



UNITED NATIONS ENVIRONMENT PROGRAMME  
INDUSTRY AND THE ENVIRONMENT

UNITED NATIONS INDUSTRIAL  
DEVELOPMENT ORGANIZATION

TECHNICAL REPORT  
N° 26 - Part 1

Mineral Fertilizer Production  
and the Environment

Part 1.

The Fertilizer Industry's  
Manufacturing Processes  
and Environmental Issues



In collaboration with the  
INTERNATIONAL FERTILIZER INDUSTRY ASSOCIATION



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PRODUCTION  
AND THE  
ENVIRONMENT

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Manufacturing Processes  
and Environmental Issues



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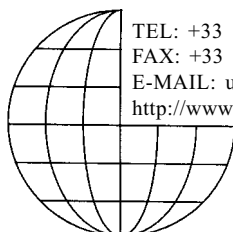
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# 1. INTRODUCTION

As with all chemical process industries, the production of mineral fertilizers gives rise to emissions, which contribute to environmental problems, both globally and locally. Over the last 25 years, much research and expenditure has been devoted to minimizing these emissions. Like other industries, the fertilizer industry started with plants which would be totally unacceptable today, both in terms of their waste emissions and their internal working environment. In the industrialized countries, the emergence of environmental conservation as a major political issue generated tight regulation of manufacturing industries, not least the fertilizer industry. Many developing countries - especially those with high population densities - are also adopting stricter environmental controls, despite the immediate economic cost which this entails.

Since the 1960s many fertilizer manufacturers have made enormous progress in reducing emission. For example, during the past 25 years, emissions to the atmosphere and effluent to water from Hydro's production plants in Norway have decreased by approximately 90%. At the same time, production has doubled. There are some intractable problems, such as the emission of CO<sub>2</sub> from ammonia production, which is an intrinsic part of the process, although some can be used down-stream in the production of certain other products, such as urea. Another difficult problem is the disposal of phosphogypsum resulting from the production of phosphoric acid. Otherwise, the environmental impact of the best fertilizer production plants is negligible. The aim is to encourage the adoption by the fertilizer industry world-wide of the most effective practices as regards environmental protection.

The purpose of this document is to provide guidelines on how environmental objectives might be achieved in the production of fertilizers by means of integrated industrial and environmental policies. The target audiences for this document are:

- Policy-making bodies outside the fertilizer industry whose decisions affect the industry;
- The fertilizer industry, in particular in countries where the industry is still being established, or where action is needed to correct past unsatisfactory practices. The information provided enables them to benefit from the experience of countries with a well-established fertilizer industry, subject to disciplines developed over a long period of time;

The processes involved in the production of mineral fertilizers give off emissions containing pollutants that may contribute to global environmental problems (e.g. green house effect) and local environmental problems (e.g. acid rain, acidification, eutrophication, chemical mist). If fertilizer production facilities are to achieve the lowest environmental impact, both locally and globally, it is important that high standards of operation and maintenance are achieved, or measures taken to reduce polluting emissions will be less effective than designed. It is also necessary to monitor the emissions to air and discharges to water from the production plants. This enables the operators of the plant to take corrective action if the effluents deviate from design conditions.

Medium-specific environmental action in resolving air, water and waste problems separately was the norm in most industries and governments until recently. In many countries it is still the main way in which environmental issues are addressed. The traditional approach to environmental policy concentrated on effects rather than causes. While some improvements in environmental quality certainly resulted from this approach, the limits also soon became apparent. The need to look at all the impacts simultaneously and to address the priority areas in a systematic way has now become more or less universally accepted.

**Environmental issues concerning the mining and beneficiation of phosphate rock and potash ores are not included.**



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## 2. THE DEVELOPMENT OF THE FERTILIZER INDUSTRY

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### ■ 2.1 THE FERTILIZER INDUSTRY

The fertilizer industry was born from a conjunction of circumstances which originated in North Western Europe in the latter part of the 18th, and the first half of the 19th centuries. These included:

- a revolutionary new concept of plant nutrition, supported by pioneering experimentation, which discovered the biological role of chemical elements;
- an industrial revolution, which stimulated technological innovation and the growth of chemical, mining and transportation industries, thus providing the infant fertilizer industry with increasingly economic sources of raw materials and access to potential markets;
- growing population densities and rapid urbanization, which created concentrated off-farm markets for food and fibre and a growing need to restore soil nutrients, in order to increase or maintain crop yields and minimize dependence on agricultural imports;
- hence, increasingly heavy, laborious manuring and cultivation, which, by the mid-19th century, were approaching their economic and physical limits.

The similarity of these circumstances with those in many of the present developing countries is obvious; and this accounts for the rapid global growth of the fertilizer industry over the last half-century. The growth of population, and its concentration in towns and cities, has made it increasingly difficult to rely wholly on traditional manuring with human, animal and crop wastes. Even in China, where the recovery of organic wastes has been practiced most efficiently, an increasingly massive use of fertilizers has become essential.

The fertilizer industry is essentially concerned with the provision of three major plant nutrients - nitrogen, phosphorus and potassium - in plant-available forms. Nitrogen is expressed in the elemental form, N, but phosphorus and potash may be expressed either as the oxide ( $P_2O_5$ ,  $K_2O$ ) or as the element (P, K). Sulphur is also supplied in large amounts, partly through the sulphates present in such products as superphosphate and ammonium sulphate. The conversion factors are  $P_2O_5 \times 0.4366 = P$ ,  $K_2O \times 0.8302 = K$ ,  $SO_3 \times 0.4 = S$ . Secondary nutrients may be supplied incidentally as a result of the production process and its raw materials. Micro-nutrients (trace elements) can be incorporated into the major fertilizers or supplied as speciality products.

The industry is generally thought to have originated with the opening of J.B. Lawes' first superphosphate plant in London in 1843. However, there are prior claimants, notably J. Murray, in Ireland, and H. Köhler, in the former Bohemia. Lord Dundonald, in Scotland, experimented with by-product ammonium sulphate in the late 18th century, and Chilean nitrate was sold to British farmers from the 1830s. Waste gas liquor also supplied some nitrogen during this initial period, and, from 1840 onwards, guano provided agriculture with substantial amounts of nitrogen and phosphorus in both Europe and America.

### □ 2.1.1 The Nitrogen Fertilizer Industry

It was not until the early years of the 20th century that processes were developed for capturing atmospheric nitrogen - firstly by passing air through an electric arc to produce nitric acid and calcium nitrate, then by reacting lime and coke in an electric furnace to produce calcium cyanamide, and then, most notably, by synthesizing nitrogen and hydrogen catalytically, using a process developed by the German scientists, F. Haber and C. Bosch. These processes revolutionized the nitrogen fertilizer industry, breaking the former dependence on the relatively rare mineral sources of nitrogen and enabling the development of products with a higher nitrogen content. The first Haber Bosch plant was opened in 1913, and nitrogen production has been largely dependent on ammonia synthesis ever since.

Ammonia synthesis requires large amounts of energy. Initially, this was provided by cheap electricity and derivatives of coal (water gas process or cryogenic separation of hydrogen from coke oven gas). These feedstocks were available only in industrialized countries. Subsequently, more economic processes were developed which involved the partial oxidation of hydrocarbons by pure oxygen and steam and the tubular reforming of natural gas or naphtha by steam. Again, these developments were initially restricted mainly to the industrialized countries, because of large investment costs and difficult logistics. However, from the 1960s onwards, the larger developing countries, especially in Asia, began increasingly to subsidize the production and consumption of fertilizers, assisted by the major international agencies.

The naphtha and fuel oil based processes were rendered relatively uncompetitive by the first oil crisis in 1974. Fortunately, more and more natural gas became available as well in Europe as in developing countries. Most new plants from the mid-60s onwards were built to use natural gas, thus enabling the former Soviet Union, certain countries in Eastern Europe and numerous developing countries with extensive gas sources to develop large ammonia-based fertilizer industries.

The early nitrogen fertilizers - sodium and calcium nitrates, calcium cyanamide and ammonium sulphate - contained only 15-21% N. Of course, this was vastly more than the typical 1-1.5% total nutrient content in animal manures, but less than could be achieved using ammonia to produce ammonium nitrates. By the 1960s, ammonium nitrate (34% N, 35% when pure) and calcium ammonium nitrate (27% N) had become the leading nitrogen fertilizers. However, the development of ever larger, gas-based ammonia plants, affording large amounts of by-product carbon dioxide allowed for utilizing this carbon dioxide in the manufacture of urea. Urea is the product of the reaction of ammonia with carbon dioxide. It contains 46% N. Consequently, it offered a further significant advance in plant nutrient concentration, and hence in savings in nutrient transportation and distribution. Today, it is one of the most common nitrogen fertilizer. Let us mention moreover the use -mainly in the USA, of liquid  $\text{NH}_3$  as a fertilizer.

Nevertheless, the less concentrated nitrogen fertilizers continue to occupy an important place in numerous countries. Among these products, ammonium sulphate is in a somewhat special position, being a by-product of the manufacture of caprolactam and coke-oven gas.

Ammonium bicarbonate became particularly important in China in the 1950s, as a fertilizer which could be relatively easily produced in small-scale coal-based plants. Ammonium chloride was another low-concentration product which had local importance in some countries, notably Japan.

## □ 2.1.2 The Phosphate Fertilizer Industry

Phosphate fertilizer technology was initially very simple. Starting with bones and coprolites as the source of phosphate, dilute sulphuric acid was introduced in 1831 in Bohemia to convert the phosphate to a largely water soluble form. The product was called superphosphate, a term already used by chemists, and apparently first used as early as 1797 by the British physician George Pearson to describe the phosphate compound found in bone (calcium dihydrogenphosphate). The need for phosphate led to extensive export of phosphoguanos from Peru. The world need for phosphate grew rapidly in the 1850s, reducing the known resources of bones, coprolites, guano and low grade phosphate minerals. The supply of phosphate was secured by the discovery of the large sedimentary phosphate deposits in South Carolina. Mining began in 1867, and in 1889 the mine supplied 90% of the world-wide phosphate industry. By 1870, several deposits of phosphorite were being exploited to supply rock to the growing superphosphate industries of Europe and America, and bones and coprolites were rapidly supplanted.

In the 1880s, the development of the basic steel making process gave rise to large amounts of by-product slag. This usually contained significant amounts of phosphorus, often as much as in superphosphate, though in a less soluble form. It was found to be a good fertilizer, especially on grassland, and a substantial part of Europe's phosphate fertilizer supply came from this source. It was known as basic slag. The growth of oxygen steel making processes in the 1960s gradually strangled this supply.

Like the early nitrogen fertilizers, these phosphate fertilizers had a nutrient content which was many times that of animal manures - typically 10-20 times greater. Superphosphate, for example, contained 14-20%  $P_2O_5$ . Nevertheless, the possibility of producing more highly concentrated superphosphate was quickly recognized when the industry learned to increase the acid/rock ratio and separate the calcium sulphate (gypsum). This gave phosphoric acid, which could then be used to acidulate more phosphate. This gave products with two or three times more  $P_2O_5$ , and they came to be known as double and triple superphosphate, or enriched and concentrated superphosphate (up to 48%  $P_2O_5$ ). The less concentrated material became known as ordinary, or single superphosphate.

The neutralization treatment of phosphoric acid with ammonia yielding ammonium phosphates (DAP with 48%  $P_2O_5$ ) started in the USA in 1917. The Haber-Boch process boosted this development, and in 1926 IG Farbenindustrie in Germany started production of multinutrient compound fertilizers based on crystalline ammonium phosphate. These fertilizers were named complex fertilizers, or often NPK fertilizers. The N content was adjusted by addition of ammonium nitrate and muriate of potash (KCl) was added in the granulation unit.

Similarly, processes involving the reaction of phosphate with nitric and hydrochloric acids were also developed. The nitric acid acidulation route was commercialized in the early 1930s in Europe. This nitrophosphate route give complex fertilizers similar to the ammonium phosphate route. The only difference is that 25-40% of the ammonium phosphate is substituted by citrate soluble dicalcium phosphate.

For various reasons, the complex fertilizer industry developed strongly in Europe and the FSU, whilst the ammonium phosphate and triple superphosphate industries developed strongly in North America where bulk blending is dominant. In other parts of the world the American example has been followed where bulk blending is favourable from a logistic and economic viewpoint, while other countries have used the European example of compound NPK fertilizers for reasons of logistics and simplicity.

Single superphosphate dominated the world phosphate fertilizer market until the 1950s. It is still a major product in Australia and New Zealand, and in various developing countries, including Brazil, China, Egypt and India where its sulphur content is particularly appreciated. It also offers low investment costs and simplicity of production.

### □ 2.1.3 The Potash Industry

The potash industry was born with the discovery of a large deposit of potassium salts at Stassfurt, in Germany, in 1859. Before this, wood ashes provided the main source of agricultural potassium, the term potash being derived from the practice of producing a lye of ashes in large pots. The first potash mine opened at Stassfurt in 1862. Thereafter, German potash dominated the market for 75 years.

Low-grade, unrefined ores were the first products. None contained more than 25%  $K_2O$ . The development of refining technology vastly improved this, and potassium chloride (60-62%  $K_2O$ ) is now the main potash fertilizer. However, the chloride form of potassium is not so acceptable for certain crops, and in certain conditions, as the sulphate and nitrate forms. Hence, the latter, though more costly, have local importance in numerous countries.

In the early 20th century, large potash deposits were discovered in other countries. Production started in France in 1910, in Spain in 1925, in the former Soviet Union and in the USA around 1930, in Canada in 1960, in Italy in 1964, in the UK in 1974 and in Brazil in 1986. In addition, first Israel and then Jordan began to recover potash from the brine of the Dead Sea, and there are similar brine-based plants in the USA and China.

Generally speaking, most developing countries have little or no potash production - Jordan being the most important exception.

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## ■ 2.2 THE FERTILIZER INDUSTRY AND ITS PRODUCTS

As suggested above, the products of the fertilizer industry are extremely diverse, and for each product there is usually a diversity of possible production processes. Moreover, the structure of the industry is also very varied. Fertilizer producers include many of the giants of the chemical and mining industries in all parts of the world, whilst, at the other extreme, there are many small companies which purchase primary fertilizer materials to make mixtures, blends and compounds.

This diversity has led to a complicated pattern of trade, involving:

- the major raw materials - energy (natural gas, other hydrocarbons, electricity), mineral phosphate, potassium salts, sulphur;
- intermediate products - ammonia and acids (phosphoric, sulphuric, nitric);
- finished fertilizers, which may or may not be further processed into mixtures, blends or compounds.

Adding to this complicated scene, mineral phosphate, potassium salts, sulphur and ammonia may all be applied to the soil directly, so that one company's raw material may be another's finished fertilizer. The type of fertilizer applied to the soil depends on such factors as soil quality, product properties, farm structure, farming intensity, and the economics of different distribution and application systems. Each product has its own advantages for a particular crop, soil and climate. It may be solid or fluid. Solids may be chemically homogeneous particles or mixtures of different products. Fluids may be salt solutions, or suspensions of solid particles, or gaseous, as in the case of anhydrous ammonia.

The content of nitrogen (N), phosphorus pentoxide ( $P_2O_5$ ) and potassium oxide ( $K_2O$ ) form the main basis of a fertilizer's commercial value, but this may also be affected by its form (powder, granules, prills, etc.) and its solubility. As far as solubility is concerned, what counts is the proportion of the applied nutrient

which is recovered by the crop. This is not necessarily maximized by greater solubility - on the contrary, in the case of nitrogen, for example, much research has been devoted to the development of fertilizers which release their nitrogen into the soil solution only slowly and in relation to the needs of the crop over its entire growing season. In this way, the nitrogen can be used more efficiently and losses to the environment can be minimized. Unfortunately, though various processes have been devised which partially achieve this goal, they have not proved to be sufficiently economic for widespread adoption.

### □ 2.2.1 Production

Annual fertilizer production amounts to more than 400 million tonnes of product.

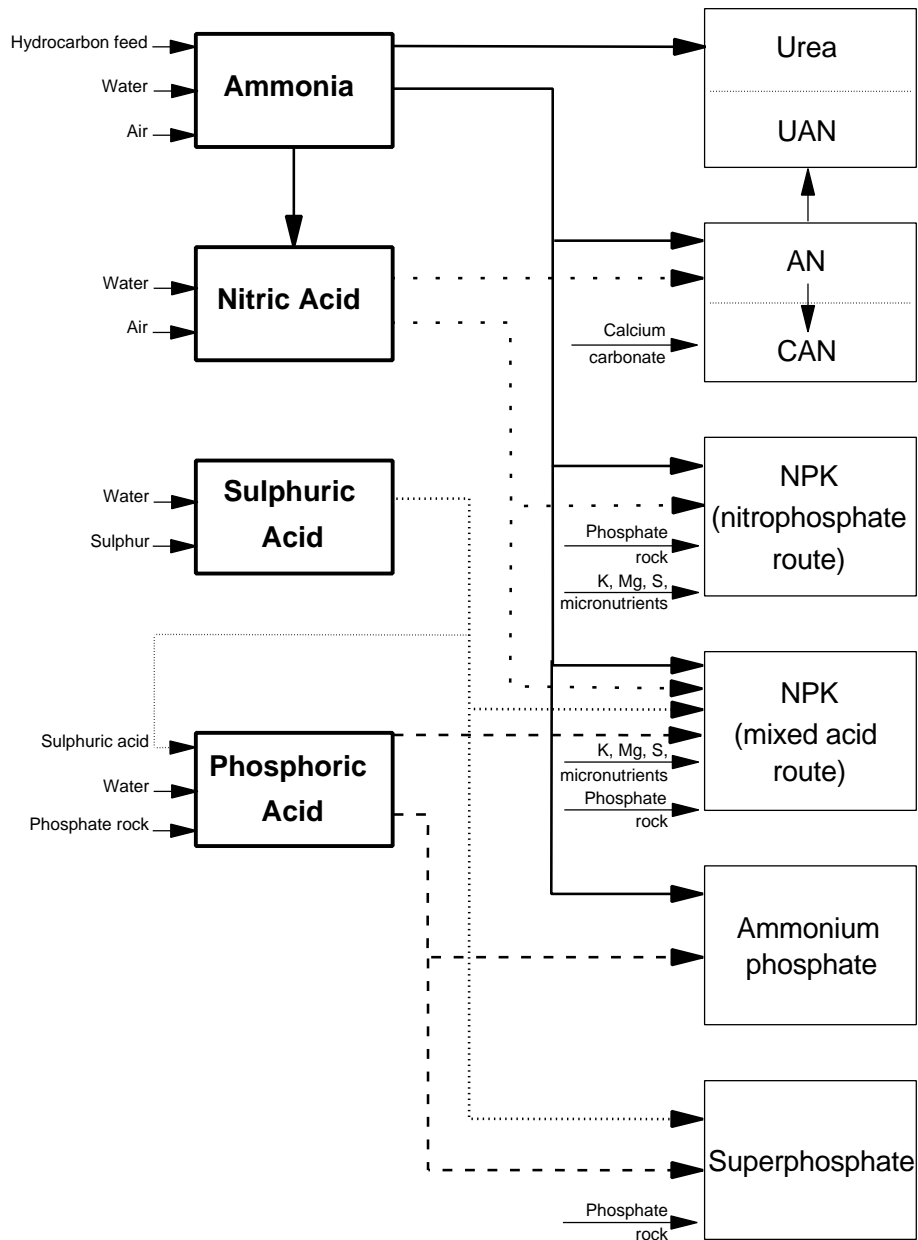
In the case of *nitrogen*, the energy required for their nitrogen production is fairly evenly distributed around the planet and there is production in every region of the world. However, there has been a trend towards increased production in locations where cheap natural gas is available, such as the Middle East and the Caribbean, but also towards the main consuming regions, such as South Asia and China. The ten largest nitrogen fertilizer producing countries account for about three quarters of world production.

In the case of phosphates, the ten largest producing countries accounting for about 80% of world production. Over the past two decades there has been a distinct trend towards the processing of phosphate rock in countries with substantial natural resources of this material, especially in North Africa and the U.S.A., but also in the Middle East, South and West Africa and China. There have been several plant closures in West Europe where phosphoric acid production capacity and output have fallen by 60% since 1980, for economic and environmental reasons, particularly the problem of gypsum disposal.

Potash is produced in the few countries where the ores are located. Between 1995 and 1997 Russia and Belarus accounted for 24% of the world's production, Canada for 36%, Germany for 14%, Israel and Jordan for 11%, these six countries thus accounting for a total of 85% of world production.

Increasingly the manufacture of fertilizers is a global industry, located near the source of the raw materials or in developing countries with expanding markets for the products. World trade in fertilizers is, therefore, tending to increase. In addition, large volumes of ammonia, phosphate rock, sulphur and phosphoric and sulphuric acids enter international trade as materials for fertilizer manufacture. In 1996, 56 million tonnes of raw materials for fertilizers, excluding the acids, and the same quantity of finished fertilizers were transported by sea, just slightly less than iron and steel as a proportion of "dry bulk cargo trade".

# FERTILIZER PRODUCTION ROUTES



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### 3. PROCESSES FOR FERTILIZER PRODUCTION

Fertilizer production involves chemical reactions, sometimes at high temperature and/or pressure, using natural raw materials. The transformation of these raw materials inevitably leads to process by-products, emissions and wastes which can be solid, liquid or gaseous. The uncontrolled release of some of these substances could harm the environment. To avoid this and also to maximize process efficiency, a wide range of processes and waste recovery and abatement techniques is available. This chapter provides a general description of the main fertilizer production processes<sup>1</sup>, together with the best available techniques (BAT)<sup>2</sup> for achieving emission limits and/or minimizing emissions to the environment. Typical plant inputs, outputs and achievable emission levels are given for the most significant types of emission, and for both new and existing plants<sup>3</sup>.

The products dealt with in this chapter are ammonia, nitric acid, urea, urea ammonium nitrate, ammonium nitrate and calcium ammonium nitrate, sulphuric acid, phosphoric acid, single and triple superphosphate and multi-nutrient fertilizers.

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#### ■ 3.1 AMMONIA

More than 99% of world nitrogen fertilizer production is based on ammonia (NH<sub>3</sub>). Ammonia is basically produced from water, air and energy. The source of energy is normally coal or hydrocarbons which are reacted with water at high temperature and electricity to drive the compressors. Natural gas is generally the preferred hydrocarbon: some 77% of world ammonia production capacity is currently based on natural gas.

A modern ammonia plant has a typical capacity of 1000-2000 t/d, although new plants are now being commonly designed up to 3000 t/d. The process and energy systems are integrated to maximize energy efficiency, in such a way that compressors are driven by recuperation steam turbines and that surplus steam and/or energy, together with by-product carbon dioxide (CO<sub>2</sub>) may be exported. However, ammonia

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<sup>1</sup> Potash and phosphate mining and their refining and beneficiation are not included.

<sup>2</sup> BAT represent standards discussed within the EU, as a guide in setting emission limits. They include some flexibility to permit local conditions to be taken into account. They should be relevant for most, if not all, industrialized countries, but local conditions are very variable, especially in Central Europe, the FSU and the developing countries. BAT generally incorporate the latest progress in plant processes and operation, without pre-determining any specific technology or methods of construction and operation. BAT techniques must be both technically and economically feasible.

<sup>3</sup> Fugitive emissions, emissions due to rainwater, heat emissions, noise and visual impacts are not covered.

plants are commonly integrated with other plants, particularly with urea plants which make use of the  $\text{CO}_2$ . Ammonia plant battery limits generally include:

- feedstock and fuel supply by pipelines at sufficient pressure for reforming,
- untreated water and air,
- ammonia product stored as liquid, either refrigerated at atmospheric pressure or non-refrigerated at ambient temperature and medium pressure.

Three main types of process are currently used for ammonia production<sup>4</sup>:

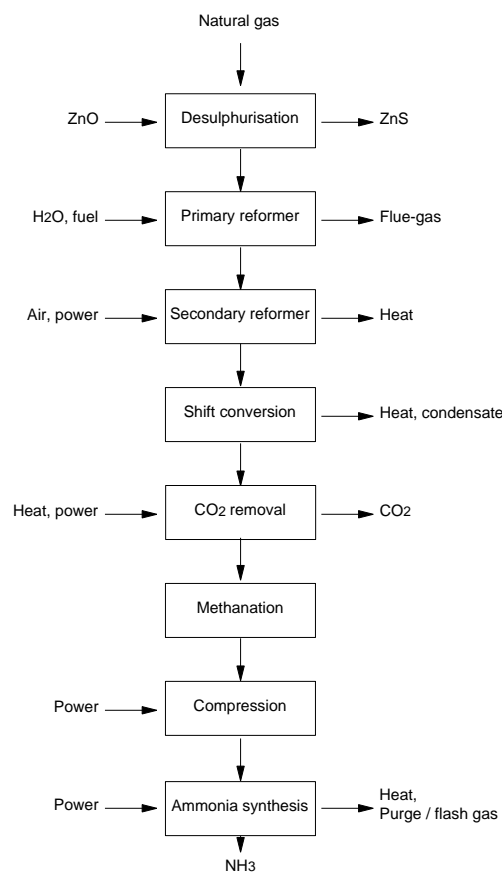
- steam reforming of natural gas or other light hydrocarbons (natural gas liquids, liquefied petroleum gas, naphtha),
- partial oxidation of heavy fuel oil or vacuum residue,
- coal gasification.

### □ 3.1.1 Processes

#### *Steam Reforming of Natural Gas*

About 85% of world ammonia production is based on steam reforming concepts.

► *Figure 3.1 Block diagram of steam reforming of natural gas*



Source: EFMA. BAT No. 1. 1995.

<sup>4</sup> Processes based on the electrolysis of water were historically significant but are no longer economic.

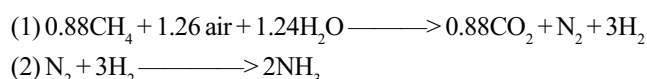


The reactions for ammonia synthesis gas production from natural gas are mainly:

- the reforming reaction:  $\text{CH}_4 + \text{H}_2\text{O} \longrightarrow \text{CO} + 3 \text{H}_2$  (endothermic) (1)
- the shift conversion reaction:  $\text{CO} + \text{H}_2\text{O} \longrightarrow \text{CO}_2 + \text{H}_2$  (exothermic) (2)

Reaction (1) takes place mainly in the primary and secondary reformer while reaction (2) takes place in both reformers but mainly in shift conversion reactors (see fig. 3.1).

Globally approximate formulae for ammonia synthesis from natural gas are as follows:



The first reaction, producing synthesis gas, normally takes place at 25-45 bar pressure, whilst the ammonia synthesis pressure ranges from 100-250 bar.

Natural gas contains sulphur compounds which would poison most of the process catalysts. Consequently, these compounds are initially removed from the feed-gas by heating it to 350-400°C and then hydrogenating the sulphur compounds to  $\text{H}_2\text{S}$  in a desulphurisation vessel, typically using a cobalt molybdenum catalyst. The  $\text{H}_2\text{S}$  is adsorbed on pelletized zinc oxide, forming zinc sulphide. The hydrogen is normally provided by the synthesis section, and the zinc sulphide remains in the adsorption bed. The resulting gas feed contains less than 0.1 ppm S and is then mixed with steam. This mixture is heated to 500-600°C and introduced to the primary reformer also called tubular reformer or fired reformer (or in some cases to an adiabatic pre-reformer preceding the primary reformer).

The primary reformer consists of a radiant box containing the process tubes. These contain nickel catalyst and are externally heated by fuel gas. The combustion of this fuel gas provides the heat necessary for reaction (1). The amount of sulphur in natural gas is usually small enough to avoid the need for desulphurisation of the fuel-gas, but if this is necessary to meet local emission standards, the plant's entire gas supply is desulphurised.

The flue gas leaving the radiant box has a temperature of about 1000°C. Only 50-60% of the fuel's heat value is directly used in the process itself, but the enthalpy of the flue gas is used in the reformer convection section, for steam generation and other process requirements. In the usual reforming process, the consumption of fuel-gas energy is 40-50% of that of feed-gas energy. The flue gas leaves the convection section at 100-200°C and is the main source of emissions from the plant. They contain mainly  $\text{CO}_2$  and small amounts of  $\text{NO}_x$ , CO and eventually  $\text{SO}_2$ .

Only 40-50% of the feed-gas is reformed in the primary reformer according to reaction (1). To complete the reforming reaction, the temperature is raised in a secondary reformer by internal combustion of part of the gas with the process air. Since the latter also provides the nitrogen for the synthesis gas, the extent of primary reforming is adjusted so that the air supplied to the secondary reformer meets both the heat balance and the stoichiometric synthesis gas requirement. The gas/air mixture is then passed over a nickel-containing catalyst which effects the remainder of the reaction (1): on emerging from the secondary reformer at a temperature of around 1000°C, about 99% of the original feed-gas has been converted. The process gas is then cooled to 350-400°C in a waste heat steam boiler or boiler/superheater.

This process gas contains 12-15% CO (dry gas basis). Most of this CO is converted to  $\text{CO}_2$  according to reaction (2) firstly by passing the process gas through a bed of iron oxide/chromium oxide catalyst at around 400°C and then over a copper oxide/zinc oxide catalyst at about 200-220°C. The residual CO content of the gas is 0.2-0.4%. At this point, the gas consists mainly of  $\text{H}_2$ ,  $\text{N}_2$ ,  $\text{CO}_2$  and the excess process steam. Most of this steam is condensed by cooling the gas before it enters the  $\text{CO}_2$  removal system. The condensate normally contains 1500-2000 ppm of ammonia and 800-1200 ppm of methanol, as well as some  $\text{CO}_2$  and catalyst metals. These impurities should be stripped out and/or recycled.

In older plants, the process condensate is simply stripped in a column into which low-pressure steam is fed in at the bottom. A mixture of steam and gases is vented to the atmosphere, whilst the stripped condensate is cooled and discharged as effluent. Although this reduces the ammonia content of the condensate, it does not solve the environmental problem of the effluents and emissions. Two main solutions are available:

- use of ion-exchange resins, passing the condensate through a strongly acid cation exchanger and then through a weakly basic anion-exchanger, and possibly through a mixed bed. This can enable reuse of the condensate as boiler feed water;
- use of the condensate for natural gas saturation, thus reducing steam consumption and avoiding the need to treat the condensate. However, this requires special equipment and additional circuitry.

Since ammonia plants are usually associated with nitrogen fertilizer plants, the ammonia process condensate can be mixed with the waste water of the fertilizer plants and treated for the recovery of useful substances. Nitric acid can be used to regenerate ion-exchange resins, and this can result in 20-28% ammonium nitrate solutions.

After the CO-CO<sub>2</sub> shift conversion, the process gas usually contains about 18% CO<sub>2</sub> which is then removed in a chemical or physical absorption process. The solvents used in chemical processes are mainly aqueous amine solutions or hot potassium carbonate solutions. Physical solvents include glycol dimethylethers and propylene carbonate. The following processes are currently recommended:

- AMDEA standard 2-stage process, or similar (amine solutions);
- GIAMMARCO-VETROVOKE process or BENFIELD process (HiPure, LoHeat), or similar (hot activated potassium carbonate solution);
- Selexol or similar (physical absorption processes);
- Pressure swing adsorption (this process is not used for large ammonia plants but for small hydrogen production).

Absorption is followed by desorption through a pressure decrease and temperature increase. The resulting pure CO<sub>2</sub> (1.3-1.4 t per t of NH<sub>3</sub>) is used for the manufacture of urea, dry ice, or in other applications.

At this point, only small amounts of CO and CO<sub>2</sub> still remain in the synthesis gas, but they must be removed, because they would poison the ammonia synthesis catalyst. This removal is achieved by reaction of the CO and CO<sub>2</sub> with a little amount of hydrogen out of the gas mixture and converting the mixture to methane (CH<sub>4</sub>) and water by passing it through a reactor filled with a nickel-containing catalyst at a temperature of around 300°C. The methane is an inert gas in the synthesis reaction, but the water must be removed; and this is achieved firstly by cooling and condensation and subsequently by condensation/absorption in the product ammonia.

The synthesis gas must then be compressed, since ammonia synthesis takes place under pressures which are normally in the range of 100-250 bar. Modern plants use centrifugal compressors, usually driven by steam turbines with the steam from the ammonia plant. The reaction uses an iron catalyst at temperatures of 350-550°C and is exothermic. Consequently, extensive heat exchange is required. Moreover, only 20-30% of the synthesis gas is converted with each pass through the converter, thus necessitating a loop arrangement, with the ammonia being separated off by cooling/condensation and fresh synthesis gas making up the difference in the loop. Inert gases left in the synthesis gas are taken out in a purge stream which is designed to leave the level of inerts in the loop at about 10-15%. The purge gas is scrubbed with water to remove ammonia and is then used as fuel or sent for hydrogen recovery.

The cooling and condensation of the product ammonia is achieved thanks to an auxiliary frigorific cycle whose refrigeration compressor is normally driven by a steam turbine. If cooling is with water or air, condensation is largely incomplete. Consequently, vaporized ammonia is used as a refrigerant in most plants, in order to achieve satisfactorily low ammonia concentrations in the gas recycled to the converter.

The liquefied product ammonia is either used directly in downstream plants or stored in tanks. These tanks are of three types:

- fully refrigerated, with a typical capacity of 10000 - 30000 t,
- pressurized storage spheres up to about 1700 t,
- semi-refrigerated tanks.

Steam reforming ammonia processes offer sufficient waste heat for steam production and electricity, but usually it is more convenient to export small amounts of steam and import electricity.

Future developments are expected to increase efficiency and decrease emissions by:

- lowering the steam to carbon ratio,
- increasing the conversion share of the secondary reformer,
- improving the purification of the synthesis gas,
- increasing the efficiency of the synthesis loop,
- improving the power energy system.

Recent improvements tending in these directions include:

- excess air secondary reforming,
- O<sub>2</sub> enriched air to the secondary reformer,
- heat exchange autothermal reforming.

#### ***Excess Air Secondary Reforming***

The low marginal efficiency of the primary reformer has prompted the design of processes which shift more of the reaction on to the secondary reformer. These processes feature:

- Decreased firing in the primary reformer, lowering the outlet temperature to about 700°C. This increases the firing efficiency, reduces the size and cost of the primary reformer, and prolongs the life of the catalyst, the catalyst tube and the outlet header;
- Increased process air supply to the secondary reformer. This increases the internal firing to achieve the same degree of total reforming. It also necessitates increased compression capacity;
- Cryogenic final purification. This removes all the methane and excess nitrogen from the synthesis gas, as well as some argon. With almost no impurities in the synthesis gas, higher ammonia conversion rates can be achieved with a lower purge flow. Since cooling is produced by depressurization, no external coolant is needed. The net result is a significantly more efficient process.

#### ***Heat Exchange Autothermal Reforming***

Reformer exit gases are at such high levels that it is thermodynamically wasteful to use them solely to raise steam. This heat can be recycled to the process itself by using the heat content of the secondary reformed gas in a primary reformer based on heat exchange, thus eliminating the fired furnace. In this case, surplus air, or oxygen-enriched air, is needed in the secondary reformer to meet the heat balance requirements. The elimination of flue-gas from the primary reformer obviously reduces atmospheric emissions. For example, compared to conventional steam reforming, NO<sub>x</sub> emissions may be reduced by 50% or more.

#### ***Partial Oxidation of Hydrocarbons or Coal by Steam or Air-Oxygen Mixtures***

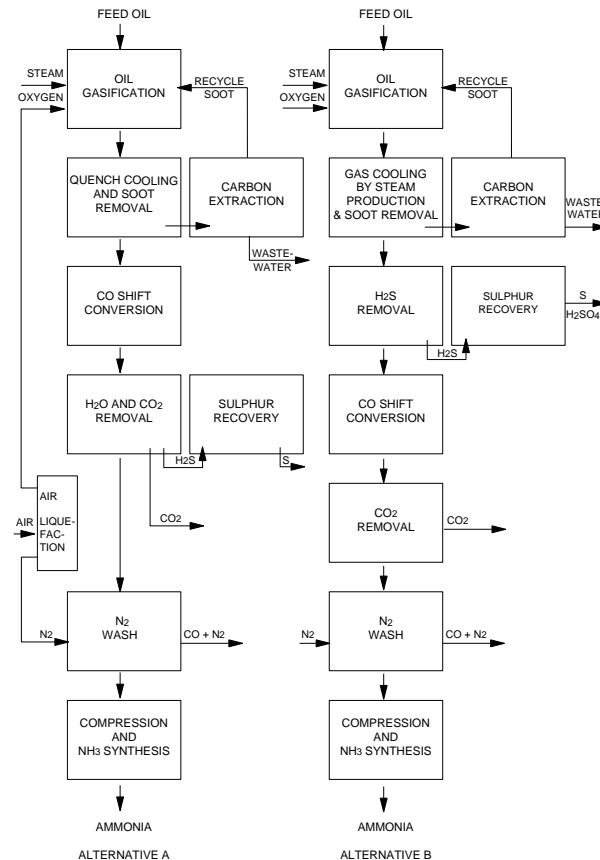
Partial oxidation processes using heavy fuel oil, residual oils or coal offer an alternative path for ammonia production, which depends on the relative availability and/or cost of these various feedstocks and oxygen in relation to investment costs and other factors such as the environmental need to use waste

materials. In this respect, extremely viscous hydrocarbons and plastic wastes can be used as part of the feed. Typical processes using oil and coal are shown in figures 3.2 and 3.3. There are several variations.

When the feedstock is heavy fuel oil with high sulphur content or coal, partial oxidation gasification is non-catalytic and occurs at high pressure and high temperature. Pressures exceed 50 bar, and temperatures are around 1400°C. Some steam is added to moderate the temperature. A preliminary air separation unit is needed to supply oxygen and nitrogen. Typical processes, using oil and coal, are shown in figs. 3.2 and 3.3.

The reaction of the hydrocarbon with oxygen produces CO and hydrogen, as well as some CO<sub>2</sub>, CH<sub>4</sub> and soot. Soot removal and recycling is difficult. Sulphur compounds in the feed are converted to H<sub>2</sub>S. This is then separated from the process gas, using a selective absorption agent, and is then converted to elemental sulphur or sulphuric acid in a separate unit. The CO is converted to CO<sub>2</sub> by passing through two high temperature catalyst beds with intermediate cooling. The CO<sub>2</sub> is then removed by an absorption agent, which could be the same as in the sulphur removal. After this, residual traces of the absorption agent and CO<sub>2</sub> are removed, before final purification of the gas by a liquid nitrogen wash. This results in a virtually pure synthesis gas, to which some nitrogen is added to provide the stoichiometric H/N ratio for ammonia. This avoids the need for a purge in the ammonia synthesis loop and improves its efficiency, compared with the steam reforming process. On the other hand, auxiliary boilers are needed, if the compressors are steam driven, and boiler fuels result in emissions of SO<sub>2</sub>, NO<sub>x</sub> and CO<sub>2</sub>, unless electricity is used.

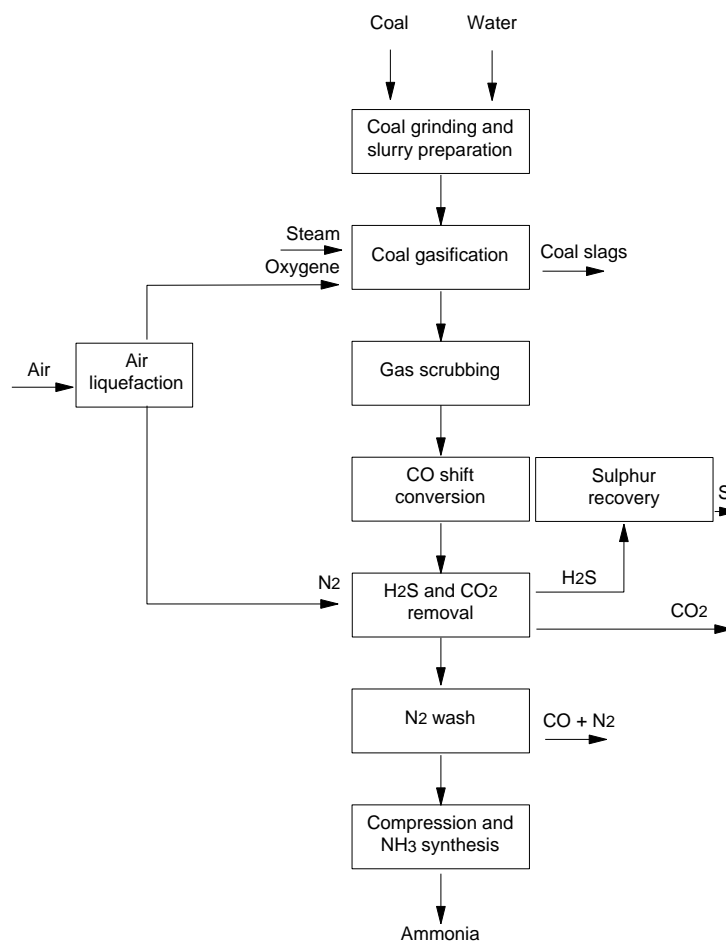
► **Figure 3.2.1** Heavy fuel oil (non catalytic) gasification process



Source: C.A. Hodge and N.N Popovici. *Pollution Control in Fertilizer Production*. Marcel Dekker Inc., New York, 1994. 502 pp..

In the case of coal gasification, the main stages include coal grinding and preparation of slurry for pulverization, in addition to those in the heavy fuel oil process. The principal effluents from the latter are waste water,  $H_2S$ ,  $CO_2$ ,  $CO$ ,  $N_2$ , and small amounts of tail gas from the ammonia synthesis. In the case of coal gasification, coal slags must be added to this list.

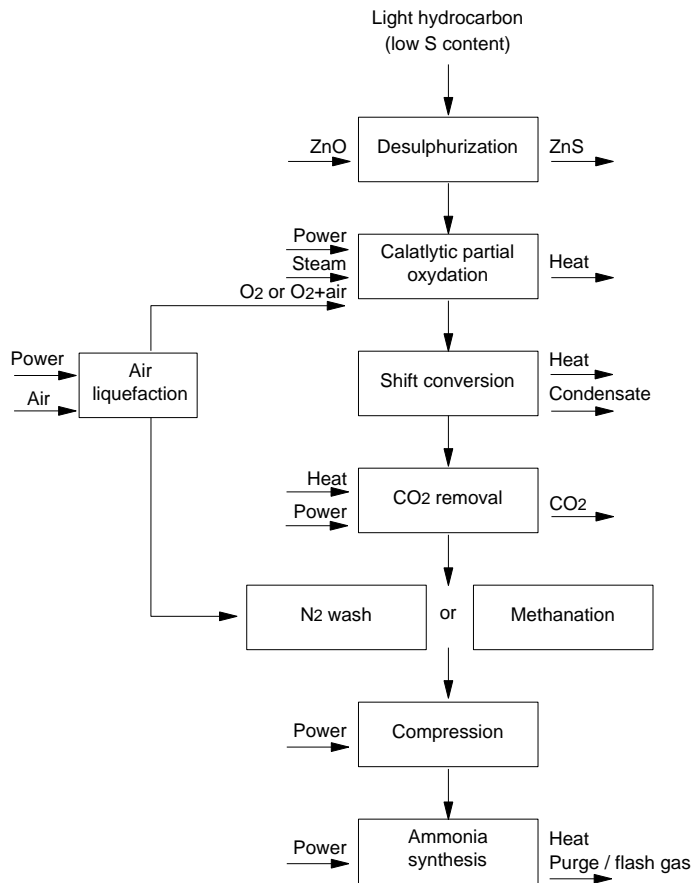
► **Figure 3.2.2** Pulverized coal (non catalytic) gasification process



Source: C.A. Hodge and N.N Popovici. *Pollution Control in Fertilizer Production*. Marcel Dekker Inc., New York, 1994. 502 pp.

When the feedstock is light hydrogen with low sulphur content (naphta, L.P.G., methane), partial oxidation is catalytic. Pressures are not limited by metallurgical problems as with tubular fired reformer. In fact, in this autothermal reformer process, pressures may exceed 40 bar and temperatures are about 1000° C after the catalyst bed. Typical process (Topsoe process) is shown in fig. 3.3. Compared to processes depicted in fig. 3.1, 3.2, this process is by far the simplest.

► **Figure 3.3** Light hydrocarbon catalytic partial oxidation process (autothermal reforming)



### □ 3.1.2 Inputs, Outputs and Emission Levels

Typical production inputs, outputs and atmospheric emission levels for modern ammonia plants, based on BAT, are shown in table 3.1. These figures are purely indicative: they are not intended to be comprehensive, and circumstances can vary considerably. The use of by-product CO<sub>2</sub>, for example, reduces the total CO<sub>2</sub> emissions very considerably, but this depends entirely on the needs of downstream facilities. Fugitive emissions of light hydrocarbons, hydrogen, NH<sub>3</sub>, CO and CO<sub>2</sub> can occur due to leaks from flanges, stuffing boxes, maintenance work, and catalyst handling. Moreover, temporary situations, such as plant start-up, involve the flaring of synthesis gas, and in this case NO<sub>x</sub> emissions may amount to an additional 10-20 kg/hr. Obviously, much depends on standards of operation and maintenance, as well as on the process and raw materials used.

We have not included sulphur as an output. As indicated above, sulphur compounds are present in very small quantities in natural gas (up to 5 mg S/Nm<sup>3</sup>) and are almost entirely recovered from the feed gas by a zinc oxide adsorber. In steam reforming, sulphur emissions from the fuel gas are almost negligible. However, larger amounts of sulphur are present in heavy oils and coal. Partial oxidation processes extract up to 95% of this in a Claus sulphur recovery unit. Even so, the amount of sulphur emissions in this case is much more than in the case of natural gas. Depending on recovery equipment, up to 3 kg SO<sub>2</sub>/t NH<sub>3</sub> could be emitted from coal- and fuel oil-based plants, compared with less than 0.01 kg in gas-based plants.

Table 3.1 clearly indicates the superiority of steam reforming over partial oxidation processes, both with regard to inputs and emissions. It also shows the wide range of achievable performances. Excess air reforming and autothermal reforming provide significant reductions in emissions, and autothermal reforming can also reduce total energy consumption by necessitating (increased) power importation and decreasing net heat loss. Energy consumption has decreased continuously in new plants over the last 25 years, and the optimal energy consumption of new plants may soon be 27-29 GJ/t NH<sub>3</sub>, the theoretical minimum being around 25 GJ (HHV).

► **Table 3.1** Typical inputs, outputs and atmospheric emission levels in modern ammonia plants

	Conventional reforming	Excess air reforming	Partial oxidation
<b>Inputs</b>			
Total energy (GJ/t NH <sub>3</sub> ) <sup>a</sup>	32-35	32-35	39-45
<i>of which:</i>			
feedstock	24.5	26.0	32.0
fuel	8-10	6-8	-
Water (t/t NH <sub>3</sub> ) <sup>b</sup>	0.7-1.5	0.7-1.5	1.2
Air (t/t NH <sub>3</sub> ) <sup>c</sup>	1.1	1.6	4.0
<b>Outputs</b>			
Ammonia (NH <sub>3</sub> ) t/d <sup>d</sup>	1000-1500	1000-1500	1000-1500
Carbon dioxide (CO <sub>2</sub> ) (t/t NH <sub>3</sub> ) <sup>e</sup>	1.15-1.30	1.15-1.30	2.0-2.6
<b>Atmospheric emissions<sup>f</sup></b>			
CO <sub>2</sub> (t/t NH <sub>3</sub> ) in flue gas <sup>g</sup>	0.5	0.4-0.5	n.a.
NO <sub>x</sub> (kg NO <sub>2</sub> /t NH <sub>3</sub> )	0.6-1.3	0.6-1.3	-
SO <sub>2</sub> (kg/t NH <sub>3</sub> )	< 0.01	< 0.01	1-3
CO (kg/t NH <sub>3</sub> )	< 0.03	< 0.03	< 0.13

a) High heat value (HHV). For steam-reforming, values are for a stand-alone plant with no energy export and no energy import except for feedstock and fuel. Where auto-production of steam is insufficient and power is imported, total energy consumption may be less. For partial oxidation, values include imported power and/or auxiliary steam.

b) Varies in steam-reforming, depending on operation of process condensate recycle. Cooling water not included, variable from site to site.

c) Cooling air not included, variable from site to site.

d) Typical modern BAT plant, but can be up to 1800 t/d. Two commercial grades: technical grade - 99.5%; and refrigeration grade - 99.8%.

e) Not including CO<sub>2</sub> in flue gases - see emissions. Depends on extent of air reforming and feedstock C/H ratio.

f) This table is not exhaustive. For example, partial oxidation plants may also emit H<sub>2</sub>S, methanol and dust traces, depending on the nature of the fuel and feedstock, and recovery procedures.

g) Figures assume by-product CO<sub>2</sub> is recovered for subsequent use and not vented. However, this depends on the CO<sub>2</sub> requirements of other plants on the site. Partial oxidation CO<sub>2</sub> depends on fuel.

Without treatment, emissions to water can arise from process condensates or waste gas scrubbing. Condensates arise mainly from cooling the process gas prior to CO<sub>2</sub> removal. About 1m<sup>3</sup> condensate/t NH<sub>3</sub> is produced, containing up to 1 kg NH<sub>3</sub> and 1 kg methanol (CH<sub>3</sub>OH). About 95% of these substances can be recovered and recycled by stripping with process steam. The stripped condensate can be further

purified by ion-exchange and then re-used as boiler feedwater. Similarly,  $\text{NH}_3$  from purge and flash gases can be recovered in a closed loop. Thus, emissions to water can be almost fully avoided, although, in the non catalytic partial oxidation process, traces of soot and coal slag occur.

BAT ammonia processes do not normally produce solid wastes. Spent catalysts and molecular sieves are removed, and their valuable metals are recovered; and, as indicated above, solid sulphur is recovered in partial oxidation processes.

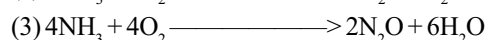
The economically achievable minimum emission levels vary between new and existing plants. Assuming steady-state production,  $\text{NO}_x$  can be limited to  $0.45 \text{ kg NO}_2/\text{t NH}_3$  ( $75 \text{ ppmv}$  or  $150 \text{ mg/Nm}^3$ ) in new plants, and about twice this in existing plants. Total energy consumption can be reduced to about  $32 \text{ GJ/t NH}_3$  in new reforming plants.  $\text{NH}_3$  in waste water can be reduced to  $0.1 \text{ kg/t NH}_3$  produced. Spent catalysts can be limited to about  $0.2 \text{ kg/t NH}_3$ . Environmental investment and operating costs are obviously variable from plant to plant, according to emission standards or targets, process design, integration with other facilities, raw materials, revamping requirements, etc.

### ■ 3.2 NITRIC ACID

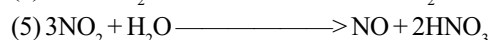
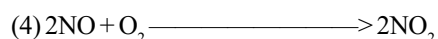
Nitric acid is used in the manufacture of ammonium nitrate, calcium nitrate and potassium nitrate. These nitrates are used as straight fertilizers or mixed into compound fertilizers. A modern nitric acid plant has a typical capacity of 1000-2000 t/d. For fertilizer purposes, the acid strength is in the range of 50-65%. Ammonia is vaporized, mixed with air and burned over a platinum/rhodium alloy catalyst. Nitrogen monoxide and water are formed according to the following reaction:



Simultaneously, some nitrogen and nitrous oxide are formed according to reactions (2) and (3):



The nitric oxide is oxidized to nitrogen dioxide, and the latter is absorbed in water to give nitric acid:



An NO yield of 97% can be achieved with burners at less than 1.7 bar. Considerable heat is evolved. In contrast, the oxidation of nitric oxide requires high pressures but low temperatures. Thus, the heat of the ammonia oxidation is used to pre-heat the waste gas and produce super-heated steam. The pre-heated waste gas drives a turbine for energy recovery and is then vented to the atmosphere. After this heat exchange, the combustion gas temperature has fallen from over  $800^\circ\text{C}$  to less than  $200^\circ\text{C}$  and is then further reduced by water cooling. The water produced in reactions (1) to (3) is condensed in a cooler/condenser and transferred to the absorption column required for reactions (4) and (5). These reactions occur simultaneously. The combustion gas receives additional air to increase the oxygen content, and  $\text{NO}_2$  is formed as the mixture cools. Since reaction (5) is exothermic, continuous cooling is required in order to promote the conversion of NO to  $\text{NO}_2$ . These reactions continue until the gases leave the absorption column. The resulting nitric acid contains dissolved nitrogen oxides and is then bleached by the secondary air.



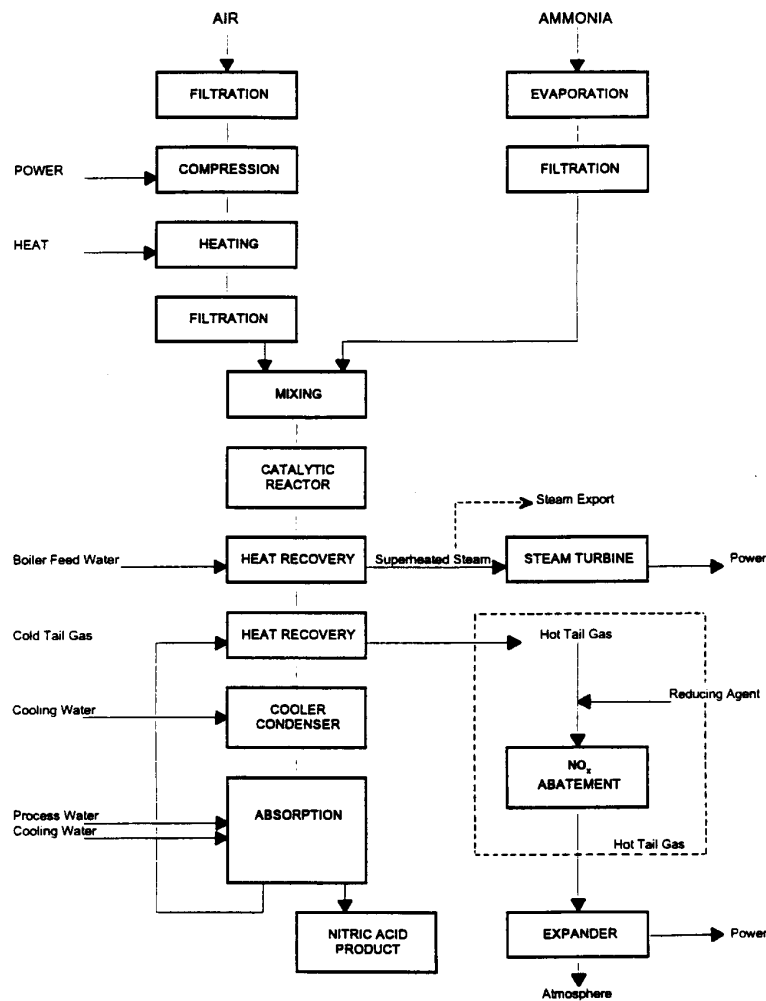
□ 3.2.1 Processes

Two types of processes are current: single pressure and dual pressure, according to the pressures used in the oxidation and absorption stages. In single pressure plants, the two stages occur at essentially the same pressure, between 1.7 and 6.5 bar for “medium” pressure plants, and between 6.5 and 13 bar for high pressure plants. In dual pressure plants, the absorption takes place at a higher pressure than the oxidation. A typical single medium pressure plant is illustrated in figure 3.4. Single high pressure plants are similar in layout, the main differences being;

- a higher operating catalyst temperature and pressure, with a lower NO yield and a higher catalyst consumption;
- a higher inlet pressure to the gas expander, allowing a higher inlet temperature, greater energy recovery and a smaller steam turbine;
- a higher pressure in the absorber, with a lower NO<sub>x</sub> content in the tail gas.

Dual pressure plants are similar as far as the cooling section. Then NO<sub>x</sub> compression and secondary cooling/condensing intervene before the absorption section. The acid condensate is mixed with the product acid. Acid solution from the absorption section passes into an NO<sub>x</sub> stripping column, and the air and stripped NO<sub>x</sub> return to the NO<sub>x</sub> gas compressor.

► Figure 3.4 Nitric acid production - single pressure plant



Source: EFMA. BAT No.2. 1995

Nitric acid is normally stored in flat bottomed, roofed tanks made from low carbon austenitic stainless steel, surrounded by suitable containment facilities. An atmospheric vent allows the tank to breathe by liquid movement or thermal effects.

### □ 3.2.2 Inputs, Outputs and Emission Levels

Apart from air and water, ammonia is the only external input, at a typical rate of 150-190 kg NH<sub>3</sub>/t of fertilizer grade nitric acid. The commonest energy system involves initial start-up steam and power, energy recovery from tail gas in a gas turbine, electric pumps, and a condensing steam turbine to drive the compressors.

Saline or poor quality water may be used for the steam turbine condensation, but other cooling requires high quality water, and process water should be demineralized. Ancillary water treatment is required for boiler feed water make-up. Cooling towers may be required for heat removal from cooling/condensing streams.

It is apparent from the reactions indicated above that the main atmospheric emission of environmental significance is NO<sub>x</sub>. During stable operation, the gas composition at the absorber outlet normally varies within the following ranges:

NO <sub>x</sub>	100 - 2,000	ppmv
O <sub>2</sub>	10,000 - 40,000	ppmv
H <sub>2</sub> O	3,000 - 7,000	ppmv
N <sub>2</sub>	balance	

and the gas flow rate is 3,130 - 3,330 Nm<sup>3</sup>/t 100% nitric acid (HNO<sub>3</sub>) (3.9 - 4.2 t/t). Plant start-up and shut-down increases the NO<sub>x</sub> emissions. In addition, small amounts of gaseous ammonia are occasionally released by the concentration of water in the ammonia vaporizer and periodic blow-downs. Maintenance operations may also generate small amounts of ammonia and nitric acid. NO<sub>x</sub> vented from acid storage depends on good tank design.

Liquid wastes originate from blow-downs of water in the cooling and water treatment systems, the boiler and the ammonia vaporizer. The waste water contains some dissolved salts and small amounts of ammonia, which are of little environmental significance. Waste waters can be cooled and neutralized, if necessary, and any significant ammonia content can be vaporized and recycled to the process. The purging and sampling of nitric acid solutions and the periodic replacement of lubricating oil may also give rise to occasional wastes, but this can be collected and recycled.

There are normally no unrecovered solid wastes in nitric acid manufacture. Catalysts have to be periodically replaced, but these are regenerated. Catalyst deposits are also recovered and recycled.

#### ***Control of Nitrogen Oxide Emissions***

The main environmental concern in nitric acid manufacture is the level of nitrogen oxides NO<sub>x</sub> (i.e. nitric acid and nitrogen dioxide) emissions. Nitrous oxide (N<sub>2</sub>O) emissions from this source, though larger than those of NO<sub>x</sub>, are small, compared with other sources. NO<sub>x</sub> can be minimized by various means:

- Extended absorption in water in a high pressure system can achieve an NO<sub>x</sub> content of about 100 ppmv;
- Alkaline absorption, treating the tail gas with sodium hydroxide; but this produces nitrite solutions which must then be treated, safely disposed of or sold, for example as sodium nitrite solution;
- Non-selective catalytic reduction: hydrogen or a hydrocarbon fuel is burned in the tail gas over a platinum, rhodium or palladium catalyst, reducing NO<sub>2</sub> to NO and, with an excess of fuel, reducing

$\text{NO}_x$  to nitrogen. Tail gases may need to be pre-heated, and the use of hydrocarbon fuel incurs the release of CO and hydrocarbons to the atmosphere. Conversely, the use of hydrogen is not possible if the ammonia plant is shut down and there is no synthesis gas. A possible advantage is the system's ability to deal with  $\text{N}_2\text{O}$  as well as  $\text{NO}_x$ .

- Selective catalytic reduction:  $\text{NH}_3$  is used to reduce  $\text{NO}_x$  to nitrogen over a catalyst. The latter can be vanadium pentoxide, platinum, iron/chromium oxides or zeolites, among others. Whether or not the tail gas needs to be pre-heated depends on the process. In all cases it needs to be at the right temperature. There is some ammonia leakage, depending on catalyst efficiency, and the tail gas must be kept above  $100^\circ\text{C}$  after expansion. On the other hand,  $\text{NH}_3$  is always available, there is no oxygen consumption and no added pollution with a high efficiency catalyst, and  $\text{NO}_x$  can be reduced to about 100 ppmv.

Consequently, extended absorption and selective catalytic reduction may be appropriate, depending on technical and economic circumstances. An SCR unit costs much less than a new absorption tower, but the latter would have much lower associated running costs. New nitric acid plants should achieve a reduction of  $\text{NO}_x$  to at least 150 ppmv (1.6 kg/t 100%  $\text{HNO}_3$ ), whilst the economic target for existing plants should be 400 ppmv (4.2 kg/t), except in the case of low pressure plants, where a realistic target would be 1000 ppmv (10.4 kg/t).

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### ■ 3.3 UREA

Urea accounts for almost 50% of world nitrogen fertilizer production (in terms of N content, and including multi-nutrient products), compared with only 30% a decade previously. It is produced by combining ammonia and carbon dioxide at high pressure (140-200 bar) and high temperature ( $180\text{-}190^\circ\text{C}$ ) to form ammonium carbamate, which is then dehydrated by heat to form urea and water, according to the following reaction:



The first stage of the reaction is exothermic and proceeds to virtual completion under industrial conditions. The second stage is endothermic, and conversion is only partial (50-80%,  $\text{CO}_2$  basis). The conversion is increased by increasing the temperature, increasing the  $\text{NH}_3/\text{CO}_2$  ratio and/or decreasing the  $\text{H}_2\text{O}/\text{CO}_2$  ratio. Process design is mainly concerned with the most efficient ways to separate product urea from the other reaction components, to recover excess  $\text{NH}_3$ , and to decompose the residual carbamate to  $\text{NH}_3$  and  $\text{CO}_2$  for recycling.

#### □ 3.3.1 Processes

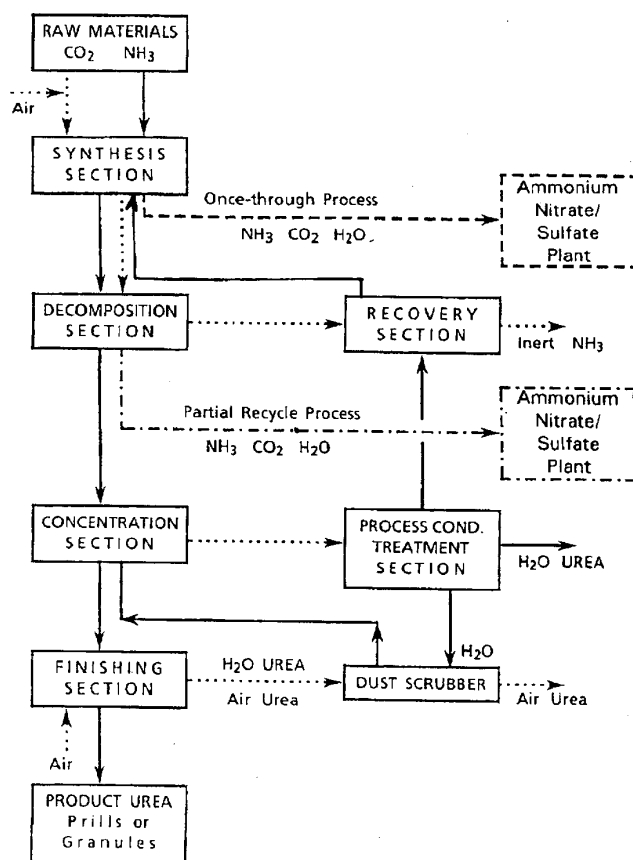
There are three main types of process:

- Once-through process: unconverted  $\text{CO}_2$  and  $\text{NH}_3$  are discharged to other plants, where the  $\text{NH}_3$  is used for the production of fertilizers such as ammonium sulphate and ammonium nitrate;
- Partial recycle process: unconverted  $\text{CO}_2$  and  $\text{NH}_3$  are partially separated in the decomposition section of the first stage and are then recovered in an absorber, the remainder being delivered to other plants as in the once-through process;
- Total recycle process: unconverted  $\text{CO}_2$  and  $\text{NH}_3$  are totally separated in multi-stage decomposers, recovered in corresponding multi-stage absorbers, and recycled to the reactor.

These possibilities are illustrated in figure 3.5.

If the residual  $\text{NH}_3$  and  $\text{CO}_2$  cannot be used in downstream plants, a total recycle process is necessary. In early urea technology, this was achieved in a series of loops with decreasing pressure, which cooled, condensed and recombined the gases to form carbamate liquor, which was then recycled to the synthesis section. This increased the  $\text{NH}_3/\text{CO}_2$  ratio, and hence the yield of urea. Better than this, however, processes were developed which decompose the carbamate in the reactor effluent without reducing the system pressure. This requires a “stripping” gas, which can be either  $\text{CO}_2$  or  $\text{NH}_3$ , or both.

► **Figure 3.5 Urea Process**



Source: C.A. Hodge and N.N Popovici. *Pollution Control in Fertilizer Production*. Marcel Dekker Inc., New York, 1994. 502 pp.

### **Carbon Dioxide Stripping**

If  $\text{CO}_2$  is used as the stripping agent, urea conversion occurs at about 140 bar and 180-185°C, with a molar  $\text{NH}_3/\text{CO}_2$  ratio of 2.95. This gives a conversion of about 60%  $\text{CO}_2$  and 41%  $\text{NH}_3$ . At or about system pressure,  $\text{CO}_2$  is added to the reactor effluent, and the stripped  $\text{NH}_3$  and  $\text{CO}_2$  are then partially condensed and recycled. Resultant heat is used to produce steam, some of which provides heat for the downstream sections of the process, and some goes to drive the turbine of the  $\text{CO}_2$  compressor.  $\text{NH}_3$  and  $\text{CO}_2$  in the stripper effluent are first vaporized and then condensed to carbamate solution, which is recycled. The process urea solution is further concentrated in an evaporation section, producing a melt of 99.7% urea, which is then prilled or granulated.

### *Ammonia Stripping*

If  $\text{NH}_3$  is used for carbamate stripping, the pressure and  $\text{NH}_3/\text{CO}_2$  ratio are somewhat higher in the synthesis section, giving a  $\text{CO}_2$  conversion rate of 65%. Excess  $\text{NH}_3$  is introduced to the reactor effluent, decomposing a large part of the unconverted carbamate. Residual carbamate and  $\text{CO}_2$  are then recovered in a two-stage process. Gas vapours from the top of the stripper are mixed with the recovered carbamate solution, condensed and recycled to the reactor. Resultant heat is used to produce steam. The urea solution is evaporated to a melt, and then prilled or granulated.

### *Advanced Cost and Energy Saving (ACES) Process*

The so-called ACES process is essentially a  $\text{CO}_2$  stripping process which operates at somewhat higher pressure (175 bar) and  $\text{NH}_3/\text{CO}_2$  ratio (4), as well as a slightly higher temperature, compared with the conventional process. Stripper gases are passed into two parallel carbamate condensers. Steam is generated for downstream heating, and the carbamate solution and non-condensed gaseous mixture are recycled to the reactor. The urea solution passes through a vacuum concentrator and is then further evaporated to about 99% urea melt.

### *Isobaric Double Recycle (IDR) Process*

This process uses both  $\text{CO}_2$  and  $\text{NH}_3$  as stripping agents. Operating at 200 bar and 185-190°C, with an  $\text{NH}_3/\text{CO}_2$  ratio of 4.5, a  $\text{CO}_2$  conversion rate of 71% is obtained, with 35% for  $\text{NH}_3$ . The reactor effluent then passes into a first stripper, which uses  $\text{NH}_3$ , and the remaining  $\text{NH}_3$  is then separated in a second stripper, using  $\text{CO}_2$ . Gases from the first stripper go directly to the reactor, and those from the second stripper pass first through the carbamate condenser. Two vacuum evaporators concentrate the urea solution to a melt for prilling or granulation.

Prilling is achieved by conveying the urea melt to the top of a tall tower and spraying it down the tower through an up-draft of air, which can be either natural or forced. As it falls, the liquid droplets solidify to prills with diameters of 1.6-2.0 mm. Granulation is achieved by spraying the melt on to recycled seed particles or prills rotating in the granulator. Granules grow larger, and the product is simultaneously solidified and dried. Traditional granulation processes involve recycling, the ratio of recycled to final product varying between 0.5-1.0. However, prill granulation has a very small recycle ratio, typically 2-4%.

## 3.3.2 Inputs, Outputs and Emission Levels

Typical inputs into modern urea plants are shown in table 3.2, although it should be noted that actual figures can vary considerably.

Urea plant sizes are normally commensurate with the amounts of  $\text{NH}_3$  and  $\text{CO}_2$  available from associated  $\text{NH}_3$  plants. A typical output in a new BAT plant is 1500 t/d of urea. Water outputs include the process condensate (up to 0.5 t/t urea) and the steam and/or turbine condensates (0.4 and 0.2 t/t urea respectively). They are normally treated and re-used as boiler feed. Low pressure steam may be used for process heating, or in turbines, or exported for other activities.

► **Table 3.2** Typical inputs in modern urea plants (per tonne urea)

	CO <sub>2</sub> stripping	NH <sub>3</sub> stripping	ACES process	IDR process
NH <sub>3</sub> (t)	0.570	0.567	0.570	0.570
CO <sub>2</sub> (t)	0.750	0.735	0.740	0.740
Steam (t) <sup>a</sup>	.770 (ST) .800 (E)	.760 (ST)	.700 (ST) .570 (E)	.760 (ST) .600 (E)
Cooling water (m <sup>3</sup> ) <sup>a</sup>	60-70	80	51-60	60-75
Electricity (MJ) <sup>a</sup>	54-396	76	108-436	72-432

a) depending on whether the CO<sub>2</sub> compressor is driven by electromotor (E) or steam turbine (ST).

Atmospheric emissions are mainly NH<sub>3</sub> and urea dust. Both arise from the prilling or granulation process. The ammonia emission results from the degradation of ammonia to form biuret in the prilling tower. Much of the dust from prilling towers and granulators is caused by condensation products of urea vapours. Some is due to the presence of isocyanic acid (HNCO) and its reaction with NH<sub>3</sub> to form urea. The remainder arises from seeding dust, undersize prills or granules, mini-prills, broken-down prills and attrition. Prilling towers with natural up-draft may have less attrition and, hence, less dust than those with forced up-draft. From the prilling tower, emissions should range from 0.5 to 1 kg NH<sub>3</sub>/t and 0.5-1.5 kg urea dust/t. With granulation, the granulator exit gas is scrubbed and losses can thereby be limited to 0.25-0.8 kg NH<sub>3</sub>/t and 0.25-0.4 kg urea dust/t. In both cases, the lower figures apply to new plants, and the higher figures are for existing plants using BAT. However, some existing plants exceed these levels. It should also be noted that, without scrubbing, dust emission from granulators would be in the range of 5-30 kg/t or more, depending on granulation efficiency.

NH<sub>3</sub> also escapes from the process absorption vents. In existing plants, NH<sub>3</sub> emitted from vents can typically be maintained within a range of 0.2-0.75 kg/t urea, depending on the process and its operating efficiency, but in new plants this can be reduced to 0.06 kg/t.

Liquid effluents relate mainly to NH<sub>3</sub>, CO<sub>2</sub> and urea in the process water, which is generated by the reaction at about 0.5m<sup>3</sup>/t urea. This normally contains some NH<sub>3</sub>, 4% CO<sub>2</sub>, and 1% urea (by weight) and must therefore be treated. The recovered gases are recycled to the synthesis, and, in a well-managed BAT plant, emissions to water can be limited to 0.0025 kg NH<sub>3</sub> and 0.0005 kg urea per tonne of product.

There are no solid wastes from urea plants, providing spillage is carefully collected.

### ■ 3.4 UREA-AMMONIUM NITRATE (UAN)

UAN solutions provide a large share of the liquid fertilizer market. Concentrated urea and ammonium nitrate solutions are measured, mixed and then cooled, and both continuous and batch processes are available. A partial recycle CO<sub>2</sub> stripping urea process may also provide unconverted NH<sub>3</sub> and CO<sub>2</sub> for conversion into UAN solutions. Typical input requirements per tonne of UAN solution (30% N) are 328 kg urea, 426 kg ammonium nitrate, 245 kg water, and steam/electricity equivalent to about 10 kWh. Corrosion inhibitor may be added for equipment protection, and there are normally traces of ammonia.

There should be no emissions to either air or water, if the process is well managed.

## ■ 3.5 AMMONIUM NITRATE AND CALCIUM AMMONIUM NITRATE

Ammonium nitrate (AN) and calcium ammonium nitrate (CAN) account for about 16% of world nitrogen fertilizer production. They are particularly important in Europe and the FSU, which account for about 75% of the world total. Ammonium nitrate is produced by neutralizing nitric acid with gaseous ammonia. The reaction is exothermic, producing AN solution and steam. In a second stage, the AN solution is evaporated to the desired concentration, depending on whether it will be finally prilled or granulated. CAN was developed to avoid the AN fertilizer being declared as dangerous goods (the AN content needs to be less than 80% AN). To produce CAN, the AN solution is mixed with a filler containing dolomite, calcium carbonate, ground limestone or, quite frequently, by-product calcium carbonate from a nitrophosphate plant (see below). This mixture can also be either prilled or granulated. Ammonium sulphate nitrate (ASN) is another mixture, produced by granulating AN and ammonium sulphate. The AN content needs to be less than 45% to avoid dangerous good declaration.

### □ 3.5.1 Processes

#### *Neutralization*

Plant design varies widely. Neutralizers, for example, may be free-boiling vessels, or circulating systems, or pipe reactors. They may operate in one or two stages, at ambient or high pressure. A two-stage neutralizer reduces total ammonia emissions but costs more than a single-stage operation. High pressure will increase steam temperature and AN concentration, and the steam can be more easily used downstream to provide the heat for evaporation and drying.

For safety and environmental reasons, temperature, pressure and pH must be strictly monitored and controlled with reliable, frequently tested equipment. An acidic AN solution is more unstable than an alkaline one, and an automatic tripping system must be in place to prevent any major temperature rise. Similarly, there must be a strict control and limitation of impurities such as chlorides and nitrites. Ammonium nitrate screenings must not be recycled if they contain an organic anti-caking additive.

#### *Evaporation*

Most of the water in the AN solution must be evaporated away before the solidification process. This may be done at about atmospheric pressure or under vacuum. Since steam always provides the necessary heat, vacuum evaporation permits the re-use of steam from the neutralizer but entails higher capital investment. During evaporation, some  $\text{NH}_3$  is boiled off and must be replaced.

Commercial evaporators include circulatory and falling film systems and shell and tube heat exchangers. Falling film evaporators occupy less space and offer a shorter residence time than other types. The product solution must be at a temperature which avoids crystallization. Its water content should normally be less than 1% for a good quality prilled product, but may be 3-8% for granulation processes.

Steam from both the neutralizer and the evaporator contain small amounts of ammonium nitrate and ammonia or nitric acid, which can be reduced by appropriate equipment design. This steam can be either purified or condensed and then purified. Purification techniques include:

- droplet separators (demister pads, wave plate separators);
- scrubbing devices (packed columns, venturi scrubbers, irrigated sieve plates).

#### *Prilling and Granulation*

The prilling of AN is similar to that of urea (see above). A large volume of air is required for the up-draft, and some  $\text{NH}_3$  and AN is carried away in the air stream. Wet scrubbing removes the  $\text{NH}_3$ , and mist eliminators remove the AN particles. Alternatively, there is an  $\text{NH}_3$ -based fume suppression technique.

AN fume is lost from the surface of prills and is difficult to remove since it is sub-micron in size. Irrigated candle filters remove this effluent effectively, but they are expensive and are not suitable for use on an CAN plant.

Granulation can be achieved with rotating drums and pans, fluidized beds and other techniques. The quantity of air required is much less than for prilling, and thus emission abatement equipment is smaller, cheaper and easier to install. The calcium carbonate can be mixed with the AN solution either before or during granulation. Drying may be required, depending on the residual water of the granules. Product granules and prills normally need cooling in rotary or fluid bed coolers, with the air cleaned by cyclones, bag filters or wet scrubbers. This air can then be recycled to the drier. The product also needs to be treated with an anti-caking agent, as it is hygroscopic. Such agents may be added to the solution before solidification or coated on to the finished particles.

### □ 3.5.2 Inputs, Outputs and Emission Levels

Typical inputs per tonne of AN in modern plants include 0.21 t NH<sub>3</sub>, 0.78 t 100% HNO<sub>3</sub> and 25-40 kWh of electricity. However, much larger amounts of electricity may be needed to achieve BAT standards in existing facilities. Steam requirements depend on the nitric acid concentration and the product concentration from the evaporator. In some plants, steam from the neutralizers may drive the evaporators, but this is not practicable in a retrofit. Thus, the net steam requirement may vary from zero to 50 kg/t, and if the final product is only AN solution, steam may be exported.

There are no by-products associated with AN and CAN production.

Atmospheric emissions of AN/CAN particulates and NH<sub>3</sub> can each be up to 2 kg/t of product (200 mg/Nm<sup>3</sup>), if BAT are not used. With new BAT plants, these figures can be reduced to 0.5 kg/t for particulates and 0.2 kg/t for NH<sub>3</sub>. Existing plants can be upgraded to BAT levels, except in the case of prilling towers, where it may be uneconomic or technically difficult to retrofit particulate abatement where insoluble solids and/or inert materials are present.

Emissions of AN and NH<sub>3</sub> to water can be up to 6 kg/t and 3 kg/t respectively (5000 and 2500 mg N/l), but achievable limits with BAT are 0.2 kg N/t (100 mg N/l) for AN and essentially nothing for NH<sub>3</sub>.

Solid wastes are not normal in AN plants, but, in addition to the emissions from an AN plant, a CAN plant can produce solid wastes based on calcium carbonate or other filler, and these could also be emitted to air and water.

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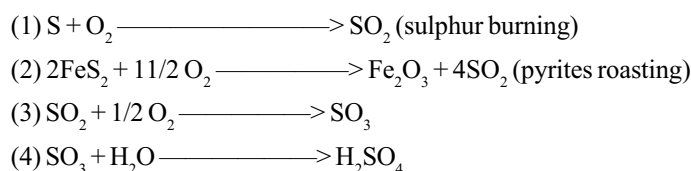
## ■ 3.6 SULPHURIC ACID

Over 60% of world sulphuric acid production (100% H<sub>2</sub>SO<sub>4</sub>) is used in the fertilizer industry, the remainder being used in a very wide variety of other industrial applications. In 1994, the amount of sulphuric acid used in fertilizer production is estimated at about 90 million t, equivalent to over 30 million t of elemental sulphur. However, elemental sulphur (brimstone) is by no means the only raw material used in sulphuric acid production: pyrites, other metal sulphides and sulphates, and sulphurous gases such as H<sub>2</sub>S all contribute significantly to this industry, and considerable amounts of spent acid are regenerated. Hence, many different production processes have been developed. The main types are summarized below. The production of oleum (H<sub>2</sub>SO<sub>4</sub>, α SO<sub>3</sub>) is not covered here, as it is not used in the fertilizer industry.



### □ 3.6.1 Sulphur Dioxide Production

Sulphuric acid results from the production of  $\text{SO}_2$ , its conversion into  $\text{SO}_3$ , and the absorption of  $\text{SO}_3$  by water, giving  $\text{H}_2\text{SO}_4$ . Typical reactions are:



Elemental sulphur is melted by heating to  $135^\circ\text{C}$  and then burned in a combustion unit at temperatures ranging from  $900^\circ\text{C}$  to  $1800^\circ\text{C}$ , followed by gas cooling. The  $\text{SO}_2$  content of the combustion gas entering the conversion process is generally 9-12% vol. but can reach 18%.

Alternatively, pyrites are roasted in various types of furnaces, producing a somewhat lower  $\text{SO}_2$  content which is diluted to 8-10%  $\text{SO}_2$  before conversion. Ores containing zinc, copper and lead sulphides are similarly roasted, usually producing somewhat lower  $\text{SO}_2$  contents. Similarly, metal sulphates - ferrous sulphate, for example - can be roasted, using elemental sulphur and pyrites, but also coke, tar, lignite, coal and oil as both fuel and reducing agent. In this case, the  $\text{SO}_2$  content of the combustion gas can vary considerably, but after cleaning and drying the process gas usually contains around 6-7%  $\text{SO}_2$ .

The combustion of hydrogen sulphide ( $\text{H}_2\text{S}$ ), carbon disulphide ( $\text{CS}_2$ ) and carbon sulphoxide ( $\text{COS}$ ) is carried out in a muffle furnace at  $800$ - $1200^\circ\text{C}$ , and combustion gases are variable, containing 0.5-12%  $\text{SO}_2$ . Iron sintering and other similar processes also give widely varying  $\text{SO}_2$  contents.

Regeneration of spent sulphuric acid is achieved by decomposition in a hot gas stream or a moving bed of solids (coke, sand, ore) at  $800$ - $1300^\circ\text{C}$ , producing gases containing 2-10%  $\text{SO}_2$ , depending on the quality of the spent acid. To compensate for varying quality, a sulphur burner can be fitted to provide supplementary  $\text{SO}_2$ . The energy requirement also varies with the quality of the spent acid, rising steeply as acid quality declines and the level of organic impurities increases. When using fuel oil, the spent acid must contain at least 60%  $\text{H}_2\text{SO}_4$ , if conversion is made in a double-contact plant (see below).

### □ 3.6.2 Sulphuric Acid Production

Four types of sulphuric acid processes are current:

- single contact,
- double contact,
- pressure contact,
- wet contact.

In single contact plants,  $\text{SO}_3$  is absorbed at the end of the process, whereas in double contact plants, it is absorbed at two stages in the process, allowing higher sulphur use efficiency. In new plants, single contact processes are now used only when the  $\text{SO}_2$  content of the combustion gas is low and widely varying.

In the case of the roasting of metallic sulphides (or possibly oxides) the  $\text{SO}_2$ -containing gases are first cooled, cleaned and dried and then oxidized to  $\text{SO}_3$  in the presence of catalysts containing alkali and vanadium oxides. In the case of sulphur units, the air is dried before combustion. The  $\text{SO}_3$  is absorbed by the water of the acid in the absorption section, the absorbing acid being kept at the desired concentration by the addition of water or dilute acid. In new plants, the conversion efficiency averages about 98.5%,

with about 98% applicable to most existing plants. The lower the  $\text{SO}_2$  content in the feed gas, the lower the conversion efficiency.

In double contact plants, there is a primary converter, followed by an intermediate absorber, a secondary converter and a final absorber. Primary conversion efficiencies fall in the range 80-93%, depending on the arrangement of the contact beds and the contact time. The absorption of  $\text{SO}_3$  in the intermediate absorber shifts the reaction equilibrium towards the formation of  $\text{SO}_3$  in the residual gas, resulting in an overall conversion efficiency averaging 99.6% (based on sulphur burning).

The oxidation of  $\text{SO}_2$  is favoured by pressure. Hence, pressure contact processes have been developed in which  $\text{SO}_2$  conversion and  $\text{SO}_3$  absorption are both achieved at high pressure. Even higher conversion efficiency is claimed for this type of process, and the tail gas  $\text{SO}_2$  content is reported to be only 200-250 ppmv. On the other hand, the high temperatures in the sulphur furnace increase nitrogen oxide formation, and a potential capital investment economy resulting from lower operating volumes of converter gases could be offset by the cost of higher grade equipment for pressure vessels. The process also consumes more power and produces less steam than the double contact process.

In contrast with the conventional contact sulphuric acid process in which dry sulphur dioxide/air mixtures are treated, wet gas is used in the wet contact process. The hydrogen sulphide in the initial gas is first burnt to  $\text{SO}_2$  and  $\text{H}_2\text{O}$  and the sulphur dioxide is converted to  $\text{SO}_3$  which together with the formed steam yields sulphuric acid. The process has been used to treat waste gases containing at least 10%  $\text{H}_2\text{S}$  from coke ovens, mineral oil refineries, fuel gasification or low-temperature carbonization plants, from natural gas cleaning installations, carbon bisulphide production plants and synthetic fibre plants. Gases with a lower  $\text{H}_2\text{S}$  content have to be burnt by additional heating (e.g. with fuel gas, oil or sulphur). The product is sulphuric acid of 78-93% concentration.

Three other processes deserve mention. Firstly, a modified lead chamber process, in which nitrogen oxides promote acid production directly from  $\text{SO}_2$ , is potentially useful for cleaning the off-gases from power plants and ore roasting plants. The conversion efficiency is very high, but emissions of  $\text{NO}_x$  occur and can amount to 1 g/ $\text{Nm}_3$ . Secondly, there is a process in which hydrogen peroxide is used to convert  $\text{SO}_2$  to  $\text{SO}_3$ . The efficiency is better than 99%, and the process leaves no waste, but the cost of the hydrogen peroxide makes it uneconomic, unless emissions of less than those of the best double contact plants are required. Thirdly, a process has been reported from Russia, in which the gas flow is periodically reversed over a single-bed converter. It is claimed that this permits the treatment of gases of low and variable  $\text{SO}_2$  contents, without the need for much of the expensive heat exchange equipment associated with other processes.

### □ 3.6.3 Inputs, Outputs and Emission Levels

Typical raw material inputs per tonne of 100%  $\text{H}_2\text{SO}_4$  are: 0.33 t brimstone; or 0.76 t pyrites (48% S); or 1.2 t zinc ores. In the case of brimstone, the process produces 1.1 to 1.2 t steam, which is used in many plants to produce electricity using turbo-alternators and to concentrate phosphoric acid in adjacent plants. Indeed, phosphoric acid production accounts for about 45% of total world  $\text{H}_2\text{SO}_4$  consumption. Sulphuric acid plant sizes vary considerably and can be up to 2700 t/d of 100%  $\text{H}_2\text{SO}_4$ , but most plants are much smaller than this.

Atmospheric emissions are limited to  $\text{SO}_2$  and acid mist. Both are released with the waste gas from the final absorber tower. Acid mist can be effectively eliminated by equipment such as Brink filters or irrigated candle filters,  $\text{SO}_3$  emission being as low as 0.15 kg/t  $\text{H}_2\text{SO}_4$  in new double contact plants (0.6 kg/t in single contact plants).  $\text{SO}_2$  emission is about 10-12 kg/t  $\text{H}_2\text{SO}_4$  in single contact plants, and only 2-3 kg/t in double contact plants. Consequently, BAT for new plants does not include the single contact process.

In sulphur burning plants, the only liquid effluent is from boiler blow-downs and water treatment. In pyrites roasting plants, effluent from gas cleaning operations may arise.

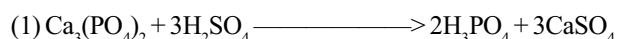
Solid waste containing vanadium results from the renewal or screening of the converter catalyst. They are returned to the catalyst supplier for recycling. Considerable amounts of cinders arise from the use of raw materials other than brimstone. Cement kilns can take some of this as a secondary raw material. Otherwise, solid wastes are usually disposed of by land-filling, subject to screening for heavy metals. Incorrect disposal can contaminate ground water.

### ■ 3.7 PHOSPHORIC ACID

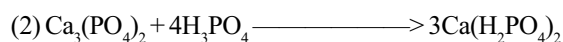
Some 70% of world phosphate fertilizer production, conventionally measured in terms of phosphorus pentoxide ( $P_2O_5$ ), uses phosphoric acid as the main intermediate. Virtually all phosphoric acid is now produced by wet processes, i.e. by acidulation of mineral phosphates. Thermal processes were previously used to produce a purer acid for applications where such purity is required, but the progress of purification techniques, and the high cost of the energy involved, have rendered such processes obsolete.

Phosphate acidulation may be achieved using nitric, hydrochloric or sulphuric acids. Nitric acid is used, particularly in Europe, for the production of multi-nutrient fertilizers (see below). Hydrochloric acid is used only in very special circumstances, since this acid is normally more expensive/less available than the other acids. The great bulk of phosphoric acid is produced using sulphuric acid, and it is processes based on  $H_2SO_4$  which are described in this section.

The variability of phosphatic ores and of the processes for their beneficiation or concentration inevitably leads to a variety of processes for phosphoric acid production. Where plants must treat different qualities of phosphate, there must be substantial technical re-adaptation for each quality. A simplified reaction equation for the dihydrate process is as follows:



This reaction suffers from the major problem of the formation of calcium sulphate (phosphogypsum) on the surface of the phosphate particles, thus blocking its continuation. This is partially overcome by (a) grinding the phosphate to a suitable particle size to increase the surface area of the reaction, and (b) recirculating phosphoric acid into the reaction to convert as much as possible of the tri-calcium phosphate to the soluble mono-calcium form, according to the following reactions:



The phosphoric acid is normally filtered away from the phosphogypsum. The latter can take numerous crystalline forms, depending on temperature,  $P_2O_5$  concentration and free sulphate content, and the form of the gypsum largely governs the filterability of the phosphoric acid.

Moreover, the mineral phosphate contains small but very variable amounts of a wide variety of impurities, including fluorine, iron, aluminium, arsenic, cadmium, copper, lead, nickel, zinc, mercury and uranium. Any radium associated with the uranium passes into the gypsum, whilst the uranium itself goes into the product acid. Consequently, the commercial value of a source of phosphate is not merely a function of its phosphorus content but also of its relative lack of impurities. Depending on the process, between 20% and 40% of the cadmium in the phosphate rock passes into the phosphogypsum, the remainder into the phosphate fertilizer.

### □ 3.7.1 Processes

There are five main phosphoric acid processes: dihydrate; hemihydrate; di-hemihydrate (double stage); hemi-dihydrate (single stage); and hemi-dihydrate (double stage). The following are their main features:

#### *Dihydrate Process*

The dihydrate process has three stages: reaction, filtration and acid concentration. 60-70% of the phosphate must have a particle size of less than 150  $\mu\text{m}$ , and where necessary, this is achieved using ball or rod mills, with either wet or dry phosphate. The reaction takes place in a series of agitated reaction tanks (or compartments of a single tank), and gypsum is precipitated in the dihydrate form at an acid concentration of 26-32%  $\text{P}_2\text{O}_5$  and a temperature of 70-80°C. The temperature is controlled by passing the reaction slurry through a flash cooler or by using an air circulating cooler.

About 5 tonnes of gypsum are produced for each tonne of  $\text{P}_2\text{O}_5$  in the product acid. The initial filtration is followed by at least two washings to maximize  $\text{P}_2\text{O}_5$  recovery, and these operations are assisted by either pressure or vacuum conditions, the latter being the practical choice. At the end of the washing sequence, the remaining liquid is removed from the filter cake as far as possible, the cake is discharged, and the filter cloth is washed.

The product acid is then concentrated, since fertilizer production requires an acid strength of 42-50%. Concentration usually takes place in a forced circulation evaporator consisting of a heat exchanger, vapour or flash chamber, condenser, vacuum pump, acid-circulating pump, fluo-silicic acid scrubber and piping. Depending on the desired concentration, more than one evaporator may be used in sequence.

This process offers low operating temperatures, high on-line time, unlimited phosphate rock quality, and easy start-up and shut-down conditions. On the other hand, it produces only weak acid, has a high energy consumption in the acid concentration stage, and incurs losses of 4-6%  $\text{P}_2\text{O}_5$ , mostly co-crystallized in the phosphogypsum.

#### *Hemihydrate Process*

With a higher operating temperature (100°C) and higher acid concentration in the reaction stage (40-52%  $\text{P}_2\text{O}_5$ ), the gypsum is precipitated in the hemi-hydrate form. This offers substantial savings in capital investment, energy, but the smaller, poorly formed crystals are more difficult to filter, unless crystal habit modifiers are used. Moreover, the  $\text{P}_2\text{O}_5$  losses run at 6-10%, again mostly entering the gypsum, which is consequently more acidic and contains more impurities (for any given phosphate quality), compared with the dihydrate process. Because of the higher temperature and acid concentration, and the instability of the hemihydrate form of gypsum, corrosion and scaling of equipment can present problems.

#### *Recrystallization Processes*

Losses of  $\text{P}_2\text{O}_5$  can be partially recovered, if the gypsum is recrystallized to its other hydrate, either before or after being separated from the acid. Thus, processes have been developed which offer the following sequences:

- acidulation under hemihydrate conditions - recrystallization to dihydrate without intermediate hemihydrate separation - product separation (HRC process);
- acidulation under hemihydrate conditions - product separation - recrystallization to dihydrate - filtration and recycling of liquors (HDH process);
- acidulation under dihydrate conditions - product separation - recrystallization to hemihydrate - filtration and recycling of liquors (DH/HH process).

All three of these processes offer substantially lower  $P_2O_5$  losses (2-3%), lower sulphuric acid consumption and a purer gypsum. The latter may possibly be used directly for plasterboard, plaster, or as a cement retarder. The HRC process normally retains a single-stage filtration, offering a slightly higher acid strength (30-32%  $P_2O_5$ ) than the normal dihydrate process. However, it requires fine rock grinding and sophisticated materials of construction. Its efficiency can be improved by re-slurrying and washing the gypsum and re-filtering it. The resulting liquor is used for washing the gypsum on the first filter.

The HDH process produces 40-52% phosphoric acid directly, and the acid is low in iron, aluminium and sulphate.

The DH/HH process produces an intermediate acid strength (32-36%  $P_2O_5$ ), has the lowest  $P_2O_5$  losses, and produces the purest gypsum. On the other hand, it requires steam for conversion, and acid evaporators, and it cannot cope with a wet rock slurry feed. Both the HDH and the DH/HH processes incur higher capital costs, including two-stage filtration.

### □ 3.7.2 Inputs, Outputs and Emission Levels

Phosphoric acid production inputs vary quantitatively according to the grade of mineral phosphate used, the concentration of the product acid, and the overall efficiency of the process. Commercial phosphoric acid is traded worldwide and is concentrated to 52-54%  $P_2O_5$ , whilst acid used directly in fertilizer production can be less concentrated. With a typical phosphate containing 32%  $P_2O_5$ , the phosphate input is about 3.3 t/t  $P_2O_5$  in the acid, and the corresponding  $H_2SO_4$  input is 2.8 t. (100%). Cooling water is used at rates varying from 100 to 150 m<sup>3</sup>/t  $P_2O_5$ , and the consumption of process water varies in a range of 4-7 m<sup>3</sup>/t  $P_2O_5$ . Electricity is used within a range of 120-180 kWh/t  $P_2O_5$ , and the steam requirement is 0.5-2.2 t/ $P_2O_5$ . When linked to a sulphuric acid plant, the high pressure steam produced in the latter's waste heat recovery boiler (see above) can be used to produce the electricity, whilst the resulting low pressure exhaust steam is used for vacuum concentration of the phosphoric acid.

Commercial mineral phosphates normally contain 2-4% of fluorine. Most of this is released in the reaction and evaporation stages and is normally recovered to produce by-product fluosilicic acid. A typical output is 20-30 kg 100%  $H_2SiF_6$ /t  $P_2O_5$ .

Modern plant sizes range up to 1600 mtpd  $P_2O_5$ , depending on the process. The main atmospheric emissions are gaseous fluorides, released during the reaction and filtration. After scrubbing, the fluorine content of these emissions is reduced to less than 10 mg/Nm<sup>3</sup>, and in an efficient plant using BAT the achievable level is 5 mg/Nm<sup>3</sup> (about 0.04 kg/t  $P_2O_5$ ). However, fluorine recovery from the hemihydrate process presents special difficulty, owing to the relatively high HF content of the gas released from the reactors.

Dust arising from the unloading, handling and grinding of mineral phosphate can also present an environmental problem, as it contains 3-4% water insoluble fluoride, which can occasionally affect animals. New plants using BAT can keep dust and particulate emissions to 50 mg/Nm<sup>3</sup>, though for existing plants a limit of three times this amount is more realistic.

Liquid effluent from the condenser also contains some fluorine, as well as small amounts of phosphoric acid. This can be recycled to the process or, where feasible, discharged into a river or sea.

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### ■ 3.8 SINGLE AND TRIPLE SUPERPHOSPHATE

Superphosphates account for over one quarter of world phosphate fertilizer production. Single superphosphate (SSP) is produced by reacting mineral phosphate with sulphuric acid in proportions which convert most of the phosphate to the water-soluble mono-calcium form. Unlike the similar reaction which produces phosphoric acid, this process retains the calcium sulphate in the product; and it is for this reason that SSP retains its importance wherever sulphur deficiency limits crop yields. Triple superphosphate contains little sulphur, because it is produced by acidulating the mineral phosphate with phosphoric acid, instead of sulphuric acid. Double, or enriched superphosphate is also produced, by using a mixture of the two acids. In all cases, the emissions to air and water are similar to those involved in phosphoric acid production, except for the problem of gypsum disposal in the latter case. Dust and fluorine removal from the off-gases exiting the reactor/curing den is usually achieved with a venturi scrubbing system involving a circulation solution of weak (less than 23 %) fluorosilicic acid. The venturi scrubber is equipped with a tail-gas scrubber in the form of a packed tower that is usually followed by an entrainment separator. A modern system can reduce fluorine emission to 0.1 kg/t  $P_2O_5$ , and dust emission to 0.3-1 kg/t of product.

Fluorine and dust in the off-gas from the granulator, dryer, cooling, and storage systems are usually removed by wet scrubbing of the off-gases and recirculating the scrubber liquor back to the process to avoid discharge.

There are always two stages in the manufacture of granulated single superphosphate, the first to manufacture powdered single superphosphate and the second to granulate. However, in the case of triple superphosphate, there are two alternatives:

- As in the case of single superphosphate, run-of-pile (ROP) material may be used. The ROP material is prepared by reacting phosphate rock with phosphoric acid with a  $P_2O_5$  concentration of 50 to 54%, but a lower concentration may be used, followed by granulation.
- A slurry of phosphate rock reacted with phosphoric acid of 35% to 38%  $P_2O_5$  concentration may be granulated directly in a traditional unit with a drum granulator, drier etc.

The advantage of this second method is that the plant can be used also for the production of other NPK fertilizers. On the other hand it can lead to higher investment costs and energy consumption and may sometimes give a product of lower solubility.

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### ■ 3.9 MULTI-NUTRIENT FERTILIZERS

Large quantities of multi-nutrient fertilizers (NP/NPK/NK/PK) are produced simply by dry mixing (or blending) single-nutrient materials without acidulation or chemical reaction. With efficient management, such operations do not normally give rise to significant environmental emissions or wastes. Consequently, we are here concerned solely with chemically compounded multi-nutrient fertilizers, and these involve a wide variety of processes and formulations, which fall broadly into three groups:

- the mixed acid route,
- the phosphoric acid route,
- the nitric acid route.

### □ 3.9.1 The Mixed Acid Route

#### *Process*

Phosphoric, nitric and sulphuric acids can be used together in various processes, to produce a wide variety of multi-nutrient formulations. If a reaction with mineral phosphate is involved, the first stage is the production of phosphoric or nitrophosphoric acid, as described above. Acids are then mixed, and an AN solution may also be added. The mixture is neutralized with gaseous  $\text{NH}_3$  and other materials may be added either during or after neutralization. These may include ammonium phosphate, ammonium sulphate, superphosphate and potassium salts. The slurry is then fed into a buffer tank, from which it passes to granulation, drying, screening, cooling and coating. A separate drying step is eliminated when a Sperodizer® is used since this device incorporates granulation and drying in a single rotary drum-type unit. Oversize and undersize particles are recycled to the process.

The acids may be mixed in reactor tanks or in pipe reactors, together with  $\text{NH}_3$ , AN solution and solid materials. Alternatively, a drum granulator may be used with a mixture of mainly solid materials, together with AN solution, and/or sulphuric acid and ammonia. For some formulations, steam is also fed in, to control the temperature.

Gases from the reactors are scrubbed as described above. Gases from the granulation, drying and cooling sections pass through venturi scrubbers, with recirculating ammonium phosphate or ammonium-sulphate-phosphate solution. The scrubber liquor is recycled, and dust is removed in cyclones. After de-dusting, air from the cooling section is normally recycled to the dryer.

#### *Emissions*

Atmospheric emissions include  $\text{NH}_3$ ,  $\text{NO}_x$ , F, fertilizer dust, and aerosols composed of ammonium nitrate, fluoride and chloride. The amounts vary according to formulation, process, and management efficiency. Normal ranges are 0.04-0.2 kg  $\text{NH}_3$ -N/t of fertilizer (10-40 mg/ $\text{Nm}^3$  wet); 0.04-0.3 kg  $\text{NO}_x$ /t (10-45 mg/ $\text{Nm}^3$ ); 0-0.02 kg fluoride/t (0-5.0 mg/ $\text{Nm}^3$ ); and 0.1-0.2 kg dust/t (25-75 mg/ $\text{Nm}^3$ ). In principle, all solid and liquid wastes can be recycled, although some N may be lost in effluent with high concentrations of ammonium nitrate. This should not exceed 0.2 kg N/t. The top of these ranges represent BAT for all formulations, all plants (whether new or existing) and all the processes described above. However, it should be noted that:

- processes involving the acidulation of mineral phosphate with nitric acid will have the highest  $\text{NO}_x$  emissions;
- ammoniation in a drum granulator will lead to higher  $\text{NH}_3$  emissions;
- the more N or P in the formulation, the more N or F (respectively) will be emitted.

### □ 3.9.2 The Phosphoric Acid Route

#### *Process*

Monoammonium phosphate (MAP) and diammonium phosphate (DAP) are made by ammoniating phosphoric acid in a neutralizer, thus producing a slurry which passes through a granulator. Some granulators can also act as ammoniators. If a potassium salt is added during granulation, an NPK compound is produced. Alternatively, granulation may be achieved by powder blending, using small amounts of  $\text{H}_2\text{SO}_4$  and  $\text{NH}_3$  to promote the process. Granules are normally dried and cooled in rotary drums. Oversize and undersize material is screened out, crushed and recycled.

### ***Emissions***

Atmospheric emissions from such processes can include  $\text{NH}_3$ , ammonium chloride ( $\text{NH}_4\text{Cl}$ ), fluorine (as  $\text{SiF}_4$  and  $\text{HF}$ ), and dusts. Emissions to water include compounds of N, P and F, as well as solids in suspension. They are mainly derived from waste gas scrubbing, but can be largely eliminated by recycling the scrubber liquor. As indicated above, slaked lime is generally used to precipitate fluorine (and any phosphates or sulphates) in waste water. Emissions for BAT plants fall broadly in the ranges mentioned in section 3.5.2 above.

$\text{NH}_3$  and fluorine compounds are contained in the waste gas leaving an ammoniator granulator or acid neutralizer. They are usually recovered by scrubbing with phosphoric or sulphuric acid, or water, and returned to the granulator. With powder blending, almost no  $\text{NH}_3$  is released unless it is used with acid to promote the granulation.

When potassium chloride is added to the process, ammonium chloride forms in both the granulator and the drier. The  $\text{NH}_4\text{Cl}$  tends to vaporize above  $130^\circ\text{C}$ , and the vapours should be removed in a mist eliminator. Wet scrubbers and bag filters are ineffective in this case. However, ammonium chloride fumes can be greatly reduced by formulating with a mixture of DAP and urea, and/or by using potassium sulphate instead of chloride.

Bag filters, wet scrubbers or dry cyclonic collectors are suitable for dust removal. The air velocity through the dryers and coolers affects the amount of dust: the higher the velocity, the more dust is emitted. Cyclones collect only the larger particles: final cleaning of exit fumes is left to the filtering/scrubbing process.

Bag filters vary greatly in design, depending largely on how they are cleaned. For dust removal, they are highly efficient and have smaller exit plumes than wet scrubbers. They recover a dry product that can be recycled without adversely affecting the water balance. On the other hand, they do not capture gases such as chlorides and fluorides. Moreover, there must be negative pressure throughout the system, and temperatures must not exceed the melting point of the bag filament. Also, they can suffer problems relating to humidity and air leaks. They are often preferred at powder blending plants.

Wet scrubbers usually use weak phosphoric acid which flows counter-current to the gas flow, the resulting liquor being recycled to the neutralizer or granulator. The most commonly used scrubber in the DAP/MAP industry is the venturi scrubber. With good management, almost no fluorine and very little ammonia is lost, and such emissions can be still further reduced if necessary by installing a tail-gas scrubber, often using phosphogypsum pond water as the medium.

### **□ 3.9.3 The Nitric Acid Route**

NP and NPK fertilizers based on the acidulation of mineral phosphate with nitric acid, instead of sulphuric acid, lead to virtually complete use of the raw materials, since the by-product is calcium nitrate (CN) instead of calcium sulphate, and this can be either granulated and used directly as a fertilizer, or incorporated into liquid fertilizer solutions, or converted into CAN, as indicated above. The only solid waste in nitrophosphate processes is a small amount of sand from the phosphate, and this can be washed and used in the building industry.

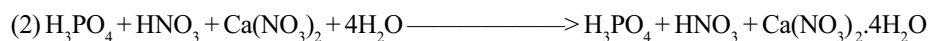
#### ***Nitrophosphoric Acid***

The basic reaction for the production of nitrophosphoric acid is:





In order to improve the solubility of the product phosphate, the calcium nitrate is precipitated out of the solution by cooling in the presence of water, according to the following reaction:



The solution of nitrophosphoric acid can then be separated from the CN crystals by filtration or centrifugation. Sand is removed by centrifuges, hydrocyclones or Lamella® separators. The solution is neutralized with ammonia, mixed (according to the desired formulation) with potassium or potassium/magnesium salts, sulphate and/or micro-nutrients, and finally granulated. The process is illustrated in figure 3.6.

The basic reaction is exothermic, leading to the emission of gases containing  $\text{NO}_x$  and fluorine. The crystallization and filtration stages also produce the same gases. These gases are collected from the various vessels and scrubbed before discharge to the atmosphere.  $\text{NO}_x$  emissions can be reduced by the addition of urea under certain conditions.

The nitrophosphoric acid solution is then neutralized with ammonia. The reaction is highly exothermic, and the evolved heat is used for evaporating the resulting slurry.

Neutralization systems vary. In one system, the NP solution and the  $\text{NH}_3$  pass through successive stainless steel reactors in different stages. Potassium salts and/or other nutrients may, or may not be added during this process. In another system, the NP solution is partially neutralized and evaporated in a series of circulating evaporators before final neutralization. In a third system, the NP solution is neutralized with pre-heated gaseous ammonia in a pressurized reactor at 1.5-2.5 bar. Evaporation occurs in all systems, and, if the product is to be prilled, a final evaporation is needed at the top of the prilling tower. All these systems operate at high temperatures and generate off-gases, which are treated with various scrubbing systems, according to the acidulation and neutralization processes and the final formulation of the fertilizer.

Neutralization under pressure produces vapour containing 2-8%  $\text{NH}_3$ . This is scrubbed with process water, and the scrubbing liquor is returned to the process. Scrubber vapours are then condensed, part of their heat being used to pre-heat the NP solution before neutralization. The remaining heat is used to make low-pressure steam for use in the NPK process or in other plants. A water cooled condenser treats any remaining vapour, and the various condensates are collected in an ammonia condenser tank.

Evaporation also produces off-gases which must be scrubbed to recover  $\text{NH}_3$  and fluorine. The scrubbing liquor is recycled to the process. The neutralization and evaporation sections may be connected to a common  $\text{NH}_3$  condensate stripping system, and the effluent from this contains some N in both ammonium and nitrate forms.

The evaporated NP or NPK solution may be prilled, granulated or “spherodized”. The latter involves a rotating drum into which the product liquor is sprayed, with a co-current of hot air evaporating the remaining water and forming dry granules. As with the solidification of other fertilizers, dust and off-gases arise with all these treatments. In the case of prilling, both dust and  $\text{NH}_3$  loss is relatively slight - of the order of 5 mg/ $\text{Nm}^3$  and 10-15 mg/ $\text{Nm}^3$  respectively. The volume of air is very large - normally more than 500,000  $\text{Nm}^3/\text{h}$  in a plant with a typical capacity of 200 t/d  $\text{P}_2\text{O}_5$  - and recovery of such small emissions is uneconomic.  $\text{NH}_3$  loss can be minimized by controlling the pH.

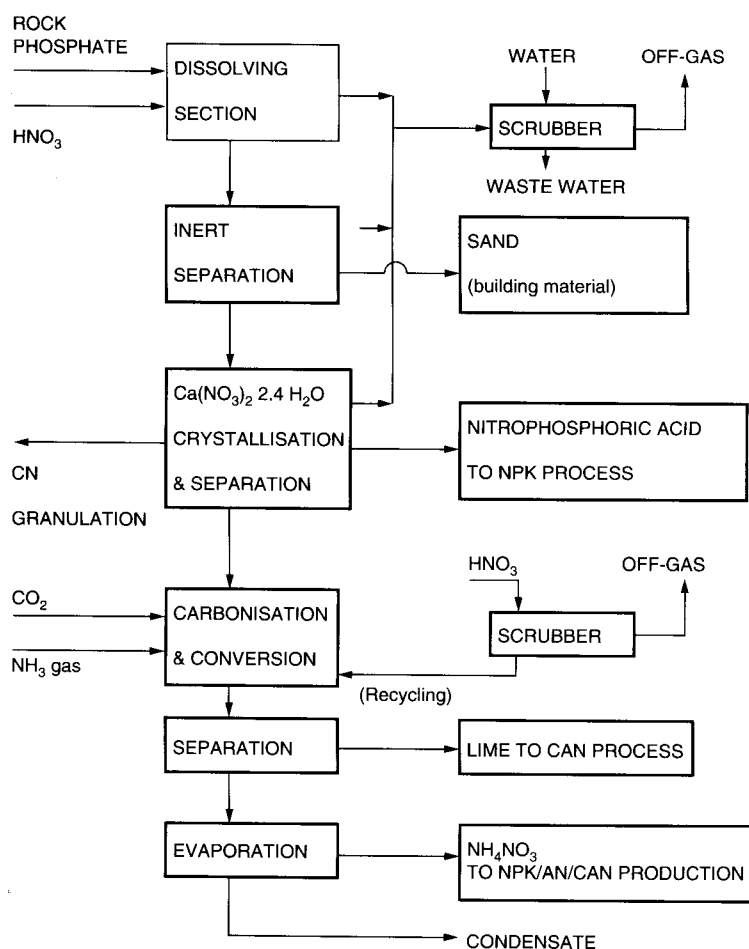
### ***Emissions***

Under BAT conditions, atmospheric emissions from a new nitrophosphoric acid plant after treatment, including NPK formulation, should be about 0.3 kg  $\text{NH}_3$  (50 mg/ $\text{Nm}^3$  wet), 0.2 kg  $\text{NO}_x$  (500 mg/ $\text{Nm}^3$  wet) (calculated as  $\text{NO}_2$ ), 0.02 kg F (5 mg/ $\text{Nm}^3$  wet) and 0.3 kg dust (50 mg/ $\text{Nm}^3$  wet) per tonne of fertilizer

produced. Achievable levels in existing plants should be about the same, except for  $\text{NH}_3$ , where a figure of 1 kg/t (250 mg/Nm<sup>3</sup>) is more realistic.

Waste water effluents from washing and scrubbing operations in new plants should typically contain about 0.06 kg  $\text{P}_2\text{O}_5$ , 0.15 kg N (mostly as  $\text{NH}_4$ ), and 0.05 kg F per tonne of fertilizer produced. In existing plants, achievable levels should be 0.11 kg  $\text{P}_2\text{O}_5$ , 0.8 kg N and 0.05 kg F. There should be no solid wastes.

► **Figure 3.6** Nitrophosphate process diagram



Source: EFMA. BAT No. 7. 1995.

### □ 3.9.4 By-Product Calcium Nitrate

Calcium nitrate precipitated from the nitrophosphate process can be either processed for direct use or converted into AN or CAN. The calcium nitrate may be converted to ammonium nitrate solution which is concentrated and prilled or granulated.

For direct use, the CN crystals are concentrated to form a melt and neutralized with gaseous ammonia. The reaction is exothermic, and the resulting steam is compressed and used to provide heat for evaporation. The concentrated melt is then prilled or granulated. Both prills and granules must be coated to minimize caking.

Off-gases are scrubbed with water before discharge to the atmosphere. In the neutralization and evaporation stages, the total amount of N (as  $\text{NO}_3$  and  $\text{NO}_4$ ) is  $< 0.003$  kg/t product, with a concentration of  $< 35$  mg N/ $\text{Nm}^3$  of off-gas. If the product is prilled, CN dust from the prilling tower is discharged directly to the atmosphere, the vented air typically containing  $< 0.2$  kg CN/t product, with a concentration of about 20 mg/ $\text{Nm}^3$ . At the bottom of the tower, the prilled CN is cooled with air in a fluidized bed. The resulting dust is separated out in a cyclone and recycled, but the air vented from the cyclone contains about 0.24 kg CN/t product, with a concentration of 300 mg/ $\text{Nm}^3$ . If the product is granulated, off-gases from the granulator and drier are scrubbed with water and process condensate, with discharge to the atmosphere being normally less than 4 mg  $\text{NO}_3$ -N/ $\text{Nm}^3$ , or 0.002 kg/t product. Liquid effluent arises from the partial discharge of condensate from the scrubbing system: it typically contains about 0.3 kg  $\text{NO}_3$  and  $\text{NH}_3$  per tonne of product when a spillage collection system is installed.

When converted to AN or CAN, the CN crystals are first dissolved in a solution of AN and pumped to a storage tank. A solution of ammonium carbonate is prepared, using  $\text{CO}_2$  from an ammonia plant and  $\text{NH}_3$  from the cooling section of a nitrophosphoric acid plant. The solution of ammonium carbonate is mixed with the CN/AN solution, and this results in ammonium nitrate and precipitated calcium carbonate. The latter is filtered off and used for CAN production. The remaining AN solution is concentrated and may be converted into solid AN, CAN, or used to produce compound fertilizers or fluid fertilizers such as UAN. In this process, there are virtually no emissions to air, and liquid effluents from the evaporator are normally recycled, used for cleaning purposes, treated and/or sent to a biological treatment plant.

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### ■ 3.10 ENERGY

Energy consumption has become an environmental issue because of the ecological impact of energy production and transport, and because of the emission of greenhouse gases from fuel burning.

Fertilizer production currently accounts for about 2 - 3 per cent of total global energy consumption. For Western Europe, the corresponding figure is about 1%. Nitrogen fertilizers account for a large majority of this consumption. Most of the energy for fertilizer production is required by the fixation of atmospheric nitrogen to manufacture ammonia. Energy is also required for the conversion of ammonia to liquid urea melt. For the manufacture of ammonium nitrate, the conversion of ammonia to nitric acid provides a net energy gain which can be used, for example, to produce electrical energy in a steam turbine. The neutralization of ammonia with nitric acid to produce ammonium nitrate also releases energy. In the case of phosphate fertilizers energy is required for the mining of the ore, for the production of phosphoric acid, for the further processing into finished products and for pollution control.

Although fertilizer production will always consume large amounts of energy in processes requiring high temperatures and pressures, the industry has become more energy efficient through improved design.

Ammonia factories built in 1990 used some 30 per cent less energy per tonne of nitrogen than those designed around 1970. Present design is thermally very efficient and further energy saving beyond another 5 - 10 per cent is not feasible in ammonia production. Other potential nitrogen fixing methods (e.g. high temperature oxidation) are much less energy efficient.

Energy use in a new plant, using natural gas in a reforming process, including raw materials, can now be as low as 30 GJ/t  $\text{NH}_3$ , compared with 75 GJ/t for the processes prevalent in the early 1960s. Partial oxidation processes use considerably more energy than reforming processes. In 1995, the average for all plants in the US fertilizer industry was about 40 GJ/t (11110 Kwh/t). (Source: *The Fertilizer Institute (TFI), USA. Averages are weighted by plant size. Figures converted from short ton basis to metric*).

Other averages reported for 1995 for the US industry (in terms of electricity) are shown below. These figures do not include small amounts of hydrocarbon fuels:

– phosphoric acid	138.0	kWh/t (100% $H_3PO_4$ )
– sulphuric acid	21.3	kWh/t (100% $H_2SO_4$ )
– DAP	34.3	kWh/t
– TSP (granular)	58.5	kWh/t
– phosphate rock	73.5	kWh/t

In the case of urea, improved efficiencies achieved by modern total recycle plants have halved the total energy input in the last 30 years to about 42 GJ/t N (steam, electricity and cooling water). The corresponding figure for ammonium nitrate is about 35 GJ/t N. The figures for old plants can be much higher.

The dependency on natural gas is a cause for long-term concern. There is a potentially large economic and environmental cost in switching back to other, more polluting hydrocarbons (mainly coal), as and when gas resources are exhausted. Hydroelectric power can also be used, though this would require higher energy consumption and major rebuilding of the factories.

#### ***Feedstock and Fuel Requirements***

In nearly all ammonia plants the same material is used as both feedstock and fuel. The fuel requirements may be 40% of the total or more, depending on the extent to which heat recovery equipment is used. In previous years when fuel was inexpensive, many ammonia plants were built with minimum heat recovery facilities.

In a natural gas-based plant 20%-30% of the gas is used for fuel and the balance for feedstock. The lower fuel values are for plants equipped with good energy recovery systems. Fuel requirements do not include electric power generation or steam generation other than that connected with heat recovery. Modern ammonia plants are self-sufficient in steam supply, and much of the mechanical power is supplied by steam rather than electricity. However, in developing countries, a captive electric generating plant usually is considered essential for a dependable supply of electricity. Also, if a urea plant is associated with the ammonia plant, additional fuel will be required to supply the steam needed for urea production. Therefore, total fuel requirements may be larger than those mentioned above.

When a high-cost feedstock is used for ammonia production, it may be advantageous to use a lower cost fuel for heating and for producing steam and electricity.

Use of heavy oil or coal for fuel could be considered for plants using expensive or scarce feedstocks. However, these fuels cannot be used to heat reformer furnaces unless some extensive modifications are made. Impurities in heavy oil or coal would adversely affect the reformer tubes by causing corrosion or erosion unless design modifications are made.

Several energy sources are used throughout the world as feedstock and fuels for ammonia production. Comparative consumption of the different energy sources per tonne of end product ammonia are given in the following table.

► **Table 3.3** *Energy consumption of different sources*

Feedstock and Fuel	Requirements per tonne of ammonia	Energy (million kcal)
Natural Gas	873 m <sup>3</sup>	7.0
Naphta	0.72 t	7.6
Fuel Oil	0.87 t	8.5
Coal	1.54 t	9.8

Source: IFDC, UNIDO, 1998.

An IFDC study gave the following relative capital investments for ammonia plants using different fuels as compared to using natural gas as feedstock:

► **Table 3.4** *Capital investment according to different sources*

Feedstock	Comparative Capital Investment
Natural Gas	100%
Naphta	114%
Fuel Oil	147%
Coal	187%
Electrolytic Hydrogen	190%

Source: Mudahar, M.S., and T.P. Hignett. *Energy and Fertilizer Policy Implications and Options for Developing Countries*. IFDC, 1982.

Because of these considerations, natural gas is presently used to produce more than 75% of the world's ammonia, and most plant being built in the foreseeable future (with perhaps the exception of China) will use natural gas as the energy source.

In the production of ammonia, the cost of natural gas represents a very large component. In the United States, the cost of natural gas represents about 63% of the total production cost of ammonia ex-plant. The capital recovery costs are very low for existing U.S. plants. In a new plant, gas cost would probably be about 10-20% of the production cost. The high cost of natural gas in the production of ammonia has stimulated a drive towards decreasing the unit consumption of natural gas. This consumption has been decreased through technological innovations and through the increase in production efficiency and increase of investment cost.

► **Table 3.5** *Natural gas and electricity used in the United States per tonne of ammonia*

Year	Natural Gas		Electricity	Total Energy Used
	million kcal	GJ	kWh	million kcal
1980	10.13	42.4	0.209	10.64
1985	9.92	41.5	0.154	10.30
1990	9.61	40.2	0.152	9.99
1995	9.46	39.6	0.188	9.93

Source: TFI Production Cost Survey, 1995.

The unit consumption decrease was very apparent until 1990. New plants are being designed for consumption of 7.2 to 7.8 million kcal/ t but in general plants are approaching the maximum economic decrease in energy consumption with the presently available technology in the USA. However, plants in some regions of the world have a much larger energy consumption. In some cases this is due to low rates of capacity utilization but “retrofits” can also be used to improve the energy efficiency of existing plants. Depending on the modifications chosen, overall energy consumption reductions in the order of about 15% can be achieved. At the same time, the adoption of specific retrofits usually allows an increase in plant capacity of up to 25% as compared to design. The costs of these retrofits are usually in the order of US \$8 to \$25 million.

Prior to performing the modifications, feasibility and characterization studies need to be performed on the particular unit to help select the retrofits that will yield economically attractive results and determine the extent of the retrofits and their integration with rest of the plant. These studies will also generate information about the required investment costs for the different options considered.

The main retrofits usually considered for improving the energy efficiency of an existing ammonia plant are as follows:

► **Table 3.6** *Potential energy savings per tonne of ammonia*

<b>Retrofit</b>	<b>million kcal</b>	<b>GJ</b>
Feed-gas saturator	0.24	1.0
Convection coils	0.22	0.9
Boiler feed water economizer	0.1	0.4
Low-heat removal of carbon dioxide	0.26	1.1
Ammonia converter	0.25 to 0.4	1.1 to 1.7
Process computer	0.15	0.6

#### ***Installation of a Feed -Gas Saturator***

A mixture of steam and natural gas with a volumetric ratio of steam to carbon of about 3.5:1 is reacted in the primary reformer of reforming ammonia plants. Most of the steam is generated from heat sources within the plant, but the balance of the steam has to be produced in auxiliary boilers. This retrofit permits the use of low-level heat from the flue gases, which would otherwise be lost, to be used in saturating the feed natural gas with water. This generates extra steam which replaces some of the steam generated in the boiler. So more MP steam is available for mechanical energy production.

#### ***Modification of Convection Coils***

As a result of other modifications, the temperature profile of the flue gases may change considerably in the cold-leg section of the primary reformer. This change can be compensated for by replacing the low steam superheat coil with a new one with additional rows of tubes and heavier fins on all tubes.

#### ***Low-heat Removal of Carbon Dioxide***

The traditional systems used for removal of carbon dioxide from the process steam uses hot potassium carbonate which requires heat for regeneration. This heat come from process heat but needs to be supplemented with external steam. A new low-heat removal system is now available, which uses flashing for part of the regeneration process, and requires less external heat.

### ***Ammonia Converter Retrofit***

The vertical quench-type converters are changed from axial flow to radial flow, greatly decreasing the pressure drop across the converter which in turn allows the use of smaller size catalyst with a larger surface area. This improved catalyst yields a higher conversion per pass, generating a lower recycle volume. The lower recycle volume and the lower pressure drop result in reduced energy requirements. This modification yields an increase effective capacity of the ammonia converter of about 35%.

### ***Addition of Process Computer***

A dedicated process computer can be installed along with other on-line analysis and control systems to monitor and control key variables. With this system, continuous setpoint changes are possible to optimize the operation of several plant areas such as hydrogen/nitrogen ratio, steam/carbon ratio, synthesis loop purge, methane leakage, converter control, and refrigeration purge.

Also:

### ***Hydrogen Recovery from the Purge Gas***

Inert gases must be pumped from the plant to avoid their buildup in the system. This purge is carried out by removing a side stream of synthesis gas after recovering the ammonia. By installing the proper recovery system, the hydrogen in this gas mixture can be recovered decreasing the energy requirements of the process by about 5% or permitting an increase of about 5% in production capacity.

The following texts are extracted from a paper by G. Kongshaug (1998).

“To-day, fertilizer production consumes approximately 1.2% of the world’s energy and is responsible for approximately 1.4% of the total emission of the Greenhouse gases in the world, consisting of 0.3% of pure CO<sub>2</sub>, 0.3% as N<sub>2</sub>O and 0.6% as flue gas CO<sub>2</sub>. Increased focus on energy issues during the last 25-30 years has already caused a positive downward trend both for energy consumption and Greenhouse gas emissions.”

“According to (our) analysis, the energy consumed for the world fertilizer production is 4400 mill. GJ/yr., of which 92.5% is used for production of the N component, 3% for the P<sub>2</sub>O<sub>5</sub> component and 4.5% for the K<sub>2</sub>O component. Approximately 53% (2350 mill. GJ/yr.) of the energy consumption is supplied as feedstock to the ammonia plants, the remaining 47% (2000 mill. GJ/yr.) is fuel energy.

By renewing the bulk of the plants with modern technology, it should theoretically be possible to reduce the total energy content by 37% to 2743 GJ/yr. The main potential is related to fuel for ammonia plants (10 GJ/t N, from 44.5 to 34.5). This will be achieved during the next 20-30 years. We have experienced that most of the European ammonia plants combine a small capacity revamp together with improvement of the energy efficiency.

A similar analysis as shown in table 3.7. has been carried out with the specific energy numbers assumed to be the best 30 years ago and with the average numbers for the European fertilizer industry:

► **Table 3.7** *Global Energy Consumption Today and for Different Scenarios*

<b>134 Mt N+P<sub>2</sub>O<sub>5</sub>+K<sub>2</sub>O</b>	<b>GJ/yr.</b>	<b>% of today</b>
BAT 1968	5040	115
<b>World today</b>	<b>4400</b>	<b>100</b>
European standard	3760	85
BAT* 1998	2743	63

\*BAT = best available techniques.

The table shows that the specific energy consumption has improved during the last 30 years, and that Europe has approximately 15% lower specific energy consumption than the world average today.

The world fertilizer production gives a gross emission of Greenhouse gases equivalent to 283 Mt (million tonnes) CO<sub>2</sub>/yr. This comprises 134 Mt CO<sub>2</sub>/yr (48%) as flue gas from energy production, 74 Mt CO<sub>2</sub>-equivalent/yr (26%) as N<sub>2</sub>O from the production of approximately 70 Mt/yr. nitric acid, and 75 Mt CO<sub>2</sub>/yr (26%) as pure CO<sub>2</sub>. Around 12 Mt/yr. of pure CO<sub>2</sub> produced by ammonia plants is used for technical, non-fertilizer applications (total global technical application of CO<sub>2</sub> is 13.5 Mt CO<sub>2</sub>/yr)

A reduction of energy consumption will also reduce the CO<sub>2</sub> emission. The theoretic reduction potential is 164 Mt CO<sub>2</sub>/yr, from 293 Mt to 119 Mt CO<sub>2</sub>/yr. A fuel reduction of 10 GJ/t N in ammonia plants will reduce the CO<sub>2</sub> emission by 47 Mt CO<sub>2</sub>/yr. Introduction of new N<sub>2</sub>O reduction technology, which Hydro Agri has developed (mainly for new plants), could also reduce the Greenhouse gas emission by 52 Mt CO<sub>2</sub>-equivalent/yr. The remaining gap of 65 Mt CO<sub>2</sub>/yr is related to several energy improvements achieved in process design during recent years”

G. Konshaug (1998) “*Energy Consumption and Greenhouse Gas Emissions in Fertilizer Production*”, IFA Technical Conference, Marrakech, Morocco, September/October 1998.

## ■ 3.11 CLEANER PRODUCTION

Reference is made to EFMA’s “Best Available Techniques” (BAT), publications for the different processes, to which several references are made in this chapter and whose titles are given at the end of this chapter.

Cleaner production is defined as “The continuous application of an integrated, preventive environmental strategy applied to processes, products and services to increase eco-efficiency and reduce risks to humans and the environment”. See also the section on Cleaner production in Part 2.

### □ 3.11.1 Nitrogen Fertilizer Plants

#### *Ammonia*

For the ammonia plant:

- Where possible, natural gas should be the feed stock for the ammonia plant to minimize air emissions; this is the most important pollution prevention option in ammonia production.
- Direct hydrogen cyanide (HCN) gas in a fuel oil gasification plant to a combustion unit to prevent its release.



- Use purge gases from the synthesis process to fire the reformer, and strip condensates to reduce ammonia and methanol.
- Use those CO<sub>2</sub> removal processes which do not release toxics such as monoethanol amine to the environment.

### *Urea*

In the urea synthesis process, recover and recycle carbamate gases and/or liquids to the reactor. Operate the top of the prilling tower at a slight vacuum. Maximize product recovery and minimize air emissions by appropriate maintenance and operation of scrubbers and baghouses.

### *Ammonium nitrate*

In ammonium nitrate plants the following pollution prevention measures are recommended:

#### Prill tower

- Reduce microprill formation.
- Reduce carryover of fines through entrainment.

#### Granulator

- Reduce dust emissions from the disintegration of granules.

#### Material Handling

- For dusty products, use covers and hoods on conveyors and transition points.

### *Nitric acid*

In the nitric acid plant, preference should be given to processes that operate nitrous gas absorption at higher pressures in order to minimize NO<sub>x</sub> releases. In nitric acid production, absorption and catalytic reduction are the common means to control nitrogen oxides emissions. The efficiency of absorption can be raised through increasing the number of trays, operating the tower at higher pressures, or cooling the weak acid liquid in the absorber.

## 3.11.2 Phosphate Fertilizer Plants

The key pollution prevention control measures for the fertilizer plant are to:

- Maximize the recovery and recycling of dust from rock and product handling;
- Minimize the discharge of sulphur dioxide from sulphuric acid plants by using the double contact double absorption process with high efficiency mist eliminators;
- Prevent spills and accidental discharges through well bunded storage tanks, through installing spill catchment and containment facilities, and through good housekeeping and maintenance practices;
- Minimize the discharge of dust and fluorine from superphosphate plants to the atmosphere by treating off-gases using an efficient wet scrubbing/fluorine recovery system.

In the phosphoric acid plant, minimize emissions of fluorine compounds from the digester/reactor by scrubbers that are well-designed, well-operated, and well-maintained. Again, design for spill containment is essential to avoid inadvertent liquid discharges. Maintain an operating water balance to avoid an effluent discharge.

The management of phosphogypsum tailing is a major problem because of the large volumes and large area required, and the potential for release of dust, radon gases and fluoride although these releases are in fact already limited by the naturally recurring phenomenon described hereafter:

1. Thanks to the tailing moisture, recrystallisation takes place inside the phosphogypsum, the smallest crystals disappear and the largest grow larger and become harder. This promotes the formation of:
  - a hard superficial layer that avoids dust blow-off.
  - hard inner layers that decrease the rate of dissolution of the already little soluble contaminants and slow down the progression of the leachate to the point of a practically impervious retention.
2. Radon is a gaseous emanation from radium; the latter is more abundant than it was in the phosphate rock and the concentration is one third less. Being volatile, the radon emitted from the tailings will be dispersed through the air by the wind.
3. The revegetation of gypsum tailing occurs naturally thanks to the seeds brought in by wind and birds.

The following will help to minimize the impacts:

- Maintain a water cover to reduce radon gas release and dust emissions;
- Where water cover cannot be maintained, keep the tailing wet or revegetate to reduce dust;
- Line the tailings storage area to prevent contamination of groundwater by fluoride. Lining may be through construction of an impervious clay layer. The construction of the gypsum tailing with compacted aged gypsum also provides adequate mechanical integrity to avoid percolation.

Where contamination of groundwater is a concern, a management and monitoring plan should be implemented.

Scrubbers are used to remove fluorides and acid from air emissions. The effluent from the scrubbers is normally recycled to the process. If it is not possible to maintain an operating water balance in the phosphoric acid plant, then treatment to precipitate fluorine, phosphorus, and heavy metals may be necessary. Lime can be used for treatment. Spent vanadium catalyst is returned to the supplier for recovery or, if unavailable, then locked into a solidification matrix and disposed in a secure landfill.

### 3.11.3 Mixed Fertilizer Plants

This section addresses the production of ammonium phosphates (monoammonium phosphate-MAP, and diammonium phosphate-DAP), nitrophosphates, potash (potassium chloride), and compound fertilizers.

In the ammonium phosphate plant, pass the gas streams from the reactor, granulator, dryer, and cooler through cyclones and scrubbers to recover particulates, ammonia, and other materials for recycling. In the nitrophosphate plant, prevent  $\text{NO}_x$  emissions by the addition of urea to the digestion stage. Prevent fluoride emissions by scrubbing the gases with water. Remove ammonia by scrubbing. Phosphoric acid may be used for scrubbing where the ammonia load is high. Balance the process water system to avoid the discharge of an effluent.

Additional pollution control devices beyond the scrubbers, cyclones and baghouses that are an integral part of the plant design and operations are generally not required for mixed fertilizer plants. Good housekeeping practices are essential to minimize the amount of spilled material. Spills or leaks of both solids and liquids should be returned to the process. Liquid effluents, if any, need to be controlled for total suspended solids, fluorides, and ammonia.

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### ■ 3.12 MAJOR HAZARDS

The following hazards are identified in EFMA's BAT booklets, to which reference should be made for information on preventive measures.

#### *Ammonia*

- Fire/explosion hazard due to:
  - leaks from the hydrocarbon feed system,
  - leaks of synthesis gas in the CO/removal/synthesis gas compression areas (75% hydrogen).
- Toxic hazards from:
  - the release of liquid ammonia from the synthesis loop,
  - accidental release during storage and handling.

#### *Urea*

- Equipment/piping failure due to corrosion,
- Explosion hazard due to the formation of an explosive gas mixture,
- Toxic hazard due to NH<sub>3</sub> release.

#### *Nitric Acid*

- Equipment piping failure because of corrosion,
- Explosion hazard due to the air ammonia mixture,
- Explosion of nitrite/nitrate salts.

#### *Ammonium Nitrate and Calcium Ammonium Nitrate*

Ammonium nitrate is an oxidizing agent and precaution must be taken in manufacturing, transport and storage. Ammonium nitrate explosions can occur in pumps and special precautions must be taken in their design and operational management. Inorganic and organic contaminants, pH, temperature, density/confinement, concentration and critical diameter strongly influence the detonability of ammonium nitrate in solid form or in solution. (also see Fertilizer Society, Shah, 1996).

#### *Phosphoric and Sulphuric Acids*

Major hazards are not expected provided the design of all the equipment has been made using the best engineering knowledge available.

#### *Compound Fertilizers (mixed acid based)*

- Slurry pump explosions,
- Slurry decomposition,
- Product decomposition (cigar combustion).

\* \* \* \* \*

**References**

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## 4. REVIEW OF ENVIRONMENTAL ISSUES

Environmental issues concerning the fertilizer industry relate to the whole chain of production, storage, transport and use. In addition to the potential pollution of air, water and soil, there are hazards to be avoided in each section of this chain, as well as questions of occupational health and safety for all who handle these products. The particular problem of phosphogypsum disposal is described below. The decommissioning of old plants presents special problems, which are also described.

While many of these issues are principally a local concern in the proximity of fertilizer plants, several have a regional or even a global significance as for example release of air pollutants and of greenhouse gases (GHG), mainly CO<sub>2</sub>. The global environmental problems are difficult to measure but the local environmental problems, such as acid rain, water acidification, eutrophication and chemical mist can directly affect people, animals, vegetation and property in the vicinity of the plant.

If fertilizer production facilities are to achieve the lowest practicable environmental impact, both locally and globally, it is important that high standards of operation and maintenance be achieved. It is also necessary to monitor the emissions to air and discharges to water from the production plants, in order to enable the operators of the plant to take corrective action. Satisfactory technology now exists for the control of most potential pollutants resulting from fertilizer manufacture, and there is considerable progress with environmental management techniques. As a result, in certain regions of the world, there have been large reductions in emissions to the air and effluents to water during the past twenty years. However, in certain other regions there is still a great deal of progress to be made with the handling and release of toxic chemicals, and the long-term management of wastes, and even the best can still improve their performance.

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### ■ 4.1 POLLUTION OF AIR, WATER AND SOIL

Atmospheric pollutants emitted by the fertilizer industry can include gaseous ammonia (NH<sub>3</sub>) and ammonium salt aerosols, nitric and nitrous oxides (NO<sub>x</sub> and N<sub>2</sub>O), fluorine (as SiF<sub>4</sub> and HF), oxides of sulphur (SO<sub>x</sub>), fertilizer dust, acid mists, and radiation (from phosphogypsum). Carbon dioxide, though not a pollutant as such, contributes to global warming and is emitted in large quantities by the fertilizer industry. A modern steam-reforming process unit generates 1.15-1.3 tonnes of carbon dioxide per tonne of ammonia, whereas the emission of NO<sub>2</sub> is less than 1.3 kg/tonne ammonia. The sulphur dioxide emission may be as low as 0.01 kg SO<sub>2</sub>/tonne ammonia. In principle no ammonia should escape to the atmosphere although this sometimes occurs. The use of by-product CO<sub>2</sub> can reduce the CO<sub>2</sub> emissions very considerably, for example in a down-stream urea plant.

Waste waters from the industry can include compounds of nitrogen, phosphate, potassium, sodium, silica, sulphur, fluorine as well as sludges and polluted wash water.

Solid wastes or by-products, which may or may not be reprocessed, can include phosphogypsum, pyrite ashes, calcium carbonate, soluble salts from potash refining, sand and, not least, the plastic bags used to transport the fertilizer. A number of chemical residues are generated from the catalysts and other associated operations, and require special management procedures. In addition, the fertilizer product itself can carry impurities to the soil, mostly in negligible amounts. One of the most notable concerns is the cadmium content of some phosphate fertilizers.

These emissions and wastes have varying effects on the environment, depending not only on their individual characteristics but on their volume, concentration and destination. Each plant needs to prepare its own mass balance of materials to identify sources and impacts on its surroundings.

#### □ 4.1.1 Nitrogen Compounds

The global balance for N compounds is composed of three separate cycles for nitrous oxide ( $N_2O$ ), ammonia ( $NH_3$ ) and nitric oxides ( $NO_x$ ) respectively<sup>1</sup>.

##### *Nitrous Oxide*

Nitrous oxide ( $N_2O$ ) is emitted in large quantities to the atmosphere through soil biological processes. The atmospheric concentration of  $N_2O$  has increased by about 8% since pre-industrial times. It is estimated that fertilizer production accounts for about 6% of man-made  $N_2O$  emissions. Global man-made emissions of this gas are estimated to amount to between 1 and 6 million t N/yr. Most of it recycles to soil and seas, but there is a small loss to the stratosphere, where it reacts in the ozone layer. It is emitted in the course of nitric acid production at rates which can vary widely within a range of 1.2 to more than 10 kg/t 100%  $HNO_3$ . A possible abatement technique is non-selective catalytic reduction, described above; but this requires the combustion of hydrogen or a hydrocarbon fuel to heat the tail gas. On the one hand, hydrogen would have to come from an adjacent ammonia plant and may not always be available, and on the other hand, CO and hydrocarbons would be emitted to the atmosphere. A commercialized and patented abatement process can be applied for new plants. By modification of the combustion unit, it is possible to achieve 75% reduction by homogeneous decomposition of  $N_2O$ .

##### *Ammonia*

Ammonia and ammonium aerosols are naturally present in the atmosphere, being released from the soil by ammonification, as well as from animals and their manure. The latter are usually by far the most dominant sources. Direct emission of  $NH_3$  and ammonium aerosols from fertilizer production, storage and handling is only a minor source, since most of these emissions can be recovered and recycled.

Atmospheric ammonia is entirely recycled to soil and waters. However, it reacts with  $SO_2$  emissions to form ammonium sulphate aerosol, which can contribute to the formation of fog, increasing its density and persistence. Irritation of the throat occurs at concentrations above  $35\text{ mg/m}^3$ , and the mucous membranes of the nose and eyes are also affected. In aquatic environments,  $NH_3$  concentrations above  $1.25\text{ mg/l}$  are harmful to some species of fish. The aqueous toxicity of ammonia is strongly dependent upon pH.

##### *Nitrogen oxides*

Nitrogen oxides ( $NO_x$ ) are also emitted from natural sources in vastly larger amounts than from artificial sources, although the latter have virtually doubled to around 100 million t in the last 20 years. In several developed countries, including the USA, Germany and Japan, emissions have begun to decrease as a result of the application of abatement techniques and slower industrial growth.

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<sup>1</sup>  $NO_x$  denotes both nitric oxide (NO) and nitrogen dioxide ( $NO_2$ ).

Nitric oxide (NO) has an atmospheric residence time of about 4 days, and is oxidized over this period to nitrogen dioxide (NO<sub>2</sub>). The latter has a residence time of about one week and is deposited either in gaseous form or in rain or as nitrate particulates. It contributes to “acid rain” and fog in respirable air. It can cause irritation of the lower respiratory tract, with more serious effects in high concentrations.

Artificial NO<sub>x</sub> emissions arise from fossil-fuel combustion and low NO<sub>x</sub> combustion processes are attracting more attention. In the fertilizer industry, as well as in other fuel-burning industries, selective catalytic reduction, using ammonia to convert NO<sub>x</sub> to N<sub>2</sub>, can be used as method of abatement, and more than 0.5 million t NH<sub>3</sub>/yr is now used globally for this purpose. About 0.7 t NH<sub>3</sub> is required to remove 1 t NO<sub>x</sub>, though this can vary with the process used.

Synthetic zeolite may also be used to adsorb NO<sub>x</sub>. By subsequently heating the NO<sub>x</sub>-loaded zeolite, the NO<sub>x</sub> can be desorbed and recycled to a nitric acid plant. Other processes, as yet commercially untried, include electron beam radiation of tail gases, precipitating fine particles of ammonium sulphate nitrate, and two wet processes which (a) use NO<sub>x</sub> to oxidize SO<sub>2</sub> to sulphate in an aqueous ammonia solution, and (b) use NO<sub>2</sub> with limestone slurry to give gypsum and NH<sub>3</sub>.

#### □ 4.1.2 Fluorine

Most atmospheric fluorine, in the form of fluoride, is thought to originate from seawater. Volcanic activity is also an important source but industrial sources account for an increasing quantity. Fluorine generating industries include the production of phosphate fertilizers, aluminium, steel, glass, bricks and ceramics.

Industrial fluoride emissions can cause problems because of their localized concentration. Hydrogen fluoride (HF) can cause discomfort above an ambient concentration of about 8 mg HF/m<sup>3</sup>, and acute discomfort between 30-50 mg HF/m<sup>3</sup>, including irritation of the eyes, nose, pharynx and upper chest. Prolonged exposure to fluoride, especially by ingestion, can cause fluorosis, the symptoms of which include mottling of the teeth, pains, stiffness, and osteosclerosis. Working conditions involving such exposure no longer exist in the industrialized countries.

Vegetation can be severely damaged by proximity to industrial fluoride emissions. Pine trees are particularly susceptible. Moreover, fluoride contamination of vegetation is cumulative and can lead to problems with herbivorous animals.

Fluoride emissions from fertilizer production are confined to operations involving the acidulation of mineral phosphate, which normally contains 2-4% of combined fluorine and varying amounts of silicon. The reaction partitions the fluorine in the phosphate between the phosphoric acid, the phosphogypsum and the tail gas. The share of the latter is about 35-40% in the form of silicon fluoride (SiF<sub>4</sub>) and HF, the respective amounts depending on reaction conditions and the amount of “active” silicon. Efficient scrubbing and removal systems can capture most of the emitted fluoride, reducing it to as little as 5 mg/Nm<sup>3</sup> (40 g/t P<sub>2</sub>O<sub>5</sub>) in the tail gas of new plants.

Waste waters from phosphate fertilizer plants also contain some fluoride.

#### □ 4.1.3 Sulphur Compounds

Although natural sources of atmospheric sulphur abound - seaspray, decaying organic matter, and volcanoes, for example - man-made emissions account for a large proportion and are mainly attributable to the burning of fossil fuels and the smelting of non-ferrous metals. The fertilizer industry contributes mainly through its production of sulphuric acid and phosphate fertilizers, and also because a minor part of the ammonia industry burns coal and heavy oil. Pollution takes the form of hydrogen sulphide (H<sub>2</sub>S), sulphur dioxide (SO<sub>2</sub>) and sulphur trioxide (SO<sub>3</sub>), which react rapidly with water in the atmosphere, as well

as with other pollutants, to form sulphate aerosols. These are a major constituent of “acid rain”. This, in turn, increases soil acidity over wide areas, some quite distant from the source of the pollution, with adverse effects on woodlands and inland waters, where it is not possible or not feasible to correct the acidity by liming.

Sulphuric acid aerosols are strong pulmonary irritants. Concentrations above 3 mg/m<sup>3</sup> produce coughing, and respiration is significantly altered above 6 mg/m<sup>3</sup>.

Most of the gaseous sulphur compounds emitted from sulphuric acid and fertilizer production can be recovered by scrubbing and filtration, but some inevitably escapes. The replacement of old single contact sulphuric acid plants by double contact plants, and the installation of modern recovery systems, represent major improvements.

#### □ 4.1.4 Heavy Metals in Fertilizers

Many elements that do not appear to be necessary for plant nutrition occur in the raw materials for fertilizers. The heavy metals occur mainly in phosphate rocks.

The table below gives some key numbers for cadmium, mercury and lead which may be of concern as regards their content in phosphate rock, soils, fertilizers and crops:

► **Table 4.1** *Heavy metals*

		<b>Cd</b>	<b>Hg</b>	<b>Pb</b>
Rock - range	mg/kg P	0.1-850	0.1-0.7	20-300
Rock - average	mg/kg P	170	0.2	40
Typical topsoil (20 cm)	g/ha	960	192	52800
Fertilizers - average	g/ha*yr	2.5	0.01	1.3
Atm. depo. -average	g/ha*yr	3	2	200
Uptake by crop - aver.	g/ha*yr	1.4	very low	7
Leaching	g/ha*yr	1.1	1.8	3.7
Net input	g/ha*yr	3	0.2	190

*Source: Norsk Hydro*

If the soil input of trace elements from phosphate rock is compared with inputs from aerial deposition, plus possibly from organic waste, and these inputs are evaluated in relation to the soil content, cadmium is the major element of concern in the very long term as regards fertilizer input.

#### **Cadmium**

Cadmium is a heavy metal which accumulates in living systems and can become toxic above certain limits. Cadmium is universally present in the earth's crust which is estimated to contain, on average, 0.2 ppm Cd, or 0.2 grams per tonne, with large variations around the average. In general the total cadmium content in soils varies widely because of the strong influence of their geological history. A survey in the United States showed variations between the averages of different states from less than 0.08 mg/kg to more than 1.2 mg/kg of soil, depending largely on their parent material. These background contents of cadmium in agricultural land are augmented by the quantities deposited from the atmosphere and those applied in phosphate fertilizers, animal manure and sewage sludge. The relative importance of these sources varies considerably.



In most industrialized countries atmospheric deposition results from town waste incineration, non-ferrous metal production, iron and steel production and fossil fuel combustion. Although airborne cadmium has been declining since the mid-1960s there is still a significant input from this source. Animal manure contains cadmium because the metal is present in grazed herbage, imported and domestically produced animal feed and cadmium impurities in phosphate feed-additives.

The quantity of cadmium contained in a phosphate fertilizer depends on the source of the rock from which it was made. The cadmium content of phosphate rocks varies from almost zero to over 300 mg/kg  $P_2O_5$  (700 mg/kg P). The acidulation of phosphate rock partitions the cadmium between the fertilizer product and the by-products, mainly the phosphogypsum arising from phosphoric acid production (see section 4.2.1).

Controlling exposure to cadmium through agricultural products can only be achieved by minimizing inputs of cadmium to soil from atmospheric deposition, animal manure, sewage sludge and phosphatic fertilizers. Certain West European countries have already applied limits to the cadmium content of phosphate fertilizers, which can be achieved economically only by using phosphate rock containing low levels of cadmium. If low limits were to be widely adopted, the use of most rocks from Algeria, Egypt, Morocco, Nauru, Senegal, Syria, Togo and Tunisia would be excluded, to the evident detriment of the economies of these developing countries. It would also exclude phosphate rocks from certain areas of the United States.

The few remaining sources of low-cadmium rocks would therefore be in great demand, with consequent increases in their price. It is not just a question of natural deposits. Geological, technical, logistic and economic factors, the physical characteristics and the presence of other contaminants also govern the availability and suitability for processing of a particular rock.

The fertilizer industry has for some decades tried to develop cadmium separation processes. All process studies so far have shown serious limitations and problems, with regard to safety, cost, energy consumption or environmental concerns. Currently available processes are too expensive and are not economically viable except for phosphates destined for human or animal consumption, which have a greater added value. A process developed for removing cadmium from phosphoric acid, which is used in the production of many phosphate fertilizers, has shown promise on a laboratory scale, but needs to be tested in a semi-industrial scale pilot plant before being used on a full industrial scale. However, it would not help single superphosphate, the production of which does not involve phosphoric acid, and which is a very important fertilizer, due partly to its high sulphur content, in countries as diverse as Australia, Brazil, China, Egypt, India and New Zealand. Similarly, it would not help nitrophosphates, nor mixed acid fertilizers incorporating phosphate rocks.

The cadmium problem cannot be resolved simply by setting low limits on the cadmium content of fertilizers. Further research and development work is required in order to find a viable solution to the problem.

#### □ 4.1.5 Radioactivity

Mineral phosphates have a natural radioactivity. In those of sedimentary origin, the main component is uranium, which exists within a range of 0.005-0.02% U. In those of igneous origin, thorium is often more prevalent than uranium, though both are present in much smaller quantities. The main product of uranium decay is radium ( $^{226}\text{Ra}$ ). Uranium in mineral phosphate is partitioned between the product phosphoric acid and the by-product phosphogypsum. Radium is carried very largely into the by-product gypsum because its sulphate is highly insoluble.

Uranium concentrations in phosphoric acid vary according to phosphate source, reaction process and acid concentration within a wide range of about 0.01-0.26 g/l for typical phosphates. Various phosphogypsums have shown uranium contents varying from 0.015 to 0.03 g/kg. The concentration of

large quantities of phosphogypsum near phosphate fertilizer complexes may be a source of radioactive pollution, if dust is blown off the stacks by wind, and also because radon gas ( $^{222}\text{Rn}$ ) is continuously evolved, although this radon is dispersed in the air.

Mineral phosphates, phosphate fertilizers, phosphogypsum and phosphoric acid plant effluents all have lower radioactivities than the international limit value prescribed by EURATOM (500 Bq/kg or 13.5 pCi/g) and are not subject to radiation regulations. Nevertheless, considerable research has been devoted to the recovery of uranium from phosphoric acid, and various processes are available, involving solvent extraction, ion exchange, the use of liquid membranes and other means. However, they are costly and closely linked with the economics of uranium fuel market, which have generally been unfavourable.

It has been established that about 40% of the radionuclides in the mined phosphate rock pass into the beneficiated product. Two thirds of this is transferred to the phosphoric acid, and the remaining third is disposed of with the phosphogypsum.

There are processes, involving the concentration of the phosphoric acid and sedimentation, for the production of the uranium in the form of "yellow cake". However, the process is not economically viable at the present price of uranium.

Work carried out in Finland has shown that the annual contribution of U-238 contained in NPK fertilizers was about 0.25% of the total uranium naturally occurring in the surface 10 cm of the soil. Similar results have been reported in Belgium, where it was found that Ra-226 contamination in phosphate fertilizers added to the soil represents only 0.25% for 14 kg/ha of P and 0.96% for 54 kg/ha of P of the total Ra-226 in the upper 20-cm layer of the soil.

The long-term effects of phosphate fertilization on radioactivity have been studied in the United States. Triple superphosphate produced from Florida phosphate rock and applied at the rate of 30 kg/ha of P during more than 50 years did not change the concentrations of U, Th, and Ra in corn leaves and grain, wheat grain and straw, or soybean leaves and bean, in comparison with non-fertilized plots. Radionuclides present in the soil solutions are absorbed by the plants but the soil conditions favouring their uptake have not been studied in detail.

In case of use of phosphate rock containing higher radionuclides in production of fertilizers, the radioactivity of phosphoric acid and phosphogypsum must be measured because the radioactive components of the rock are concentrated to a degree in various parts of the plant during processing, particularly during vacuum filtration. To avoid ingestion of radioactive elements, a high level of hygiene should be observed when maintenance is carried out in these parts of the plant and when scale is removed.

Source: IFDC and UNIDO (1998). *Fertilizer Manual*. Kluwer Academic Publishers, Dordrecht, The Netherlands.

#### 4.1.6 Dust

Filters permit the removal of dust in fertilizer manufacture but there is also the question of the handling of bulk materials. Fertilizers and their raw materials are an important constituent of sea-borne bulk trade. They take fourth place among bulk commodities in world shipping trade after iron ore, coal and grains. In 1995 some 120 million tonnes of fertilizers and phosphate rock were shipped, accounting for 8% of all sea-borne bulk trade, which compares for example with some 192 million tonnes for grain. Spillage and dust emissions from bulk handling operations can be an environmental problem as well as representing an economic loss. The state of Florida does not permit the discharge of dry sulphur. In certain ports bulk material is handled using old equipment which is far from meeting today's standards. It is important that bulk materials should be handled in carefully engineered equipment using dust free continuous systems.

## ■ 4.2 THE DISPOSAL OF WASTE

### □ 4.2.1 Phosphogypsum

All phosphate ores contain traces of radioactive elements and a number of metals. During processing, these are partitioned between (1) beneficiation process wastes, (2) the waste from the further processing into intermediate and finished fertilizer production, and (3) some end up in the final product.

The main waste is phosphogypsum. Approximately 1.5 tonnes of phosphogypsum is produced per tonne of phosphate rock fed in phosphoric acid production, or 5 tonnes per tonne of  $P_2O_5$ . The nitric acid route for the production of multinutrient fertilizers avoids the production of by-product gypsum.

Gypsum (calcium sulphate dihydrate) is a mineral which also occurs in nature. Phosphogypsum is produced by the reaction of phosphate rock with sulphuric acid during the process of producing phosphoric acid. The term “phosphogypsum” (PG) is used to specify the particular gypsum arising from the acidulation of phosphate rock, because it contains trace amounts of many of the mineral impurities that accompany phosphate rock. One of these impurities is radium, the parent of radon. Other trace impurities found in PG include arsenic, nickel, cadmium, lead, aluminium as well as fluoride and phosphoric acid. Mainly because of the radon content, the United States Environmental Protection Agency restricts use of PG and stipulates that no PG with radium over 10 pCi/g can be removed from the PG stacks adjacent to the chemical plants. It should, however, be noted that:

- No radium being brought into the system by any other raw material than phosphate rock, the amount of radium in the PG is the same as in the phosphate rock and the concentration is two thirds.
- The radon emissions from PG are thus exactly the same as from the corresponding phosphate rock.
- Being a gas, the radon will be carried away from gypsum stack with the air while radon emanating from underground, naturally-occurring materials such as certain granites may enter houses and accumulate in them if they are not properly vented. This situation may create higher and more dangerous concentrations of radiations.

Previously it was common practice for phosphoric acid plants situated on coasts to pump gypsum into the sea, where it rapidly dissolves if the ocean currents are sufficiently strong and not along-shore. In some places, restrictions on the disposal of phosphogypsum into the sea have been introduced. In other areas, disposal into the sea is permitted subject to restrictions on the cadmium content of the gypsum.

When phosphogypsum is discharged to the sea or estuary the environmental impact will depend to a great extent on the location of the plant. In landlocked waters or in sea with weak currents, the discharge of phosphogypsum affects aquatic life adversely, whereas in open sea the contained fluoride precipitates as sodium fluoride, and the strong currents disperse the sediments.

The use of waste phosphogypsum for other purposes has been widely encouraged, but economic and/or quality problems and/or the demand for the resulting products frequently inhibit or prevent this. These problems relate not only to the impurities in the phosphogypsum, but also to its relatively high moisture content. Plasterboard, plaster and cement are the main possibilities, but it is also possible to recycle phosphogypsum in sulphuric acid production. Gypsum and phosphogypsum are also used in large quantities as a soil amendment for sodic soils. The ready availability of natural gypsum and the high cost of gypsum-based sulphuric acid are the main obstacles to its use. But in countries where gypsum and other sulphurous raw materials are scarce, phosphogypsum has been successfully used for these purposes. In these cases the DH/HH process which produces the purest and driest PG is best suited. Gypsum is an excellent and economic road-making material and large quantities could be used for this purpose. In the USA, the environmental authorities hesitate to permit this use in view of the radon emissions. Submissions demonstrate the very low degree of risk and it is possible that this use will be approved in due course.

For phosphogypsum disposal to the sea, the North Sea Declaration of 1990 called for a 70% reduction of cadmium to the North Sea by 1995 on a 1985 baseline and a further reduction has been targeted to 90% by the year 2000 based on 1985. The target for plants around the North Sea is 0.5 g cadmium per tonne of phosphogypsum disposed to the sea.

For phosphogypsum storage on land, water used for gypsum transportation is usually recycled after the gypsum settles. The water normally contains traces of the impurities contained in the gypsum. The water balance in gypsum settling ponds must be carefully managed.

Dumping on land is not possible everywhere because the material settles and dries slowly and requires an adequate land area and certain climatic and soil conditions where the gypsum stack is situated.

Dry gypsum from the filter in some plants is transported by belt conveyors to the gypsum storage pile. The pile area is completely surrounded by a ditch which collects the run-off water including any rain water.

In other plants the filter cake is slurried with recycled pond water and pumped to special storage areas where the phosphogypsum eventually dries in stacks. The area receiving the phosphogypsum slurry is sub-divided into smaller areas, with each section being used in rotation. Slurry is discharged on top of the storage pile and the phosphogypsum rapidly settles out of the effluent. Clear water runs off and drains to the adjacent cooling ponds. The water is recycled within the system to ensure that the contaminants are kept within the plant. The phosphogypsum stack is surrounded by a ditch which contains any water that might spill accidentally.

While the stack is in operation, the smallest PG crystals are dissolved in the PG moisture and recrystallized on the larger crystals; this on-going process creates very hard layers of PG which are practically impervious, and thus limits the effect of contaminants leaching (in fact, their hardness decreases largely the rate of dissolution of the already poorly soluble contaminants, and also it decreases the rate of progression of the leachate down the stack).

Similarly, the top layer of the stack becomes harder and this avoids any dust blow-off, while it still allows the growing of vegetation based on the seeds brought in by wind and birds.

Nevertheless, the following consideration in the design and construction of phosphogypsum disposal areas have been advised:

– ***Site selection***

The height of the stacks depends on the engineering properties of the underlying soil and its load bearing strength.

– ***Cooling ponds***

The cooling pond surfaces will have to be adapted to local climatic conditions and the water balance in the plant.

– ***Percolation control***

The process water associated with phosphogypsum is highly acidic and contains high levels of contaminants. Some of the following techniques may be necessary to prevent this water from reaching the ground water:

- seepage collection ditches,
- intercept wells,
- lining systems (natural or synthetic),
- fixing of soluble  $P_2O_5$  and trace elements by neutralization.

Florida, USA, has over 20 phosphogypsum stacks. Ground water monitoring at these stacks began in 1986. Stacks 200 feet (60 m) high are common in Florida, and based on a final 4:1 horizontal: vertical slope, a land area of approximately 300 acres (121 ha) is covered. The top surface area is about 70 acres (28 ha).

According to the U.S. Phosphogypsum Management Rule of March 1993, gypsum produced after 2001 will have to be contained in lined systems. TFI estimates that the “Rule” raises the capital cost of phosphogypsum disposal from about \$ 1.5/ton gypsum to \$ 3.5/ton, an increase of approximately \$ 10/ton P<sub>2</sub>O<sub>5</sub>.

The “Rule” is in fact Chapter 62-673, Florida Administrative Code, Phosphogypsum Management, of January 1993. The “Rule” specifies performance criteria and location requirements for new stacks. It describes requirements for the liner systems and leachate collection. It covers operational procedures, including ground water monitoring and surface water and leachate management. It describes provisions for the closure of a phosphogypsum stack system, including the cover and the long-term care of the stack through monitoring and maintenance for 50 years after the closure. The “Rule” requires that a bond be posted or other means adopted for insuring long-term financial responsibility.

In June 1994 a “sinkhole” some 50 metres wide and 55 metres deep was discovered in an unlined, gypsum stack in Florida which was closed and replaced in 1992 by a new stack which complies with the new requirements. In nature, sinkholes are caused by limestone dissolution over a long period of time. When the void space becomes too large to support the terrain above, the roof collapses. Normally a lake is formed. In this case the collapse occurred under a gypsum stack and solid and slurry gypsum collapsed downwards. There was concern that this material might pollute the aquifer that supplies water to the surrounding area. Immediate action was taken by the company involved in order to prevent his happening. New measures have been worked out between the Florida Department of Environmental Protection and the phosphate industry in order to prevent a recurrence of such an incident.

Upon closure of a gypsum stack, the stack should be covered by a barrier and soil cap to prevent additional runoff of contaminated water cause by rainfall. Stacks have to be closed at the end of their useful life, generally when the stack reaches about 200 feet (61m). Cargill Inc. closed a stack in 1990, capping it with HDPE, and 46 cm of soil. The stack is now growing grass, trees and brush and is home to numerous rabbits and bird life. The stack now appears from the distance as a green flat-topped hill. A typical cost for a stack closure might be \$10 million. Closures include a drainage system with contaminated water recovery and monitor wells. Companies in Florida re required to monitor a closed stack for up to 50 years.

In a paper entitled “*Phosphogypsum; a waste (more or less harmful) or a resource?*” presented at the IFA Technical conference held in Marrakech, Morocco, in September 1998, A. Davister describes the nature, properties and possible uses of phosphogypsum. The present direction of research and development as regards phosphogypsum in Florida is given in *The Programs of the Florida Institute of Phosphate Research*, by P. Clifford et al., presented at the meeting of The Fertilizer Industry Round Table, Annapolis, USA, October 1998.

#### 4.2.2 Disposal of Spent Catalysts

The steam reforming process for ammonia requires that the catalysts be replaced after every 2 to 6 years in service. Partial oxidation plants use typically 2 to 3 different catalysts.

Spent catalysts, also contain oxides of hexavalent chromium, zinc, iron and nickel. They are returned to the manufacturer or other metal recovery companies. The carbon dioxide removal stage can use potassium hydroxide solutions containing activators, aqueous amine solutions or other chemicals.

Most of the catalysts can be recycled to catalyst manufacturers or other metal handling firms for reclamation of valuable metals. The other catalysts can be used by other companies for various purposes.

The following text is extracted from an article by Parkans International, entitled *Recycling in Ammonia Plants - A Catalyst Perspective*, which was published in "Arab Fertilizer", n° 17, January/March 1998, Arab Fertilizer Association, Cairo.

### ***Environment***

Questions to be asked to help develop a strong, environmentally sensitive program would include:

- Does the ammonia plant management feel comfortable with the environmental impact of their recycling company and each of the third party sites they utilize? Do they meet your internal standards as an environmentally friendly operation?
- What types of by-products, if any, are formed from recycling and recovery of the spent catalyst? How are they handled or disposed? Are there any recycling routes that form no by-products? Is the recycling operation a potential "sham recycling"?
- If landfills have to be used, are the environmental impacts of the landfilled catalyst well understood? Does the landfill meet the company's standards; does the landfill meet "world class" standards for construction and operation?
- Are there countries with weak environmental standards or existing large pollution problems (especially in the third world)? Your company may not want to further burden the environmental in these areas, or to make itself a potential future target for the inevitable search for the parties responsible for pollution.

### ***Liability and Risk***

The following are some questions and ideas that can assist members of the fertilizer industry in developing their corporate recycling programs to minimize such liabilities and risks:

- Do local landfill sites meet the minimum world wide standards? Are they up to par with what you know will be required as standards soon? If not, what type of specific problems would you foresee by continuing shipments to the disposal sites?
- When dealing with a local or foreign recycler, do you know everything about them? Financial strength, personnel, history, operations? Is all the information before you verifiable?
- Would your company be better served by conducting a thorough audit of the disposal site or the recycling company before any business takes place?
- Has the recycler explained clearly the procedures to be used in utilizing the spent catalyst? Do you ask the questions: "Where, who, when, and how?" Where is our material taken; who is the actual recycler; when will it be used; and how will it be used?

### ***Operations***

Several options are available for the plants to consider:

Option I- All inclusive catalyst handling program in which the recycling company handles the entire catalyst removal and recycling process, beginning with catalyst removal from reactors, to oxidation, packaging, shipment, and eventual recycling. One problem here is that logistics issues and existing subcontracting arrangements at the plant might make this approach not feasible.

Option 2-Strictly catalyst recycling program in which the plant contracts, or uses its own personnel or organization, to perform catalyst changeouts, oxidation, storage, and packaging, and shipment to the recycler. This process is the standard one across the world.

Option 3-A middle ground between the first two options, in which the plant controls certain aspects of the turnaround and catalyst handling process, and the recycler provides limited in-plant services such as labeling, final packaging, and shipment.

Ammonia plants have significant catalyst recycling potential and all ammonia plant spent catalysts should be recycled. The economics are favorable and all the materials are non-hazardous.

Finally, we recommend to:

- minimize the number of locations handling your spent catalyst;
- use a legitimately audited recycler,
- try to audit your recycler yourself, or be a part of a group that conducts audits on behalf of its members,
- use a recycler that operates its own facilities, has the appropriate local, regional and national permits with an excellent record of compliance, and has knowledgeable and trained personnel, adequate financial strength and relevant insurance coverages.
- be extra careful with brokers;
- fully oxidize catalysts before shipment;
- properly pack spent catalysts in good quality containers, and ship spent catalysts as soon as reasonably possible, and, finally;
- avoid landfills to the greatest extent possible.

#### 4.2.3 Other Wastes

Apart from the catalysts, the phosphogypsum and the cinders from the production of sulphuric acid from sources of sulphur other than brimstone, the quantities of other wastes generated by well-run nitrogen, phosphate and fertilizer plants should be small. However, in spite of their low volumes, the environmental hazards of some of these solid wastes can be significant.

These wastes could include:

- PCBs from electrical equipment,
- waste oils and lubricants from the site,
- waste or spent batteries used on the site,
- herbicides,
- laboratory wastes,
- asbestos,
- CFCs and halons still in use or in old equipment,
- spilt chemicals,
- contaminated soil or equipment,
- obsolete equipment incorporating hazardous materials,
- waste resulting from process modifications.

Specialized techniques of handling and disposal apply in each case. In view of the difficulty of properly disposing of such wastes, companies should look carefully at waste avoidance approaches, through substitution by different chemicals, through great care to avoid spills, and in arranging for suppliers to take back chemicals at the end of their life (e.g. catalysts). There should be an attempt to reuse or recycle materials where possible, and to arrange with the authorities for disposal of the remainder.

Other significant sources which may be generated in significant amounts include:

- wastewater treatment sludges,
- scrubber wastes and filter dusts,
- filter bags, and other obsolete items of treatment plants,
- empty chemical containers.

In some countries the national infrastructure is incapable of dealing properly with such special wastes. In these circumstances, the company may run its own landfill, an operation which requires careful management supervision, with well-defined procedures. A disposal site has to be designed and built by appropriate experts after appropriate evaluation and approval by the authorities. The operation of the site should be by designated, trained personnel with the power to refuse entry to wastes not conforming with rigid entry criteria that are established at the outset. Wastes entering such a facility should be chemically stabilized, to avoid leaching of toxic components. Regular monitoring is essential, with appropriate backup, emergency and repair services.

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### ■ 4.3 DECOMMISSIONING OLD PLANTS

There are three aspects:

- old plant and equipment,
- old dump-sites,
- polluted soil.

Old fertilizer plants are being shut down for economic or environmental reasons, and phosphate and potash mines are being mined out. The problem of site remediation and clean-up of past contaminated sites is fast becoming a fact of life for many plants that have been careless about leakage of chemicals and on-site disposal in the past. The process of cleaning and restoring polluted soil and water is a complex and costly undertaking, for which the plant/site owner is normally liable. Legal prudence dictates a regulated framework for plant decommissioning and site remediation. No matter how thorough a voluntary cleanup may be, there can be no protection from the possibility of subsequent litigation. In any case, the industry has a “duty of care” obligation with respect to disposal to external disposal sites. Many governments are now requiring by law that companies clean up their sites. This is often under specific ‘contaminated sites’ legislation, or general environmental regulation

The diverse range of chemicals, and the difficulty of recovering them from the surrounding soil groundwater, means that clean-up is very expensive. Many of the contaminated sites requiring most urgent attention are former landfills.

To date there are no clear guidelines to ‘how clean is clean’, with the result that many companies are unsure of how far to go. A number of countries such as the USA, Canada, France, Germany, The Netherlands, Switzerland, the U.K. and Australia have attempted to prepare guidelines as to soil standards expected from successful clean-up operations.



In the USA, the Comprehensive Environmental Response, Compensation and Liability Act, popularly known as Superfund, addresses this problem with procedures including preliminary assessment, site inspection, remedial investigation, feasibility study (including a definition of remedial methods and a calculation of the respective costs), public comment and/or hearing, and design and construction of the remedial project. This process can take several years before the project is actually implemented, and subsequent periodic monitoring may also be involved.

As regards the options, removal of soil has the advantages of being quick and certain, factors which are important for a developer. Removal of the contaminated soil to a landfill has generally been the cheapest method of remediation to date, but with the tighter regulation of landfill this method may become more expensive. Cleaner soil is brought in from another part of the site or elsewhere to replace the soil removed. Removal to landfill does not eliminate the contaminants and the transport adds to environmental costs but the transfer of contaminants to properly designed and managed disposal sites has its advantages.

Capping involves covering the contaminated soil. The top layer is usually clay in order to minimize the amount of rainwater reaching the contaminated layer. Below the clay layer is a capillary break, often of rubble, to prevent water from the contaminated layer rising towards the surface through capillary action. There may be vertical barriers to prevent the horizontal movement of the contaminants.

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## ■ 4.4 GLOBAL WARMING AND OZONE DEPLETING SUBSTANCES

### □ 4.4.1 Greenhouse Gases

The earth's atmosphere is largely transparent to visible light radiation which heats up the earth. The earth in turn radiates heat back to the atmosphere, but this is absorbed by water vapor and many atmospheric gases and re-emitted back to earth. Gases such as CO<sub>2</sub>, CH<sub>4</sub>, other hydrocarbons, NO<sub>x</sub>, halocarbons and O<sub>3</sub> are all important in this process, to varying degrees, as a result of their physical characteristics and lifetime in the atmosphere.

Global levels of these greenhouse gases have increased significantly over this century, and significant temperature rises are hypothesized as a result. This may affect climatic patterns with consequent implications for ecosystems, agriculture and coastlines. Many national and international initiatives are now being implemented to improve scientific understanding of climate change and to stabilize and eventually reduce emission levels.

The increasing atmospheric concentration of these gases is due to human, domestic and industrial activities. The increase appears to have started with industrialization, the intensification of agriculture and population growth, and became especially noticeable after the Second World War.

The main concern is the increasing concentration of carbon dioxide (CO<sub>2</sub>). The annual net addition of CO<sub>2</sub> to the atmosphere, resulting from human activities, has been estimated at about 8.5 billion tonnes of carbon, of which the share of the fertilizer industry is thought to be around 2%. Although the total anthropomorphic emissions are only about 7% of the quantity naturally released annually by biological processes, and despite the fact that most of the additional CO<sub>2</sub> is absorbed by the oceans, there has been a significant increase in the CO<sub>2</sub> content of surface air, the estimated average annual growth rate being in the range of 0.2-0.5%.

The importance of cleaner, safer technology and procedures for manufacturing emphasized by the Kyoto protocol on climate change. The Kyoto Protocol adopted in December 1997 during the Third meeting of the Conference of Parties of the United Nations Framework Commission on Climate Change established

an obligation on countries which ratify the Protocol to reduce the overall emission of these gases by at least 5% below 1990 levels in the commitment period 2008 to 2012. Six gases are covered, two of which are particularly relevant to the fertilizer manufacturing industry, carbon dioxide, CO<sub>2</sub>, and nitrous oxide, N<sub>2</sub>O. Technology is available for reducing emissions from fertilizer plants to very low levels. Proper operation, maintenance and house-keeping are important in reducing emissions to a minimum. The installation in 1993 of an “Integrated process control system” by Norsk Hydro in Norway reduced emissions to almost zero.

It is incumbent on all industries to keep CO<sub>2</sub> emissions as low as possible, and the fertilizer industry contribute to this through technological progress in achievable energy efficiencies. The projected growth of fertilizer use makes such progress all the more necessary. But as technological progress nears its limits, further significant limitation of CO<sub>2</sub> emissions must be mainly expected from the replacement of old, inefficient plants by new ones.

► **Table 4.2** *Greenhouse gases*

	Surface air concentration ppm (vol)			Recent growth percent/year	Expected relative contributions to global warming (1980-2050) Percent
	Year				
Gas	1600	1880	1985		
CO <sub>2</sub>	280	280	345	0.2-0.5	47
CH <sub>4</sub>	0.7	1.15	1.65	1.2	14
N <sub>2</sub> O	0.28	0.28	0.3	0.2-0.3	10
CFC's	0	0	0.0005	5.8	29

The relative weightings of the global warming potential per unit of emission are CO<sub>2</sub>=1, N<sub>2</sub>O=310, CF-gases=6600, SF<sub>6</sub>=23900, HFC 134a=1300.

Source: Norsk Hydro.1990.

Although emitted in smaller quantities, certain other gases are more active than carbon dioxide in terms of global warming. Nitrous oxide (N<sub>2</sub>O) is 310 times as active as carbon dioxide.

See section 4.1.1 for further information on emissions of nitrous oxide (N<sub>2</sub>O) and nitrogen oxides (NO<sub>x</sub>) in fertilizer manufacture.

#### □ 4.4.2 Photochemical Oxidants

Many of the emission gases can not only be harmful in the forms in which they are emitted, but may react in the atmosphere to form secondary pollutants with properties and effects quite different from those of their precursors. The photochemical action of sunlight forms a complex mixture of primary and secondary pollutants, particularly NO<sub>x</sub> and volatile organic compounds (VOC). Ozone (O<sub>3</sub>) is naturally occurring in the stratosphere, but in the troposphere, up to 18 km above the ground, ozone is present in smaller amounts. Its presence is greatly enhanced by photochemical reactions with NO<sub>x</sub> and VOC, and becomes a powerful oxidant, with low concentrations being toxic to both animals and plants. It may impart breathing difficulties in humans at elevated levels, and cause infectious disease and irritations. Observed effects on plants include visible foliar damage and leaf collapse, loss of chlorophyll, loss of yield, growth alterations, reduced nitrogen fixation, and changes in plant physiology.

Oxidants can cause physical damage to structures through chemical corrosion, particularly in relation to metals.

Photochemical oxidants and secondary pollutants are particularly difficult to deal with because of their complexity. Decisions concerning air quality which are based solely on the properties of primary pollutants will be of limited value for secondary pollutants. Of increasing concern is the possibility that two or more substances combining together may cause a more significant health or environmental effect than any one on its own.

#### 4.4.3 Ozone Depletion

In the upper atmosphere (stratosphere), ozone acts to shield the earth from excessive levels of ultra-violet radiation. The amount of UV radiation reaching the ground depends on the amount of ozone in the stratosphere at a particular place and time. An increase could have significant effects on human health, particularly epidemiological problems, on the biota, particularly the efficiency of photosynthesis, and on climate. It has been demonstrated that the synthetic gases chlorofluorocarbons (CFC) and halons among others deplete the stratospheric ozone and there is now international agreement through the Montreal Protocol that the use of ozone depletion substances (ODS) be greatly reduced and eventually eliminated.

#### 4.4.4 Acid Deposition

Acid deposition in dry or dissolved forms is primarily related to the compounds of sulphur and nitrogen as atmospheric pollutants, not only of local origin, but also transported over large distance from the areas of emission. This deposition can cause significant changes to soil and water chemistry, with consequent effects upon vegetation and freshwater organisms. The effects of acidity in freshwater ecosystems are perhaps the best documented, particularly those related to fisheries and declining catches. Increasing acidity is known to impair physiological and reproductive processes in fish, and fish eggs and fry are particularly susceptible to acidic water. Indirect effects also impact fish populations, through reduction in invertebrate species diversity, and excessive algal and moss growth.

Terrestrial ecosystems are also affected, with most attention focused on forests, tree growth and performance.  $\text{SO}_2$ ,  $\text{NO}$  and  $\text{NO}_2$  in the levels associated with atmospheric pollution reduce the yield of some crops. Many sensitive ecosystems are at risk of damage from acid deposition through long range transport of atmospheric pollutants. Dry deposition is thought to be of greatest significance close to emitting sources, particularly where long term chronic deposition occurs. Effects on the ocean are minimal since the sea is effectively buffered against any impact from acid deposition. In fact, the Gulf Petrochemical Industries Co. in Bahrain has established a thriving fish farm around their complex, demonstrating that the discharges from the plant are innocuous, while producing a substantial harvest of healthy fish which are given free of charge to under-privileged people.



## 5. APPENDICES

### ■ 5.1 ABBREVIATIONS

AAPFCO	American Association of Plant Food Control Officials
ADR	Agreement on the Carriage of Dangerous Goods by Road
AOAC	Association of Official Analytical Chemists
APELL	Awareness and Preparedness for Emergencies at the Local Level
API	American Petroleum Institute
AQS	Air Quality Standard
BAT	Best Available Techniques
BATNEEC	Best Available Techniques Not Entailing Excessive Cost
BOD	Biological Oxygen Demand
BPM	Best Practical Means
BCSD	Business Council for Sustainable Development
CAER	Community Awareness and Emergency Response
CEFIC	European Chemical Industry Council
CEN	European Standardization Organization
CFI	Canadian Fertilizer Institute
CMA	Chemical Manufacturers' Association (USA)
COD	Chemical Oxygen Demand
CP	Cleaner Production
EFMA	European Fertilizer Manufacturers' Association
EIA	Environmental Impact Assessment
EIS	Environmental Impact Statement
ELV	Emission Limit Value
EMAS	Eco-Management and Audit Schemes
EMS	Environmental Management System
EPA	Environment Protection Agency
ESCAP	Economic & Social Commission for Asia and the Pacific
ETA	Environmental Technology Assessment
EU	European Union, formerly European Economic Community, EEC
FADINAP	Fertilizer Advisory, Development & Information Network for Asia & the Pacific
FAI	Fertiliser Association of India
FAO	Food and Agriculture Organization
GEMI	Global Environmental Management Institute
GHG	Greenhouse Gases
IATA	International Air Transport Association

ICC	International Chamber of Commerce
ICCA	International Council of Chemical Associations
IFA	International Fertilizer Industry Association
IFDC	International Fertilizer Development Center
ILO	International Labour Organization
IMDG	International Maritime Dangerous Goods (Code)
IMO	International Maritime Organization
IPC	Integrated Pollution Control
IPCS	International Programme for Chemical Safety
IPPC	Integrated Pollution Prevention and Control
ISO	International Standards Organization
LCA	Life Cycle Analysis
MACT	Maximum Achievable Control Technology
NPRI	National Pollutant Release Inventory (Canada)
OEL	Occupational Exposure Limit
OECD	Organization for Economic Cooperation and Development
OSHA	Occupational Safety and Health Administration
RC	Responsible Care <sup>®</sup>
RCRA	Resource Conservation and Recovery Act
RID	Regulations concerning the carriage of Dangerous Goods by Rail
SHE	Safety, Health and Environment
STEL	Short Term Exposure Limit
TFI	The Fertilizer Institute (USA)
TLV	Threshold Limit Value
TQM	Total Quality Management
TQEM	Total Quality Environmental Management
TRI	Toxic Release Inventory (USA)
UNCED	United Nations Conference on Environment and Development
UNEP	United Nations Environment Programme
UNIDO	United Nations Industrial Development Organization
VOC	Volatile Organic Compounds
WHO	World Health Organization

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## ■ 5.2 CONTACT ORGANIZATIONS

### IFA

IFA, the International Fertilizer Industry Association, comprises around 500 member companies worldwide, in over 80 countries. The membership includes manufacturers of fertilizers, raw material suppliers, regional and national associations, research institutes, traders and engineering companies.

IFA collects, compiles and disseminates information on the production and consumption of fertilizers, and acts as forum for its members and others to meet and address technical, agronomic, supply and environmental issues.

IFA liaises closely with relevant international organizations such as the World Bank, FAO, UNEP and other UN agencies.

***IFA's Mission***

- To promote actively the efficient and responsible use of plant nutrients to maintain and increase agricultural production worldwide in a sustainable manner.
- To improve the operating environment of the fertilizer industry in the spirit of free enterprise and fair trade.
- To collect, compile and disseminate information, and to provide a discussion forum for its members and others on all aspects of the production, distribution and consumption of fertilizers, their intermediates and raw materials.

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**UNEP**

UNEP's Industry and Environment centre in Paris was established in 1975 to bring industry, governments and non-governmental organizations together to work towards environmentally-sound forms of industrial development. This is done by:

- encouraging the incorporation of environmental criteria in industrial development
- formulating and facilitating the implementation of principles and procedures to protect the environment
- promoting the use of low- and non-waste technologies
- stimulating the worldwide exchange of information and experience on environmentally-sound forms of industrial development.

The Centre has developed a programme on Awareness and Preparedness for Emergencies at Local Level (APELL) to prevent and to respond to technological accidents, and a programme to promote worldwide Cleaner Production.

United Nations Environment Programme

Industry and Environment

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Web: <http://www.unepie.org>

**UNIDO**

The United Nations Industrial Development Organization works with 169 Member States to help people in developing countries attain their economic and social goals by means of environmentally sustainable industrial development. Its services are also available to countries seeking to strengthen their industrial base as part of their transition towards a market economy.

UNIDO was established on 1 January 1967 by General Assembly resolution 2152 (XXI) of 17 November 1966. It became the sixteenth specialized agency of the United Nations on 17 December 1985 with the mandate to act as the central coordinating body for industrial activities within the UN system.

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Vienna International Centre  
P.O. Box 300, 1400 Vienna, Austria  
Tel: +43 1 26026 3883 - Fax: +43 1 26026 6819  
Tel: +43 1 26026 3938 (direct I. Volodin)  
Web: <http://www.unido.org>

### **Some International Organizations Providing Recommendations and Standards**

International Standards Organization (ISO)  
1, rue de Varembe, Case Postale 56, CH-1211 Geneva, Switzerland  
Tel: (41) 22 749 0111 Fax: (41) 22 733 3430  
Web: <http://www.iso.ch>

European Chemical Industry Council (CEFIC)  
Avenue E. van Nieuwenhuysse 4, 1160 Brussels, Belgium  
Tel: (32) 2 676 7211 - Fax: (32) 2 676 73 00  
Web: <http://www.cefic.be>

International Chamber of Commerce (ICC)  
38, cours Albert 1<sup>er</sup>, F-75008 Paris, France  
Tel: (33) 01 49 53 28 28 - Fax: (33) 01 42 25 86 63  
Web: <http://www.cci.org>

### **Fertilizer Organizations Cited**

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Email: [main@efma.be](mailto:main@efma.be)  
Web: <http://www.efma.org>

The Fertiliser Association of India (FAI)  
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The Fertilizer Institute (TFI)  
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