Chapter 4

FERTILISER MANUFACTURING PROCESSES AND ITS ENVIRONMENTAL PROBLEMS

Chemical fertiliser production aims at making available natural nutrients to plants as water-soluble compounds so that absorption is easy. This chapter provides a general description of the main fertiliser production processes. An understanding of these processes is essential in identifying the pollutants and the environmental issues that arise out of these plants. The products dealt with in this chapter are ammonia, urea, nitric acid, ammonium nitrate and calcium ammonium nitrate, sulphuric acid, phosphoric acid, single and triple super phosphate and complex fertilisers.

AMMONIA

Nitrogen, plentifully available in atmosphere, all around cannot be directly absorbed by plants and hence require proper fixation. It is usually converted first to ammonia and then to ammonium salts, most of which are highly water soluble. Ammonia is produced by the direct synthesis from elemental hydrogen contained in water and nitrogen present in the air. Isolation of these two gases in its elemental form from water and air necessitate the requirement of a large input of energy. Usually this energy requirement is provided by fossil fuels such as petroleum fractions, coal etc. Natural gas, coke oven gas, light hydrocarbon such as naphtha, fuel oil, vacuum residues from refining, coal etc., are the common feedstock for ammonia plants. Various technologies and processes are available for ammonia manufacture depending on feedstock. Steam reforming of natural gas and light hydrocarbons and partial oxidation of fuel oil; vacuum residue and coal are the commonly employed technologies for ammonia synthesis (Appl, Max. 1992).
Natural gas is preferred over the other feedstock for Ammonia (NH₃) synthesis from an environmental perspective. Ammonia production from natural gas includes process steps such as desulphurisation of the feedstock; primary and secondary reforming, carbon monoxide shift conversion and removal of carbon dioxide, which can be later used for urea manufacture; methanation; and ammonia synthesis (Fig.4.1).

Catalysts used in the process reaction may include cobalt, molybdenum, nickel, iron oxide/chromium oxide, copper oxide/zinc oxide, and iron. Around 77% of world ammonia production capacity is currently based on steam reforming of natural gas. A modern ammonia plant has a typical capacity of 1000-1800 MT per day (FM, 1998) and new plants are now being designed up to 3000 MT per day. The process and energy systems in these plants are integrated to maximize energy efficiency and reduce effluents and emission to the environment. More than 99% of world nitrogen fertiliser production is based on ammonia (UNEP, 1996).

Chemistry of the Process

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

the reforming reaction: \( \text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3 \text{H}_2 \) \hspace{1cm} (1)

the shift conversion reaction: \( \text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2 \) \hspace{1cm} (2)

Reaction (1) takes place mainly in the primary and secondary reformer. Reaction (2) takes place in both reformers to a lower extent, but mostly in the downstream shift conversion reactors (Fig.4.2).
Fig. 4.1: Flow Sheet of Ammonia Plant Based on Steam Reforming
Fig.4.2: Chemistry of the Ammonia Process
Thus, the ammonia synthesis from natural gas can be represented generally as follows:

(1) \[0.88 \text{CH}_4 + 1.26 \text{Air} + 1.24 \text{H}_2\text{O} \rightarrow 0.88 \text{CO}_2 + \text{N}_2 + 3\text{H}_2\]

(2) \[\text{N}_2 + 3\text{H}_2 \rightarrow 2 \text{NH}_3\]

The front-end reaction producing synthesis gas, normally takes place at 25-45 bar pressure, while the ammonia synthesis unit operate under pressure ranges from 100-250 bars.

**Feedstock Desulphurisation.**

Natural gas and light hydrocarbon invariably contains small quantities of sulphur compounds, which would poison most of the process catalysts. Consequently, these compounds are removed from the feed-gas by hydrogenating it at 350-400°C when the sulphur compounds are converted to \(\text{H}_2\text{S}\) in a desulphuriser, in presence of cobalt molybdenum (Comox) catalyst (Twigg, 1989).

The hydrogen sulphides (\(\text{H}_2\text{S}\)) from the feedstock stream is adsorbed on palletized zinc oxide, to form zinc sulphide. The hydrogen is normally provided by the synthesis section, and the zinc sulphide remains in the adsorption bed, which are deactivated over a period and then replaced.

**Primary Reforming**

The resulting gas feed contains less than 0.1 parts per million (ppm) sulphur and is then mixed with superheated process steam. This mixture is heated to 500-600°C and introduced to the primary reformer. The reformer is usually a rectangular tubular furnace in which the feedstock—steam mixture is heated using externally fired burners. In some cases, an adiabatic pre-reformer is also placed
before the primary reformer to ease the duty of the main reformer. The primary reformer tubes contain nickel catalyst and are externally heated by fuel. The combustion of this fuel provides the heat necessary for reaction (1).

The flue gas leaving the radiant box has a temperature of about 1100°C. Only 50-60% of the heat supplied is directly used in the process. The remaining enthalpy of the flue gas is recovered in the flue gas heat recovery train to pre-heat the incoming feedstock, for steam generation, superheating steam and for other process requirements. The flue gas leaves the convection section and is sent to the atmosphere at 100-200°C and this is the main source of emissions from the plant. They contain mainly CO₂ and small amounts of Nitrogen Oxides (NOₓ), CO and SO₂ (James G.R. and Slack A.V., 1973).

**Secondary Reforming**

Secondary reforming is partial oxidation of residual methane in the process gas from primary reformer. For this, hot process air is added to the gas stream in a specially designed water-jacketed reactor, because of which internal combustion takes place. It 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 where the reforming reaction (1) proceeds to near completion. The gases exit from the secondary reformer at a temperature of around 950-1000°C with most of the hydrocarbon in the feed converted to CO, CO₂ and H₂ together with added nitrogen (FM, 1998). The process gas is then cooled to 350-400°C in a process heat recovery steam boiler or boiler feed water heater.
CO Conversion

The cooled reformed gas contains 12-15% CO, balance being hydrogen, nitrogen, CO₂ and small amounts of argon and methane (dry basis). Most of the CO is converted to CO₂ according to reaction (2) by passing the process gas through a bed of iron oxide/chromium oxide catalyst at around 370-400°C in a high temperature converter and then over a copper oxide/zinc oxide catalyst at about 200-220°C in a low temperature converter. The residual CO content of the gas is 0.2-0.4%. At this point, the gas contain mainly of H₂, N₂, CO₂ and the excess process steam, which was supplied at the primary reforming stage. Most of this steam is condensed by cooling the gas before it enters the CO₂ removal system. The condensate normally contains 1500-2000 parts per million (ppm) of ammonia and 800-1200 ppm of methanol, as well as some CO₂ and catalyst dust etc.

In older plants, the process condensate is 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 after polishing is used as boiler feed water. (ECE/CHEM 1978, 1991).

Carbon Dioxide Removal

The converted gas usually contains about 18-22% CO₂ which is then removed by chemical or physical absorption process. The solvents used in chemical processes are mainly aqueous amine solutions or hot potassium carbonate solutions. For physical absorption solvents like glycol dimethylethers and propylene carbonate are used. The following converted processes are currently employed for absorption of CO₂.
Hot activated potassium carbonate processes

- Benfield Process (UOP)
- Catacarb Process (Eickmeyer)
- Gimmarcco Vetrocoke Process (GV)

Amine processes

- MDEA (Activated Methyl Di Ethanolamine) Process (BASF)

Physical absorption processes

- Selexol Process (UOP)
- Rectisol Process (Linde Process Technologies)
- Pressure Swing Adsorption (PSA)

In the hot potassium carbonate process CO₂ is absorbed by potassium carbonate solution to produce potassium bicarbonate, which is subsequently stripped of the absorbed gases through pressure reduction and heating up.

\[ \text{K}_2\text{CO}_3 + \text{CO}_2 + \text{H}_2\text{O} \rightarrow 2 \text{KHCO}_3 \quad \text{(absorption)} \]

\[ 2 \text{KHCO}_3 + \text{heat} \rightarrow \text{K}_2\text{CO}_3 + \text{CO}_2 + \text{H}_2\text{O} \quad \text{(regeneration)} \]

Vanadium pentoxide (Benfield), arsenic trioxide (GV), piperazine (BASF) and certain other compounds depending on the process are used as promoters or Catalysts.

In the amine processes absorption of CO₂ takes place with the formation of amine adducts that are heat sensitive and are regenerated by heating the solution.

In the physical absorption process, CO₂ is dissolved under pressure in methanol without combining in a chemical sense and regeneration take place by simple flashing of the solution.

Pressure Swing Absorption is also employed for CO₂ removal in smaller plants. The regenerated CO₂ (1.3-1.4 tonne per tonne of NH₃) is cooled and used for the manufacture of urea.
Methanation

The gas from the absorber after CO₂ removal contain only small amounts of CO and CO₂ it must be removed, because it would poison the ammonia synthesis catalyst. This is achieved by the methanation reaction in which the CO and CO₂ are converted to methane (CH₄) and water by passing it through a reactor containing nickel catalyst at a temperature of around 350 to 400°C. The methane is an inert gas in the synthesis reaction and the water formed is removed by cooling and condensing it. The gas after methanation and cooling contain hydrogen and nitrogen in the stoichiometric ratio of 3:1 and is called the synthesis gas.

Ammonia Synthesis

The synthesis gas is compressed to 100-200 bars using centrifugal compressors, usually driven by high-pressure steam turbines. The reaction uses an iron catalyst at temperatures of 350-550°C (FM, 1998). Ammonia formation reaction is exothermic, heat thus generated is used for producing steam. Usually only 20-30% of the synthesis gas is converted with each pass through the converter, thus necessitating a loop arrangement for separating the ammonia from the converter effluent and also for admitting fresh make up gas to the system. During operation inert gases contained in the synthesis gas (argon, methane etc.) tend to build up in the synthesis loop and is maintained at about 10-15% by a continuous purge. The purge gas is first cooled to separate NH₃ contained in it as then scrubbed with water to remove remaining ammonia and is then used as fuel or sent for hydrogen recovery. (FM, 1998; Strelzoff, 1981).
The cooling and condensation of the product ammonia is achieved by a refrigeration system and the product ammonia is sent to the storage.

The liquefied product ammonia is either used directly in downstream plants or stored in tanks. These tanks are usually of the fully refrigerated type in the capacity range of 10000 to 50000 MT, pressurized spheres (3000 MT) and bullets (20 MT) (Hodge C.A. and Popovici N.N., 1994).

Future developments are expected to increase the efficiency of the process, reduce emissions by lowering the steam to carbon ratio. Improvements in the secondary reforming stage and increase in the efficiency of gas purification and the synthesis loop are intended in this direction. (Czuppon T.A. and Knez S.A., 1991; LeBlanc J.R, 1986).

Partial Oxidation of Hydrocarbon or Coal

Partial oxidation processes using heavy fuel oil, vacuum residue from petroleum refining or coal offer an alternative route for ammonia production. Economics of the process depends on the relative availability and cost and quality of these feedstock and oxygen in relation to investment costs and other factors such as the environmental need to use waste materials that are otherwise difficult to dispose off.

When the feedstock is heavy fuel oil with high sulphur content or coal, non-catalytic partial oxidation at around 50 bar pressure and 1400°C is employed for gasification. Some steam is added to the gasifier to moderate the gasification temperature. A cryogenic air separation unit is needed to supply oxygen and nitrogen for the process (Fig.4.3).
Fig. 4.3: Flow Sheet of Ammonia Plant Based on Partial Oxidation
The reaction of the hydrocarbon with oxygen in the gasifier produces CO and hydrogen, as well as some CO$_2$, CH$_4$ and soot. After heat recovery from the hot and dusty gases in specially designed boiler soot is removed by scrubbing with water and separated as carbon slurry. Sulphur compounds in the feed are converted to hydrogen sulphide and it is separated from the process gas, using a selective absorption agent (which could be the same as in the CO$_2$ removal). The regenerated H$_2$S is then converted to elemental sulphur by the Claus sulphur recovery process (UNEP, 1998).

The CO is then converted to CO$_2$ by the water shift reaction upon passing through two beds of iron catalyst with intermediate cooling. The CO$_2$ is then removed by an absorption agent as in the case of the reforming route. The residual traces of CO and CO$_2$ are removed in the final purification of the gas by a liquid nitrogen wash. This results in a pure synthesis gas, to which more nitrogen is added to provide the stoichiometric hydrogen–nitrogen ratio for ammonia. As the synthesis gas so produced contain only H$_2$ and N$_2$, without any inerts, there is no need for a purge in the ammonia synthesis loop and hence loop efficiency is better, compared to the steam reforming process.

In coal gasification, the main stages are coal grinding and preparation of slurry for pulverization, in addition to those in the heavy fuel oil process.

**UREA**

Urea or Carbamide accounts for almost 50% of world nitrogenous and fertiliser production in terms of nitrogen content, and including multi-nutrient products. Urea is produced by a reaction of liquid ammonia with carbon dioxide. The process steps include synthesis, where liquid ammonia and carbon dioxide react to
form ammonium carbamate, which decomposes to form urea solution, concentration by vacuum, crystallization or evaporation to produce a melt, decomposition and recycle of unconverted reactants, prilling or granulating the melt, cooling and screening of solids, coating of the solids; and bagging or bulk loading of the product. The carbon dioxide for urea manufacture is produced from the front end of the ammonia plant.

**Reaction Chemistry**

The reaction between ammonia and carbon dioxide takes place at high pressure (140-200 bar) and high temperature (180-190°C) to form ammonium carbamate, which is then dehydrated by heat to form urea and water, according to the following reaction:

\[ 2\text{NH}_3 + \text{CO}_2 \rightarrow \text{NH}_2\text{COONH}_4 \rightarrow \text{CO(NH}_2)_2 + \text{H}_2\text{O} \]

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% on CO₂ basis). The conversion is increased by increasing the temperature, increasing the NH₃/CO₂ ratio and/or decreasing the H₂O/CO₂ ratio. Process design is mainly concerned with the most efficient separating of product urea from the other components recovery of excess NH₃ and decomposition of the residual carbamate to NH₃ and CO₂ for recycling.
Urea Processes

There are three main types of process depending upon the recovery of unconverted reactants (Zardy F., 1995).

Once-through process where the unconverted CO₂ and NH₃ are discharged to other plants, where the NH₃ is used for the production of ammonium sulphate and ammonium nitrate. Partial recycle process in which unconverted CO₂ and NH₃ 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 in which unconverted CO₂ and NH₃ are totally separated in multi-stage decomposers, recovered in corresponding multi-stage absorbers, and recycled back to the reactor.

If the unconverted NH₃ and CO₂ from the reactor outlet stream do not find use in downstream plants, a total recycle process is necessary. This was achieved in a series of decomposition stages with decreasing pressure, which cooled, condensed gases to form carbamate liquor, which was then recycled to the synthesis section. This increases the NH₃/CO₂ ratio, and hence the yield of urea. Modern stripping processes were developed which decompose the carbamate in the reactor effluent without reducing the system pressure using NH₃ or CO₂ as the stripping medium (FM, 1998).

Carbon Dioxide Stripping

If CO₂ is used as the stripping agent, urea conversion occurs at about 140 bar and 180-185°C, with a molar NH₃/CO₂ ratio of 2.95. This gives a conversion of about 60% CO₂ and 41% NH₃. CO₂ is added to the reactor effluent at about system pressure, and the stripped NH₃ and CO₂ are then partially condensed and recycled.
(Nitrogen, 1990). 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 CO₂ compressor. NH₃ and CO₂ in the stripper effluent are first vaporized and then condensed to form 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 (Fig. 4.4).

**Ammonia Stripping**

If ammonia is used for carbamate stripping, the pressure and NH₃/CO₂ ratio are somewhat higher in the synthesis section, giving a CO₂ conversion rate of 65%. Excess NH₃ is introduced to the reactor effluent, decomposing a large part of the unconverted carbamate. Residual carbamate and CO₂ 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 (Fig. 4.5).

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

The ACES process is essentially a CO₂ stripping process which operates at somewhat higher pressure (175 bar) and NH₃/CO₂ 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 (Uchino H and Morikawa H., 1995).
Fig. 4.4: Flow Sheet of Urea Manufacturing Process by Stripping
Fig. 4.5: Flow Sheet of Urea Manufacturing Process by Total Recycle
Isobaric Double Recycle (IDR) Process

This process uses both CO₂ and NH₃ as stripping agents. Operating at 200 bar and 185-190°C, with an NH₃/CO₂ ratio of 4.5, a CO₂ conversion rate of 71% is obtained, with 35% for NH₃ (Pagani et al., 1982). The reactor effluent then passes into a first stripper, which uses NH₃, and the remaining NH₃ is then separated in a second stripper, using CO₂. 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 (EFMA, 1995).

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% (Granelli F, 1996).

NITRIC ACID

Nitric acid is used in the manufacture of ammonium, calcium and potassium nitrates. These nitrates are used as straight or mixed into compound fertilisers. A modern nitric acid plant has a typical capacity of 1000-2000 tonnes per day. For fertiliser manufacturing purposes, the acid strength is usually maintained in the range of 50-65%.
The production stages for nitric acid manufacture include vaporizing the ammonia; oxidation (mixing the vapour with air and burning the mixture over a platinum/rhodium catalyst), cooling the resultant nitric oxide (NO) and oxidizing it to nitrogen dioxide (NO₂) with residual oxygen; and absorbing the nitrogen dioxide in water in an absorption column to produce nitric acid (HNO₃) (Twigg M.V., 1989).

Chemistry of the Process

Ammonia is vaporized, mixed with air and burned over a platinum/rhodium alloy catalyst. Nitrogen monoxide (nitric oxide) and water are formed according to the following reaction:

\[ 4\text{NH}_3 + 5\text{O}_2 \rightarrow 4\text{NO} + 6\text{H}_2\text{O} \]

Simultaneously, some nitrous oxides are also formed according to the following reaction:

\[ 4\text{NH}_3 + 4\text{O}_2 \rightarrow 2\text{N}_2\text{O} + 6\text{H}_2\text{O} \]

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

\[ 2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2 \]

\[ 3\text{NO}_2 + \text{H}_2\text{O} \rightarrow \text{NO} + 2\text{HNO}_3 \]

An yield of 97% NO can be achieved with burners at less than 1.7 bar with evolution of heat. The oxidation of nitric oxide requires high pressures but low temperatures. The heat of ammonia oxidation is used to pre-heat the waste gas and produce superheated steam. The pre-heated waste gas drives a turbine for air compression to recover energy and is then vented to the atmosphere. After this heat exchange, the combustion gas temperature drop from over 800°C to less than 200°C and is further reduced by
water cooling. The water produced is condensed in a cooler/condenser and transferred to the absorption column.

These reactions occur simultaneously. The combustion gas receives additional air to increase the oxygen content, and NO₂ is formed as the mixture cools. Since the formation of acid is exothermic, continuous cooling is required in order to promote the conversion of NO to NO₂. 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 (FM, 1998).

Processes

Two types of processes are currently in vogue. They are classified as single pressure and dual pressure, according to the pressures used in the oxidation and absorption stages. The second option is broken into high pressure and medium pressure designs. In mono 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 (Slack A.V., 1968).

Mono Pressure Plants

This design is generally used in smaller plants. Ammonia oxidation and absorption of nitrogen dioxide occur at the same relative pressure (Fig.4.6). This reduces the complexity and capital cost of the dual pressure plant, but at a compromise of efficiency loss, potentially for both the front and back ends of
Fig. 4.6: Flow Sheet for Nitric Acid Process
the plant. Single pressure plants can be designed to operate at low to medium pressure to favor the ammonia oxidation reaction; at high pressure to favour the absorption reactions; or at any operating pressure in between (FM, 1998).

Dual pressure plants are similar as far as the cooling section. Then compression of nitrogen oxides 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 NOx stripping column, and the air and stripped NOx return to the NOx gas compressor.

**Dual Pressure Plants**

This design is generally used in medium and larger plants. Ammonia oxidation occurs at low pressure. This decreases the gas density and the nitrogen loading on the gauze. The result is an increase in efficiency of the ammonia oxidation reaction and minimization of platinum catalyst loss. Absorption of nitrogen dioxide occurs at high pressure to maximize the partial pressure of the gas phase reactants. The result is an increase in the rate of the nitrogen monoxide oxidation reaction and the solubility of oxygen and nitrogen dioxide in the aqueous solution. A nitrous gas compressor boosts the pressure from the front end of the process (ammonia oxidation) to the back end (absorption) (FM, 1998).

**SULPHURIC ACID**

Sulphuric acid is produced from elemental sulphur, pyrites as well as other scrubbing gas stream. Over 60% of world sulphuric acid production (100% H₂SO₄) is used in the fertiliser industry, the remainder being used in a very wide variety of other industrial applications.
Chemistry of the Process

The principal steps in the process consist of burning sulphur (S) in air roasting of pyrites to form sulfur dioxide (SO₂), combining the sulphur dioxide with oxygen (O₂) to form sulphur trioxide (SO₃), and combining the sulphur trioxide with water (H₂O) to form a solution containing sulphuric acid (H₂SO₄).

(1) \( S + O_2 \rightarrow SO_2 \) (sulphur burning)
(2) \( 2FeS_2 + 1\frac{1}{2}O_2 \rightarrow Fe_2O_3 + 4SO_2 \) (pyrites roasting)
(3) \( SO_2 + \frac{1}{2}O_2 \rightarrow SO_3 \) (oxidation)
(4) \( SO_3 + H_2O \rightarrow H_2SO_4 \) (absorption)

Elemental sulphur is melted by heating to 135°C and then burned in a combustion unit at temperatures ranging from 900°C to 1800°C, followed by gas cooling. The SO₂ content of the combustion gas entering the conversion process is generally 9-12% vol. (EFMA, 1995).

Alternatively, pyrites are roasted in various types of furnaces, producing a lower SO₂ content, which is diluted to 8-10% SO₂ before conversion. Ores containing zinc, copper and lead sulphides are also similarly roasted, usually producing lower SO₂ contents. Metal sulphates are also roasted using elemental sulphur and pyrites. Coke, tar, lignite, coal or oil are used as both fuel and reducing agents. In this case, the SO₂ content of the combustion gases vary considerably, but after cleaning and drying, the process gas usually contains around 6-7% SO₂.

The combustion of hydrogen sulphide (H₂S), carbon disulphide (CS₂) and carbonyl oxide (COS) is carried out in a muffle furnace at 800-1200°C, and
combustion gases are variable, containing 0.5-12% SO₂. Iron sintering and other similar processes also give widely varying SO₂ 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°C, producing gases containing 2-10% SO₂, depending on the quality of the spent acid. To compensate for varying quality, a sulphur burner can be fitted to provide supplementary SO₂.

Processes

Four types of sulphuric acid processes are currently used in the industry i.e., single contact, double contact, pressure contact, and wet contact.

In single contact plants, SO₃ 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 SO₂ content of the combustion gas is low and widely varying.

In the case of the roasting of metallic sulphides (or possibly oxides) the SO₂ containing gases are first cooled, cleaned and dried and then oxidized to SO₃ in the presence of catalysts containing alkali and vanadium oxides (Monsanto, 2000).

In the case of sulphur burning acid units, the air is dried before combustion. The SO₃ 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 SO₂ content in the feed gas, the lower the conversion efficiency.
The oxidation and absorption steps in the manufacture of sulfuric acid from sulphur are all highly exothermic. The excess heat generated at each step of the process is recovered in the waste heat boiler, super heater, and economizers. The recovered heat is in the form of high-pressure superheated steam, which can be used to generate electric power in a turbo generator. The process is designed to give a conversion of sulphur dioxide to sulfuric acid of over 99.7% in the acid plant as well as a high conversion of process heat to steam. Atmospheric air is drawn through an air filter through a drying tower with 98% circulating acid and into the main compressor. Some of the sensible heat of the acid in the drying tower is transferred to the air. This sensible heat, plus the heat of compression by the main compressor, raises the temperature of the air entering the horizontal spray sulfur burner where sulfur is burned to sulfur dioxide. The SO₂ gas stream is typically 11.5% SO₂, 9.5% O₂ and 79% N₂ by volume (Duecker and West, 1959). The temperature of the SO₂ gas from the sulfur burner is cooled in a waste heat boiler, by generating as high pressure saturated steam.

Double Absorption

The basic concept of the double absorption process is to further increase the conversion reaction and reduces tail gas SO₂ emissions from the acid plant by providing secondary SO₂ to SO₃ conversion and SO₃ absorption stages following the primary conversion and absorption stages. In general, primary conversion consists of three catalyst passes and secondary conversion consists of just one catalyst pass. This final pass achieves further conversion because the SO₃ formed in the primary passes is removed in the inter-pass absorption step (Fig.4.7).
From the waste heat boiler, the gas flows to the first pass of the converter system where it is partially converted to sulfur trioxide gas in the presence of vanadium catalyst. The heat of conversion reaction is cooled by superheating steam to improve the yield of the sulfur dioxide oxidation in the next catalyst pass. The temperature of the steam and inlet gas temperature is controlled in the proper range by bypassing a portion of the steam flow around the super heater. The cooled gas stream flows from the super heater to the second converter pass where additional conversion of the sulfur dioxide to sulfur trioxide takes place accompanied by the generation of additional heat. Hot gases leaving the second converter pass are cooled by sending them through the hot interpass gas heat exchanger.

Cooled gases leaving the heat exchanger flow to the third converter pass where additional conversion of sulfur dioxide to sulfur trioxide takes place. Hot gases
leaving the third converter pass are cooled by the cold interpass heat exchanger and an economizer, in route to the interpass, or intermediate, absorption tower.

In the interpass tower, the SO$_3$ is removed from the gas stream by absorbing it in the circulating sulfuric acid, in order to allow further conversion of the remaining SO$_2$ to SO$_3$.

The temperature of the 98-99% H$_2$SO$_4$ circulated over the interpass absorbing tower increases due to the sensible heat of the gas stream entering the tower and from the heat of formation of H$_2$SO$_4$. Acid from the bottom of the interpass absorbing tower drains to the pump tank where it is combined with acid from the other towers, and is then pumped through the coolers and circulated back to the top of the tower.

Sufficient water is added to control the strength of acid circulated over the towers between 98-99%. Cool gas leaving the interpass-absorbing tower, containing unreacted SO$_2$ is heated and sent to the third converter pass.

From the hot interpass heat exchanger, the gas stream flows to the fourth converter pass where final conversion of SO$_2$ to SO$_3$ is accomplished. The temperature to the fourth converter pass is controlled by bypassing a portion of gas around the cold and hot interpass heat exchangers.

The gas stream leaving the fourth pass enters the split water flow economizer where it is cooled by boiler feed water. Gas leaving the economizer enters the final absorbing tower prior to exhausting to the atmosphere through a stack.

In the final absorbing tower, SO$_3$ in the gas stream is absorbed by water in the 98-99% circulating acid. The temperature of the strong acid circulated over the final absorbing tower increases due to the heat of formation and the sensible heat of the gas.
stream entering the tower. The acid from the bottom of the final absorbing tower flows into the pump tank, where it is combined with acid from the other towers, and then it is pumped through the coolers and circulated back to the top of the towers. Some of the 98% acid from the acid circulation system is pumped to the dilution system where it is diluted to 93% for storage, use, or sales.

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 SO$_2$ in the intermediate absorber shifts the reaction equilibrium towards the formation of SO$_3$ in the residual gas, resulting in an overall conversion efficiency averaging 99.6% (based on sulphur burning).

**Pressure Contact Process**

The oxidation of SO$_2$ is favored by pressure. Hence, pressure contact processes have been developed in which SO$_2$ conversion and SO$_3$ absorption are both achieved at high pressure. Even higher conversion efficiency is claimed for this type of process, and the tail gas SO$_2$ content is reported to be only 200-250 parts per million by volume (ppmv).

**Wet 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 SO$_2$ and H$_2$O and the sulphur dioxide is converted to SO$_3$, which together with the formed steam yields sulphuric acid. The process has been used to treat waste gases containing at least 10% H$_2$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 fiber plants. Gases with a lower H₂S 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 (UNEP, 1998).

PHOSPHORIC ACID

Plants require large quantities of phosphorus which is involved in its numerous functions, especially those requiring energy. Phosphorus is indeed the energizer in food production by plants.

Some 70% of world phosphate fertiliser production, conventionally measured in terms of phosphorus pentoxide (P₂O₅), uses phosphoric acid as the main intermediate. Virtually all phosphoric acid is now produced by wet processes, i.e. by acidulation of mineral phosphates. Phosphate acidulation may be achieved using nitric, hydrochloric or sulphuric acids (Slack A.V., 1968).

If nitric acid is used the product would be for the multi-nutrient fertilisers called nitro phosphates. Hydrochloric acid is used only in very special circumstances, since this acid is normally more expensive than other acids. The great bulk of phosphoric acid is produced using sulphuric acid.

Chemistry of the Process

A simplified reaction equation for the dihydrate process is as follows:

\[
\text{Ca}_3(\text{PO}_4)_2 + 3 \text{H}_2\text{SO}_4 \rightarrow 2\text{H}_3\text{PO}_4 + 3\text{CaSO}_4
\]
This reaction proceeds with the formation of calcium sulphate (gypsum) on the surface of the phosphate particles, thus blocking its continuation. This is mostly overcome by grinding the phosphate to a suitable particle size to increase the surface area of the reaction, and recirculating phosphoric acid into the reaction, according to the following reactions:

\[
(2) \text{Ca}_3(\text{PO}_4)_2 + 4\text{H}_3\text{PO}_4 \rightarrow 3\text{Ca(H}_2\text{PO}_4)_2
\]

\[
(3) 3\text{Ca(H}_2\text{PO}_4)_2 + 3\text{H}_2\text{SO}_4 \rightarrow 3\text{CaSO}_4 + 6\text{H}_3\text{PO}_4
\]

The phosphoric acid is normally filtered away from the phosphogypsum (Becker P, 1989). Mineral phosphate contains small quantities 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 purity. Depending on the process, between 20% and 40% of the cadmium in the phosphate rock passes into the phosphogypsum, the remainder into the phosphate fertiliser.

Processes

There are five main phosphoric acid processes viz, dihydrate; hemihydrate; di-

hemihydrate (double stage); hemi-dihydrate (single stage); and hemi-dihydrate (double stage).
Dihydrate Process

The dihydrate process has three stages: reaction, filtration and acid concentration. The reaction takes place in a series of agitated reaction tanks or compartments of a single tank to which ground phosphate (particle size <150 microns) is added and gypsum is precipitated in the dihydrate form at an acid concentration of 26-32% P₂O₅ (Fig.4.8).

Fig.4.8: Flow Sheet of Phosphoric acid Process (Dihydrate)
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. (A.V. Slack, 1968)

About 4.5 to 5 tonnes of calcium sulphate dihydrate (CaSO₄ or gypsum) are produced for each tonne of P₂O₅ in the product acid. The initial filtration is followed by at least two washings to maximize P₂O₅ recovery under vacuum conditions. 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 fertiliser 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, fluoro-silicic acid scrubber and piping.

**Hemi Hydrate Process**

In this process operating at around a temperature of 100°C and at higher acid concentration in the reaction stage (40-52% P₂O₅), the gypsum is precipitated in the hemi-hydrate form. There is substantial savings in capital investment, energy, but the smaller, poorly formed crystals are more difficult to filter, unless crystal habit modifiers are used. P₂O₅ losses are more (6-10%) compared to the dihydrate process (FM, 1998) (Fig. 4.9).
Losses of P$_2$O$_5$ can be partially recovered, if the gypsum is crystallized to its other hydrate, either before or after being separated from the acid. The following processes have been developed on these lines (Fig.4.10).
Fig. 4.10: Flow Sheet of Phosphoric Acid Process (Dihemihydrate)

i) HRC process: Acidulation of rock under hemihydrate conditions, recrystallization to dihydrate without intermediate hemihydrate separation and product separation;

ii) HDH process: Acidulation under hemihydrate conditions, product separation, recrystallization to dihydrate and filtration and recycling of liquors;

iii) DH/HH process: Acidulation under dihydrate conditions, product separation, recrystallization to hemihydrate and filtration and recycling of liquors (Phosphorous and Potassium, 1991).
All the three processes offer substantially lower P<sub>2</sub>O<sub>5</sub> losses (2-3%), lower sulphuric acid consumption and purer gypsum. The latter may possibly be used directly for plasterboard, plaster, or as a cement-retarding agent.

**Ammonium Sulphate**

Ammonium sulfate one of the oldest mineral fertilisers, is produced through direct neutralization of ammonia with sulfuric acid. It is also obtained as a Caprolactam by-product from the petrochemical industry.

\[ 2 \text{NH}_3 + \text{H}_2\text{SO}_4 \rightarrow (\text{NH}_4)_2\text{SO}_4 + \text{H}_2\text{O} \]

The reaction between ammonia and sulfuric acid produces an ammonium sulfate solution that is continuously circulated through an evaporator to thicken the solution and to produce ammonium sulfate crystals. The crystals are separated from the liquor in a centrifuge, and the liquor is returned to the evaporator. The crystals are fed either to a fluidized bed or to a rotary drum dryer and are screened before bagging or bulk loading (FM, 1998; Gopinath N.D., 1968; George K.C. and Gopinath N.D., 1963).

**Ammonium Nitrate (AN) and Calcium Ammonium Nitrate (CAN)**

Neutralizing nitric acid with gaseous ammonia produces ammonium nitrate.

\[ \text{NH}_3 + \text{HNO}_3 \rightarrow \text{NH}_4\text{NO}_3. \]

The reaction is exothermic, producing ammonium nitrate solution and steam. In a second stage, the ammonium nitrate solution is evaporated to the desired concentration, depending on whether it will be finally prilled or granulated.

To produce calcium ammonium nitrate (CAN), the ammonium nitrate solution is mixed with a filler containing dolomite, calcium carbonate, ground
limestone or, quite frequently, by-product calcium carbonate from a nitro phosphate plant. This mixture can also be either prilled or granulated.

The neutralization reaction takes place in free-boiling vessels, 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 ammonium nitrate 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.

Most of the water in the ammonium nitrate solution must be evaporated away before the solidification process. This may be done at about atmospheric pressure or under vacuum. During evaporation, some ammonia is boiled off in the falling film evaporators and heat exchangers (Nebel R., 1985). The product solution is maintained at a temperature, which avoids crystallization. The water content shall be maintained at less than 1% for a good quality prilled product and 3-8% for granulation processes. The prilling of ammonium nitrate is similar to that of urea. The product sprayed from the top dries up in the upward draft of air from the bottom of the tower. Some ammonia and ammonium nitrate is carried away in the air stream. Wet scrubbing of the exit air stream removes ammonia contained in it and mist eliminators remove the product particles.

Granulation is done with rotating drums and pans or fluidized beds. 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 ammonium nitrate solution either before or during granulation.
Product granules and prills are cooled in rotary or fluid bed coolers, with the air cleaned by cyclones, bag filters or wet scrubbers. This air is then recycled to the drier. The product is treated with an anti-caking agent to avoid lump formation.

**Single Super Phosphate (SSP) and Triple Super Phosphate (TSP)**

Super phosphates account for over one quarter of world phosphate fertiliser production. Single super phosphate (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 single super phosphate retains its importance wherever sulphur deficiency limits crop yields.

Triple super phosphate contains little sulphur, because it is produced by acidulating the mineral phosphate with phosphoric acid, instead of sulphuric acid. Double or enriched super phosphate 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. There are always two stages in the manufacture of granulated single super phosphate, the first to manufacture powdered single super phosphate and the second to granulate (FM, 1998). However, in the case of triple super phosphate, there are two alternatives as in the case of single super phosphate, run-of-pile (ROP) material may be used. The run of pile material is prepared by reacting phosphate rock with phosphoric acid with a $\text{P}_2\text{O}_5$ concentration of 50 to 54%, but a lower concentration may be used, followed by granulation (UNEP, 1996).
Multi-Nutrient Fertilisers

Large quantities of multi-nutrient fertilisers (NP/NPK/NK/PK) are produced simply by dry mixing (or blending) single-nutrient materials without acidulation or chemical reaction (FM, 1998) (Fig. 4.11).

Fig. 4.11: Flow Sheet of Compound Fertilisers (NPK) Process
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 nitro phosphoric acid, as described above. Acids are then mixed, and an ammonium nitrate solution may also be added. The mixture is neutralized with gaseous ammonia and other materials may be added either during or after neutralization. These may include ammonium phosphate, ammonium sulphate, super phosphate and potassium salts.

The slurry is then fed into a buffer tank, from which it passes to granulation, drying, screening, cooling and coating. The acids may be mixed in reactor tanks or in pipe reactors, together with ammonia, ammonium nitrate solution and solid materials. Alternatively, a drum granulator may be used with a mixture of mainly solid materials, together with ammonium nitrate solution, and/or sulphuric acid and ammonia (Bhandarkar P.G. and Paudpiece, 1995).

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 dedusting, air from the cooling section is normally recycled to the dryer.

Phosphoric Acid Route Process

Monoammonium phosphate (MAP) and diammonium phosphate (DAP) are made by ammoniating phosphoric acid in a neutralizer to produce a slurry, which is granulated. 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 sulphuric acid (H$_2$SO$_4$) and ammonia (NH$_3$) to promote the reaction. Granules are dried and cooled in rotary drums. Oversize and undersize material is screened out, crushed and recycled.

The Nitric Acid Route Process

Complex grade (NP and NPK) fertilisers 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 instead of calcium sulphate, and this can be either granulated and used directly as a fertiliser, made into liquid fertiliser solutions, or converted into calcium ammonium nitrate CAN.

Nitrophosphates

The basic reaction for the production of nitro phosphoric acid is:

$$Ca_3F(PO_4)_3 + 10HNO_3 \rightarrow 3H_3PO_4 + 5Ca(NO_3)_2 + HF$$

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:

$$H_3PO_4 + HNO_3 + Ca(NO_3)_2 + 4 H_2O \rightarrow H_3PO_4 + HNO_3 + Ca(NO_3)_2.4H_2O$$

The solution of nitro phosphoric acid can then be separated from the calcium nitrate crystals by filtration or centrifugation (FM, 1998). The solution is neutralized with ammonia, mixed with potassium and magnesium salts or micronutrients, and finally granulated (Fig.4.12).
Fig. 4.12: Flow Sheet of Nitro Phosphoric Acid Process

The nitro phosphoric acid solution is then neutralized with ammonia. The reaction is highly exothermic, and the evolved heat is used for evaporating the resulting slurry and the product is prilled. Neutralization under pressure produces vapour containing 2-8% NH₃. This is scrubbed with process water, and the scrubbing liquor is returned to the process. Scrubber vapours are condensed, part of the 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 all the condensate are collected in an ammonia condenser tank (UNEP 1998) (Fig.4.13).
Evaporation also produces off-gases, which must be scrubbed to recover NH$_3$ and fluorine. The scrubbing liquor is recycled to the process. The neutralization and evaporation sections may be connected to a common NH$_3$ condensate stripping system, and the effluent from this contains some nitrogen in both ammonium and nitrate forms.

The evaporated NP or NPK solution may be prilled or granulated (Fig.4.14). 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.
ENVIRONMENTAL PROBLEMS ASSOCIATED WITH FERTILISER MANUFACTURING

Like any other chemical processing industry, mineral fertiliser plants also contribute to atmospheric emission, effluent and solid waste generation. These environmental problems have repercussions at the local as well as global levels. Over the last 25 years considerable developments in technology has taken place in order to minimize the adverse environmental impacts. Even with the latest technology it has not been possible to fully ward off the ill effects arising out of the thermodynamic inefficiencies of the available systems and equipment. With the development of an overall awareness of the environmental degradation in the seventies of the last Century and consequent enactment of a host of national and international legislation, the issue of environmental protection has emerged as a major political issue which led to tight regulation of manufacturing industries including the fertiliser industry.

The environmental impact of a fertiliser plant depends on a wide variety of circumstances, including the nature of the plant, its design integrity, vintage, the processes and raw materials or feedstock which it uses, the location of the site, the nature of its surroundings, the regulations to which it must conform and the expertise of its operation and management network. Table 4.1 lists the potential sources of pollutants from fertiliser plants.

It includes plant wise solid, liquid and gaseous pollutants and the streams containing such pollutants. Let us discuss these issues plant wise.
Table 4.1
Fertiliser Industry Effluents and their Sources

<table>
<thead>
<tr>
<th>Plant</th>
<th>Solid Waste</th>
<th>Liquid Effluent</th>
<th>Gaseous Emissions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ammonia</td>
<td>Spent Catalysts</td>
<td>Process condensate</td>
<td>Ammonia</td>
</tr>
<tr>
<td></td>
<td>Sludge from equipment</td>
<td>CO₂ removal solutions</td>
<td>Carbon dioxide</td>
</tr>
<tr>
<td></td>
<td>Insulation debris</td>
<td>Cooling tower blow down</td>
<td>Furnace flue gas</td>
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<tr>
<td></td>
<td>Construction debris</td>
<td>Boiler blow down</td>
<td>Vent gases</td>
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<td></td>
<td>Oil Sludge</td>
<td></td>
<td></td>
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<tr>
<td>Urea</td>
<td>Nil</td>
<td>Process condensate</td>
<td>Prilling tower dust</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Gland leakages from pumps</td>
<td>Ammonia</td>
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<tr>
<td></td>
<td></td>
<td>Floor washings</td>
<td></td>
</tr>
<tr>
<td>Sulphuric Acid</td>
<td>Sulphur sludge</td>
<td>Water treatment effluents</td>
<td>Acid mists</td>
</tr>
<tr>
<td></td>
<td>Spent Catalyst</td>
<td></td>
<td>SO₂/SO₃ in stack</td>
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<td></td>
<td>Packing etc.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Phosphoric Acid</td>
<td>Gypsum</td>
<td>Plant washings</td>
<td>Fluorine</td>
</tr>
<tr>
<td></td>
<td>Sludges</td>
<td></td>
<td>Particulate matter</td>
</tr>
<tr>
<td></td>
<td>Radioactivity</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nitric Acid</td>
<td>Spent Catalysts</td>
<td>Plant washings</td>
<td>Nitrogen oxides</td>
</tr>
<tr>
<td>Complex</td>
<td>Spillages</td>
<td></td>
<td>Ammonia</td>
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<tr>
<td></td>
<td>Slurry from drainage/washing</td>
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<td></td>
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<tr>
<td>Ammonium Sulphate</td>
<td>Spillages</td>
<td>Plant leakages</td>
<td>Particulate matter</td>
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<td></td>
<td>Chalk slurry</td>
<td></td>
<td>Ammonia fumes</td>
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<tr>
<td>Power Generation</td>
<td>Oil sludge</td>
<td>Water treatment effluents</td>
<td>Sulphur dioxide in flue gas</td>
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<td></td>
<td></td>
<td>Oil spillage</td>
<td></td>
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<tr>
<td>Water Treatment</td>
<td>Used resins</td>
<td>Regeneration effluents</td>
<td>Nil</td>
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<td></td>
<td>Sludge from equipment</td>
<td></td>
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</tr>
</tbody>
</table>
AMMONIA PLANT

Emissions

Emissions from ammonia plants comprise of light hydrocarbons from storages, hydrogen, carbon dioxide, sulphur dioxide, ammonia, carbon monoxide and gaseous leak from flanges, stuffing boxes and dust and particulate matter from catalyst handling operations (Pachayappan V, 1980). Plant start-up may involve the flaring of synthesis gas, and in this case some oxides of nitrogen emissions may also come. Typical ammonia process based on steam reforming generate around 2.2 tonne of carbon dioxide, and less than one kilogram of nitrogen oxides and 0.2 kilogram of sulphur dioxide per tonne of ammonia produced. In the partial oxidation process 2.7-2.8 tonnes of carbon dioxide, 1.8 kilogram of nitrogen oxides and 3 kilogram of sulphur dioxide are produced per tonne of ammonia.

Carbon dioxide (CO$_2$) is a greenhouse gas and contributes to global warming. The production of urea requires about 1.6 tonnes of CO$_2$ per tonne of nitrogen. The fertiliser industry’s share of the annual net addition of CO$_2$ to the atmosphere resulting from human activities is estimated at 2%; and human activities account for only 7% of the quantity released annually by biological processes. Consequently, the share of fertiliser production in the total annual release of CO$_2$ to the atmosphere is very small—in the range of 0.1-0.2%. Nevertheless, the projected growth of fertiliser use makes it all the more desirable that the industry should keep CO$_2$ emissions as low as possible. Since technological limits to energy efficiency have been almost attained in new generation plants whose energy consumption is less than 20% of the theoretical requirement future limitation of CO$_2$ emissions will have to come from the replacement of old, inefficient plants.
The fixation of by-product carbon dioxide as urea reduces the total carbon dioxide emissions considerably. Hence ammonia plants are most often associated with equivalent capacity urea plants also. Emissions also depend on the process and raw materials used as well as on the standards of operation and maintenance. Conventional combustion in the reformer furnace gives rise to nitrogen oxides (NOx) in the flue gas and it increases with increase in the combustion temperatures (Stern A.C. et al., 1984). Steam injection and use of low NOx burners are control mechanisms adopted to reduce formation of nitrogen oxides. Usually the furnace is operated with excess air and hence the chances of formation of carbon monoxide (CO), usually a product of incomplete combustion, is remote.

Sulphur, an impurity invariably present in all petroleum fractions, get converted to its compounds that are major sources of pollution during the manufacturing process. Natural gas, unlike other petroleum feedstock, contains only very small quantities of sulphur (up to 5 mg/Nm$^3$) and is entirely removed by hydrogenation. In the case of naphtha the sulphur content in the range of 1000-1500 parts per million (ppm) and is usually removed by hydrofining or hydrodesulphurisation process prior to reforming. Thus in steam reforming of natural gas or light hydrocarbons sulphur emissions are negligible. However, larger amounts of sulphur are present in heavy oils and coal. Partial oxidation processes extract up to 95% of sulphur in the elemental form in a Claus sulphur recovery unit. Depending on recovery equipment, up to 3 kilogram sulphur dioxide per tonne of ammonia could be emitted from coal and fuel oil based plants, compared with less than 0.01 kilogram in gas-based plants. Plants employing steam-reforming technology have lower emissions compared to partial oxidation processes.
There shall be no ammonia emission (odour concentration 18-35 mg/Nm³) from plants unless there is a leak or so. All ammonia bearing streams such as high pressure loop purge gas from the synthesis unit etc., are scrubbed with water, ammonia is recovered and the rest is used as fuel in the reformer furnace.

During plant start up and shutdown when nickel catalyst temperatures are in the range of 100-150°C, in presence of carbon monoxide, there is a chance of formation of poisonous Nickel Carbonyl (NiCO₄) in the reformer (Twigg M.V., 1989). Usually this situation is avoided by careful manipulation of the operating temperatures.

Modern developments in gasification and ammonia process technology such as excess air reforming and auto thermal reforming provide significant reductions in emissions. Auto thermal reforming also reduce total energy consumption by necessitating (increased) power import and decreasing net heat loss. (Czuppan T.A and Knez S.A., 1991). Specific energy consumption has decreased continuously in new plants over the last 25 years, and the optimal energy consumption of new plants are in the range of 6.5-7 Giga Calories (GCal) per tonne of ammonia as against the theoretical minimum of around 6 GCal.

Effluents

Process condensate, from excess steam put to the primary reformer, is produced upon cooling the converted gas upstream of carbon dioxide removal unit is a source of liquid effluent from the plant. Usually around one cubic metre of condensate per tonne of ammonia is generated and it contain up to 1000 ppm each of ammonia and methanol as pollutants. Most of this condensate can be recovered as steam and recycled by stripping with process steam feed to the primary reformer. The
stripped condensate which contains not more than 50 ppm each of these pollutants can be further purified by ion exchange method and then used as boiler feed water. (ECE/CHEM'78, 1991). Similarly, ammonia from purge and flash gases from the synthesis loop are recovered by absorption in water followed by distillation in a closed loop. The lean gases from the stripper and purge recovery system are routed along with other off gases to the furnace.

Blow down from boilers, cooling tower and regeneration effluents from water conditioning plants also contribute to generation of wastewater.

In addition to the above in the non-catalytic partial oxidation process, water containing suspended and dissolved impurities; soot and slag are produced, which necessitates treatment using mechanical, chemical and biological means.

**Solid waste**

Spent catalysts and molecular sieves, used up resins, sludge from process vessels, packaging materials, insulation rejects etc., are sources of solid waste generated in modern ammonia plants. Usually eight or nine different catalysts are used in a steam-reforming based ammonia plant and most of these catalysts have an average useful life of around 2 to 6 years after which they are replaced. In the case of partial oxidation plants the number of catalysts used are only three or four. These catalysts contain heavy and toxic metals such as hexavalent chromium, nickel, zinc, iron, mineral supports etc., and hence cannot be disposed as landfills. Some of these spent catalysts are used for metal recovery.
Additives used in the potassium carbonate solution used for absorption of carbon dioxide such as vanadium pentoxide, arsenic tri oxide, amines are also hazardous.

Start up and shut downs cause majority of the process emissions from the ammonia plant. Reduction in start up time, recovery of vent gases as fuel and use of flare will reduce air pollution during start up and shut down.

The economically achievable minimum emission levels vary among old and new plants. Assuming steady-state production, oxides of nitrogen can be limited to 0.45 kilogram nitrogen oxides per tonne of ammonia (75 ppmv or 150 mg/Nm$^3$) in new plants, and about twice this in olden plants. Ammonia in wastewater can be reduced to 0.1 kilograms per tonne of ammonia produced. Spent catalysts can be limited to about 0.2 kilogram per tonne of ammonia. Environmental investment and operating costs vary according to emission standards or targets to be achieved, process design, integration with other facilities, raw materials, revamping requirements etc.

The modern ammonia plant is characterised by large capacities and involves the storage, transport and handling of several hazardous and toxic materials in huge quantities. These involve petroleum feedstock and fuel, carbon monoxide, hydrogen, ammonia etc., that are hazardous. Hence it is necessary that a comprehensive safety and risk analysis be carried out to operate and maintain these plants safely.
NITRIC ACID

Emissions

The main atmospheric emission from nitric acid plants are oxides of nitrogen (NOx)-nitrous oxide (N₂O), nitrogen peroxide (NO₂) and nitric oxide (NO). The concentration of these gases vary between 75 and 2000 ppmv depending on final acid concentration, pressure of the process, cooling temperatures, and degree of tail gas treatment available. Reduction in nitrogen oxides is usually achieved by absorption in cold dilute 25 to 30% nitric acid followed by stripping desorption and recycling the gas back to the process, acid or alkaline chemical absorption, adsorption on molecular sieves, catalytic reduction with natural gas or other hydrocarbon fuel or selective catalytic reduction with ammonia (Hodge C.A. and Popovici N.N., Ed. 1994).

Effluents

Wastewaters from nitric acid plants come from water treatment unit, cooling towers and boiler blow down. The wastewater contains some dissolved salts and small amounts of ammonia, which are of little environmental significance. Wastewaters are cooled and neutralized if necessary and any significant ammonia content is vaporized and recycled to the process. The purging and sampling of ammonia and nitric acid solutions and the periodic replacement of lubricating oil in rotating equipment may also give rise to occasional generation of effluents which can be collected and recycled.
Solid waste

Spent catalysts and resins are major solid waste generated from nitric acid plants. The platinum/rhodium catalyst after use is usually returned to the manufacturer for recovery of precious metals. Spent resins are burned in kilns.

Nitrous oxide ($N_2O$) emissions can be minimized by various means such as extended absorption in water to achieve a concentration of 100 ppmv. Alkaline absorption by treating the tail gas with sodium hydroxide solution produces nitrite solutions which is then be treated and safely disposed or sold. In non-selective catalytic reduction hydrogen or a hydrocarbon fuel is burned along with the tail gas over a platinum, rhodium or palladium catalyst to reduce nitrous oxide to nitric oxide. Tail gases may need to be pre-heated, and the use of hydrocarbon fuel release of carbon monoxide and hydrocarbons to the atmosphere. In selective catalytic reduction ammonia is used to reduce nitrogen oxides to nitrogen over a catalyst such as vanadium pentoxide, platinum, iron/chromium oxides or zeolites. If there is some ammonia leakage, depending on catalyst efficiency, and the tail gas must be kept above $100^\circ C$ after expansion. On the other hand with ammonia addition and with a high efficiency catalyst, and nitrogen oxides can be reduced to about 100 parts per million by volume (ppmv).

Extended absorption and selective catalytic reduction are appropriate treatment techniques depending on their technical and economic feasibility. A Selective Catalytic Reduction (SCR) unit costs less than a new absorption tower, but the latter would have much lower associated running costs. With the above systems it is possible to achieve a reduction of nitrogen oxides to at least 150 ppmv (1.6 kilogram per tonne of 100% nitric acid), whilst the economic target for existing
plants should be 400 ppmv (4.2 kilogram per tonne), except in the case of low-pressure plants, where a realistic target would be 1000 ppmv (10.4 kilogram per tonne).

**Urea Plant**

*Emissions*

Urea plant capacities are normally commensurate with that of ammonia and carbon dioxide that are available from associated ammonia plants. Atmospheric emissions from this plant are mainly ammonia and urea dust arise out of the prilling or granulation process.

The ammonia emissions are from leaks in the plant and degradation of urea to form biuret in the prilling tower. Much of the dust from prilling towers and granulators is caused by condensation products of urea vapours.

Particulate emissions occur from seeding dust, undersize prills or granules, broken prills and also due to attrition. Prilling towers with natural draft may have less attrition and, hence, less dust than those with forced draft. Prilling tower, emissions range from 0.5 to 1 kilogram ammonia and 0.5-1.5 kilogram urea dust per tonne of product. With granulation, the granulator exit gas is scrubbed and losses can thereby limited to 0.25-0.8 kilogram of ammonia and 0.25-0.4 kilogram of urea dust per tonne. Without scrubbing, dust emission from granulators would be in the range of 5-30 kilogram per tonne or more, depending on granulation efficiency. In older plants, ammonia emitted from vents are typically be maintained within a range of 0.2-0.75 kilogram per tonne of urea, depending on the process and its operating efficiency, but
in new plants this is reduced to as low as 0.06 kilogram per tonne (Hodge C.A. and Popovici N.N., Ed. 1994).

**Effluents**

Waste water from urea plants include the process condensate from the vacuum concentration stages (around 0.5 tonne per tonne urea) and the steam and turbine condensate (0.4 and 0.2 tonne per tonne urea respectively) and small quantities of oily water from equipment. The process condensate is normally treated and reused as boiler feed. Low-pressure steam so generated is used for process heating, in turbines, or exported to other plants. The waste water normally contains about 2% ammonia, 4% carbon dioxide, and 1% urea by weight and must therefore be treated in a thermal Hydrolyser-Stripper (Lammen W., 1994). The recovered gases are recycled to the synthesis section and the effluents now contain only around 0.0025 kilogram ammonia and 0.0005 kilogram urea per tonne of product. Alternatively the ammonia bearing effluents are also biologically treated, initially oxidizing to nitrate and then by de-nitrifying to nitrogen gas (Dave J.M., 1992).

**Solid waste**

There are no solid wastes from urea plants except spillages of product and mechanical refuse which can be fully retrieved.

**Ammonium Nitrate (AN) and Calcium Ammonium Nitrate (CAN) Plants**

Atmospheric emissions from these plants are particulates and ammonia which on an average comes to around 2 kilogram per tonne of product. In new generation plants using the best available technology (BAT) the above content is reduced to as
low as 0.5 kilogram per tonne for particulates and 0.2 kilogram per tonne for ammonia. Emissions of ammonium nitrate and ammonia to water are of the order of 6 kilogram per tonne and 3 kilogram per tonne respectively (5000 and 2500 mg/litre) and it is reduced to 0.2 kilogram of nitrogen per tonne for ammonium nitrate and essentially nothing for ammonia by resorting to best available techniques of pollution control in these plants.

Liquid effluent from these plants comprise of condensates from neutralization, evaporation, blow down from air scrubbing and contain some amounts of ammonium nitrate and nitric acid. A thermal hydrolyser system will be able to strip out the ammonia content and after polishing through a demineraliser unit, the condensate can be recycled (Hodge C.A. and Popovici N.N., Ed., 1994).

Solid wastes problems are not encountered in AN plants. In addition to the emissions from an ammonium nitrate plant, a calcium ammonium nitrate plant produce solid wastes such as calcium carbonate or other filler used. These could be used elsewhere or safely disposed as landfill.

SULPHURIC ACID

Emissions

Atmospheric emissions from sulphuric acid plants consist of sulphur dioxide, sulphur trioxide, particulate matter 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. Sulphur trioxide emission being as low as 0.15 kilogram per tonne of sulphuric acid in new double conversion and double absorption (DCDA) plants where as it is usually around 0.6 kilogram per
tonne in single contact plants. Sulphur dioxide emission is about 10-12 kilogram per tonne of sulphuric acid in single contact plants and only 2-3 kilogram per tonne in double contact plants (UNEP, 1998). In plants where sulphur is burnt to produce \( \text{SO}_2 \) the only liquid effluent is generated from boiler blow-down and water treatment. In plants where \( \text{SO}_2 \) is received from pyrites roasting, effluent from gas cleaning operations also arise.

*Solid wastes*

Solid wastes from these plants are spent catalyst and sulphur muck. Spent catalyst is returned to the catalyst supplier for recycling. Otherwise, solid wastes are usually disposed of by land-filling, subject to screening for heavy metals.

**PHOSPHORIC ACID**

*Emissions*

The main atmospheric emissions from these plants are gaseous fluorides from the reaction and filtration stages and dust from rock phosphate grinding and handling operations. After scrubbing, the fluorine content of these emissions is reduced to less than 10 mg/Nm\(^3\), and in an efficient plant using BAT a level is 5 mg/Nm\(^3\) is easily achieved. However, fluorine recovery from the hemihydrate process presents special difficulty, owing to the relatively high hydrogen fluoride (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. New plants using BAT can keep dust and particulate emissions to 50 mg/Nm\(^3\), 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 (UNEP, 1998).

A major solid waste from phosphoric acid plant is phosphogypsum. For every tonne of acid produced 4.5 tonnes of gypsum is generated, part of which is sold as chemical or soil conditioner. Earlier it was used to make ammonium sulphate by the Merceberg process which is not in extensive application now-a days (Gopinath N.D., 1968; George K.C. and Gopinath N.D., 1963 and Vyas V.M., 1992).

Bulk remains to be disposed and there is no cost effective value added products that could be made from this waste product. Usually gypsum is disposed in open sites as a stack over an impervious layer of polythene so that leaching will not occur and cause pollution for ground water. The lechetes from the stack are collected and safely discharged after necessary treatment (Isherwood K.F., 1992).

Complex Fertilisers (NP, NPK) Plant

Atmospheric emissions from complex fertiliser plants include ammonia, oxides of nitrogen, fluorine, dust, and aerosols composed of ammonium nitrate, fluoride and chloride. The amounts vary with the kind of process employed and its efficiency of operations and management (EFMA, 1995). Normally it ranges from 0.04 to 0.2 kilogram of ammoniacal nitrogen, 0.04 to 0.3 kilogram of nitrogen oxides, up to 0.02 kilogram fluoride and 0.1 to 0.2 kilogram of particulate matter per tonne of product. In principle, all solid and liquid wastes can be recycled, although some nitrogen (0.2 kilogram per tonne) may be lost in effluent with high concentrations of ammonium nitrate. The processes involving the acidulation of mineral phosphate with nitric acid has the highest emission of nitrogen oxides. Ammoniation in a drum granulator will lead to higher ammonia emissions and the
more nitrogen or phosphorous in the formulation, the more nitrogen or fluorine respectively will be emitted (UNEP, 1998).

The fluoride and phosphate bearing effluents are treated with lime and they are precipitated as their insoluble calcium salts and are filtered. The calcium fluoride cake is either sold or disposed with out any chance for leaching and consequent contamination of ground water. The precipitated calcium phosphate is fed to the process.

**COMPLEX FERTILISERS (MAP, DAP)**

Atmospheric emissions from the manufacture of complex fertilisers such as mono ammonium phosphate (MAP) and diammonium phosphate (DAP), include ammonia, ammonium chloride (NH₄Cl), fluorine as silicon tetra fluoride (SiF₄), hydrogen fluoride (HF), and particulate matter. Dust and fines are separated from these emissions by water scrubbing. The liquid effluent is subjected to further treatment.

Emissions to water include compounds of nitrogen, phosphorous and fluorine, as well as solids in suspension. They are mainly derived from waste gas scrubbing and can be recovered by recycling the scrubber liquor. Lime is generally used to precipitate fluorine (and any phosphates or sulphates) in waste water. Ammonia and fluorine compounds are contained in the waste gas leaving an ammoniator granulator or acid neutralizer. They are recovered by scrubbing with phosphoric or sulphuric acid, or water, and returned to the granulator. With powder blending, no ammonia is released unless it is used with acid to promote the granulation.
When potassium chloride is added to the process to introduce the potassium content, ammonium chloride forms in both the granulator and the drier, it tends to vaporise above 130°C due to sublimation, and the vapours are 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 diammonium phosphate and urea, and/or by using potassium sulphate instead of potassium 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 and final cleaning of exit fumes is to be done by water scrubbing. Bag filters 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. They do not capture gases such as chlorides and fluorides and are operated under slight vacuum and lower temperatures. 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 ammonium phosphate industry is the venturi type of scrubber. With this system the fluorine and ammonia recovery is very efficient and emissions are further reduced by installing a tail-gas scrubber in series often using phosphogypsum pond water as the medium for scrubbing.
SINGLE SUPER PHOSPHATE (SSP) AND TRIPLE SUPER PHOSPHATE (TSP)

Emissions

The emissions from these plants are gases from the reaction section and particulate matter. The gaseous fluorine compounds are absorbed in a recirculating stream of a solution of fluorosilicic acid (Hodge C.A. and Popovici N.N., 1994). For TSP plants multistage venturi type cyclonic scrubbers are used. Dust control is usually by effective dust recovery systems either wet or dry, by changing the grain size or by adding chemical agents that lower dust formation.

Atmospheric emissions from a new nitrophosphate plants consist of ammonia, fluorine, nitrogen oxides and dust. The exhaust gaseous streams after treatment, including complex (NPK) formulation, shall be about 0.3 kilogram ammonia, 0.2 kilogram of oxides of nitrogen, 0.02 kilogram fluoride and 0.3 kilogram dust per tonne of fertiliser produced.

Waste water effluents from washing and scrubbing operations in new plants shall typically contain about 0.06 kilogram P₂O₅, 0.15 kilogram nitrogen (mostly as NH₃), and 0.05 kilogram of fluorine per tonne of fertiliser produced. In existing plants, achievable levels shall be 0.11 kilogram P₂O₅, 0.8 kilogram nitrogen and 0.05 kilogram fluoride. There are no solid wastes emanating from this plant.

NOISE LEVEL IN PLANT ATMOSPHERE

Noise sources in fertiliser plants are furnaces and fired heaters, burners, blowers and fans, air coolers, pumps, compressors, cooling tower fans, steam venting and let down, grinders, crushers, centrifuges, compressed air, vibration of equipment
and pipelines, moving machinery, conveyors and so on. Insulating the source from the operators console is usually adopted as the basic strategy to combat sound pollution. Special refractory linings for furnaces, insulation, low noise burners, installation of silencers for fans, blowers, vent stacks etc., special noise attenuation for ducting and pipe work, control valves with special trims to reduce noise, low air velocity and low fin tip air coolers, special protective enclosures for machinery such as pumps, turbines, compressors etc., are the available techniques by which the impact of sound pollution in plants are reduced to an acceptable level (Johansen T. et al., 1992).

The major plant nutrients that are supplemented through mineral fertiliser industry, as described above, are nitrogen, phosphorus and potassium. These nutrients are made into the form of water-soluble compounds that are mostly ammonium salts. The various chemicals and intermediates used in the manufacture of mineral fertilisers are ammonia, nitric acid, sulphuric acid, phosphoric acid, urea, ammonium nitrate, muriate of potash and to a lesser extent certain other chemicals.

The process of manufacture involve, chemical reactions at high pressure, temperature and concentration, consumption of large quantum of energy, most severe corrosive environments, and handling and storage of inflammable, toxic and hazardous chemicals and intermediates in large quantities. The raw materials and reactants used in the chemical processes pose concerns to human health, safety and the environment.

Pollution to air, water and land caused by emissions and effluents containing oxides of nitrogen, sulphur and carbon, ammonia, hydrogen sulphide, fluorine, other greenhouse gases, acid mist, dust and particulates, radiation, phosphogypsum, heavy
metals, toxic chemical, used catalysts, resins, chemical residues and spillages, waste oil and lubricants, chlorofluorocarbons, laboratory wastes, redundant equipment, mechanical refuse, plastics etc. are the major environmental issues and concerns from the fertiliser industry.

These concerns are addressed in fertiliser production in such a way to keep the environmental impact of emissions and waste to a minimum by increasing the efficiency of production processes and adopting techniques of reducing pollution and through effective abatement. The extent of pollution, risk to human beings and damage to the environment, arising out of the production processes vary with the different fertiliser materials and thus call for specific control strategies and abatement facilities suitable to each of them. With the currently available technologies, it is possible to control the impact of these concerns within an acceptable level. To achieve the lowest levels of environmental consequences, the operation and maintenance of these plants are to be held in good order with a high standard of adherence to established and innovative control measures.
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