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

Booklet No. 8 of 8:

PRODUCTION OF NPK FERTILIZERS
BY THE
MIXED ACID ROUTE

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## CONTENTS

PREFACE 4

DEFINITIONS 6

1. INTRODUCTION 7

2. DESCRIPTION OF PRODUCTION PROCESSES 9
   2.1 Granulation with a Pipe Reactor System 9
   2.2 Drum Granulation with Ammoniation 11
   2.3 Mixed Acid Process with Phosphate Rock Digestion 13

3. DESCRIPTION OF STORAGE AND TRANSFER EQUIPMENT 16
   3.1 Solid Raw Materials 16
   3.2 Products 16

4. ENVIRONMENTAL DATA 17
   4.1 Emission Sources 18
   4.2 Granulation with a Pipe Reactor System 19
   4.3 Drum Granulation with Ammoniation 20
   4.4 Mixed Acid Process with Phosphate Rock Digestion 21

5. EMISSION MONITORING 22
   5.1 Emissions to Air 22
   5.2 Emissions to Water 22

6. MAJOR HAZARDS 23
   6.1 Slurry Pump Explosions 23
   6.2 Slurry Decomposition (reactor processes) 23
   6.3 Product Decomposition 23

7. OCCUPATIONAL HEALTH & SAFETY 25

8. SUMMARY OF BAT EMISSION LEVELS 26
   8.1 Achievable Emission Levels for New and Existing Plants 26
   8.2 Cost of Pollution Control Measures 27

9. REFERENCES 28

GLOSSARY OF TERMS 29

APPENDIX 1 Emission Monitoring in NPK Plants 32

APPENDIX 2 General Product Information on Nitrate Based NPK Fertilizers 35
The European Fertilizer Manufacturers Association (EFMA) has prepared eight Booklets on Best Available Techniques (BAT) in response to the proposed EU Directive on integrated pollution prevention and control (IPPC Directive). The Booklets have been prepared 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
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 proposed IPPC Directive (see below). 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/m³ or mg/l) 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, 1 March 1995
DEFINITIONS

The following definitions are taken from the proposed EU Directive of September 1993 on Integrated Pollution Prevention and Control:

«Best Available Techniques» (BAT) signify the latest stage in the development of activities, processes and their methods of operation which indicate the practical suitability of particular techniques as the basis of emission limit values for preventing or, where that is not practicable, minimising emissions to the environment as a whole, without pre-determining any specific technology or other techniques.

«Techniques» include both the technology used and the way in which the installation is designed, built, maintained, operated and decommissioned. The techniques must be industrially feasible, in the relevant sector, from a technical and economic point of view.

«Available» techniques mean those developed on a scale which allows implementation in the relevant industrial context under economically viable conditions and being reasonably accessible to the operator.

«Best» means most effective in achieving a high level of protection for the environment as a whole, taking into account the potential benefits and costs which may result from action or lack of action.
INTRODUCTION

Straight fertilizers such as Calcium Ammonium Nitrate (CAN), Ammonium Nitrate (AN), Ammonium Sulphate (AS), Urea, Single Superphosphate (SSP), Triple Superphosphate (TSP), Potash (Potassium Chloride) (MOP) and combined types such as Mono-Ammonium Phosphate (MAP), Di-Ammonium Phosphate (DAP) are well-defined products made using well-defined processes.

Compound or complex fertilisers such as NPK, are more difficult to define as there is an infinite number of N/P/K-ratios and the processes applied in their production are numerous.

The product name «NPK» is normally followed by three numbers to indicate the percent of N, P₂O₅ and K₂O which the product contains, e.g. 24–6–12 indicates that this particular grade contains 24% N (nitrogen compounds), 6% P₂O₅ (phosphorus compounds) and 12% K₂O (potassium compounds). In addition, the fertilizer may contain magnesium, boron, sulphur, micronutrients, etc. The typical content of nutrients (N + P₂O₅ + K₂O) will normally be in the range of 40-60%.

Grades with no P₂O₅ or no K₂O are also included in the «NPK» product range but they are normally named NP and NK fertilizers. These types of fertilizers can normally be produced in NPK plants and emission levels will typically be within the limits valid for NPK grades.

The most widespread NPK fertilizers in Europe contain nitrate and/or ammonium salts.

NPK fertilizers can be produced in four, basically different, ways:–
- ammonium phosphate/ammonium nitrate-based NPK fertilizers
- nitrophosphate-based NPK fertilizers (mixed acid route)
- nitrophosphate-based NPK fertilizers (ODDA-route)
- mechanical blending of single or multi-nutrient components

This Booklet will only focus on the two first ways, which are characterised by the following technologies:–

1. Processing of raw materials
   - Mixed acid slurry processes with digestion of rock phosphate
   - Phosphoric acid slurry processes
   - Mixing of solid raw materials

2. Granulation techniques
   - Drum granulation
   - Blunger/pugmill granulation
   - Spherodiser granulation
   - Prilling

The selection of the basic techniques is based on several factors:–
- Target product range (N/P/K ratio)
– Raw material basis
– Quality parameters
– Flexibility of process
– Size of production plant
– Integration with other processes
– Economic factors

Nevertheless, having made a proper selection, almost all production sites will continue their own development to improve
– Production flexibility
– Production efficiency
– Environmental impact
– Product quality

One NPK grade (15–15–15 / N–P₂O₅–K₂O) using all the technologies is used in this Booklet to present comparable figures and the production rate has been standardised to 50t/h.

Emission figures and production rates in a specific production unit will depend on the product grade, but the grade selected for this Booklet can be considered an average grade. The raw material basis has also been standardised and only commercially available raw materials have been selected, although many production sites have access to other, alternative raw materials.

The technologies covered are all well-known and well-proven. The main developments within fertilizer technology have primarily taken place in the areas of instrumentation, process control (computers), measurement, waste recycling and gas cleaning. Many older plants have already been revamped and such developments have been incorporated.

The Booklet covers NPK production technology including gas scrubbing and materials handling equipment and the storage needed to handle solid raw materials and finished products. The Booklet does not cover the production of any intermediates such as nitric acid, phosphoric acid, sulphuric acid, ammonium nitrate solution or superphosphates.

The descriptions of technologies which can apply at BAT level have been limited to three processes with the following characteristics.

1. Granulation with a pipe reactor system
   – Broad range of formulations
   – Direct neutralisation of phosphoric and sulphuric acid in a pipe reactor
   – No phosphate rock digestion
   – High costs of raw materials (P₂O₅)
   – Simple gas scrubbing
   – Low costs of labour and maintenance
   – Low cost of investment

2. Drum granulation with ammoniation
   – Broad range of formulations
Neutralisation of phosphoric and sulphuric acids in the granulation drum
- No phosphate rock digestion
- High costs of raw materials (P₂O₅)
- Simple gas scrubbing
- Low costs of labour and maintenance
- Low cost of investment

3. Mixed acid process with phosphate rock digestion
- Broad range of formulations
- Phosphate rock digestion enabling a considerable part of the phosphorus to be supplied from the low cost raw material, phosphate rock
- Flexible control of the reactions of raw materials in the liquid phase
- High product quality
- Complex gas scrubbing
- Medium costs of labour and maintenance
- Medium cost of investment

It should be understood that the technologies selected above are not the only three which can meet the BAT emission levels described in chapter 8. Any process which can meet the figures in chapter 8 is BAT.

2. DESCRIPTION OF PRODUCTION PROCESSES

Three different processes are described:
- 2.1. Granulation with a pipe reactor system
- 2.2. Drum granulation with ammoniation
- 2.3. Mixed acid process with phosphate rock digestion

These three production principles can be combined with different types of granulation and drying equipment and different types of air effluent treatment systems. The descriptions are generalised but should cover a major part of the NPK fertilizer technologies (except the nitrophosphate process) which exist today.

2.1 Granulation with a Pipe Reactor System

The process works with a classical granulation loop but incorporates one or two pipe reactors. One pipe reactor is fitted in the granulator and another may be used in the dryer. (see Figure 1).
Phosphoric acid or a mixture of phosphoric and sulphuric acids is neutralised in the pipe reactors with gaseous or liquid ammonia. A wide range of grades, including ammonium phosphates, can be produced. The process is flexible and easy to operate and the pipe reactors can be operated with a high turn-down ratio.
2.1.1 Granulation and drying section

The required solid raw materials such as potassium chloride, potassium sulphate, superphosphate, secondary nutrients, micronutrients and filler are metered and fed into the granulator together with the recycle. The pipe reactor fitted in the granulator is designed to receive phosphoric acid, part of the ammonia, and all other liquid feeds such as sulphuric acid and recycled scrubber liquor.
Concentrated ammonium nitrate solution may be added directly into the granulator and ammoniation rates in the pipe reactor vary according to the product. Further ammoniation may be carried out in the granulator.

A pipe reactor fitted in the dryer is fed with phosphoric acid and ammonia. The N/P mol ratio is 1.00 (essentially production of mono-ammonium phosphate). The MAP produced consists of very fine particles and passes via the cyclones and screens back to the granulation drum. The granules obtained are dried in a drying section using a heated air stream.

2.1.2 Screening, crushing, cooling and coating
The dry granules are screened into three fractions. The over-size is removed and returned via the crusher to the granulator, together with the fines. The product-sized fraction is removed with the possibility of returning part of this fraction to the granulator to stabilise the recycle loop.

Finally the on-spec fraction is cooled in classical cooling equipment such as a fluidised bed cooler or a cooling drum.

The cooled product is fed into a coating drum where a surface coating is applied to prevent caking.

2.1.3 Gas scrubbing and dust removal
Gases from the granulator and the dryer are scrubbed in venturi scrubbers with recirculating ammonium phosphate or ammonium sulpho-phosphate solution. Make-up phosphoric and/or sulphuric acid is/are added for pH control if necessary. The scrubber liquor which is being recycled is fed to the pipe reactor in the granulator.

Finally, the gases are vented through cyclonic columns irrigated with an acidic solution. The gases coming from the dryer are de-dusted in high efficiency cyclones to remove the majority of the dust before scrubbing. The air coming from the cooling equipment is generally recycled as secondary air to the dryer after de-dusting. General de-dusting equipment is installed in the entire plant.

2.2 Drum Granulation with Ammoniation
The process consists of a classical granulation loop using mainly solid raw materials. Ammonium nitrate solution and/or steam is/are fed into the granulator. The process is very flexible, and is able to produce a broad spectrum of grades including products with a low nitrogen content. (see Figure 2).

2.2.1 Granulation and drying
The required solid raw materials such as potassium chloride, potassium sulphate, superphosphates, ammonium phosphates, secondary nutrients, micronutrients and filler are metered and fed into the granulator together with the recycle.
Ammonium nitrate solution is sprayed directly into the granulator and sulphuric acid may be fed into the granulator followed by ammoniation. For some NPK grades steam is also used to keep the temperature at the required level.
The granules obtained are dried in a drying section using a heated air stream.

2.2.2 Screening, crushing, cooling and coating

The dry granules are screened into three fractions and the over-size is removed and returned via the crusher to the granulator together with the fines. The product-sized fraction is removed with the possibility of returning part of this fraction to the granulator to stabilise the recycle loop. Finally, the on-spec fraction is cooled in classical cooling equipment such as a fluidised bed cooler or a cooling drum and the cooled product is fed into a coating drum where a surface coating is applied to prevent caking.

2.2.3 Gas scrubbing and dust removal

Gases from the granulator and dryers are scrubbed in venturi scrubbers with recirculating ammonium phosphate or ammonium sulfo-phosphate solution. Makeup phosphoric and/or sulphuric acid is/are added for pH control if necessary. The scrubber liquor which is being recycled is fed into the granulation drum.

The gases coming from the dryer are de-dusted in high efficiency cyclones to remove the majority of the dust before scrubbing. The air coming from the cooling equipment is generally recycled as secondary air to the dryer after de-dusting. General de-dusting equipment is installed in the entire plant.

2.3 Mixed Acid Process with Phosphate Rock Digestion

The process is very flexible and produces grades with varying degrees of phosphate water solubility. The process is able to use cheap raw materials such as phosphate rock (see Figure 3).

2.3.1 Phosphate rock digestion and ammoniation

This type of process is characterised by the way the phosphates, or at least a part of them, are made «available» (soluble).

The first step of the process is the digestion of phosphate rock with nitric acid resulting in a solution of phosphoric acid and calcium nitrate. Acid gases such as oxides of nitrogen and fluorine compounds are formed during the digestion, depending on the type of phosphate rock.

Other raw materials such as phosphoric, sulphuric and nitric acids or AN solution are added after the digestion, which is an exothermic process. The acid slurry is ammoniated with gaseous ammonia and after the neutralisation, other components such as ammonium phosphates, superphosphates, ammonium sulphate and compounds containing potassium and magnesium, are added. Most of these materials may also be added before or during the neutralisation but if the raw
material contains chloride the pH of the slurry should be 5 – 6 to avoid production of hydrogen chloride.

*Figure 3 - Mixed Acid Process with Rock Digestion*
The design of the reactor battery can vary from a few large reactors to many, smaller reactors. Common for all the designs of the reactor battery is that the row of reactors ends with a buffer tank.

Depending on the type of raw material, the amount of gas scrubber liquid to be recycled and the degree of ammoniation, the water content of the slurry in the buffer tank can vary between 5% and 30% and the temperature from 100°C to 140°C.

2.3.2 Granulation, drying, screening, crushing, cooling and coating
In principle, the dry section can be divided into a granulation part, a drying part, a screening/crushing part, a cooling part and a coating part.

The granulation can be performed by different equipment such as drum, blunger and spherodiser. The spherodiser granulation also incorporates the drying operation.

A broad spectrum of grades can be produced by these processes, but NPK fertilizers with a very low content of nitrogen are not convenient for the spherodiser process because in such cases a sprayable slurry will demand an unrealistic, high content of water.

In all the granulation processes mentioned above the off-spec fraction from the screening/crushing operation is recycled to the granulation equipment.

All granulation processes, except the spherodiser process, require a drying operation after the granulation. This drying is normally carried out in a drying drum.

The fertilizer may be cooled in a cooling drum or in a fluidised bed cooler.

The coating can be a combination consisting of a treatment with an organic agent and an inorganic powder. Both additions can be made in one drum.

2.3.3 Gas scrubbing and dust removal
2.3.3.1 Reactor gases
The gases from the digestion reactors, where phosphate rock is digested in nitric acid, are treated separately in a spray tower scrubber to recover NO\textsubscript{x} and fluorine compounds. The pH is adjusted by the addition of ammonia.

The ammoniation reactor gases are scrubbed in several stages of counter-current scrubbing. The pH is adjusted to the most efficient scrubbing condition, pH 3-4, with a mixture of HNO\textsubscript{3} and/or H\textsubscript{2}SO\textsubscript{4}. The first scrubbing stage ensures a saturation of the gases; the second high pressure venturi stage is designed to remove aerosols. The subsequent stages make the recovery efficiency high and the final stage operates with the cleanest scrubbing liquid. A droplet separator is installed in the stack or immediately before it.

2.3.3.2 Drying gases
The gases from the dryer (granulator/dryer) are led through cyclones before entering the scrubber. The scrubber consists of a variable throat venturi with subsequent two-
stage scrubbing. The last stage should be operated with the cleanest liquid. A part of the liquor, after the circulation, goes to a settler for the separation of solids. The thickened part is fed to the reactors and the overflow returned. The pH is adjusted with acids to pH 3-4.

2.3.3.3 Cooling gases
The cooler uses ambient air or cooled and conditioned air. The warm air from the cooler is recycled to the inlet of the dryer.

2.3.3.4 General de-dusting
Screens, crushers and conveyor discharge points are de-dusted and the de-dusting air is cleaned in a bag filter before recycling or discharge into the atmosphere.

3. DESCRIPTION OF STORAGE AND TRANSFER EQUIPMENT

3.1 Solid Raw Materials
The main solid raw materials are potash and phosphate rock. These raw materials are transported to the production site by ships, trains or lorries.

3.1.1 Ship unloading
Grab cranes are traditionally used for the unloading of ships and with this method there is the risk that some fine material may spread to the environment in the harbour area. It is recommended that closed unloading methods (such as screw or pneumatic ship unloading machines) be used in new plants to avoid impact on the environment.

3.1.2 Unloading of rail waggons or lorries
The raw materials are tipped from waggons and lorries into hoppers which feed the materials to conveyors. The roads and the area near the unloading are asphalted and sloped so that the rainwater with nutrients flows to the pumping sump which is connected to the recycle system of the NPK plant.

3.1.3 Conveyors
Belt conveyors are totally enclosed in tunnels.

3.1.4 Storage
Raw materials are stored in closed buildings or silos. Materials in storage are handled by payloader, scraper or crane.

3.2 Products
Products are granulated fertilizers of different grades.

3.2.1 Conveyors
Belt conveyors are placed in closed 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 (Reference [1]). Bulk storage is in closed buildings with walls to separate different grades of product. Materials are handled by payloader or scraper. Fertilizers are hygroscopic and thus it is recommended that the storage atmosphere is air-conditioned.

3.2.3 Screening
Fines and lumps must be screened out from the product after bulk storage for quality reasons. The separated over- and under-sized material is recycled back to the NPK plant.

3.2.4 Bulk delivery
Part of the product may be supplied to customers in bulk. Bulk products are loaded onto lorries, rail waggons or ships and there is the risk of spreading some dust from the filling spouts to the environment. The use of a dust collecting system in the filling spouts is recommended to avoid waste. Rainwater from asphalt areas near the bulk loading system is collected and returned to the recycle system in new plants.

3.2.5 Bagging
Part of the product may be bagged in 40-50kg bags and in 500-1200kg big bags. Bagged products are normally stored under cover.

3.2.6 Solid waste products
Waste products, such as under-size from screening, dust from filters and spillages from bagging and bag storage, are recycled to the NPK plant by conveyors or container vehicles.

3.2.7 Emissions
There is practically no emission to the environment from materials handling when this is done correctly. There is no contaminated waste water and the only emission to air is the dust collection air from the bagging plant and screening station. The average air volume through dust filters is 40,000Nm³/h and the typical dust content after the filters is 30mg/Nm³.

4. ENVIRONMENTAL DATA
The environmental data for all the processes described relate to one grade, (15–15–15). The grade chosen makes it possible to recycle more waste water than a grade with a higher nitrogen content. This makes it easier to recycle all the liquids but, in principle, the aim should be to recycle all the waste liquids from the production of all grades.
Excess condensate from the production of ammonium nitrate solution is not included in this Booklet, but is referred to in EFMA BAT Booklet No. 6.

To make it easier to compare the processes a capacity of 50t/h was chosen even though the two processes (pipe reactor system and drum granulation with ammoniation) generally have a smaller capacity than the third (mixed acid process).

4.1 Emission Sources

4.1.1 Ammonia
The majority of the ammonia emissions originate from the ammoniation reactors. The amount depends on pH, temperature, and slurry viscosity. Some ammonia evaporates at the inlet of the spherodisers, in the drying drums and in the drums with ammoniation because of high temperature and/or drying rate.

4.1.2 Nitrogen oxides
Nitrogen oxides, NO\textsubscript{x}, are mainly NO and NO\textsubscript{2} with some nitric acid. The main source of NO\textsubscript{x} is the dissolution of phosphate rock in nitric acid. The nature of the rock, for example organic matter and iron contents and the reaction temperature, affect the amount of NO\textsubscript{x}. The emission can be reduced by cooling the reactor and by adding urea solution to the reactor.

4.1.3 Fluorine compounds
The fluorine compounds originate from the phosphate rock and thus, indirectly, from the phosphoric acid. In practice, the main part of the fluorine goes through the process into the fertilizer and only a minor part is released into the gaseous phase.

4.1.4 Aerosols
The main aerosol components are ammonium nitrate, ammonium fluoride and ammonium chloride which are formed in the gas-phase reaction between ammonia and acidic components as well as by sublimation from the boiling reaction mixture.

4.1.5 Fertilizer dust
The main source of fertilizer dust is the drying drum with a minor amount being released in the cooling drum. Dust collection is necessary from the screens, crushers and conveyors.

4.1.6 Carbon dioxide and sulphur dioxide
Drying requires hot air which is normally produced using heavy fuel oil or natural gas. The amounts of carbon dioxide and sulphur dioxide depend on the content of carbon and sulphur in the fuel used. Part of the sulphur dioxide will be retained in the gas scrubbing system. The amount of fuel needed is decreased by using the neutralising heat in the reactors to reduce the water content of the slurry. Recirculation of the
cooling gases to the drying drum also produces economies and low pressure process steam from other plants is often used to heat the dryer inlet air.

4.2 Granulation with a Pipe Reactor System

4.2.1 Input requirements

<table>
<thead>
<tr>
<th>Water solubility of phosphates</th>
<th>85%</th>
<th>95%</th>
</tr>
</thead>
</table>

Typical raw materials
- Nitric acid* kg/t (100%) 280 242
- Ammonia* kg/t 107 122
- Phosphoric acid P₂O₅ kg/t 105 154
- SSP (21% P₂O₅) kg/t 212 -
- Potash (60% K₂O) kg/t 250 250

Filler kg/t - 150

Utilities
- Electricity kWh/t 30 30
- Total energy for drying MJ/t 320 320

*Includes the part added as AN solution

4.2.2 Output production

The production rate is fixed at 50t/h (1,200t/d or 350,000t/a)

There is no export of energy related to the process.

4.2.3 Emissions and waste

There are no solid and liquid wastes when these streams can be recycled to the process. Some liquid effluent will arise when manufacturing NPK grades containing high levels of ammonium nitrate. There are no measurable fugitive emissions and the total amount of air is estimated to be 120,000Nm³/h (wet).

Typical values for the emissions to air are listed below.

<table>
<thead>
<tr>
<th>Component</th>
<th>Emission at 50t/h</th>
<th>Emission at 50t/h</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>kg/h</td>
<td>kg/t NPK</td>
</tr>
<tr>
<td>NH₄–N*</td>
<td>2.5 (2–5)</td>
<td>0.05 (0.04–0.1)</td>
</tr>
<tr>
<td>Fluorides</td>
<td>0.3 (0.2–0.6)</td>
<td>0.005 (0.004–0.01)</td>
</tr>
<tr>
<td>Dust</td>
<td>6 (5–9)</td>
<td>0.12 (0.1–0.2)</td>
</tr>
</tbody>
</table>

*Including any free ammonia.

The ranges in brackets are the variations of the emissions which can be expected when different grades are produced.

4.3 Drum Granulation with Ammoniation
4.3.1 Input requirements

Typical raw materials.
- Nitric acid* kg/t (100%) 301
- Ammonia* kg/t 101
- Sulphuric acid kg/t (100%) 32
- SSP (18% P$_2$O$_5$) kg/t 11
- TSP (45% P$_2$O$_5$) kg/t 329
- Potash (60% K$_2$O) kg/t 250

Utilities
- Electricity kWh/t 33
- Total energy for drying MJ/t 300

*Including the part added as AN solution

4.3.2 Output production

The water solubility of the phosphates is 85%.
The production rate is fixed at 50t/h (1,200t/d or 350,000t/a)
There is no export of energy related to the process.

4.3.3 Emissions and waste

Emissions and wastes are the same as those given in paragraph 4.2.3.
4.4 Mixed Acid Process with Phosphate Rock Digestion

4.4.1 Input requirements

<table>
<thead>
<tr>
<th>Water solubility of phosphates</th>
<th>60%</th>
<th>80%</th>
</tr>
</thead>
</table>

**Typical raw materials**

- Phosphate rock (38.5% P₂O₅) kg/t: 151 128
- Nitric acid* kg/t (100%): 298 282
- Ammonia* kg/t: 107 111
- Phosphoric acid P₂O₅ kg/t: 96 104
- Sulphuric acid kg/t (100%): 53 76
- Potash (60% K₂O) kg/t: 251 251

**Utilities**

- Electricity kWh/t: 50 50
- Total energy for drying MJ/t: 450 450

*Includes the part added as AN solution

4.4.2 Output production

The production rate is fixed at 50 t/h (1,200 t/d or 350,000 t/a)

There is no export of energy related to the process.

4.4.3 Emissions and waste

Emissions and wastes are the same as those given in paragraph 4.2.3. The total amount of air is estimated to be 200,000 Nm³/h (wet).

 Typical levels for the emissions to air are listed below.

<table>
<thead>
<tr>
<th>Component</th>
<th>Emission at 50 t/h</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>kg/h</td>
</tr>
<tr>
<td>NH₄–N*</td>
<td>5 (2–8)</td>
</tr>
<tr>
<td>NHₓ–N</td>
<td>5 (2–9)</td>
</tr>
<tr>
<td>Fluorides</td>
<td>0.5 (0–1)</td>
</tr>
<tr>
<td>Dust</td>
<td>10 (5–15)**</td>
</tr>
</tbody>
</table>

*Including any free ammonia.
  **These levels do not include aerosols formed in reactions between acid gases and ammonia. These aerosols are included in NH₄–N, NOₓ–N, and fluoroide.

The ranges in brackets are the variations of the emissions which can be expected when different grades are produced.
5. Emission monitoring

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

5.1 Emissions to air

5.1.1 Components to be monitored
The components to be monitored are:
- Ammonia nitrogen (NH$_4$–N)
- Nitrous nitrogen (NO$_x$–N)
- Fluoride (F–)
- Dust

5.1.2 Frequency of monitoring
The frequency of monitoring depends on the harmfulness of the components. Cumulative sampling for all components and the measuring frequency are determined by the consistency of the emission figures.

On-line monitoring at critical emission points is suggested for ammonia nitrogen (NH$_4$–N) and fluoride (F–). This provides the operators with direct information about the effect of malfunctions in the process on the environment and consequently the process conditions can be corrected more efficiently.

5.2 Emissions to Water

Most plants using BAT have very low emissions to water under normal operating conditions. All liquid wastes are normally recycled into the process. There may, however be an overall site requirement for monitoring the effluent flow.
6. MAJOR HAZARDS

This chapter covers the following main hazards:–

6.1. Slurry pump explosions
6.2. Slurry decompositions
6.3. Product decompositions

The hazards involved in manufacturing, transport and storage of NPK fertilizers depend on the formulation.

The IFA/EFMA «Handbook for the Safe Storage of Ammonium Nitrate Based Fertilizers» gives details of the potential hazards (Reference [1]).

6.1 Slurry Pump Explosions

The main reasons for pump explosions are:–
– No (or insufficient) flow through the pump
– Incorrect design and maintenance practices

Special precautions must be taken in design and operational management to avoid slurry pump explosions.

6.2 Slurry Decomposition (reactor processes)

The main reasons for slurry decompositions are:
– Low pH
– Incorrect or contaminated raw materials
– Too high temperature

6.3 Product Decomposition

The risk of decomposition, the extent and possible consequences depend entirely on the hazardous properties of the product.

6.3.1 During manufacturing

The main reasons for product decomposition during manufacturing are:–
– Overheating of the product
– During drying
– Through an external heat source
– Through friction
– Low pH
– Contamination of the formulation with elements which favour decomposition
The following precautions must be taken:

6.3.1.1 Design equipment
- Avoid build-up on the inlet vanes in the dryer
- Uniform temperature profile of the air inlet (no hot spots) to be guaranteed.

6.3.1.2 Operational management
The hazardous properties of each formulation must be known:
- Self-sustaining decomposition or not (trough test)
- Decomposition temperature (stationary oven test)

Note: Both the above tests can be found in Reference [2].

The process control and safety instructions must take into consideration:
- pH control
- Alarms and interlocks on all process parameters that by deviation may lead to overheating of the product
- Documented control of the raw materials and safety precautions
- Possibility of a self-sustaining decomposition during production
- Emergency procedures

6.3.2 During transport and storage
Decomposition during storage represents the biggest hazard, bearing in mind the large quantities of fertilizer involved.

The main reasons for decomposition are:
- Initiation by an external heat source
- Contamination by organics and/or other materials causing initiation through heating by chemical reactions

6.3.3 Precautions
Refer to chapters 8 and 9 of the IFA/EFMA, «Handbook for the Safe Storage of Ammonium Nitrate Based Fertilisers» (Reference [1]), for the design and operational management.
7. OCCUPATIONAL HEALTH & SAFETY

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

- **Acids:** Nitric acid, phosphoric acid, sulphuric acid
- **Gases:** Ammonia, nitrogen oxides and compounds of fluorine, chlorine and sulphur (see threshold limit values in Reference [3])
- **Dust:** NPK dust is regarded as inert
- **Hot salt melts:** Can cause severe burning on contact

There are special safety regulations for work with acids or ammonia.

Decomposition may occur when fertilizer or fertilizer slurry containing ammonium nitrate is heated above a certain temperature, for certain periods of time. Large quantities of toxic gases may be evolved and 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.

8.1 Achievable Emission Levels for New and Existing Plants

The following emission levels can be achieved for new and existing plants because existing plants can be revamped with new gas cleaning systems. These levels relate to steady-state production and do not take account of peaks which can occur during the unsteady transient conditions of start-up and shut-down and during emergencies.

It should be emphasised that all data are based upon the following BAT assumptions:—

− All solid and liquid wastes are recycled, except that some liquid effluent may arise when manufacturing NPK grades containing high concentrations of ammonium nitrate. In this case an achievable emission level to water is 100mg N/l or 0.2kg N/t of product.
− General dedusting is incorporated in the processes

General remarks:

The BAT levels cover all the described processes and all possible NPK grades, so the following general comments should be mentioned:—

− processes with nitric acid digestion of phosphate rock (chapter 2.3) will have the highest NO\textsubscript{x} emissions
− processes with drum ammoniation will have a higher ammonia emission than pipe reactor or slurry phase ammoniation systems
− high nitrogen grades will give the highest total nitrogen emissions
− high phosphorus grades will give the highest fluoride emissions.

<table>
<thead>
<tr>
<th>Component</th>
<th>BAT-values</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ppm</td>
</tr>
<tr>
<td>NH\textsubscript{3}–N</td>
<td>80</td>
</tr>
<tr>
<td>NO\textsubscript{x} as NO\textsubscript{2}</td>
<td>35</td>
</tr>
<tr>
<td>Fluorides</td>
<td>6</td>
</tr>
</tbody>
</table>

Wet Dust (expressed as dry matter, excluding aerosols, which are included in gaseous components) 50 0.2

Conversion factors to convert:—

N → NH\textsubscript{3} : multiply by 1.214  
N → NO\textsubscript{2} : multiply by 3.286  
F → HF : multiply by 1.053
8.2 Cost of Pollution Control Measures

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

- the emission target or standard to be obtained.
- the type of process, the degree of integration with other processes on site, the production volumes, the type of raw materials being used, etc.
- whether the plant is new so that the design can be optimised with respect to pollution abatement, or whether the plant is an existing one requiring revamping or «add on» 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 at a later stage.

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. In new plants, however, the process design would integrate environmental control with the need for high efficiency and productivity and hence it is difficult to single out the costs of environmental control.

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

The figures relate to an NPK plant with an annual capacity of 350,000t.

<table>
<thead>
<tr>
<th>Equipment</th>
<th>Investment cost</th>
<th>Operating cost</th>
</tr>
</thead>
<tbody>
<tr>
<td>MFK plant, incl. BAT equipment</td>
<td>20 million ECUs * ±10%</td>
<td>4 – 8ECU/t**</td>
</tr>
<tr>
<td>BAT equipment***, integrated</td>
<td>2.4 million ECUs ±10%</td>
<td>0.4 – 0.8 ECU/T****</td>
</tr>
<tr>
<td>BAT equipment***, added later</td>
<td>4 million ECUs ±40%</td>
<td>0.4 – 0.8 ECU/T****</td>
</tr>
</tbody>
</table>

* The NPK plant investment estimate does not include any raw material storage, bagging or off-site facilities.
** Excluding costs of raw materials and fixed costs.
*** BAT equipment is considered to be two-stage scrubbing of reactor and dryer gases and bag filter for cooling gases, with total recycling of liquid wastes. Excluded are cyclones for dryer and cooler gases and a very simple reactor gas scrubber.
**** Operating cost estimates are based on 15-20kWh/t additional electricity consumption, based on estimated additional motor power for blowers and pumps (about 1000kW total addition). Some additional maintenance costs are also needed.
9. REFERENCES


GLOSSARY

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

ACGIH American Conference of Governmental Industrial Hygienists
AFNOR Association Française de Normalisation (France)
AN Ammonium Nitrate
AQS Air Quality Standard
AS Ammonium Sulphate
BAT Best Available Techniques
BATNEEC Best Available Technology Not Entailing Excessive Cost
BOD Biological Oxygen Demand
BPL Basic Phosphate of Lime (Bone Phosphate of Lime)
BS British Standard
CAN Calcium Ammonium Nitrate
CEFIC Conseil Europeen de l’Industrie Chimique (European Chemical Industry Council)
COD Chemical Oxygen Demand
DAP Di-Ammonium Phosphate
DIN Deutsches Institut für Normung (Germany)
EEC European Economic Community
EFMA European Fertilizer Manufacturers Association
ELV Emission Limit Value
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
CaCO₃  Calcium Carbonate
Cd  Cadmium
CH₃OH  Methanol
CH₄  Methane
CO  Carbon Monoxide
CO₂  Carbon Dioxide
F  Fluorine
F⁻  Fluoride
H  Hydrogen
H₂O  Water
H₂S  Hydrogen Sulphide
H₂SiF₆  Hydrofluorosilicic Acid (Hexafluorosilicic Acid)
H₂SO₄  Sulphuric Acid
H₃PO₄  Phosphoric Acid
HNO₃  Nitric Acid
K  Potassium
KCl  Potassium Chloride (Muriate of Potash) («Potash»)
K₂O  Potassium Oxide
N  Nitrogen
N₂  Dinitrogen Monoxide (Nitrous Oxide)
NH₃  Ammonia
NH₄⁻  Nitrogen Monoxide (Nitric Oxid
3  Nitric Nitrogen
O (O₂)  Oxygen
P  Phosphorus
P₂O₅  Phosphorus Pentoxide
S  Sulphur
SO₂  Sulphur Dioxide
SO₃  Sulphur Trioxide
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**: Kilogrammes per hour
- **kWh**: Kilowatt hour (1000kWh = 3.6GJ)
- **l**: Litre (liquid volume)
- **m**: Metre
- **m³**: Cubic Metre (liquid or solid volume)
- **mg**: Milligramme
- **mg/l**: Milligrammes per litre
- **MJ**: Mega Joule
- **mm**: Micrometre
- **Nm³**: 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**: Tonnes per day
- **t/y**: Tonnes per year
- **°C**: Degree Celsius (Centigrade)
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 Section 8 of this Booklet are briefly described below.

2. Emissions to Air

2.1 Dry Gas Monitoring – Particulates
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.

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\(^-\), P\(_2\)O\(_5\) (P), K\(_2\)O and SO\(_4\)\(^-\)S, 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 P\(_2\)O\(_5\) (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 monochloramine is reacted with phenol to form an indo-phenol blue compound. This method is particularly suitable for the determination of ammonia in cooling waters derived from saline sources (dock, estuarine or sea water) and may be used in continuous flow colorimetry.

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

Note that free ammonia exists in equilibrium with NH\(_4^+\) as follows:

\[
\text{NH}_4^+ + \text{H}_2\text{O} \rightleftharpoons \text{NH}_3 + \text{H}_3\text{O}^+
\]

and that the equilibrium depends on pH. The above method determines the NH\(_4^+\) ammonia. Free ammonia is particularly toxic to fish and should an incident occur, it may be more important to relate the result to free ammonia. Any suitable pH determination may be used and the free ammonia estimated as given in «Hampson B L, J Cons Int Explor, Mer, 1977, 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 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 nitrates to an end point determined by coloration of an indicator dye such as Alizarin Red S or Eriochrome Cyanine R.

2.6 Phosphate ($P_2O_5$ or P)
Low concentrations of $P_2O_5$ can be measured spectrophotometrically by reacting the sample with acidic molybdate reagents to form a reduced phosphomolybdenum blue complex.

Higher concentrations of $P_2O_5$ 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 ($K_2O$ or K)
Atomic absorption spectrometry is used for low concentration levels of K and flame emission spectrometry for higher concentrations.

2.8 Sulphate ($SO_4$–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 to Water

Most plants employing BAT will have low emissions to 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:

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flow</td>
<td>Ultrasonic</td>
</tr>
<tr>
<td>pH</td>
<td>Applicable national standard for pH electrodes.</td>
</tr>
<tr>
<td>F⁻</td>
<td>See 2.3 above.</td>
</tr>
<tr>
<td>P₂O₅ or P</td>
<td>See 2.3 above.</td>
</tr>
<tr>
<td>NH₄⁺N</td>
<td>See 2.3 above.</td>
</tr>
<tr>
<td>NO₃⁻N</td>
<td>See 2.3 above.</td>
</tr>
</tbody>
</table>

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
  - Trace elements (micro nutrients)
  - 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 : Depending on composition.
Explosive properties point : Very high resistance to detonation.
Oxidising properties : Not classified as oxidising according to EEC
Directive 88/379/EEC
Best Available Techniques Booklets
issued by EFMA 1995

1. Production of Ammonia
2. Production of Nitric Acid
3. Production of Sulphuric Acid
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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