate are classified as oxidising substances under the U N Transport Regulations. Details can be found in Reference [15].

Ammonium Nitrate declared as EC Fertilizer may only be supplied to the end user in packages. The legislation of the appropriate country must be consulted for the precise details of local requirements. Some further guidance is contained in References [3] and [4]. Conformance to these requirements ensures that ammonium nitrate is safer for the customer. The manufacturer must select a process route that satisfies the specified limits and must also control the raw materials which are to be used (in respect of trace element analysis) to ensure that the limits are met. This also applies to anticaking and conditioning additives which are used to improve the final product.

This 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 THE PRODUCTION PROCESS

The production process comprises three main unit operations:-

- Neutralisation
- Evaporation
- Solidification (prilling and granulation)

There is no single process route which can be identified as BAT for the production of ammonium nitrate. The main reasons for this are:-

- Commercial considerations will influence the choice of the form of the final product, therefore no solidification process can be preferred
- BAT can be achieved for the various unit operations of the process by a number of techniques. Whilst it is preferable for a manufacturer to employ BAT to prevent or to minimise emissions, it is also acceptable for the manufacturer to render the emission harmless by end-of-pipe treatment provided that the same environmental result is achieved

Individual plants vary widely in process detail although the process may appear simple at first sight. More details may be found in Reference [2].

Ammonium nitrate solution may also be supplied to the AN/CAN plant from a separate process such as a nitrophosphate process (see Fertilizers Europe BAT Booklet No 7).

2.1 Neutralisation

The exothermic neutralisation of nitric acid with ammonia gas produces ammonium nitrate solution and steam. The nitric acid is commonly pre-heated using equipment of suitable corrosion resistance especially if the available concentration of nitric acid is towards the lower limit of the range 50-70%. Pre-heating can best be performed (BAT) by using steam or hot condensate from the ammonium nitrate process.

The amount of pre-heat can be calculated from the concentration of the nitric acid and the required concentration of the resultant ammonium nitrate solution by calculating an enthalpy balance. Neutralisation can be performed in a single stage or in two stages. A two-stage neutraliser operates with a low pH in the first stage (acidic conditions) and a neutral pH in the second stage. The equipment can operate at a variety of operating pressures and temperatures. In most neutralisers the pressure, temperature and concentration are linked by the boiling point characteristics of ammonium nitrate solutions with only two of these variables being independent.

Ammonia gas may contain small quantities of inerts such as hydrogen, nitrogen, and methane. These will be vented from the neutraliser system at a point which depends upon the detail of the particular process.

2.1.1 Neutralisers

Neutralisers may be free-boiling vessels, circulating systems, or pipe reactors. At least 10 different types and designs of neutralisers are in use in Europe. The environmental factors which influence the choice of neutraliser are:-

- A two-stage neutraliser produces most of the boil-off steam in the first stage and most of the ammonia emission from the second stage. This reduces the total emission of ammonia
- A single-stage neutraliser is inherently simpler and cheaper
- Neutralisation at an elevated pressure will produce steam at a higher temperature (and ammonium nitrate at a higher concentration). Such steam could be used more readily in down-stream processes such as evaporation and drying
- The control of the neutraliser is a critical parameter. The pH and the temperature must both be strictly controlled to limit the losses from the neutraliser. All installations must include pH and temperature controls using reliable equipment which must be tested on a routine basis. It is essential that the process staff are informed of excursions by audible and/or visual alarms which are backed up by automatic, independent trips which will make the neutraliser safe in the event of a major temperature rise as this could lead to a major environmental incident. Such safety equipment frequently incorporates a system for drenching the contents of the neutraliser with excess clean water in the event of a significant temperature rise
- The control of impurities has been mentioned above. At the operating temperature of the neutraliser, impurity control is of great importance because a safety incident will also be a significant environmental incident. Some manufacturers do not

recycle ammonium nitrate screenings to the neutraliser for this reason. Recycling is especially to be avoided if the screenings are contaminated by an organic anticaking additive. It should be noted that an acidic solution of ammonium nitrate is more unstable than an alkaline solution

BAT requirements for neutralisers should include the following:-

- Whenever the operating conditions allow the addition of water to the neutraliser, this water (for example, contaminated steam condensate) should be used to recycle ammonium nitrate solution provided this can be performed safely
- Impurities should be rigorously excluded. However, fines and oversize removed from the final product should be recycled to the process as far as practicable
- The steam which is evolved from the neutraliser vessel contains ammonia and ammonium nitrate in quantities to a few thousand ppm of each. This can be reduced to a few hundred ppm by careful design of the neutraliser

2.1.2 Steam purification

The steam leaving the neutraliser can be purified, or it can be condensed and then purified. The steam may be used in the evaporator (see below) or it may be used to preheat and evaporate ammonia and it can be used to preheat the nitric acid.

The following techniques have been used commercially for the purification of the steam and should be considered to be “available”:-

Droplet separation techniques

- Knitted wire mesh demister pads
- Wave plate separators
- Fibre pad separators using, for example, PTFE fibres

Scrubbing devices

- Packed columns
- Venturi scrubbers
- Irrigated sieve plates

Some details of such devices (and others) can be found in Reference [6].

Ammonium nitrate emissions from neutralisers are very difficult to remove because the particles are very fine. A combination of droplet separators and scrubbers can be used.

For all the above scrubbers BAT would require the addition of acid, normally nitric acid, to neutralise any free ammonia and to optimise its removal.

Process interchange is preferred where practicable for condensation of the steam. Alternatively, water or air cooled exchanger(s) are required.

2.1.3 Condensate treatment

Re-use or purification of the contaminated condensate by an end-of-pipe scheme must be considered whenever the condensate does not achieve BAT. This can be achieved by various techniques including:-

- Stripping with air or steam with the addition of alkali to liberate ionised ammonia if required
- Distillation
- Membrane separation processes such as reverse osmosis

Ion exchange can also be considered but there are some safety concerns which must be addressed. The recycle of organic resins to the ammonium nitrate process must be prevented, and the resin must not be allowed to become nitrated.

The choice of technique will depend on whether nitrate removal is required and this will depend on the receiving water.

The condensate which is finally produced from the steam which leaves the neutraliser could be discharged in one of the following ways:-

- To drain
- To a nitric acid plant for use as absorption water provided safety and purity requirements of nitric acid are met
- To other uses on the site such as in the manufacture of solution fertilizers
- To boiler water feed, possibly after further purification
- To a lagoon for control/analysis purposes
- To a lagoon for subsequent evaporation by the heat of the sun or for disposal to land, although neither of these is practicable in many countries in Europe because of the climate or the amount of land required

Biological treatment has been considered for removal of nitrogen from fertilizer plant effluents but this has not been used on a commercial basis in Europe, except in the case of an existing public utility or on a large integrated chemical site.

The product from the neutraliser is ammonium nitrate solution with a concentration which depends on the feed materials and the operating conditions. It may be fed to storage without further processing but, if it is to be used in the manufacture of solid ammonium nitrate, CAN, or NPK fertilizer, it is normally concentrated by evaporation.

2.2 Evaporation

The evaporator is normally required to remove the majority of the water which is present in the ammonium nitrate solution. The acceptable water content depends on the process which is to be used in the manufacture of the finished product, but is normally below 1% for a prilled product. A water content up to 8% is required for the feed to some granulation processes.

Evaporation is always performed using steam which can come from the ammonium nitrate process (neutraliser) or from a steam raising facility on the site.

It is advisable to ensure that steam cannot contribute to the decomposition of ammonium nitrate by using saturated steam at an appropriate temperature. Evaporation may be performed at substantially atmospheric pressure or under vacuum. The latter allows the re-use of neutraliser steam but requires more capital expenditure.

During evaporation some ammonia is lost from the ammonium nitrate solution and this must normally be replaced prior to solidification. The steam which is boiled off is contaminated with the ammonia which must be removed and droplets of ammonium nitrate will also be present.

Evaporators in commercial use include circulatory systems, shell and tube heat exchangers and falling film types. The falling film evaporator has the advantages of a small working volume and a short residence time. All commercial evaporators produce contaminated steam which must be significantly purified before discharge to the environment to qualify the plant as achieving BAT. Techniques to purify this steam include:-

- Droplet separators similar to those used for neutralisers (see above)
- Scrubbers used on fine dust and fume similar to those used in the production of solid product (see below)
- The steam could also be condensed and fed to a system used for the purification of neutraliser condensate as described above in 2.1

The evaporator must produce an ammonium nitrate solution of the required concentration at a temperature which avoids crystallisation. It may be necessary to cool the solution from the evaporator to reduce effluents from down-stream equipment.

2.3 Prilling and Granulation

“Prilling” refers to the formation of granules by the solidification of droplets of fertilizer materials. “Granulation” is a more general term and refers to techniques using processes such as agglomeration, accretion, or crushing to make a granular fertilizer. There are currently no plants in Europe which use either a crushing or a compaction/flaking technique to make ammonium nitrate or CAN. One process uses prills as the feed to a layering-type granulation unit to produce a larger (fattened) granule when compared with the prilled feed.

The prilling technique is used in many plants for the production of ammonium nitrate and in some plants for CAN. Granulation of ammonium nitrate may be performed in a dedicated plant, or in one which can also produce CAN. Dedicated CAN plants exist where the CAN is granulated. CAN may also be manufactured in a plant which produces NPK fertilizers.

2.3.1 Prilling

The feed of ammonium nitrate to a prilling plant must be substantially anhydrous. It is formed into droplets which then fall down a tall tower (prill tower). Air is made to flow up the tower using fans (counter-current to the prills) and the droplets cool and solidify. There are two main techniques for droplet formation, a rotating perforated bucket and a static sys-

tem of fixed orifices such as a shower head. Ground calcium carbonate (limestone or dolomite) is added prior to the formation of the droplets when CAN is being made.

Atmospheric effluents result from the loss of ammonia and ammonium nitrate (and calcium carbonate in CAN production) to the air stream. A lower melt temperature can reduce emissions. Ammonia is normally removed by neutralisation in a wet scrubber. Small particles of ammonium nitrate (miniprills) are carried out with the air and these can be removed using comparatively simple equipment. However, ammonium nitrate fume is also lost from the surface of the prills and this is sub-micron in size which makes it much more difficult to remove. It is very noticeable as it gives a persistent blue haze which can be seen at a long distance from the plant. The development of irrigated candle filters (with candles incorporating fine glass fibre) has given the ammonium nitrate industry an effective means of scrubbing this effluent, albeit at a cost to the manufacturer of at least 3.75 million EURs, for a unit with a capacity of about $1,500\text{t}\cdot\text{d}^{-1}$, which is a significant proportion of the total plant cost. Candles incorporating fine glass fibre are generally most efficient but other packings can be effective in certain applications.

Candle filters cannot be used for the abatement of the effluent from CAN prilling towers because the insoluble calcium carbonate fouls the surface of the filter in an unacceptably short time. The same situation will apply if any insoluble materials are added to the ammonium nitrate.

Other scrubbing systems have been used on prill towers but they do not achieve the same improvement in effluent abatement. Most conventional scrubbers are less efficient for the removal of particles which are below 1 micron (prill tower fume) but comparatively efficient for coarser particles. One plant has installed a system whereby the prill tower air is cooled, cleaned, and recycled but this is not in general use at the present time (Reference [1]).

It is possible for the prill tower to be provided with an insert (shroud) which collects the most highly polluted air (perhaps 30% of the total) for treatment in a candle filter. This can reduce the capital and operating costs of the abatement system and the overall environmental impact.

2.3.2 Granulation

In contrast to the prilling technique, granulation requires a more complicated plant and a variety of equipment is used in the industry including rotating pans and drums, fluidised beds and other more specialised equipment. The main advantage of granulation with respect to the environment is that, although the nature of the effluent may be comparable, the quantity of air to be treated is much smaller and abatement equipment is cheaper and thus easier to install. The energy consumption of the abatement equipment is normally lower for a granulation plant. If the ammonium nitrate feed to the granulator has a high moisture content, then the emission may contain only coarser particles, rather than “fume” and can therefore be scrubbed with cheaper equipment than a candle filter. Granular product can be made in a wider range of particle size than prills, (and in particular can be made larger than prills) but this is primarily of commercial, rather than environmental concern.

Some granulation processes can use ammonium nitrate containing up to 8% water but this water must still be removed in the process, though at a lower temperature (with possibly greater overall energy economy).

Some types of process equipment can be used to manufacture both granulated AN and CAN. Other types of equipment can be used to produce both granulated CAN and NPK (compound) fertilizers.

Examples of granulators used in AN/CAN plants include rotary pans and drums, "Sphero-disers", pugmills and fluidised beds. The filler will normally be added in the process before the granulator if CAN is to be produced and the ammonium nitrate is added in the granulator as a spray of hot concentrated solution. No further drying of the granules will normally be required. The granules are screened and the fines and crushed oversize returned to the granulator.

Examples of CAN and CAN/NPK granulators include drums and pugmills. The filler may be mixed with the ammonium nitrate solution before granulation or in the granulator itself. Granules from this process will normally require drying in a fluidised bed or rotary drier. It may not be necessary to add any additional heat when drying CAN as the granules can have sufficient heat to provide the necessary driving force. Such a process is known as an autothermal process. The granules are screened after the drier

Gases from the granulator (if applicable) and from the drier may be cleaned by a combination of dry cyclones or bag filters and wet scrubbers. Candle, venturi and cyclonic devices are frequently used for the latter. Candle filters are most suitable if the emission contains a large proportion of sub-micron particles but they are not suitable for use on a CAN plant. Dry devices must be kept warm, above the dewpoint of the air and below the critical relative humidity of the dust. Wet scrubbers normally use a circulating solution (with purge and makeup facilities) and pH control with acid may be required. The gases may be saturated with water in a separate unit before passing to the scrubber.

The solution from a wet scrubber will normally be recycled to the process but it may not always be possible for all the solution to be recycled without adversely affecting the granulation. Further concentration may be needed. It is important that the wet scrubbers on a CAN plant are suitably designed to handle the inert solids without choking and a solid waste may be produced from such scrubbers.

2.3.3 Emissions into air from prilling and granulation plants

The ammonia and ammonium nitrate emissions into air from the prilling and granulation sections of AN and CAN plants can be abated by a range of abatement equipment. The resultant emission depends upon two main factors, the efficiency of the abatement equipment for the particular emission, and the volume to be abated.

Particulate material from some types of granulation plants is relatively coarse in particle size, whereas from a prilling process the prill tower emission contains very fine particles. Abatement equipment can in principle be designed for either case. Candle filters are

normally required for a prill tower emission and these can abate particulate emissions to 15mg.m^{-3} of air. For coarser materials dry devices such as bag filters or dry cyclones can achieve BAT and may provide a better option. Particulate emissions can be of higher concentration, perhaps up to 30 or 50mg.m^{-3} , but the recovered material is a solid that can more readily be recycled to the process without problems of water balance.

The volume of air cannot normally be changed on an existing plant. Plants that were designed to use a given volume would need to have their design concept changed completely. This would also have implications for product quality – for example a change from a prilled to a granulated product would make a product with different spreading characteristics – and this would have important repercussions on the customers. More modern plants generally tend to use lower air volumes, but a reduction in air volume on an existing plant, in most cases, would be excessively expensive.

2.4 Cooling

Both granulators and prill towers normally produce a product which requires further cooling in rotary or fluid bed coolers with the air cleaned by high efficiency cyclones, bag filters or wet scrubbers such as those listed above. Air cleaned in a dry system can be generally re-used as secondary air to the drier after de-dusting (where possible).

A bulk flow heat exchanger may be used. The product is cooled by rejecting the heat to water from a cooling tower in a development of a plate heat exchanger. (Reference [10]) This has no atmospheric effluents.

2.5 Conditioning

Ammonium nitrate and CAN are prone to caking during storage and are conditioned to prevent caking. Anticaking agents may be internal to the finished particle or applied as a coating to the outside. They may be of various chemical species and are generally specified by the individual manufacturer. A discussion on anticaking can be found in Reference [9].

These additives may also prevent dust formation and moisture pick-up during storage.

2.6 Other Losses

There may be other losses to atmosphere, but these are mostly unique to the specific plant design and cannot be listed in a general Booklet.

Loss of ammonium nitrate to drain from a large number of sources is a potential problem for all ammonium nitrate plants. A common cause is the losses from pump seals, but losses can be simply leaks from flanges, passing valves etc., or they may be deliberate washings of process equipment because of build-up in solids handling equipment, or the preparation of equipment for maintenance. The particular problems that will be experienced on a specific plant will be unique to the plant design, but the general points must be considered by all manufacturers.

Design

Provision should be made in the initial design of a new plant, where possible, to collect miscellaneous losses into a system which is separate from the storm-water systems. This is not practicable for an existing plant with combined drains, where the total water flow may be contaminated.

Operation

There must be a management system to monitor losses and to repair leaks as soon as practicable. The collected solutions should be reprocessed if they are uncontaminated; used in other plants as makeup solutions; sold as dilute solution for use in liquid fertilizer manufacture; or processed/treated in equipment as described above. The practicable options will depend upon individual plant circumstances.

Solid wastes are not normally a feature of an ammonium nitrate plant. Clean spillage can be reprocessed and contaminated spillage can usually be sold at a discounted price. There will normally be small quantities of general factory waste.

3. DESCRIPTION OF STORAGE AND TRANSFER EQUIPMENT

The storage and transfer of ammonia and nitric acid are described in the Fertilizers Europe BAT Booklets 1 and 2 respectively. Solid ammonium nitrate in packages must be stored in a general warehouse which has been approved for ammonium nitrate duty. The specific requirements vary between countries and the appropriate authorities must be consulted. General guidance can be obtained from References [3] and [4].

Bulk ammonium nitrate and CAN must be protected from moisture as both products are hygroscopic. Large bulk warehouses may be air-conditioned depending upon the local climatic conditions and the anticaking additive used to protect the product. Some additives can reduce the water uptake rate. Safety rules must be followed as appropriate to the locality.

Ammonium nitrate solution may be stored prior to use in down-stream plants or prior to sale. It must be stored at a temperature above the crystallising temperature of the solution. Tanks may be lagged and/or heated; the solution may be circulated through a heat exchanger or heated with a (steam) coil. Tanks normally have protection against over-filling and are commonly surrounded by a bund of a sufficient volume to hold the entire contents of the tank. Detailed recommendations are given in Reference [7].

Ammonia in gaseous form is normally added in small quantities to maintain the solution at the correct pH because ammonium nitrate solutions lose ammonia during storage. Small quantities of ammonia may be lost from tank vents.

4. ENVIRONMENTAL DATA

The quantities of contamination, as discussed in Chapter 2, are very variable and may eventually be emitted into different media (air or water). Chapter 8 gives details of achievable levels.

4.1 Input Requirements

The raw materials, ammonia and nitric acid, are required in virtually stoichiometric quantities. Nitric acid is typically around 60% strength; the water in the nitric acid will be emitted from the process in one form or another or recycled to another plant.

Proprietary anticaking additives are normally used in the process. The amounts required cannot be generalised but must be determined by the individual plant for the specific marketing requirements.

Water may be imported to the process as make-up to the cooling towers, but on some plants the cooling towers are a central facility. Water is not normally required for other process purposes. Water for process duties, for washing and flushing of equipment to clear blockages and to prepare equipment for maintenance is normally available from the process.

Electricity requirements are relatively modest for a new ammonium nitrate facility for solid product and can range from 25 to 60kWh.t⁻¹ of product. However, large amounts of electricity may be needed to retrofit existing facilities to BAT. This could mean up to 70kWh.t⁻¹ over the above figures. The production of ammonium nitrate solution requires less electricity eg 5kWh.t⁻¹.

Steam is required to evaporate the ammonium nitrate solution but the amount will depend on the concentration of the nitric acid and the required product concentration and it is not possible to generalise. Steam from the neutralisers may be used in some plants to drive the evaporation process but this is not practicable as a retrofit to an existing process. In some plants, energy is required to evaporate liquid ammonia and this would normally be supplied from the process, for example, by using the steam from the neutraliser. It is therefore possible for the steam requirements to vary from zero to 50kg.t⁻¹ of product. Steam can be exported at a rate up to 170kg.t⁻¹ of ammonium nitrate if the plant only makes ammonium nitrate solution. Some plants can export hot water.

The plants to make solid CAN also require steam and electricity and a the process will require around 150-200kg steam per tonne of product together with 10-50kWh.t⁻¹ of product.

4.2 Output Production

There are no by-products or co-products normally associated with the production of ammonium nitrate or CAN. There are no plants which can export electricity and steam export is only possible at a small rate on a small number of plants. The export of steam condensate is common on plants which use a larger quantity of steam in the process. Contaminated condensate may be exported to other plants.

4.3 Emissions and Wastes

As mentioned above an ammonium nitrate plant will always produce a surplus of water. Some other plants on the site may be able to consume all or part of this water, but these routes are specific to the particular site.

A stand alone ammonium nitrate plant may emit the following:-

- To atmosphere – ammonium nitrate
- ammonia

These can arise from neutralisers, evaporators, prill towers, granulators, driers and coolers as discussed above.

- To drain – ammonium nitrate
- ammonia or nitric acid (which should normally be neutralised)

These can arise from neutraliser and evaporator boil-off, equipment cleaning, and a wide range of points which are specific to a given site.

All these emissions can be abated to BAT levels (see Chapter 8) by a range of techniques. Emissions into air can be up to 200mg.Nm^{-3} of particulates and of ammonia (2kg.t^{-1} of product for each) if BAT is not employed.

Unabated emissions into water can be up to $5,000\text{mg AN N.l}^{-1}$ and $2,500\text{mg NH}_3 \text{ N.l}^{-1}$ (6 and 3kg.t^{-1} of product respectively).

Solid wastes are not normal.

A CAN plant may produce all the above emissions, together with solids based on calcium carbonate or other solid filler which could be released to any of the three environmental media.

5. EMISSION MONITORING

The significant parameters which should be measured are, in general,

To atmosphere:-

- Particulate solids (ammonium nitrate and possibly calcium carbonate and/or CAN dust)
- Ammonia and possibly
- Oxides of nitrogen

To drain:-

- Ammonia/Ammonium – N
- Nitrate – N
- Flow rate
- Particulate solids on a CAN plant

There may be a specific further requirement for other parameters, depending on the plant and the receiving waters. Such parameters may include:-

- pH
- Temperature
- Suspended solids
- BOD or other measurement of organic species
- Parameters specific to the process, for example, for process additives

Important operating parameters which could have environmental implications must be defined and monitored by operators. It is impossible to define these fully in a general document but a few examples are:-

- Levels in operating vessels
- Levels in storage vessels
- Operating pressures
- Operating temperatures
- Operating flows
- pH in neutralisers and storage tanks

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

6. MAJOR HAZARDS

There are three hazardous chemicals which are present in Ammonium Nitrate and CAN plants:-

- Ammonia
- Nitric acid
- Ammonium nitrate

It is more common for the major storage of these chemicals to be located within their own manufacturing plants, full details of their hazards are given in BAT booklets 1 and 2.

Ammonium nitrate is considered to be an oxidising agent and precautions must be taken in manufacturing, transport and storage.

6.1 Ammonium Nitrate

The main chemical hazards associated with ammonium nitrate are:-

- Fire
- Decomposition
- Explosion

Burns caused by hot AN solution should also be considered from a safety point of view.

Fire

Ammonium nitrate itself does not burn. Being an oxidising agent, it can facilitate the initiation of a fire and intensify fires in combustible materials.

Hot AN solution can initiate a fire in rags, wooden articles etc., on coming into contact with them. Similarly, fertilizer products or dust contaminated with oil or other combustible materials can also start fires when left on hot surfaces.

Fires involving AN cannot be extinguished by the prevention of air ingress (eg smothering with steam) because of the *in situ* provision of oxygen from the AN.

Decomposition

Pure solid AN melts at 169°C. On further heating it decomposes by way of a complex set of reactions. Up to about 250°C it decomposes primarily into N₂O and H₂O. Above 300°C reactions producing N₂, NO, NO₂ etc., become significant. These reactions are exothermic and irreversible. They are accompanied by the vapour pressure dependent endothermic dissociation into HNO₃ and NH₃ vapours which can provide a temperature limiting mechanism, provided the gases can escape freely. If they cannot, the endothermic dissociation is suppressed and a run-away decomposition can develop, leading to explosive behaviour.

A number of materials have a strong catalytic effect on the thermal decomposition of AN. These include acids, chlorides, organic materials, chromates, dichromates, salts of manganese, copper and nickel and certain metals such as zinc, copper and lead.

The decomposition of AN is suppressed or prevented by an alkaline condition. Thus the addition of ammonia offers a major safeguard against the decomposition hazard.

The release of toxic fumes is one of the main hazards associated with the decomposition of AN.

Explosion

AN is especially difficult to detonate and neither flame, spark nor friction is known to cause detonation. Shocks derived from detonating gas mixtures (hydrogen/oxygen or acetylene/oxygen) have been found to be incapable of producing detonation in AN. AN fertilizer dust, being non-combustible in nature, does not give rise to a dust explosion such as those commonly associated with grain and organic dusts. Shock initiation in solid prilled AN needs a fairly substantial stimulus. Heating under confinement and shock initiation of hot or contaminated AN by projectile impact appear to be more credible mechanisms in the context of industrial operations.

Strongly acidic conditions and the presence of contaminants should be avoided to counter the explosion hazard in AN solutions. Explosions can occur when ammonium nitrate is heated under confinement in pumps. Reasons for pump explosions include:-

- No (or insufficient) flow through the pump
- Incorrect design (Design may incorporate low flow and/or high temperature trips)
- Poor maintenance practices
- Contamination

Burns Caused by Hot AN Solutions

These solutions are dangerous because of their high temperatures (commonly in the range 120-180°C) and because they attack the skin on account of their oxidising properties.

6.2 Ammonium Nitrate Storage

See Reference [7] for details of the storage of AN solutions. In many countries there are specific legal requirements which must be followed. These are generally based upon the EC Fertiliser Directives EC 76/116 and EC 80/876 and the COMAH Directive 96/82/EC. See Reference [3] for details of the legislative requirements. These requirements generally cover the storage areas with respect to their structural and operational requirements and must be consulted for the relevant country. The following are included here as an illustration of the nature of the possible requirements:-

- Materials of construction used in the building of the store
- Other buildings in the locality
- Storage of other product in the same building
- Absence of drains
- Fire detection and fire fighting systems
- Layout and size of stacks

Legislation may require the operator to conduct a detailed safety survey and report the results to the appropriate authorities. The legislation may be supported by a series of industry guidance notes which are produced by manufacturers and by trade associations. See Reference [4] for an example.

Selected tests are available which may be used to assess the safety of ammonium nitrate and CAN (Reference [8]).

7. OCCUPATIONAL HEALTH & SAFETY

The chemicals which must be considered for occupational health and safety in all plants are:-

- Ammonia
- Nitric acid (and nitrogen oxides)
- Ammonium nitrate.

Other chemicals, such as processing aids, maintenance chemicals and anticaking agents, added to improve the storage characteristics of the product, may be used in the plant but these cannot be discussed in such a general document. Safety data sheets should be available for all who come into actual or potential contact with these chemicals.

7.1 Ammonia

Ammonia is a gas at atmospheric pressure and temperature and is normally stored as a liquid. It has a pungent, suffocating odour which is readily recognisable. The liquid gives severe cold burns, and the vapour is toxic and corrosive to all parts of the body.

ACGIH [11] occupational exposure limits for ammonia are 25ppmv for 8 hour TWA and 35ppmv for short term exposure (15 min). Advice on the correct medical treatment for exposed persons must be available at all points of potential contact.

7.2 Nitric Acid

Nitric acid is a corrosive aqueous solution of a strong acid and the liquid may give off toxic fumes of oxides of nitrogen. These, and nitric acid fume, are toxic and corrosive to all parts of the human body. ACGIH [11] occupational exposure limits are 2ppmv for 8 hour TWA and 4ppmv for short term exposure (15 min). First aid procedures must be specified on safety data sheets but a particular hazard is that fluid may build up in the lungs up to 48 hours after exposure. Appropriate protective clothing must be worn for tasks which have the potential for the spillage of nitric acid.

7.3 Ammonium Nitrate

Ammonium nitrate does not have any specific occupational health problems. The dust arising from ammonium nitrate (or CAN) is of low toxicity and is generally regarded as a nuisance dust with 10mg.Nm⁻³ (8 hour exposure) being accepted as the permitted level provided the particle size is above 5µm. Ammonium nitrate may decompose in a fire situa-

tion and thus stores should be suitably designed with consideration for factors such as access to stacks, spacing between stacks, presence of other chemicals (such as combustible materials). Oxides of nitrogen will be emitted during a decomposition.

Full health and safety data is given in Safety Data Sheets. Guidance on Safety Data Sheets is given in reference [12]. General product information on ammonium nitrate and calcium ammonium nitrate is given in Appendix 2.

8. SUMMARY OF BAT EMISSION LEVELS

Emission levels are generally associated with the efficiency of the abatement equipment which has been installed. Such equipment has an efficiency which is related to both the quantity of the effluent stream (water or air) and to the concentration of the pollutant. Emission levels are often quoted in legislation as a residual concentration of the pollutant because this is normally defined once the BAT equipment has been selected. The quantity of pollutant (in kg.t^{-1} of product, for example) will depend upon the volumetric flow of the stream.

8.1 Achievable Emission Levels For New Plants

The following emission levels can be achieved for new plants. These levels relate to steady-state production and take no account of peaks which may occur during the unsteady transient conditions of start-up and shut-down or during emergencies.

8.1.1 Emissions into air

Ammonium nitrate production when no insoluble solids are present

Prill towers and granulators using molten ammonium nitrate	15 mg.Nm^{-3} particulates 10 mg.Nm^{-3} ammonia
Other individual emission points	30 mg.Nm^{-3} particulates 50 mg.Nm^{-3} ammonia

Ammonium nitrate production when insoluble solids are present, including CAN production

	50 mg.Nm^{-3} particulates 50 mg.Nm^{-3} ammonia
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The balance of losses between the various atmospheric emission points varies with the technology employed but in total, should not exceed 0.5kg particulates and 0.2kg ammonia per tonne of product.

8.1.2 Emissions into water

Ammonium nitrate	100 mgN.l^{-1} (0.2 kgN.t^{-1} product)
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8.1.3 Solid wastes

Nil

8.2 Achievable Emission Levels for Existing Plants

Existing plants can be upgraded to the above levels using end-of-pipe technology except for prilling plants where insoluble solids are present because no suitable technology exists for the abatement of the prill tower fume which contains inert material. Certain plants may have specific problems where abatement equipment cannot be retro-fitted because of the detailed design of the original major items of equipment. The justification for the installation of end-of-pipe abatement must be considered on a site-specific basis, taking into account factors such as:-

- The environmental impact of the emission
- The improvement created by abatement
- Any energy use by the abatement equipment
- The cost of the equipment
- Any cross-media effects

CAN plants and AN plants with insoluble solids may produce small quantities of sludge containing inert solids.

8.3 Cost of Pollution Control Measures

The costs of pollution control measures in ammonium nitrate plants are difficult to generalise. 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, 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 economic to incorporate the pollution abatement equipment at the process design stage rather than revamping or “adding-on” equipment later.

For an existing plant the cost of pollution control equipment 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. The process design in new plants 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, type of equipment to be installed and the pollution control which is needed to meet the requirements of the local receiving medium.

Examples

i) Atmospheric abatement of an ammonium nitrate plant.

The capital cost of adding a Brink filter to the prill tower, plus cyclones for the fluid bed cooling air, for a large single-stream ammonium nitrate plant with a capacity of about $1,500\text{t}\cdot\text{d}^{-1}$, can be as much as 7.5 million EUR because all the air has to be brought to a point on the ground for treatment. The revenue cost of electricity for the fan which is required to move the large volume of air can be up to $70\text{kWh}\cdot\text{t}^{-1}$ of ammonium nitrate.

ii) Recycle of water to a separate facility.

This is only feasible if such a separate facility exists. Examples are where the site possesses a facility to use contaminated water in a solution fertilizer plant or a nitric acid plant. In the latter case, due consideration must be given to safety and efficiency on the nitric acid plant. The cost of such recycle is impossible to estimate as it largely depends on local factors.

iii) Minimisation within the plant

The condensate from the neutraliser boil-off steam could be concentrated by methods such as reverse osmosis, ion exchange and single/multi-effect evaporation. These schemes will all produce two streams – a concentrated stream and a “cleaned” stream. The flow rate of the two streams and their concentration can vary widely. For example, the flow rate of the concentrate could be between 5 and 30% of the initial flow. The cost of such schemes will be in the region of 1 to 2 million EUR for a large plant of around $1,500\text{t}\cdot\text{d}^{-1}$ of ammonium nitrate.

iv) End-of-pipe treatment of aqueous effluents.

End-of-pipe treatment has been installed using air or steam stripping and ion exchange systems. No information has been published on the costs of such installation but capital costs will be of the order of 1-3 million EURs. Revenue costs (chemicals plus steam) will depend upon local costs. Note that steam stripping requires the addition of an alkali to liberate free ammonia and will not reduce the nitrate content of the effluent. This may or may not be a problem depending upon the receiving waters.

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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
CEFCI	Conseil Européen 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
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 Compound
NP	fertilizer containing Nitrogen and Phosphate Compound
NPK	fertilizer containing Nitrogen, Phosphate and Potash Fertilizer
NS	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 ₃ OH	Methanol
CH ₄	Methane
CO	Carbon Monoxide
CO ₂	Carbon Dioxide
F	Fluorine
F ⁻	Fluoride
H (H ₂)	Hydrogen
H ₂ O	Water
H ₂ S	Hydrogen Sulphide
H ₂ SiF ₆	Hydrofluorosilicic Acid (Hexafluorosilicic Acid)
H ₂ SO ₄	Sulphuric Acid
H ₃ PO ₄	Phosphoric Acid
HNO ₃	Nitric Acid
K	Potassium
KCl	Potassium Chloride (Muriate of Potash) (“Potash”)
K ₂ O	Potassium Oxide
N (N ₂)	Nitrogen
N ₂ O	Dinitrogen Monoxide (Nitrous Oxide)
NH ₃	Ammonia
NH ₄ -N	Ammoniacal Nitrogen
NH ₄ NO 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 ₂ O 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
K	Degree Kelvin

APPENDIX 1 EMISSION MONITORING IN AN/CAN 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

Particulate emissions 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 the 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 in the duct. These can be combined to give mass emissions.

Wet gas systems need to be analysed using a combined iso-kinetic system with an extraction system designed to trap/separate the pollutant components for manual analysis. Extractive sampling need not be iso-kinetic if a fume in a dry gas is to be monitored.

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

The use of trained staff is essential.

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

2. Emissions into Air

2.1 Ammonia and Particulate Solids

Extractive sampling with appropriate sample conditioning and the following methods are commonly used:-

Ammonia, Ammoniacal and Nitric N

Sample dissolution in water or standard sulphuric acid solution and chemical analysis by ion selective electrode, colorimetry or ion chromatography after removing insoluble solids by filtration, if necessary.

Particulate solids

Iso-kinetic sampling followed by gravimetric or chemical analysis. Note that even trained staff may obtain results with significant errors and repeat measurements may be necessary.

2.2 Ammonia and Ammonium Nitrate Fume

Non iso-kinetic extractive sampling may be used with trapping and dissolution of fume and ammonia. The combined solution may be analysed chemically.

2.3 On-Line Methods

Continuous monitoring for ammonia and ammonium nitrate fume is not generally applicable for AN/CAN plants.

Particulate solids can be measured in dry gases using transmissometers, which may use the attenuation of light or Beta radiation. In a light attenuation system, light from a source is reflected back from the opposite side of the duct and the attenuation, measured against a reference beam, is used to evaluate the particulate loading in the duct.

Similar methods apply for Beta radiation but iso-kinetic sampling is also used to deliver a representative sample of the particulate-laden air to a Beta beam.

3. Emissions into Water

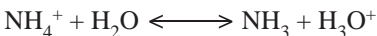
Typical monitoring methods rely on flow proportioned sample collection or high frequency spot sampling and continuous flow measurement. Spot sampling may be sufficient but in either case the samples obtained may be analysed as follows:-

3.1 Ammonia/Ammoniacal N

The spectrophotometric method for ammonia relies on the reaction in which monochloramine is reacted with phenol to form an indophenol 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 can 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:-



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 NH_4^+ 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, 1977,37, 11" and "Whitfield M, J Mar Biol. Ass UK, 1974,54, 562".

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

3.2 Nitric N

The nitrate in the sample is reduced to nitrite using a solution of hydrazinium sulphate and copper sulphate. A colour reagent of sulphanilamide and N-1 naphthylethylene diamine dihydrochloride is then added to produce a pink coloration which can be measured spectrophotometrically. Ion selective electrodes can also be used to measure nitrate nitrogen but it should be noted that chloride ions interfere.

3.3 Particulate/Suspended Solids

Solids are analysed gravimetrically after filtering, appropriate washing and drying.

3.4 Flow Rate

A wide range of industrial flow meters is available.

APPENDIX 2 GENERAL PRODUCT INFORMATION ON AN AND CAN

1. Ammonium Nitrate (AN)

1.1 Identification

Chemical name	: Ammonium Nitrate
Commonly used synonyms	: AN, Ammonium Nitrate Fertilizer
C.A.S. Registry number	: 6484-52-2
EINECS Number	: 299-347-8
Molecular formula	: NH_4NO_3

1.2 Hazards to Man and the Environment

To man

Ammonium nitrate is basically harmless when handled correctly.

To the environment

Ammonium nitrate is basically harmless when handled correctly.

1.3 Physical and Chemical Properties

Appearance	: White or off-white granules or prills
Odour	: Odourless
PH water solution (10g/100ml)	: >4.5
Melting point	: 160-170°C depending on moisture content
Boiling point	: >210°C (decomposes by dissociation)
Explosive properties	: Not explosive as per EEC test A14 (67/548/EEC). The fertilizer has a high resistance to detonation. This resistance is decreased by the presence of contaminants and/or high temperatures
Oxidising properties	: Can support combustion and oxidise. Not classified as oxidising according to EEC Directive 88/379/EEC and test A17
Solubility in water	: 1,900g.l ⁻¹ at 20°C
Bulk density	: 830 to 1,100kg.m ⁻³

2. Calcium Ammonium Nitrate (CAN)

2.1 Identification

Chemical name	: Mixture of ammonium nitrate and calcium Carbonate Calcium ammonium nitrate, CAN
Composition	: Mixture of ammonium nitrate with calcium carbonate and/or dolomite containing not more than 80% of ammonium nitrate

2.2 Hazards to Man and the Environment

To man

CAN is basically harmless when handled correctly.

To the environment

CAN is basically harmless when handled correctly.

2.3 Physical and Chemical Properties

Appearance	: White, off-white or grey granules or prills
Odour	: Odourless
pH water solution (10g/100ml)	: >4.5
Explosive properties	: Not explosive as per EEC test A14. The fertilizer has a very high resistance to detonation. This resistance is decreased by the presence of contaminants and/or high temperatures
Oxidising properties	: Not classified as oxidising material according to EEC Directive 88/379/EEC. Can support combustion
Solubility in water	: NH_4NO_3 highly soluble $\text{CaCO}_3/\text{MgCO}_3$ sparingly soluble
Bulk density	: 900-1,100 kg.m^{-3}



Best Available Techniques Booklets were first issued by Fertilizers Europe in 1995. Second revised edition 2000.

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



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