CLEANER PRODUCTION GUIDELINES IN FERTILIZER MANUFACTURING SECTOR

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INTRODUCTION TO FERTILIZER INDUSTRY

India is the second biggest consumer of fertilizer in the world next only to China. The Indian Fertilizer companies produced around 37.6 million tones of fertilizer in the year 2012-13 with a 9% rise in comparison to 34.6 million tones of last year (2011-12) production.

Fertilizers are materials used to provide plant nutrients which are deficient in soils. 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 (P₂O₅, K₂O) 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.

**Nutrient content of common fertilizers**

<table>
<thead>
<tr>
<th>No.</th>
<th>Material</th>
<th>N</th>
<th>P₂O₅</th>
<th>K₂O</th>
<th>MgO</th>
<th>S</th>
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</thead>
<tbody>
<tr>
<td>1.</td>
<td>Ammonium Nitrate</td>
<td>35</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
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<td>2.</td>
<td>Ammonium Sulfate</td>
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<td>0</td>
<td>0</td>
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<td>3.</td>
<td>Calcium Nitrate</td>
<td>15.5</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
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<tr>
<td>4.</td>
<td>Diammonium Phosphate</td>
<td>18</td>
<td>46</td>
<td>0</td>
<td>0</td>
<td>0</td>
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<tr>
<td>5.</td>
<td>Monoammonium phosphate</td>
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<td>52</td>
<td>0</td>
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<td>0</td>
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<tr>
<td>6.</td>
<td>Muriate of Potash</td>
<td>0</td>
<td>0</td>
<td>60</td>
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<td>0</td>
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<tr>
<td>7.</td>
<td>Potassium Nitrate</td>
<td>13.5</td>
<td>0</td>
<td>44</td>
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<td>0</td>
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<td>8.</td>
<td>SKMG or SULPOMAG</td>
<td>0</td>
<td>0</td>
<td>22</td>
<td>18</td>
<td>22</td>
</tr>
<tr>
<td>9.</td>
<td>Sulphate of Potash</td>
<td>0</td>
<td>0</td>
<td>50</td>
<td>0</td>
<td>18</td>
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<td>10.</td>
<td>Single Super Phosphate</td>
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<td>22</td>
<td>0</td>
<td>0</td>
<td>14</td>
</tr>
<tr>
<td>11.</td>
<td>Triple Super Phosphate</td>
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<td>46</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>12.</td>
<td>Urea</td>
<td>46</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
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</table>
Highlights of processes for different Fertilizers

➢ Urea

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 naphta by steam.

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 (180-190°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%, 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 ways to separate product urea from the other reaction components, to recover excess NH₃, and to decompose the residual carbamate to NH₃ and CO₂ for recycling.

There are three main types of process:

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

➢ 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 CO₂ stripping urea process may also provide unconverted NH₃ and CO₂ 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.

- 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.
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 venture scrubbing system involving a circulation solution of weak (less than 23%) fluorosilicic acid.

The venture 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 P2O5, and dust emission to 0.3-1 kg/t of product.

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 P2O5 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% P2O5 concentration may be granulated directly in a traditional unit with a drum granulator, drier etc.

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.

Environmental Issues in Fertilizer Industry and CP options

Cleaner Production means, “the continuous application of an integrated, preventative environmental strategy to processes, products and services to increase eco-efficiency and reduce risks to humans and the environment”. Cleaner Technology may be “thought of a subset of Cleaner Production activities with a focus on the actual manufacturing process itself and considers the integration of better production systems to minimize environmental harm and maximize production efficiency from many or all inputs.”

NITROGEN FERTILIZER PLANTS

➢ Urea

Cleaner production in Air Emission

• 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.
• Use synthesis NH3 purge gas treatment to recover NH3 and H2 before combustion of the remainder in the primary reformer.
• Increase the residence time for off-gas in the high temperature zone of the primary reformer;
• Ammonia emissions from relief valves or pressure control devices from vessels or storages should be collected and Sent to a flare or to wet scrubber;
• Install leak detection methods to detect fugitive emissions of ammonia from process and storage;
• Implement maintenance programs, particularly in stuffing boxes on valve stems and seals on relief valves, to reduce or eliminate releases.
• Reduction of dust emissions by producing granular rather than prilled product;
• Installation of prilling towers with natural draft cooling instead of towers with forced/induced draft air cooling;
• Scrubbing of off-gases with process condensate prior to discharge to atmosphere, and reprocessing the recovered urea solution;
• Use of baghouse filters to prevent the emission of dust laden air from transfer points, screens, bagging machines, etc., coupled with an urea dust dissolving system which allows recycling of urea to the process;
• Flash melting of solid urea over-size product which allows urea recycling to the process;

**Cleaner production in Water Emission**

An urea plant generates a significant stream of process water containing NH3, CO2 and urea (ie, a 1000 tons per day (t/d) plant generates approximately 500 cubic meters per day (m3/d) of process water). Other sources are ejector steam, flush, and seal water.

Recommended pollution prevention and control measures include the following:

- Improve evaporation heater/separator design to minimize urea entrainment;
- Remove NH3, CO2, and urea from the process water in a process water treatment unit, and recycle the gases to the synthesis to optimize raw material utilization and reduce effluents;
- Provide adequate storage capacity for plant inventory to prepare for plant upset and shutdown conditions
- Install submerged tanks to collect plant washings and other contaminated streams from drains for recycling to process or conveying to the process water treatment unit.

**Cleaner production in Solid waste**

- Catalysts used in the process need to be disposed off after their activities are significantly reduced. Normally, the catalyst used in the plant needs to be replaced at intervals of 5 to 7 years. These catalysts are normally pyrophoric and have to be removed by taking certain standard precautions and stored in closed containers. These spent catalysts have ready market and are normally sold off, thus, as long as proper precautions are taken are not likely to pose any environment problem. The recovery of valuable elements from spent catalysts become on unavoidable task not for lowering the catalysts cost but also for reducing the catalysts waste to prevent the environmental pollution.
- Safe disposal of hazardous waste.

**AMMONIUM NITRATE/ CALCIUM AMMONIUM NITRATE**

**Cleaner production in Air Emission**

In ammonium nitrate plants the following pollution prevention measures are recommended:
- Install steam droplet separation techniques (e.g., knitted wire, mesh demister pads, wave plate separators and fiber pad separators using, for example, polytetrafluoroethylene (PTFE) fibers) or scrubbing devices (e.g., packed columns, venturi scrubbers and irrigated sieve plates) to reduce emissions of ammonia and ammonium nitrate in the steam from neutralizers and evaporators. A combination of droplet separators and scrubbers should be used to remove ammonium nitrate particulate emissions. Nitric acid should be used to neutralize any free ammonia.

- Treat and re-use contaminated condensate using techniques including stripping with air or steam with the addition of alkali to liberate ionized ammonia if required, or use distillation and membrane separation processes such as reverse osmosis.

- Adopt the lowest practical melt temperature to reduce emissions of ammonia and ammonium nitrate (and calcium carbonate in calcium ammonium nitrate (CAN) production) from prilling and granulation emissions.

- In Prill tower, Reduce micro prill formation & Reduce carryover of fines through entrainment.

- In Granulator reduce dust emissions from the disintegration of granules.

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

- Remove ammonia emissions from prilling and granulation by neutralization in a wet scrubber. Wet scrubbers normally use an acid circulating solution. The solution from a wet scrubber will normally be recycled to the process.

- Remove ammonium nitrate fumes from prilling through scrubbing.

- Remove small particles of ammonium nitrate (miniprills), carried out with the air stream through cyclones, bag filters and wet scrubbers.

- Adopt an enclosed granulation process instead of prilling technique where feasible.

- Install an extraction, capture and filter system for ventilation air from areas with dust-generating product-handling activities to prevent fugitive emissions of particulates.
Cleaner production in Water Emission

Ammonium nitrate (AN) / calcium ammonium nitrate (CAN) plants produce a surplus of water to be treated for discharge or possibly recycled to other units in the nitrogenous fertilizers production complex. Their process effluents typically include condensates containing up to 1% ammonia and up to 1% ammonium nitrate from reactors (neutralizers) and evaporator boil-off, and ammonium nitrate and nitric acid from plant wash-down. Unabated emissions into water can be up to 5,000mg AN as N/l and 2,500mg NH3 as N/l (6 and 3 kilograms per ton (kg/t) of product respectively). Pollution prevention and control measures for A/CAN plants include the following.

- Internally recovery of ammonium nitrate and ammonia (e.g. scrubber liquor from the granulation plant air cleaning section being recycled through the further evaporation stages on the granulation plant).
- Integrate AN/CAN plants with nitric acid production.
- Treat steam contaminated with ammonia or ammonium nitrate, before condensation, by droplet separation techniques and scrubbing devices.
- Treat process water (condensate) by stripping with air or steam with the addition of alkali to liberate ionized ammonia as needed, ion exchange, distillation, or membrane separation processes.

Cleaner production in Solid waste

- Solid wastes are principally spent catalysts that originate in ammonia production and in the nitric acid plant. Other solid wastes are not normally of environmental concern.

Phosphate Fertilizer Plants

Cleaner production in Air Emission

- 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 bonded 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.

- 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.

**Cleaner production in Water Emission**

- The discharge of sulfur dioxide from sulfuric acid plants should be minimized by using the double-contact, double-absorption process, with high efficiency mist eliminators. Spills and accidental discharges should be prevented by using well-bonded storage tanks, by installing spill catchment and containment facilities, and by practicing good housekeeping and maintenance. Residues from the roasting of pyrites may be used by the cement and steel manufacturing industries.
- 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, treatment to precipitate fluorine, phosphorus, and heavy metals may be necessary.

**Cleaner production in Solid waste**

- Lime can be used for treatment. Spent vanadium catalyst is returned to the supplier for recovery, or, if that cannot be done, it is locked in a solidification matrix and disposed of in a secure landfill.
- Opportunities to use gypsum wastes as a soil conditioner (for alkali soil and soils that are deficient in sulfur) should be explored to minimize the volume of the gypsum stack.
- Consider the use of phosphor gypsum to produce gypsum board for the construction industry.
- Design and operate phosphor gypsum disposal facilities to minimize impacts.
- Prepare and implement an emergency preparedness and response plan (required because of the large quantities of sulfuric and phosphoric acids and other hazardous materials stored and handled on the site).
- Consider providing pyrite-roasting residues to the cement or steel-making industry.
Mixed Fertilizer Plants

Cleaner production in Air Emission

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 NOx 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.

Cleaner production in Water Emission

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.

Cleaner production in Solid Waste

- There is no solid waste except sand which can be used as a building material after washing and separation.
- By-products are converted into commercial products and spillages and off-specification products are recycled into the NPK production.

Problems with Superphosphate or N-P-K Fertilization of the Soil

- Depletion of the soil traces minerals.
- This occurs for at least two reasons.
• The increased yield of acreage or tonnage of crops means that more trace elements go into the crops, and these trace minerals are then removed from the soil when the crop is harvested.

• Superphosphates seem to speed up the oxidation rate of the plants, weeds, and the soil microorganisms.

• Other damage to the soil micro-organisms.

  ➢ Topsoil erosion.
  ➢ Reduced soil permeability.
  ➢ More severe poisoning of the soil, plants, animals, humans and the environment with newer toxic pesticides and insecticides.
  ➢ Reduced general soil fertility.
  ➢ More toxic metals in the soil.

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