

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

Booklet No. 7 of 8:

**PRODUCTION OF
NPK FERTILIZERS**
by the
NITROPHOSPHATE ROUTE

2000

EFMA
European Fertilizer Manufacturers' Association

Ave. E van Nieuwenhuysse 4
B-1160 Brussels
Belgium

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

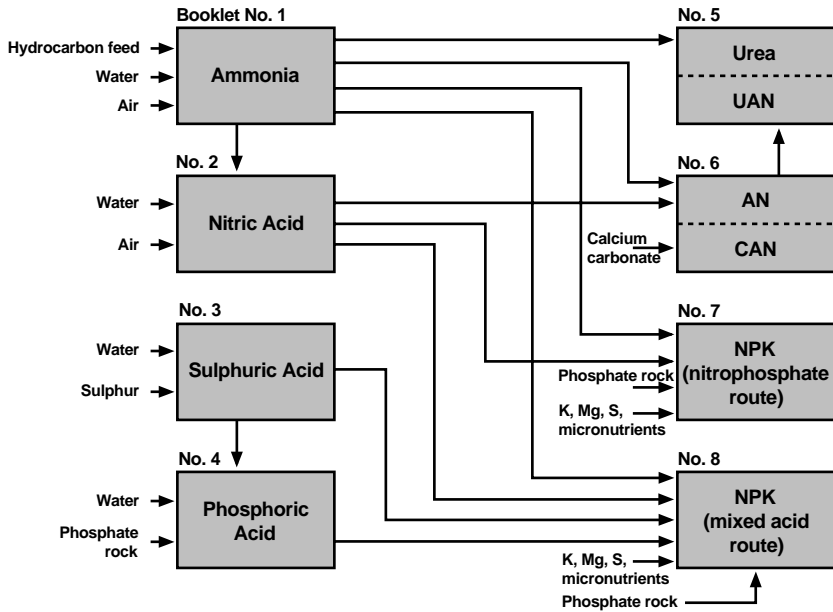
Booklet No. 7 of 8:

**PRODUCTION OF
NPK FERTILIZERS**
by the
NITROPHOSPHATE ROUTE

Copyright 2000 – EFMA

This publication has been prepared by member companies of the European Fertilizer Manufacturers' Association (EFMA). Neither the Association nor any individual member company can accept liability for accident or loss attributable to the use of the information given in this Booklet.

EFMA's BAT Booklets



CONTENTS

PREFACE	4
DEFINITIONS	6
1. INTRODUCTION	7
2. DESCRIPTION OF THE PRODUCTION PROCESSES	7
2.1 Basic Concept	7
2.2 Technologies of the Nitrophosphate Process	8
2.2.1 Ammonia plant	10
2.2.2 Nitric acid plant	10
2.2.3 Nitrophosphoric acid unit	12
2.2.4 The calcium nitrate tetrahydrate conversion unit	13
2.2.5 Compound fertilizer production unit	14
2.2.6 Calcium nitrate fertilizer production unit	16
3. DESCRIPTION OF STORAGE AND TRANSFER EQUIPMENT	18
3.1 Solid raw materials	18
3.2 Finished Products	18
4. ENVIRONMENTAL DATA	20
4.1 Emissions into Air	20
4.2 Emissions into Water	21
4.3 Solid Wastes	21
5. EMISSION MONITORING	22
5.1 Emissions into Air	22
5.2 Emissions into Water	22
6. MAJOR HAZARDS	22
7. OCCUPATIONAL HEALTH & SAFETY	23
8. SUMMARY OF BAT EMISSION LEVELS	24
8.1 Achievable Emission Levels for New Plants	24
8.2 Achievable Emission Levels for Existing Plants	24
8.3 Cost of Pollution Control Measures	25
9. REFERENCES	25
GLOSSARY OF TERMS	26
APPENDIX 1 Emission Monitoring in NPK Plants	29
APPENDIX 2 General Product Information on Nitrate Based NPK Fertilizers	32

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

Most producers of compound fertilizers in Western Europe are producing nitrate based mineral compound fertilizers under the product name “NP” or “NPK”. These products contain nitrogen in ammoniacal (NH_4) and nitrate (NO_3) form, phosphorus expressed as P_2O_5 , and normally also potassium expressed as K_2O . The content of nutrients ($\text{N} + \text{P}_2\text{O}_5 + \text{K}_2\text{O}$) will normally be between 40 and 50%. In addition the fertilizers may contain magnesium, boron, sulphur and micro-nutrients.

These compound fertilizers are made by one of the two following important production routes:-

- The nitric acid route or nitrophosphate process, described in this Booklet
- The sulphuric acid route or mixed-acid process, described in EFMA BAT Booklet No. 8

The two processes are based on different technologies, having different investment costs, economic impact, energy consumptions, emission values and process integration.

This Booklet describes compound fertilizer production based on a nitrophosphoric acid plant with a capacity of $200\text{t}\cdot\text{d}^{-1}$ of P_2O_5 (equivalent to about $700\text{t}\cdot\text{d}^{-1}$ of phosphate rock depending on the rock). This production capacity makes it possible to produce $1,300\text{t}\cdot\text{d}^{-1}$ of NPK 15+15+15 and also $2,000\text{t}\cdot\text{d}^{-1}$ of calcium ammonium nitrate fertilizer (CAN, 27% N), or $1,000\text{t}\cdot\text{d}^{-1}$ of calcium nitrate ($\text{Ca}(\text{NO}_3)_2$, 15.5% N).

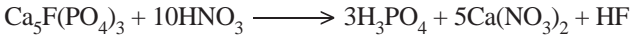
This Booklet describes the principles for production, pollution prevention and control and defines achievable levels for waste and emissions to air and water for new and existing nitrophosphate based NPK plants. CAN and calcium nitrate production associated with the nitrophosphate route are described in EFMA BAT Booklet No. 6 and Section 2.2.4 of this Booklet respectively. 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 figures in Chapter 8 is to be considered as BAT.

2. DESCRIPTION OF THE PRODUCTION PROCESS

2.1 Basic Concept

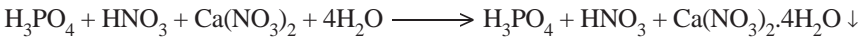
Phosphate sources must be converted into a form which can be taken up by plants (“available”). This can be achieved by using the integrated “Nitrophosphate” process which produces compound fertilizers containing ammonium nitrate, phosphate and potassium salts. This process aims to produce nitrate-containing straight and compound fertilizers starting from rock phosphate and using all the nutrient components in an integrated process without solid wastes and with minimal gaseous and liquid emissions.

The integrated process starts with the dissolution of the rock phosphate in nitric acid following the reaction:-



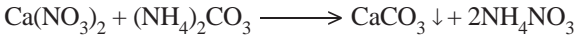
Varying amounts of volatile compounds such as carbon dioxide (CO_2), nitrous gases (NO_x) and hydrogen fluoride (HF) may be liberated, depending on the rock phosphate.

The mother liquor obtained contains too many calcium ions to guarantee the production of plant available P_2O_5 . The solution is therefore cooled so that calcium nitrate tetrahydrate (CNTH) crystallises out following the reaction:-



The solution of phosphoric acid, remaining calcium nitrate and nitric acid, called nitrophosphoric acid, can be separated from the CNTH crystals by filtration. The nitrophosphoric acid is then neutralised with ammonia, mixed with potassium/magnesium salts, sulphate and/or micro-nutrients and converted in a rotary granulation drum, fluidised bed, prilling tower or pug-mill to obtain solid compound fertilizers containing nitrate.

The separated calcium nitrate crystals are dissolved in ammonium nitrate solution and treated with ammonium carbonate solution following the reaction:-



This solution is filtered and the calcium carbonate crystals are removed and used for the production of granular calcium ammonium nitrate fertilizer. The resulting dilute ammonium nitrate solution is concentrated and also used to produce calcium ammonium nitrate fertilizer or NPK.

The calcium nitrate solution may also be neutralised and evaporated to obtain a solid fertilizer.

Depending on the phosphate rock and the cooling temperature around 2.2 tonnes of calcium carbonate or 3.6 tonnes of calcium nitrate per tonne of P_2O_5 are obtained.

2.2 Technologies of the Nitrophosphate Process

All the nutrients are totally used in the production of nitrate-containing fertilizers. This can only be realised through corresponding investment, together with a high integration of the different plants. The process is restrictive in the sense that only nitrate-containing fertilizers can be produced.

A modern compound fertilizer plant, based on the nitrophosphate route, requires an integrated production complex of different units. The links between the different units are shown in Figure 1.

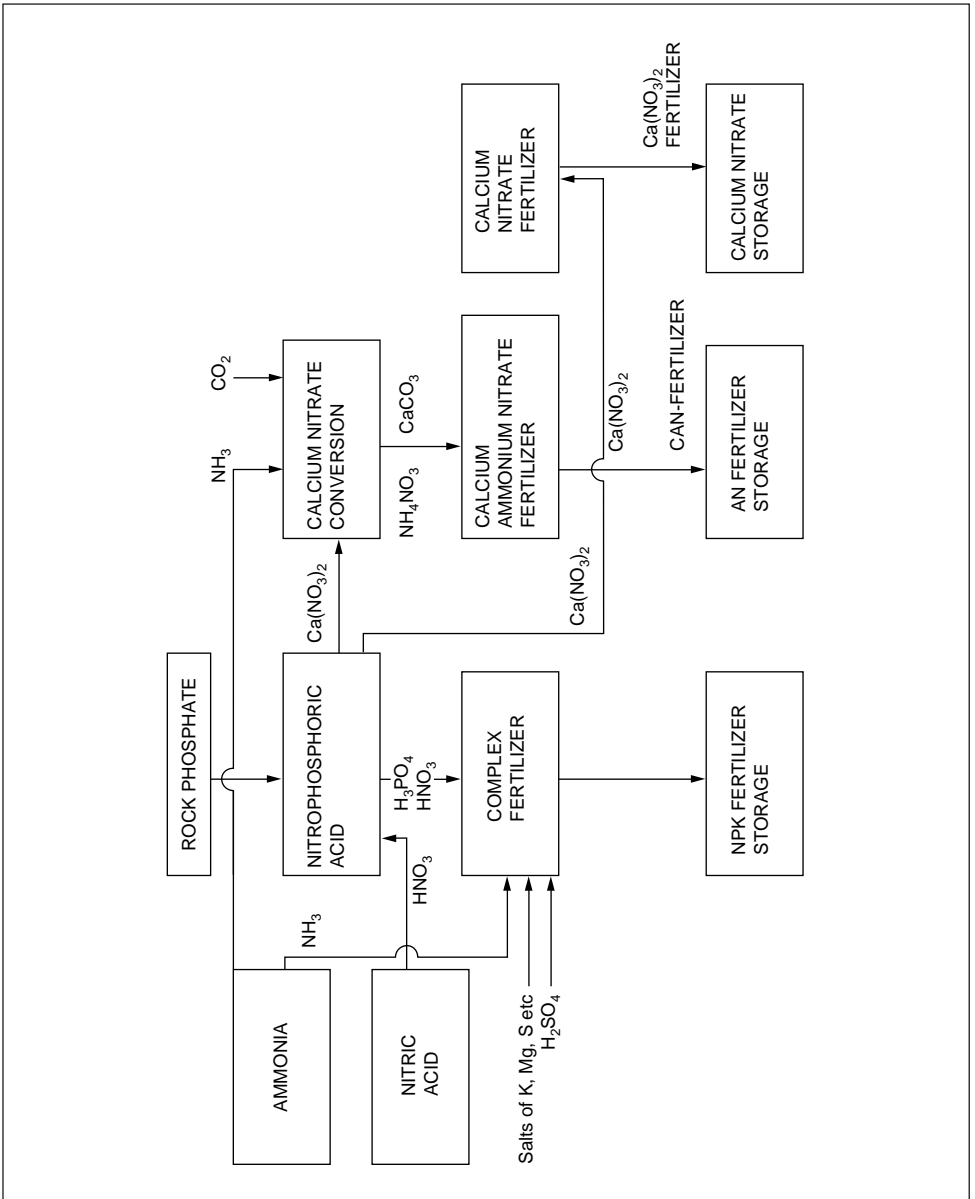


Figure 1 – Integrated Nitrophosphate Process.

2.2.1 Ammonia plant

A full description of ammonia production is given in EFMA BAT Booklet No. 1.

Ammonia is of importance in the nitrophosphate process because:-

- Liquid ammonia is used in the nitrophosphoric acid section (see 2.2.3) for cooling and this is more economic than the use of cooling compressors with high energy consumption
- Gaseous ammonia is used for the neutralisation of the remaining acid (see 2.2.4 and 2.2.5)
- The ammonia plant delivers carbon dioxide for the conversion unit (see 2.2.4) and thus reduces the CO₂ emission from the ammonia plant. Other sources of CO₂ such as ethylene oxide or incineration plants, can also be used

2.2.2 Nitric acid plant

A full description of the production of nitric acid is given in EFMA BAT Booklet No. 2.

A nitric acid plant on site is not a prerequisite because nitric acid can be bought and stored without problems but there are important advantages from energy and environmental points of view if it is included in the integrated process:-

- The nitric acid plant provides surplus steam for concentration purposes in the other units and thus saves energy
- The nitric acid plant can, under certain conditions, also process waste waters from the neutralisation and evaporation stages of ammonium nitrate production, leading to a saving of expensive demineralised water and thus also saving energy

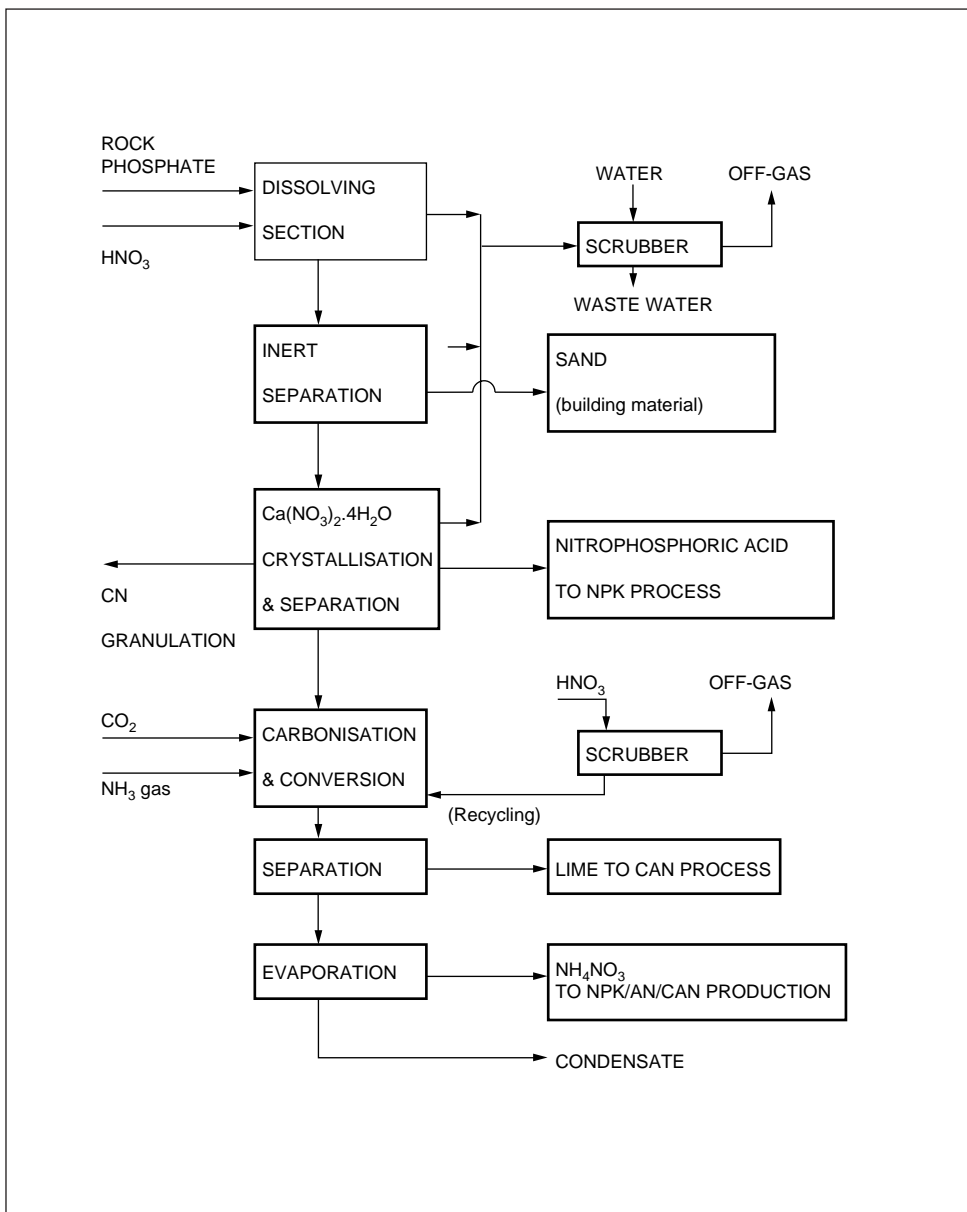


Figure 2 – Process Diagram of the Production of Nitrophosphoric Acid.

2.2.3 Nitrophosphoric acid unit

A process diagram for the production of nitrophosphoric acid is shown in Figure 2.

The production of this nitrophosphoric acid takes place in a special unit. In this unit natural rock phosphate, containing 30-40% P_2O_5 , is first dissolved in about 60% HNO_3 .

The reaction is exothermic and raises the temperature of the solution. The temperature is controlled at about 70°C because of the high corrosion rate above 70-75°C. The exothermic reaction leads to the emission of off-gases containing NO_x due to the reaction of the nitric acid with reducing agents such as organic matter and ferrous salts in the rock. The emission of NO_x and fluorides is controlled by collecting and combining the off-gases from the different vessels and treating them in a scrubbing unit before discharge to the atmosphere. The addition of urea can reduce this NO_x formation under certain conditions.

The resulting digestion solution containing different amounts of suspended solids, mostly quartz sand, the amount depending on the origin of the different rocks, is then treated to remove most of this sand. Sand is an undesirable diluent of the nutrients in the final product and a cause of equipment and piping damage by erosion. It can be removed by centrifuges, hydrocyclones or, more recently, by lamella separators. The overflow solution flows into a storage tank and is subsequently used in the crystallisation stage of the process. The sand is separated from the slurry and washed. The liquid effluent from this washing, if any, which contains P_2O_5 and NO_3^- , can be sent to a treatment unit. The neutral sand is used, for example, in the building industry.

The digestion solution still containing minor amounts of sand is fed discontinuously to a number of standard batch-wise operating crystallisers. The solution is cooled with water and liquid NH_3 to the required final crystallisation temperature and most of the calcium crystallises out as CNTH. These crystals are subsequently removed from the remaining solution by centrifuge, rotating drum filter or, more recently, by belt filter. The remaining nitrophosphoric acid ("NP solution") having a CaO/P_2O_5 ratio varying between 0.21 and 0.65 (typical composition at $CaO/P_2O_5 = 0.25$ is 23% P_2O_5 , 5.8% CaO , 6% NO_3-N and 33% H_2O), is the basic starting material for the production of nitrate containing compound fertilizers.

The washing and crystallisation section also produces off-gases, which contain NO_x and fluorides. The off-gases are treated in scrubbers before discharge to atmosphere. The volume of off-gases is low compared to that from the dissolving section.

Final emission levels depend on the kind of rock phosphate and on other treatment possibilities available on the production site, such as a biological treatment.

There is no solid waste as all the sand can be used for other purposes.

2.2.4 The calcium nitrate tetrahydrate conversion unit

This unit contains two important production stages:-

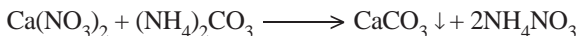
- The production of calcium carbonate
- The production of concentrated ammonium nitrate solution

2.2.4.1 Production of calcium carbonate

As described above, calcium nitrate tetrahydrate crystals are separated from the nitrophosphoric acid solution by various separation techniques. These crystals are dissolved in an ammonium nitrate solution and pumped to a storage tank.

In another section of the plant a solution of ammonium carbonate in dilute ammonium nitrate is prepared. Carbon dioxide from an ammonia plant and gaseous ammonia from the refrigeration section of the nitrophosphoric unit are the raw materials for the ammonium carbonate production. Around 1.0t of CO₂ is used per tonne P₂O₅ produced.

The ammonium carbonate solution is mixed with the calcium nitrate solution and the following reaction takes place:-



The resulting reaction mixture passes to a belt filter where the precipitated CaCO₃ is filtered off. The calcium carbonate is sent to storage before being used in the production of granular calcium ammonium nitrate or in other applications. The remaining ammonium nitrate solution (50-65% AN) is pumped to a storage tank and can be used for the production of compound fertilizers or calcium ammonium nitrate.

This production stage has no liquid effluents because all the water used is recycled in the different production stages. Nevertheless, the carbonisation and conversion sections have off-gases which are treated in a scrubbing column and the scrubbing liquor is recycled. The off-gases, containing small amounts of NH₃ and F after scrubbing, are discharged to atmosphere.

2.2.4.2 Production of concentrated ammonium nitrate solution

The solution from the belt filter is treated in a second filtration step to remove the remaining CaCO₃ crystals. The excess ammonium carbonate is neutralised with nitric acid and the resulting neutral clean dilute ammonium nitrate solution is stored in an AN solution tank from where it is pumped to the AN evaporation section. The AN evaporation section may consist of a series of falling film evaporators and may constitute a double or triple-effect evaporation depending on the capacity and cost of energy at the given location.

Saturated steam of max. 9bar, provides the necessary energy for this concentration unit. The concentrated AN solution can be stored before use in the production of granular fertilizers.

This section has practically no emission into air. Liquid effluents are generated by the condensation of the evaporated gases and are normally recycled, used for cleaning purposes, purified by an appropriate method and/or sent to a biological treatment plant.

2.2.5 Compound fertilizer production unit

Nitrate containing fertilizers can be produced from the nitrophosphoric acid produced as described in Section 2.2.3, by neutralising with ammonia and with the possible addition of nitric acid, ammonium sulphate or sulphuric acid, potassium and magnesium salts and micro-nutrients. This production is carried out in three sections; neutralisation, particle formation and conditioning. A process diagram for this unit is shown in Figure 3.

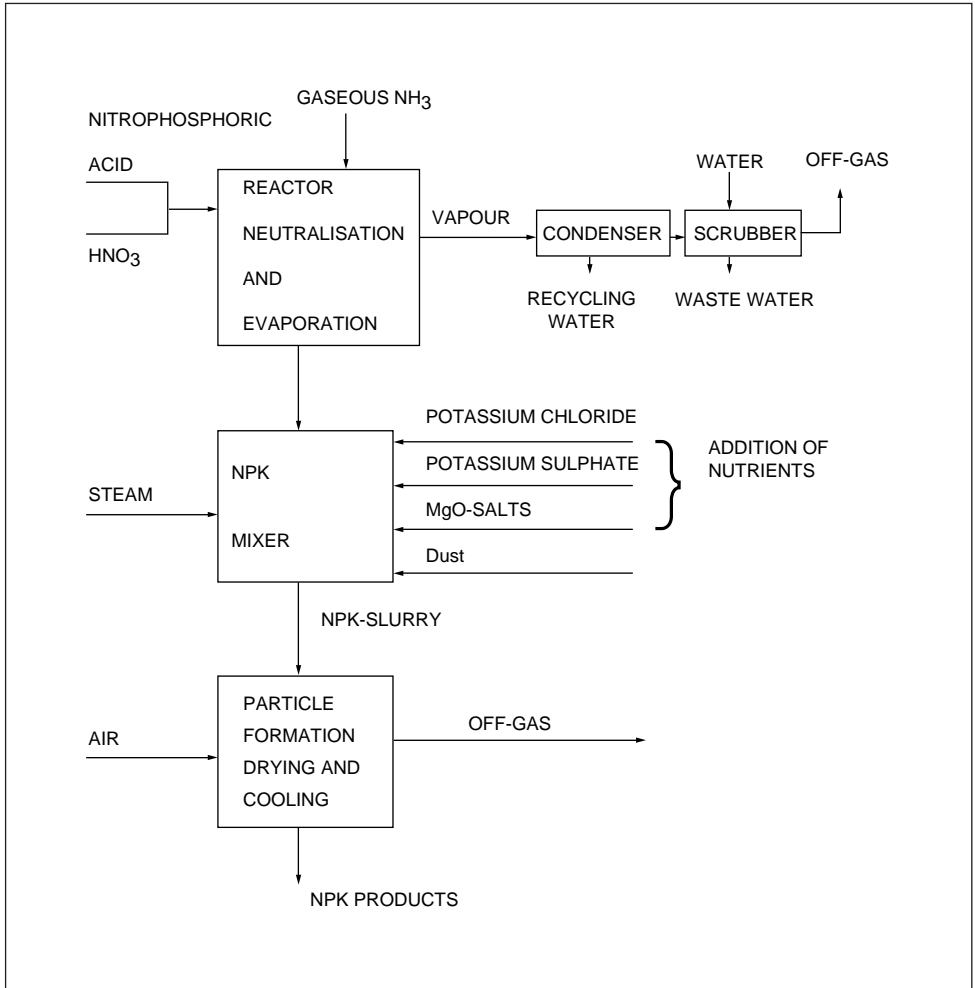


Figure 3 – Process Diagram of the Production of Nitrate Containing Compound Fertilizers (NPK) by the Nitrophosphate Route.

2.2.5.1 Neutralisation

The nitrophosphoric acid solution with a $\text{CaO}/\text{P}_2\text{O}_5$ ratio of 0.21-0.65 is neutralised with gaseous ammonia to around pH 5 in stainless steel reactors in different stages. This reaction is very exothermic and raises the temperature to around the boiling point (125-145°C). The reaction heat is normally used for economic evaporation of the slurry and cooling the slurry.

More or less water is evaporated depending on the kind of granulation, so that after mixing the solution with potassium salts and other nutrients the following water contents are reached:-

- Sphero-diser : 10-28%
- Granulation drum : 4-12%
- Prill tower : 0.5%

All the processes involve treatment with ammonia and operate at high temperature, generating off-gases. It is possible to use various condensing or scrubbing systems for these off-gases as the different kinds of processes work under different conditions. Energy costs, type of raw material, investment costs, type of granulation and the grades of fertilizers all influence the choice of the emission reduction technique. The recycling of the condensates or scrubber liquor is dependent on the water balance of the grade which is produced.

2.2.5.2 Particle formation

Three types of processes are normally used for the production of NPK fertilizers; prilling, drum or pugmill granulation and Sphero-diser granulation. The three types of particulation give different amounts of emissions to air and require different treatment systems. The air and water emission levels proposed in Chapter 8 are levels for all the particulation processes.

Prilling

Evaporated NP liquor from the neutraliser is mixed with the required salts and recycled product. The final water content is about 0.5%. The mixer overflows into a rotating prill bucket from which the slurry is sprayed into the prill tower. Fans at the top of the tower cause ambient air to flow counter-current to the droplets formed by solidification. The solid prills fall onto a rotating tower bottom and are scraped off and forwarded to the dry handling system. The product leaving the prilling tower is screened to meet product specifications. Over- and under-size material is returned to the process and the on-size NPK product is sent to the conditioning section.

Dust emission from the prilling tower itself is very low. No special air treatment system is needed for the vast amounts of cooling air because the dust concentration is less than $5\text{mg}\cdot\text{Nm}^{-3}$. Total dust emission is dependent on the ammonium nitrate content and is normally less than $2.5\text{kg}\cdot\text{h}^{-1}$ as the total air volume passing through the prilling tower is more than $500,000\text{Nm}^3\cdot\text{h}^{-1}$. The concentration of ammonia is also low, being typically $10\text{-}15\text{mg}\cdot\text{Nm}^{-3}$ ($5\text{-}7.5\text{kg}\cdot\text{h}^{-1}$). The amount of ammonia escaping is related to several process parameters, especially pH, high temperature and the $\text{NH}_3/\text{P}_2\text{O}_5$ ratio of the NP liquors. Recovery of ammonia from such large volumes is unrealistic and the only way to minimise this ammonia loss is to control the pH.

Drum and pugmill granulation

The NP liquor at approximately 135°C and with a water content around 4-12% is mixed with the required salts and recycled products and is pumped and sprayed into a rotating drum granulator. The water evaporated in the drum is carried away by a co-current flow of air. The granules so formed are dried in a rotating drying drum with hot air. The water content of the granules is normally below 1.5%. The air leaving the drums, about 100,000Nm³.h⁻¹ for the production of 55t.h⁻¹ 15-15-15, contains water vapour, dust, ammonia and combustion gases.

The air from the granulation and drying drums is treated in high performance cyclones, giving low dust levels (< 50mg.Nm⁻³) after passing the cyclones. As with the prilling tower, the amount of ammonia lost in the granulation and drying drum depends on the operating temperature and the final pH of the neutralised slurry.

The average ammonia content is less than 150mg.Nm⁻³ under normal conditions, if the final pH is maintained at about 5.0. The NPK product, after drying, is screened and the on-size hot product is sent to the conditioning section. The under-sized and over-sized granules, are returned to the granulator after crushing. Screens, crushers and conveyor discharge points are de-dusted in one mode of operation using the air going to the drums.

Spherodiser granulation

The NP liquor with a temperature of 115-120°C is mixed with the required salts and recycled products. The resulting slurry with a water content of 10-28% is pumped and sprayed into a special rotating drum, called a spherodiser. Warm air, heated to 300-400°C by gas or fuel flows co-currently in the spherodiser evaporating the water from the NP liquor and building up dry granules with a water content of <1.5%.

The air from a spherodiser, about 100,000 Nm³.h⁻¹ is treated in high performance cyclones. The remaining dust and NH₃-content is dependent on the grade, the operating temperature and pH of the NP liquor.

The dry granules are screened and the over-size taken out, crushed and returned to the spherodiser together with the under-size. The on-size fraction passes to the conditioning process. The screen, crusher and conveyor discharges are de-dusted using the air required for granulation.

2.2.5.3 Conditioning

The commercial product from the drying and screening is cooled in a fluidised bed, a bulk flow heat exchanger or rotating drum. Off-gases from these latter stages, containing minor amounts of dust and generally no ammonia, are de-dusted in cyclones. Finally, the product is cooled and coated before storage in order to minimise the subsequent caking of the material.

2.2.6 Calcium nitrate fertilizer production unit

The calcium nitrate crystals from the nitrophosphate process can be processed to a solid calcium nitrate (CN) fertilizer, using prilling or pan-granulation technology, as an alternative to the combination of CNTH conversion and subsequent processing to CAN. (See EFMA BAT Booklet No. 6)

2.2.6.1 Neutralisation and evaporation

The CNTH crystals from the nitrophosphoric acid unit are heated to form a melt which is pumped to a two-stage atmospheric tank reactor system for neutralisation with gaseous ammonia. The reaction between ammonia and the remaining acids in the CNTH melt is exothermic. The ventilation gases from the two reactors are scrubbed with water before being discharged to atmosphere. The total discharge from the scrubbers is $<0.3\text{kg}\cdot\text{h}^{-1}$ ($\text{NO}_3\text{-N}$ and $\text{NH}_4\text{-N}$) for a $100\text{t}\cdot\text{h}^{-1}$ plant and the concentration is $<35\text{mg N}\cdot\text{Nm}^{-3}$ of off-gas.

The 60% CNTH melt, containing small amounts of ammonium nitrate is evaporated in one or two stages to a final concentration of 85% and this concentrated solution is then transferred to the prilling or pan granulation process.

The process steam containing ammonia is scrubbed with condensate and compressed for energy recovery for use in the evaporators. Part of the condensate is discharged into water and the remainder is returned to the process. The discharge of NO_3 and NH_4 nitrogen into water from a $100\text{t}\cdot\text{h}^{-1}$ CN plant is around $30\text{kg}\cdot\text{h}^{-1}$, when a spillage collection system is installed in the wet part of the process. The collected spillage is returned to the process.

2.2.6.2 Pan granulation

The concentrated melt from the evaporator system is sprayed into the pan granulator together with the recycled fines. The granules are smoothed in a smoothing drum and air-cooled in a fluid bed. The cooled product is screened in two stages and the on-size product is transferred to a coating drum and finally to storage. The over-size material is crushed, mixed with the fines and recycled to the granulator.

The ventilation gases from the granulation and dry part of the process are scrubbed with water and process condensate from the wet part of the process, in a lamella separator before discharge to atmosphere. The emission of CN-containing aerosols to air is normally $<4\text{mg NO}_3\text{-N}\cdot\text{Nm}^{-3}$ of off-gas. The volume of ventilation air from a pan granulator producing $50\text{t}\cdot\text{h}^{-1}$ CN fertilizer is $170,000\text{Nm}^3\cdot\text{h}^{-1}$.

The condensate from the lamella separator, containing calcium nitrate, is mixed with collected spillage from the dry part of the process and returned to the neutralisation section.

There is no discharge of $\text{NO}_3\text{-N}$ into water from the dry part of the process.

2.2.6.3 Prilling

The concentrated melt from the evaporators is mixed with recycled fines and fed to a rotating prill bucket. The melt leaving the bucket solidifies due to the heat exchange with counter-current air in the prill tower. Air from the prill tower is discharged to atmosphere without dust removal. The volume of air from a $40\text{t}\cdot\text{h}^{-1}$ CN plant is $370,000\text{Nm}^3\cdot\text{h}^{-1}$, normally with a CN dust concentration of $20\text{mg}\cdot\text{Nm}^{-3}$.

The prills from the base of the tower are cooled with air in a fluid bed cooler and screened to remove off-size material. The product-size prills are coated before storage. Over-size material is dissolved in neutralised CN solution and returned to the evaporator feed tank. Under-size material is mixed into the evaporated melt before prilling.

Dust from the fluid bed cooler is removed in a cyclone separator and returned to the evaporator feed tank. The volume of air leaving the cyclones is $32,000\text{Nm}^3\cdot\text{h}^{-1}$, with a dust concentration of $300\text{mg}\cdot\text{Nm}^{-3}$.

3. DESCRIPTION OF STORAGE AND TRANSFER EQUIPMENT

3.1 Solid raw materials

The main solid raw materials are phosphate rock and potassium salts (potassium chloride (potash)) and/or potassium sulphate and these are transported to the production site by ships, trains and lorries.

3.1.1 Ship unloading

Ships are traditionally unloaded by grab cranes. It is important that the content of fine material under $75\mu\text{m}$ should be below 1% to avoid dust emission or, as in the case of potash, to have conditioned material. The use of closed cranes and transport equipment can minimise dust emission originating from the unloading site. A screw or pneumatic ship unloading machine may be used.

3.1.2 Unloading of rail waggons or lorries

The raw materials are tipped from waggons and lorries under a roofed structure into hoppers which feed the material to conveyors. The roads and the area near the unloading site are preferably asphalted and sloped so that the rainwater – possibly containing nutrients – can be collected and recycled or discharged in a controlled manner.

3.1.3 Conveyors/pneumatic transport

All types of conveyors are preferably placed in totally enclosed tunnels. Pneumatic transport of some solid raw materials directly into bins or silos is possible. Air filters must be provided on these bins or silos.

3.1.4 Storage

Raw materials are stored in closed buildings or silos. Material in storage is handled by payloaders, scraper or crane.

3.2 Finished Products

Finished products are granulated or prilled fertilizers of many different grades. They are stored and transported in bulk or bagged. The external – as well as internal – treatment given to the granular or prilled fertilizers ensures good physical properties. Dusting, abrasion, resistance to temperature changes and caking are such that handling is simple and does not normally require special precautions.

3.2.1 Conveyors

Belt conveyors may be placed in enclosed tunnels.

3.2.2 Bulk storage

The storage of bulk product is described in the EFMA handbook on safe storage and handling of AN-based fertilizers [1]. Bulk storage is in closed buildings with walls to separate the different grades of product.

Material is handled either by payloader or scraper. Fertilizers are hygroscopic and thus it is recommended that the storage area is air-conditioned.

3.2.3 Screening

Fines and lumps must be screened out from the product after bulk storage to ensure high quality. The separated over- and under-size material is recycled to the NPK plant.

3.2.4 Bulk delivery

Product may be supplied to customers in bulk form. Bulk products are loaded into lorries, rail waggons or ships. There is the risk of spreading some dust from the filling spouts to the environment and to avoid this, a dust collecting system in the filling spouts is recommended.

Rainwater collection from asphalt surfaces near the bulk loading areas is not normally required but may be considered.

3.2.5 Bagging

Part of the product may be supplied in 40-50kg bags and in big bags of 500-1,200kg. Bagged products are normally stored under cover.

3.2.6 Off-spec solid materials

Off-spec products, such as under-size and over-size from screening, dust from filters and spillages from bagging and bag storage, are recycled to the NPK plant by conveyors or wheeled vehicles.

3.2.7 Emissions

Practically, there is no emission into the environment from material handling which is done correctly. There is no waste water and the only emission into air is the dusty air collected from the bagging plant filling spouts and the screening station. The average air volume through such dust filters is $40,000\text{Nm}^3\cdot\text{h}^{-1}$. The dust content of the air after passing through the filters is typically $30\text{mg}\cdot\text{Nm}^{-3}$.

4. ENVIRONMENTAL DATA

The environmental data for the processes described relate to one grade (15–15–15). The amount of waste water that can be recycled depends, at a given capacity, on the grade of product being produced. In principle, the aim should be to recycle all the waste liquids from the production of all grades. However, some liquid effluent may occur when manufacturing NPK grades which contain high concentrations of ammonium nitrate.

The emissions sources in the nitrophosphate process are described below. Achievable emission levels are summarised in Chapter 8. No account is taken of the co-production of CAN or calcium nitrate.

The typical advantages of the process from an environmental point of view are:-

- The process is not dependent on sulphur and thus no sulphur oxides are emitted
- The process produces no phosphogypsum and no gypsum waste water
- There is no solid waste. By-products are upgraded to commercial products and spillages are recycled
- The cooling energy necessary for the CNTH crystallisation comes from the evaporation of liquid ammonia required for ammoniation
- The production of CaCO_3 needs 1 tonne of CO_2 per tonne P_2O_5 produced, thus reducing the overall CO_2 emission by this amount

The disadvantage of the process is the emission of nitrogen oxides and fluorides.

4.1 Emissions into Air

4.1.1 Nitrogen oxides

Nitrogen oxides, NO_x (mainly NO and NO_2) are emitted from the dissolution of phosphate rock in nitric acid. These oxides result from the nature of the rock e.g. organic and iron contents and also from the reaction temperatures in the different steps. Emissions can be reduced by adding urea solution or by cooling the reactors to the lowest possible digestion temperature.

The off-gases are treated in scrubbers but it is not possible to eliminate the NO_x emission entirely. Emission values will normally be $< 500\text{mg.Nm}^{-3}$.

4.1.2 Fluorides

Phosphate rocks contain about 4% fluorine and the majority of this passes through the process into the fertilizer with only a minor part released into the gaseous phase. The fluorides are normally removed in scrubbers. Emission values will normally be $< 5\text{mg F/Nm}^{-3}$.

4.1.3 Ammonia

The major ammonia emissions originate from the CNTH conversion section, the AN evaporation section, the neutralisation of the nitrophosphoric acid and partly from the granulation or prilling sections.

The high process temperatures and the technical difficulties in neutralising nitric acid with ammonia without over-neutralisation make it impossible to avoid NH_3 emission. The ammonia off-gases from the nitrophosphoric neutralisation steps are removed in scrubbers. The resulting ammonia in the exhausted air is $60\text{mg}\cdot\text{Nm}^{-3}$ air. The ammonia emission from the granulation and drying sections is on average $<150\text{mg}\cdot\text{Nm}^{-3}$. This depends on the nature of the fertilizer, the operating temperatures and in particular, on the pH value.

The ammonia emission can be reduced to around $60\text{mg}\cdot\text{Nm}^{-3}$ after scrubbing with acidic solutions.

4.1.4 Aerosols

Aerosols of NH_4NO_3 and NH_4Cl may be formed during the different production steps. It is therefore important to avoid contact between NO_x and NH_3 containing waste gases.

4.1.5 Fertilizer dust

The main sources of dust are the drying and granulation drums and/or prilling towers with a minor amount of dust coming from the cooling drum, screens, crushers and conveyors. The best way for de-dusting this waste air is to pass the off-gases through a battery of high performance cyclones with suitably sized air streams, velocity, temperature and pressure. It is also important to have well-trained staff who continuously controls the granulation step and the emissions. Generally the emission value for dust is $50\text{mg}\cdot\text{Nm}^{-3}$. The values can go up to $75\text{mg}\cdot\text{Nm}^{-3}$ when producing grades with high solid or sulphate content of the slurry to be granulated.

4.2 Emissions into Water

The main effluent components are ammonia, nitrate, fluoride and phosphate. Ammonia emissions into water occur when not all condensates of the ammonium nitrate evaporation or the neutralisation of the nitrophosphoric acid solution can be recycled. The main sources of the nitrate and fluoride emission are the scrubber liquor of the phosphate digestion and the sand washing. Phosphate emissions to water originate from the sand washing.

Two methods for the reduction of emissions have been demonstrated in nitrophosphoric acid plants. One reduces the P_2O_5 emission from 0.4kg to 0.02kg $\text{P}_2\text{O}_5\cdot\text{t}^{-1}$ P_2O_5 produced, by recycling the liquor of the sand washing. The other method reduces the emissions of N and F from 1.2 and 0.7 to $0.6\text{kg N}\cdot\text{t}^{-1}$ P_2O_5 and $0.02\text{kg F}\cdot\text{t}^{-1}$ P_2O_5 respectively, by recycling of the NO_x scrubber liquor. In theory a reduction of N, P_2O_5 and F is possible when using nitric acid of more than 63% but this has not yet been demonstrated.

4.3 Solid Wastes

There is no solid waste except sand which can be used as a building material after washing and separation.

By-products are converted into commercial products and spillages and off-specification products are recycled into the NPK production.

5. EMISSION MONITORING

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

5.1 Emissions into Air

5.1.1 Dry gas

Dust in dry gases from stacks and vents with a temperature above the dewpoints, can be easily measured. The gases are taken isokinetically and passed through a fine glass filter and the aerosols and clean gases pass through the filter and the dust is retained. The emission, expressed as mg.Nm^{-3} is determined by weighing the mass on the filter and measuring the volume of the gas extracted from and in the stack as described in ISO standards. The correct determination of free ammonia is difficult because of the presence of aerosols such as NH_4Cl , $(\text{NH}_4)_2\text{CO}_3$ and NH_4NO_3 .

5.1.2 Wet gas

Measuring dust and ammonia in a wet gas on a continuous basis is problematical. The best available technique for atmospheric monitoring is for trained staff to take routine manual samples and a measuring frequency of once per day or shift is recommended but the problem of aerosols still makes the determination of free ammonia very difficult.

5.2 Emissions into Water

In the nitrophosphate process the most significant parameters to be monitored are pH, ammonia, nitrate, phosphate and fluoride. On-line monitoring for all of these parameters is possible without difficulty and this makes controlling and correction by trained staff easy.

6. MAJOR HAZARDS

The following hazardous chemicals are handled during the production of compound NP(K) fertilizers from rock phosphate and nitric acid, i.e. by the nitrophosphate route:-

- Nitric acid and mixtures of nitric and phosphoric acids
- Ammonia
- Ammonium nitrate (with concentrations >90%)
- Sulphuric acid

In general the inventory of these chemicals in a nitrophosphate plant is rather small. Ammonia and nitric acid are normally stored within the limits of their own production facilities and supplied to the nitrophosphate plant by pipeline. Production, storage and transfer of ammonia and nitric acid as well as the related environmental, occupational health & safety aspects are described in the EFMA BAT Booklets Nos 1 and 2.

Ammonium nitrate (AN) is produced and processed within a nitrophosphate production facility in varying concentrations. High concentrations of AN solutions or melts are considered to be hazardous. The inventory of such hazardous AN solutions may vary in existing plants but new plants can be designed to limit the inventory to less than 100t on average.

A reduced inventory also implies shortened residence times and this too is beneficial from a safety point of view. The production, storage and transfer of ammonium nitrate are described in EFMA BAT Booklet No. 6.

Further hazards involved in the manufacturing, storage and transport of NP(K) fertilizers may be found in the use of gases (e.g. CO₂ for the production of ammonium carbonate and lime), hot air (for drying granules), high pressure steam and the use of advanced equipment (granulator drums, elevators, chain mills etc.). These hazards are general in nature and not specific to NP(K) production.

Special care must be taken when handling and pumping AN containing solutions, slurries or melts (see EFMA BAT Booklet No. 6) and precautionary measures must be considered to avoid pump explosions. These are well described in the literature on this subject.

Further hazards directly related to the manufacturing, storage and transport of NP(K) fertilizers are self-sustaining decompositions at temperatures above 130°C. These potential hazards depend entirely on the product grades and the formulations. Various precautionary measures can be taken to reduce these potential hazards, such as temperature control of the product during production and adjustment of the product formulations and reduction of the impurity content.

The storage and handling of ammonium nitrate based fertilizers is described in an EFMA handbook [1].

7. OCCUPATIONAL HEALTH & SAFETY

The fertilizer plants described in this Booklet pose some chemical and physical risks regarding personal health. The main chemicals which must be considered for occupational health and safety include:-

- Acids : Nitric, phosphoric and sulphuric acids
- Gases : Ammonia, nitrogen oxides, compounds containing fluorine, chlorine and sulphur
- Dust : NPK dust is regarded as inert
- Hot salt melts : Can cause severe burning on contact

Special safety regulations exist for work with acids or ammonia.

Decomposition can occur when fertilizer or fertilizer slurry containing ammonium nitrate is heated above a certain temperature. Large amounts of toxic gases can be given off. Special precautions should be taken against these gases because they can cause lung oedema a long time after exposure.

Good operating practices – including personal protection (gloves, safety spectacles, safety footwear, helmet, gas mask, etc.), first aid (shower, eye wash), emergency procedures (alarm signals, escape routes, emergency plans) full information to personnel about safety and health aspects (use of data sheets) – should be followed.

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

8. SUMMARY OF BAT EMISSION LEVELS

The following emission levels are considered to be achievable for new and existing plants. Emissions are quoted separately for the process steps of producing nitrophosphoric acid and for the processing and granulation of NPK. The given BAT-values for NPK relate to average values for most NPK formulations. Approximately 10% of the annual production will typically cover grades with difficult formulations where the BAT-values cannot be met. The concentrations given are indicative and will depend on how the various gas streams are treated and mixed before discharge. Emissions into water only cover process wastes and no other side pollutions related to material handling.

8.1 Achievable Emission Levels for the Nitrophosphoric Acid and Conversion Units (Sections 2.2.3 and 2.2.4)

8.1.1 Emissions into air

NH ₃	0.2kg.t ⁻¹ P ₂ O ₅	60mg.Nm ⁻³ wet
NO _x (as NO ₂)	1.0kg.t ⁻¹ P ₂ O ₅	500mg.Nm ⁻³ wet
Fluoride	0.01kg.t ⁻¹ P ₂ O ₅	5mg.Nm ⁻³ wet

8.1.2 Emissions into water

Total Nitrogen	1.2kg.t ⁻¹ P ₂ O ₅
P ₂ O ₅	0.4kg.t ⁻¹ P ₂ O ₅
Fluoride	0.7kg.t ⁻¹ P ₂ O ₅

8.1.3 Solid wastes

No solid waste except sand after washing and separation which can be used as a building material.

8.2 Achievable Emission Levels for NPK Production (Section 2.2.5)

8.2.1 Emissions into air

8.2.2 Emissions into water

Total Nitrogen	0.2kg.t ⁻¹ NPK
Fluoride	0.03kg.t ⁻¹ NPK

8.2.3 Solid wastes

No solid waste.

8.3 Cost of Pollution Control Measures

The costs of pollution abatement equipment and the operating costs are high in relation to the total investment and operating costs.

The total investment costs for a $350,000\text{t}\cdot\text{y}^{-1}$ NPK plant, including the nitrophosphoric acid and conversion unit are 80 to 100 million EUR. This figure does not include raw material storage, bagging or off-site facilities. The estimated cost for BAT pollution abatement equipment is 20% of the total.

The operating costs are estimated to be 10% of this equipment cost.

Cost figures of adding-on equipment to an existing NPK plant are similar to those given in EFMA BAT Booklet No. 8 (Section 8.2).

9. 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.

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
CEFCIC	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
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 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 NPK 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 to 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 Dry Gas Monitoring – Particulate

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.

Light scattering measurements as opposed to transmission methods can also be used. Tribo electric effect meters allow the detection of a higher emission level.

2.2 Wet Gas Monitoring

This system typically involves analysing solutions which have been continuously separated from the gas stream taken by the iso-kinetic sampler. The use of the initial solution or a probe dilution solution is determined by the need to obtain continuous determination of ammoniacal N, Nitric N, F⁻, P₂O₅ (P), with any aerosols being collected separately and combined for weekly manual analysis of residual ammoniacal N, nitric N and fluoride.

The analytical methods employed can be either colorimetric or ion selective electrode, except for P₂O₅ (P) which is only achievable using coloration methods. The following analytical methods can be used for both on-line or manual techniques.

2.3 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 NH₄⁺ as follows:-



and that the equilibrium depends on pH. The above method determines the NH₄⁺ 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, 37. 11" and "Whitfield M, J Mar Biol. Ass UK, 1974, 54, 562".

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

2.4 Nitric N

The spectrophotometric method for nitric nitrogen relies on the reduction of the nitrate in the sample to nitrite, using a solution of hydrazinium sulphate and copper sulphate. A colour reagent consisting of sulphanilamide and N-1 naphthylethylene diamine dihydrochloride is then added to produce a pink solution. Kjeldahl methods are also available.

Ion selective electrodes can be used to measure nitric nitrogen but it should be noted that chloride ions interfere.

2.5 Fluoride F⁻

Commonly used methods for the determination of fluoride in solutions from the gas sampling system are colorimetric and ion selective electrode methods.

Colorimetric methods include the zirconium SPADNS (sulpho phenyl azo dihydroxy naphthalene disulphonic acid) method as the most widely used. Fluoride reacts with zirconium lake dye to produce a colourless complex for spectrophotometric determination.

A fluoride selective electrode using a lanthanum fluoride membrane may be used.

A volumetric method may also be used which relies on the titration of fluoride ion against lanthanum nitrate to an end point determined by coloration of an indicator dye such as Alizarin Red S or Eriochrome/Cyanine R.

2.6 Phosphate (P₂O₅ or P)

Low concentrations of P₂O₅ can be measured spectrophotometrically by reacting the sample with acidic molybdate reagents to form a reduced phosphomolybdenum blue complex.

Higher concentrations of P₂O₅ can also be measured spectrophotometrically by acidifying with nitric acid and reacting with a solution of ammonium molybdate/ammonium metavanadate to produce a yellow colour.

2.7 Potash (K₂O or K)

Atomic absorption spectrometry is used for low concentration levels of K and flame emission spectrometry for higher concentrations.

2.8 Sulphate (SO₄-S)

Inductively-coupled plasma atomic emission spectrometry is recommended for very low concentrations of S. Ion chromatography may be used for slightly higher concentrations and gravimetric methods are recommended for samples with high concentrations.

3. Emissions into Water

Most plants employing BAT will have low emissions into water under normal operating conditions. However, problems associated with start-up, shut-down and maintenance may mean that there may be an overall site consent which requires monitoring. This will require the measuring of effluent flow and proportional or high frequency sampling and continuous on-line analysis as follows:-

Flow	-	Ultrasonic
pH	-	Applicable national standard for pH electrodes
F ⁻	-	See 2.3 above
P ₂ O ₅ or P	-	See 2.3 above
NH ₄ -N	-	See 2.3 above
NO ₃ -N	-	See 2.3 above

APPENDIX 2 GENERAL PRODUCT INFORMATION ON NITRATE BASED NPK FERTILIZERS

1. Identification

Chemical name:	Ammonium Nitrate based Compound Fertilizers (NPK, NP, NK Fertilizers)
Nature of ingredients:	These fertilizers contain ammonium nitrate and some or all of the following:- Other ammonium salts Phosphate salts Potassium salts Inert fillers Secondary nutrients Micro-nutrients (trace elements) Coating agents

2. Hazards to Man and the Environment

To man

These fertilizers are basically harmless products when handled correctly.

To the environment

These fertilizers are basically harmless products when handled correctly.

3. Physical and Chemical Properties

Appearance	: White/grey granules or prills
Odour	: Odourless
pH water solution (10%)	: 4-6
Melting point	: Depending on composition
Explosive properties	: Very high resistance to detonation
Oxidising properties	: Not classified as oxidising according to EEC Directive 88/379/EEC

**Best Available Techniques Booklets
were first issued by EFMA 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