Egyptian Environmental Affairs Agency (EEAA)

Egyptian Pollution Abatement Project (EPAP)

Inspection Manual

Fertilizers Industry

July 2002

List of Acronyms

BOD	Biological Oxygen Demand
COD	Chemical Oxygen Demand
O&G	Oil and Grease
CO	Carbon Monoxide
CO_2	Carbon Dioxide
VOCs	Volatile Organic Compounds
NPK	Nitrogen, Phosphtae & Potassium Fertilizers (complex fertilizers)
CoO	Cobalt Oxide
ZnO	Zinc Oxide
A.N	Ammonium Nitrate
NH_3	Ammonia
HNO_3	Nitric Acid
NO	Nitrogen Oxide
CH_3OH	Methanol
NiO	Nickel Oxide
MEK	Methyl ethyl Ketone
SO_x	Sulfur Oxides
NO_x	Nitrogen Oxides
TDS	Total Dissolved Solids
CP	Cleaner Production
WWTP	Wastewater Treatment Plant

µm	Micro meter 10^{-6} m
BAT	Best Available Technology
MHUUC	Ministry of Housing, utilities and urban Communities
EoP Treatment	End-of-Pipe Treatment
RBOs	Regional Branche Offices for EEAA
EMUs	Environmental Management Units

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1. Introduction

The Egyptian Pollution Abatement Project (EPAP) sponsored by FINIDA has assigned Finnish and Egyptian consultants for the task of developing sector-specific inspection and monitoring guidelines.

A General Inspection Manual, GIM, has been developed covering inspection aspects common to all sectors. The manual:

- Discusses the strategy, objectives and tasks of the inspectorate management.
- Identifies the team leader responsibilities and tasks.
- Presents a methodology for performing all types of inspection. Tasks during the various phases of planning, performing field inspection, report preparation and follow-up are discussed. Several checklists are included.

Sector specific inspection manuals have been developed for the following industries:

- Textile industry
- Pulp and paper industry
- Food industry
  - Grain milling industry
  - Dairy industry
  - Carbonated beverages industry
  - Confectionery industry
  - Fruits and vegetables industry
- Metallurgical industry
- Fabricated metal industry
- Motor vehicle assembly

The developed manuals were tested through a number of training programs that targeted RBOs and EMUs.

The inspectors involved in the training used these manuals to inspect a number of industrial facilities. Feedback from the concerned parties led to the improvement of these manuals and their continuous update.

1.1 Preface

As a continuation of the previous effort, the following manuals are developed

- Paint industry
- Detergent oil and soap industries
- Cement and ceramic industry
- Fertilizer industry

1.1.1 Project Objectives

The project aims at the development of sector-specific guidelines for inspection to be used by inspectors. These manuals are meant to be simplified but without abstention of any information necessary to the targeted users. Flowcharts, tables and highlighted notes are used for easy representation of information.

1.1.2 Organization of the Inspection Manual

The inspection manual for the fertilizers industry includes ten chapters. The first chapter represents an introduction to the whole project and to the specific sub-sector of the industry. Chapters from two to five describe the fertilizers industry and its environmental impacts.

The description of the industry in chapter (2) includes the inputs and outputs, a description of the different production lines with their specific inputs and outputs, a brief description of the service and auxiliary units that could exist in the fertilizers plants with their potential sources of pollution and the various emissions, effluents and solid wastes generated from the different processes.

Chapter (3) describes the environmental and health impacts of the various pollutants, whereas chapter (4) gives a summary of the articles in the Egyptian environmental laws relevant to the fertilizers industry. Chapter (5) gives examples of the pollution abatement techniques and the applicable measures to the fertilizers industry.

The inspection procedures are described in chapters (6) to (10) starting with a brief description of the inspection process in chapter (6). The planning aspects that should be considered at the inspectorate level are explained in chapter (7), while the different tasks at the inspectors level specific to the fertilizers industry are described in chapters (8) to (10). The tasks before field inspection are presented in chapter (8), whereas the inspection tasks for actually performing the field visit are defined in chapter (9). Chapter (10) is concerned with the conclusions of the field visit, including the preparation of the inspection report, supporting the enforcement case and following-up the compliance status of the facility.

1.2 Introduction to the Fertilizers Industry

Fertilizers industry is one of the most polluting industries in Egypt. It is considered a sub-sector of the chemical industries which is based on the usage of numerous types of chemicals in large quantities. This industry is considered a large industry in which several chemical processes beside physical operations take place. Several companies in Egypt are producing two basic types of fertilizers, which include nitrogenous or phosphates fertilizers. Table (1) gives a brief information about those companies, their products and locations.

Table (1) Different Fertilizers Companies in Egypt

Company	Location	Products	Raw materials
Abu Qir Fertilizers and Chemicals	Alexandria	- Ammonia - Nitric Acid - Urea (prilled and granulated) - Ammonium Nitrate (granulated)	- Natural Gas
Delta Fertilizers and Chemicals	Talkha	- Ammonia - Nitric Acid - Urea (prilled) - Ammonium Nitrate - Methanol - Urea - Ammonium Nitrate solution	- Natural Gas
Egyptian Chemical Industries (KIMA)	Aswan	- Ammonia - Nitric Acid - Ammonium nitrate (prilled) - Ferrosilicon Alloy (up to 75 % silicon content)	- Water and air - Coke, Quartz (SiO_2) and iron turnings
El Nasr Fertilizers and Chemicals (SEMADCO)	Suez	- Ammonia - Nitric Acid - Sulphuric Acid - Ammonium Nitrate (granulated) - Ammonium Sulphate Crystalline - Calcium Nitrate Solution	- Natural Gas - Sulphur
El Nasr Coke and Basic Chemicals	Helwan- El Tebbin	- Ammonia - Nitric Acid - Ammonium Nitrate (prilled) - Ammonium Sulphate (by-product)	- Coke Oven Gas
Egyptian Fertilizers and Chemicals	El Ein El Sokhna-Suez Gulf	- Ammonia - Urea (granulated)	- Natural Gas
Abu Zaabal Fertilizers and Chemicals	Abu Zaabal	- Sulphuric Acid - Phosphoric Acid - Powder Single Superphosphate - Granulated Triple Superphosphate - Sulphuric Acid	- Elemental Sulphur - Phosphate Rock - Phosphoric Acid
Egyptian Financial and Industrial Company	Kafr El Zayat and Assuit	- Sulphuric Acid - Powder and granulated Single Superphosphate	- Elemental Sulphur - Phosphate Rock

2. Process Description

Fertilizers industry is a form of secondary chemical production. It is necessary to understand the inputs and processing techniques in order to identify the pollution sources and abatement measures in this industry.

Fertilizers may be categorized into two groups, natural and synthetic fertilizers. Synthetic fertilizers include different types according to their chemical composition, physical status and solubility in water. According to their chemical composition, fertilizers are categorized into three main groups as follows:

- Phosphatic fertilizers containing phosphorous as a base element, which is expressed by P_2O_5 %.
- Nitrogen fertilizers containing nitrogen as a base element, which is expressed by N_2 %.
- Potassium fertilizers containing potassium as a base element, which is expressed by K_2O %.

In addition to the straight fertilizers containing single nutrient (N or P or K) there are the complex fertilizers containing two or three major plant nutrient N.P.K. Enormous varieties of NPK according to their contents of nutrients are available. Liquid fertilizers are also produced worldwide including hundreds of forms containing one or more nutrients together with trace elements. NPK fertilizers are produced in the Egyptian Fertilizer Development Center Pilot Plant, located in Talkha, in limited quantities according to the clients requests. Also in Delta Company there is a plant that produces urea- ammonium nitrate liquid fertilizer (32 % N).

The liquid fertilizers must be free of solids to avoid clogging the slurry nozzles. Concentrated phosphoric acid is used as the basis for high analysis liquids. When reacted with ammonia, it gives neutral solution which does not crystallize at low temperature. If ammoniated under pressure, ammonium polyphosphate forms. This can be stored and shipped as a solid and dissolved readily when needed. Another liquid fertilizer is anhydrous ammonia, vaporized to a gas and ploughed directly into the soil. A combination of solution/ suspension containing 13 % nitrogen and 43 % P_2O_5 has been developed, to which custom blenders can add potash and trace elements if needed.

2.1 Raw Materials, Chemicals and Other Inputs

2.1.1 Main Raw Materials

Inputs for the fertilizers industry vary according to the fertilizer type. Phosphate rock is considered the main raw material for the production of phosphate type fertilizers, while in case of nitrogenous fertilizers, ammonia is considered the main raw material. Ammonia is produced by synthesis of nitrogen and hydrogen. The latter is generated either by steam reforming of natural gas, or electrolysis of water. On the other hand, nitrogen is produced either from air liquification as in KIMA- Aswan, or combustion of natural gas.

Large quantities of acids are also used, namely sulphuric acid, nitric acid and phosphoric acid. In all fertilizers plants those acids are produced on-site. Raw sulphur is considered the main raw material for the production of sulphuric acid, whereas phosphoric acid production depends on phosphate rock as raw material. The production of nitric acid is based on the on-site produced ammonia.

The involved catalysts in the fertilizers industry are as follows:

- In ammonia production:
  - CoO, MoO_3 and ZnO for sulphur removal.
  - NiO for primary and secondary reformers.
  - Iron oxide and chromium for CO high shift conversion and copper oxide and zinc oxide for low shift.
  - NiO catalyst for methanation.
  - Iron promoted catalyst for ammonia synthesis.
- In nitric acid production: platinum/ rhodium catalyst.
- In sulphuric acid production: vanadium pentoxide catalyst.

These catalysts are usually not considered as inputs, instead they are considered part of the equipments. This is related to nature of the reactors in this industry, which are fixed bed reactors. Hence the catalysts only aid the reaction, without reacting themselves. According to several factors, catalysts loose their activity after long operating hours which defer from a catalyst to another. Consequently, they need to be regenerated, usually on-site except for the very expensive catalysts such as platinum alloy catalyst which is regenerated in the manufacturing company.

Solvents, carbon dioxide, ground dolomite as coating materials and limestone are also used in fertilizers industry. Table (2) summarizes the major inputs according to the involved operation.

2.1.2 Other Inputs (Water, Fuel and Steam)

Large quantities of water are consumed for several purposes involving cooling, process, steam generating, floor washing and cleaning, ..etc. Steam is generated in these plants in huge quantities for heating, reforming, stripping and other purposes. This steam is generated in boilers by fuel combustion. The fuel type differs from one facility to the other, including fuel oil (mazot), gas oil (solar) or natural gas. Fuel oil (mazot) is widely used due to its cheap cost. On burning, it generates on burning air emissions with high concentration of sulphur oxides (SO_x).

Air is also necessary for some operations such as drying and cooling.

Table (2) The Main Inputs in Fertilizers Industry

Operation	Inputs
Single superphosphate Production	
Acidulation	- Phosphate rock - Strong sulphuric acid - Water
Drying	- Air
Bagging	- Polyethylene bags
Triple Superphosphate Production	
Reaction	- Ground phosphate rock - Phosphoric acid
Drying	- Hot air
Bagging	- Polyethylene bags
Phosphoric Acid Production	
Washing	- Ground phosphate rock - Weak phosphoric acid
Reaction	- Sulphuric acid
Sulphuric Acid	
Melting	- Sulphur
Drying of air	- Sulphuric acid (98 %)
Absorption	- Diluted sulphuric acid
Synthetic Ammonia Production	
Desulphurization	- Natural gas - Adsorbent
Primary reforming	- Steam
Secondary reforming	- Compressed hot Air
CO_2 separation	- Solvent mono-ethanol amine or potassium carbonate and other solvents
Nitric Acid	
Filtration	- Air
Vaporization	- Ammonia
Oxidation	- Gaseous NH_3 - Air
No_x absorption	- Nitric acid
Absorption	- Process and cooling water
Bleaching	- Air
Methanol Unit	
Methanolation	- Synthetic gas - Water
Distillation	- Steam

Ammonium Nitrate	
Reaction (neutralization)	- Gaseous ammonia - Nitric acid
Concentration	- Ammonium nitrate solution
Mixing	- Dolomite, Kaolin or limestone - Ammonium nitrate melt
Coating	- Diatomaceous earth, limestone or dolomite
Bagging	- Polyethylene bags
Ammonium Sulphate	
Evaporation	- Ammonia - Steam
Reaction & crystallization	- Sulphuric acid
Drying	- Steam heated air
Bagging	- Polyethylene bags
Ammonium Phosphate	
Reaction	- Ammonia - Phosphoric acid
Coating	- Coating materials
Bagging	- Polyethylene bags
Calcium Nitrate	
Reaction (dissolving tower)	- Lime stone - Flakes - Nitric acid
Neutralization	- Ammonia
Packaging	- Plastic barrels
Urea	
Synthesis	- Carbon dioxide - Liquid ammonia
Evaporation	- Steam
Prilling	- Cold air
Bagging	- Polyethylene bags

2.2 Production Processes

Fertilizers industry is considered one of the complex chemical sector, which includes several production lines and service units. These are given in table (3).

Table (3) Production Lines and Service Units

Production Lines	Service Units
1. Phosphatic Fertilizers	Boilers
- Super phosphate production	Water treatment unit
- Triple superphosphate production	Wastewater treatment plant
- Phosphoric acid production	Compressors
- Sulphuric acid production	Cooling towers
2. Nitrogenous Fertilizers	Storage facilities
- Ammonia production	Workshops
- Nitric acid production	Garage
- Ammonium nitrate production	
- Diammonium phosphate production	
- Ammonium sulphate production	
- Urea production	
- Methanol	
- Calcium nitrate	

2.2.1 Phosphates Fertilizers

Phosphate fertilizers industry is considered one of the most polluting industries in Egypt. No modernization or pollution abatement plans and technologies were set for this industry, in spite of the implementation of such technologies world wide. It is worth mentioning that the production of phosphate fertilizers in Egypt is limited (installed capacities 1.2 millions tons 15.5 P_2O_5) compared with nitrogenous fertilizers (installed capacities 12 million tons estimated as 15 % N_2).

The various phosphate fertilizers, depending on their composition, have different solubility in soil solutions and are, therefore, assimilated by plants differently. Phosphate fertilizers include single superphosphate and triple superphosphate. The single superphosphate is a mixture of monocalcium phosphate and gypsum (available P_2O_5 almost 16- 22 %), while triple-superphosphate is composed mainly of monocalcium phosphate (available P_2O_5) almost 46 %).

a) Single supephosphate Fertilizer

Fig (1) presents the block flow diagram for manufacturing of mono superphosphate fertilizers and the related raw materials and pollution sources.

The manufacturing process depends on reacting phosphate rock with sulfuric acid and the fertilizer contains about (16- 20 %) P_2O_5. The net reaction proceeds as follows:

$$CaF_2 . 3Ca_3(PO_4)_2 + 7H_2SO_4 + 14H_2O \rightarrow 3Ca(H_2PO_4)_2 + 7CaSO_4 . 2H_2O + 2HF$$

The process can be divided into two stages as follows:

- The first stage represents the diffusion of sulfuric acid to the rock particles accompanied by a rapid chemical reaction on the particle surface, which continues until the acid is completely consumed, and crystallization of calcium sulphate.
- The second stage represents the diffusion of the formed phosphoric acid into the pores of the rock particles which did not decompose. This stage is accompanied by a second reaction.

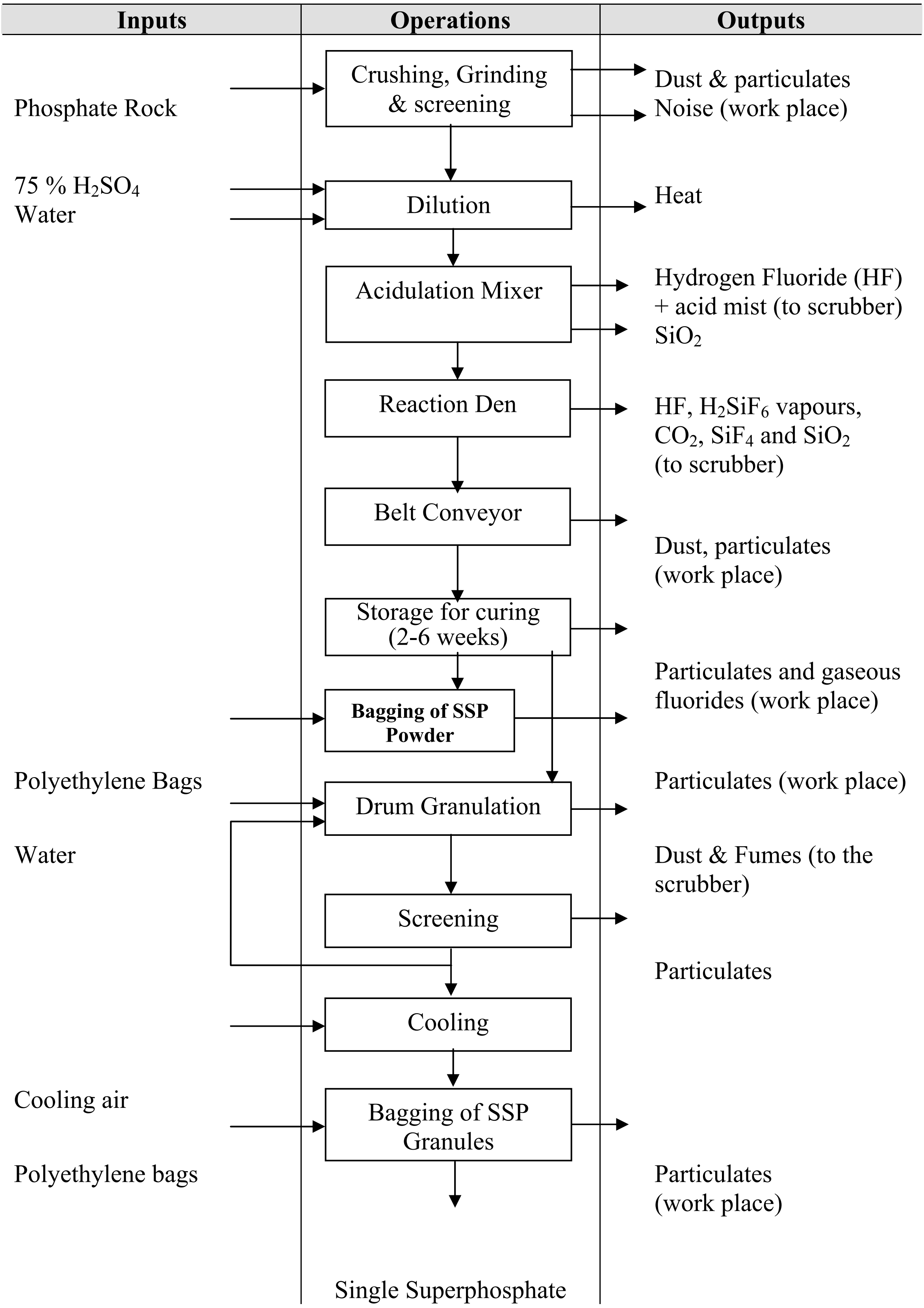
In this process ground phosphate rock is transported from the storage site to automatic weight, by a system of belt and screw conveyors and elevators, which feed the continuous action double conical mixer. The sulfuric acid is continuously diluted with water in a batch mixer to a 75 % concentration, then fed to the mixer to react with ground phosphate rock where a first reaction takes place. This reaction ends in the reaction mixer in 30- 60 minutes, during the period of settling and hardening of the superphosphate slurry, which is caused by the relatively rapid crystallization of the low solubility calcium sulphate. The next stage of the process is ageing of the superphosphate, i.e. the formation and crystallization of monocalcium phosphate in the den. The formed slurry is transported to the continuous-action reaction den which has a very low travel speed to allow for solidifying (see fig 2), where formation of superphosphate takes place (settling and hardening of the slurry in the first stage of ageing). Considerable quantities of fluoride compounds are evolved from the acidulation, they are sent to the scrubbers shown in fig (3).

The superphosphate powder, from the den, is transferred for ageing by a belt conveyor, located below the den, to the pile storage for curing, or completion of chemical reaction, which takes 2-6 weeks to a P_2O_5 availability acceptable for plant nutrient. The raw fertilizer is uniformly distributed by a scattering device and in order to accelerate the ageing operation, the superphosphate is agitated during storage by means of a grab-bucket crane. The end product still contains a certain amount of uncombined phosphoric acid, which makes the fertilizer more hygroscopic. Neutralizing admixtures are used to remove the free acid of the superphosphate, or it is treated with gaseous ammonia. These procedures improve the physical properties of the superphosphate. They lower the moisture content, the hygroscopic and the tendency to cake. If ammonia treatment is used, an additional nutritional component (N_2) is also introduced into the fertilizer.

During reaction of the phosphate with sulphuric acid in the den, hydrogen fluoride evolves and reacts with the silica contained in the phosphates and forms gaseous silicon-tetrafluoride (SiF_4) and fluo slicic acid (H_2SiF_6). The continuous den is, therefore, enclosed so that fumes of these compounds do not escape into the working place. The fluorous gases, containing H_2SiF_6 vapors, are withdrawn through an opening in the den roof into a ventilation pipe to an absorption unit and are utilized for making sodium fluo silicates.

Superphosphate is granulated in drum granulators to improve its physical properties. In the granulator, the superphosphate powder (after being cured for 2-6 weeks) is wetted with water fed into the drum through nozzles, and rolled into granules of different size which are then dried, screened into size fractions cooled and the product is bagged in plastic (polyethylene) bags. The over size granules are ground and recycled, with the undersize granules, to the den.

Fig (1) Process Flow Diagram for Single Superphosphate Manufacturing



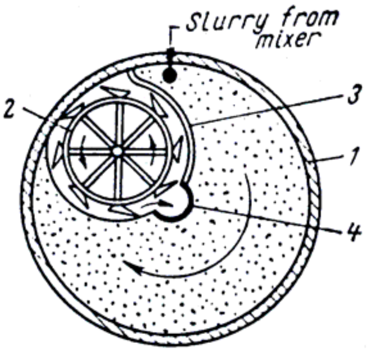


Fig (2- a) Continuous- Action Single Superphosphate Den

(1) rotating shell; (2) cutter; (3) partition; (4) stationary discharge pipe

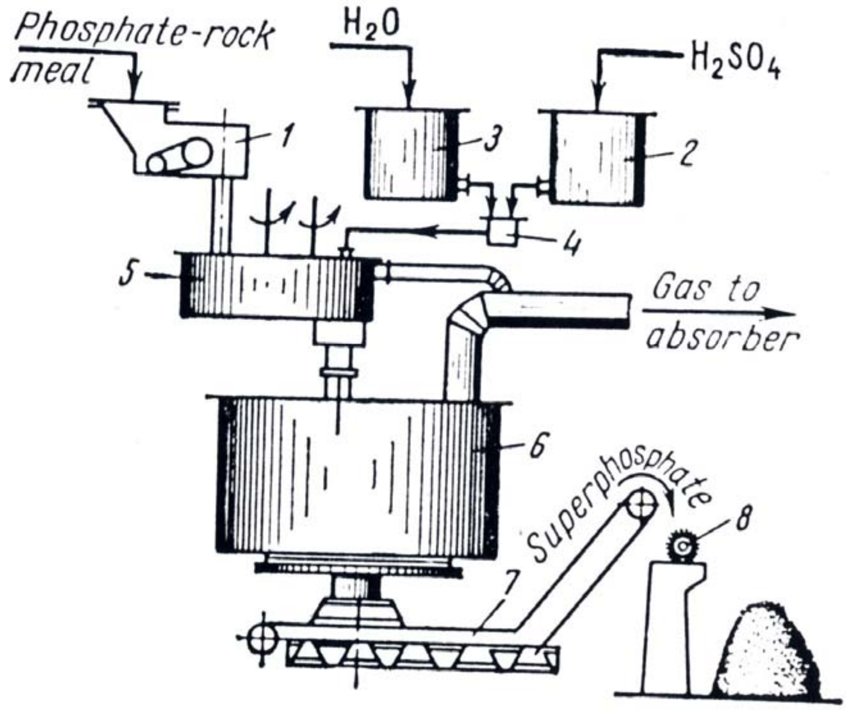
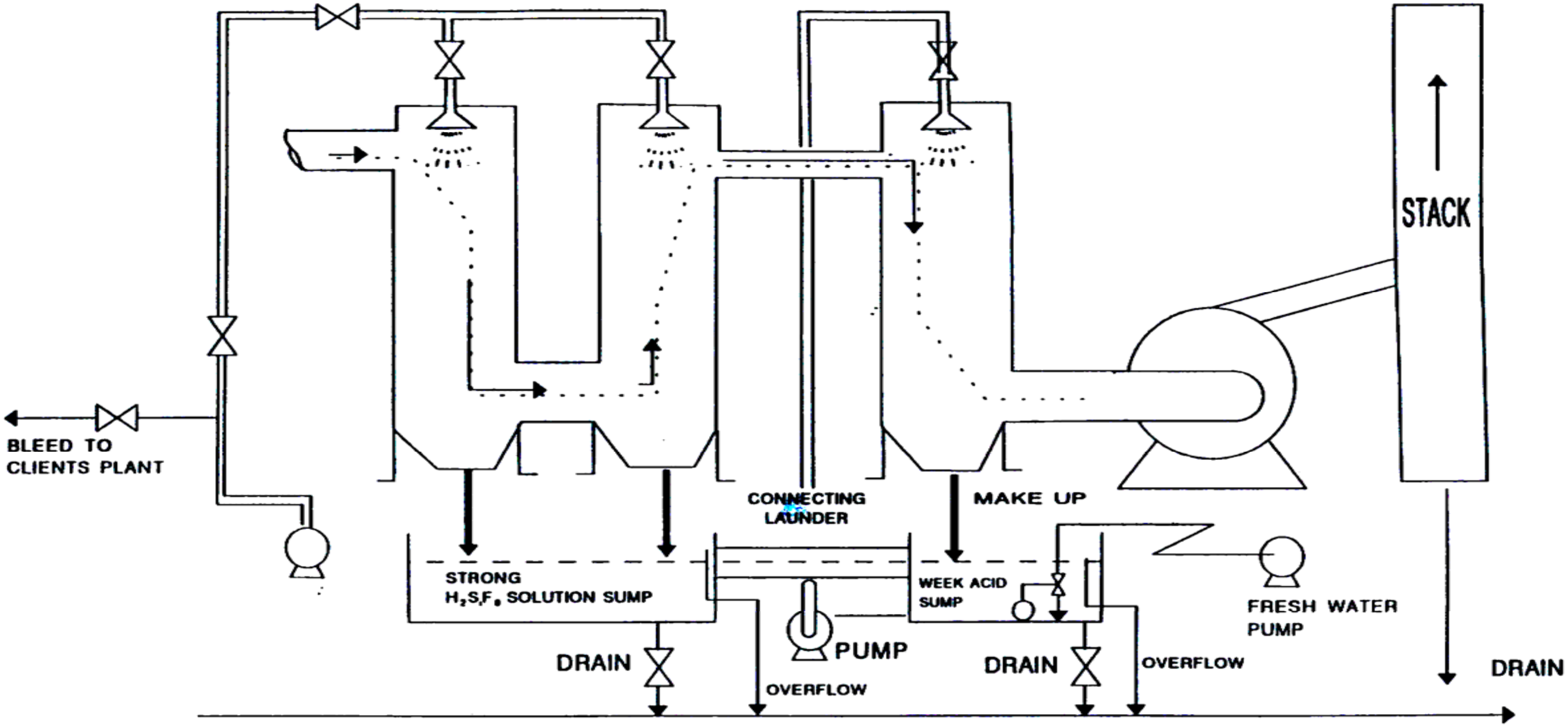


Fig (2- b) Single Superphosphate Manufacturing Processing

(1) phosphate weigh feeder; (2, 3) head tank for sulphuric acid and water; (4) acid feeder; (5) mixer; (6) superphosphate den; (7) superphosphate conveyor; (8) supephosphate scatter at the storage site


STACK
BLEED TO CLIENTS PLANT
CONNECTING LAUNDER
MAKE UP
STRONG H_2SiF_6 SOLUTION SUMP
WEEK ACID SUMP
FRESH WATER PUMP
PUMP
DRAIN
OVERFLOW
DRAIN
OVERFLOW
DRAIN

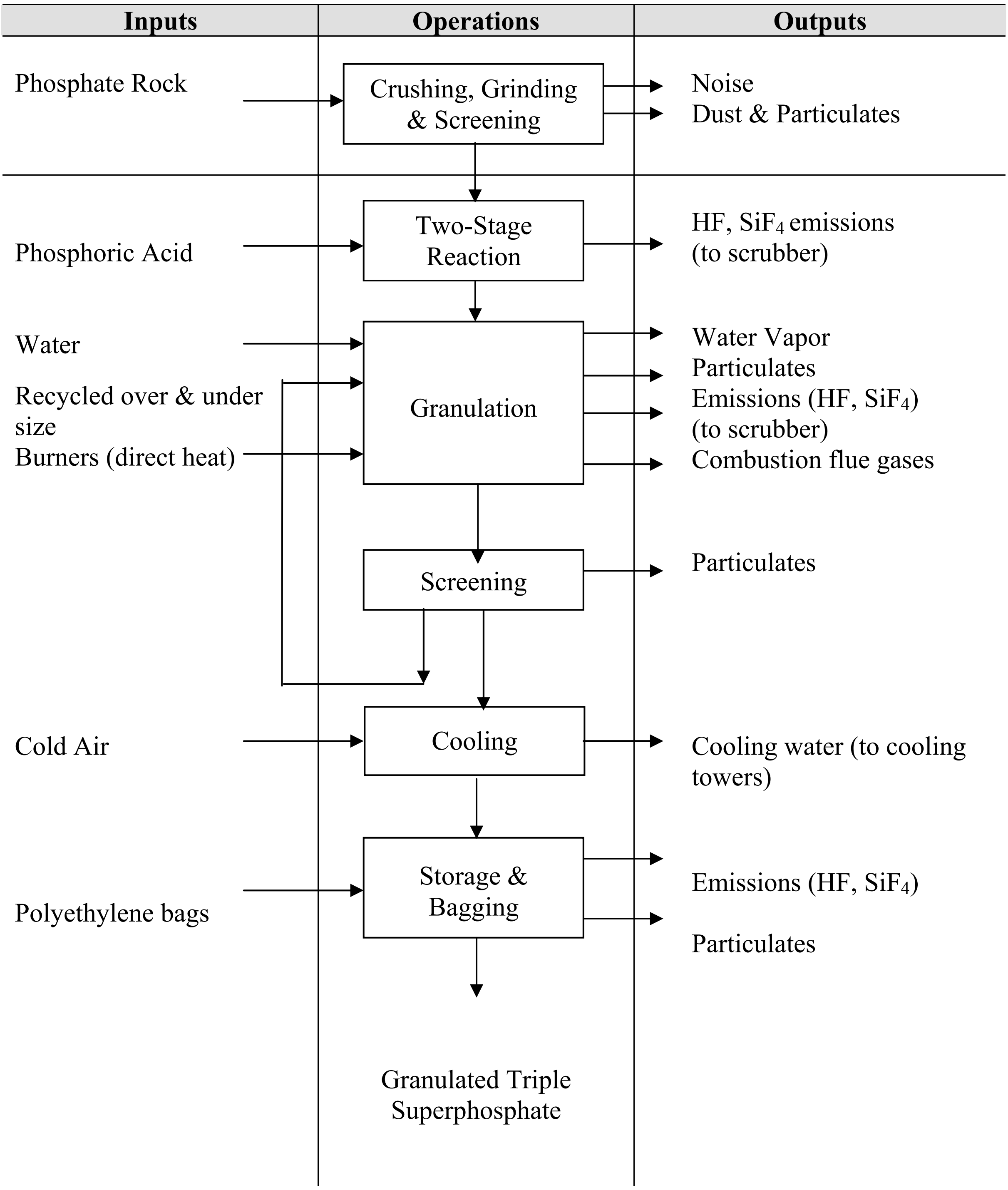
b) Triple Superphosphate Fertilizer

Fig (4) shows the block flow diagram for manufacturing of triple superphosphate. This type of fertilizers is much more concentrated than the ordinary superphosphate, containing 45- 46 % of available P_2O_5. Triple superphosphate is manufactured by the action of phosphoric acid on phosphate rock. The main reaction is:

$$\underset{\text{(Phosphate Rock)}}{CaF_2 . 3Ca_3 (PO_4)_2} + 14H_3PO_4 \rightarrow \underset{\text{(Triple Superphosphate)}}{10Ca (H_2PO_4)_2} + 2HF \uparrow$$

A process similar to single superphosphate production is used, in which pulverized phosphate rock is mixed with phosphoric acid in a two-stage reactor. The resultant slurry is sprayed into the granulator. The slurry is sprayed into the drum granulation co-current with flue gases of fired fuel (natural gas or fuel oil and air). The product is screened and off-size is recycled back to the granulator. The on-size product is cooled and stored ready for being bagged. The exhaust gases from the reactor, granulator and cooler are scrubbed to remove fluoric compounds.

Fig (4) Process Flow Diagram for Triple Superphosphate Manufacturing



c) Wet Process of Phosphoric Acid Production

The main process for producing phosphoric acid is by the use of sulfuric acid as shown in fig (5). The major reaction is

$$\underset{\text{(Phosphate Rock)}}{CaF_2 . 3Ca_3(PO_4)_2} + 10H_2SO_4 + 20H_2O \rightarrow \underset{\text{(Gypsum)}}{10CaSO_4 . 2H_2O} + 2HF + 6H_3PO_4$$

Raw phosphate rock, ground to less than 200 mesh size, is fed to a chute where a recycled stream of weak H_3PO_4 washes it into a reaction tank and digested with strong sulfuric acid. The retention time ranges from 1.5 to 12 hr, and conditions are controlled to produce gypsum crystals that are readily filterable. Considerable heat is generated in the reactor when the sulphuric acid and phosphate rock react. In older plants, this heat was removed by blowing air over the hot slurry surface. In modern plants, a portion of the slurry is cooled by vacuum flash, and then recycled back into the reactor. The reaction mixture is filtered using a tilting-pan filter. The feed to the filter continuously enters the pans, which are connected to the vacuum source. The circular frame supporting the pans rotates so that each pan is moved successively under the desired number of washes. After the final wash liquor has completely drained off, the vacuum is released and the pan is inverted a full 180 degree. The cake drops off, its removal is being ensured by a reverse blast of air through the filter medium, which is then scoured fresh and cleaned by a high-pressure shower while the pan is still inverted. The filter medium and drainage area are then purged by vacuum, and the pan returned to the feed position.

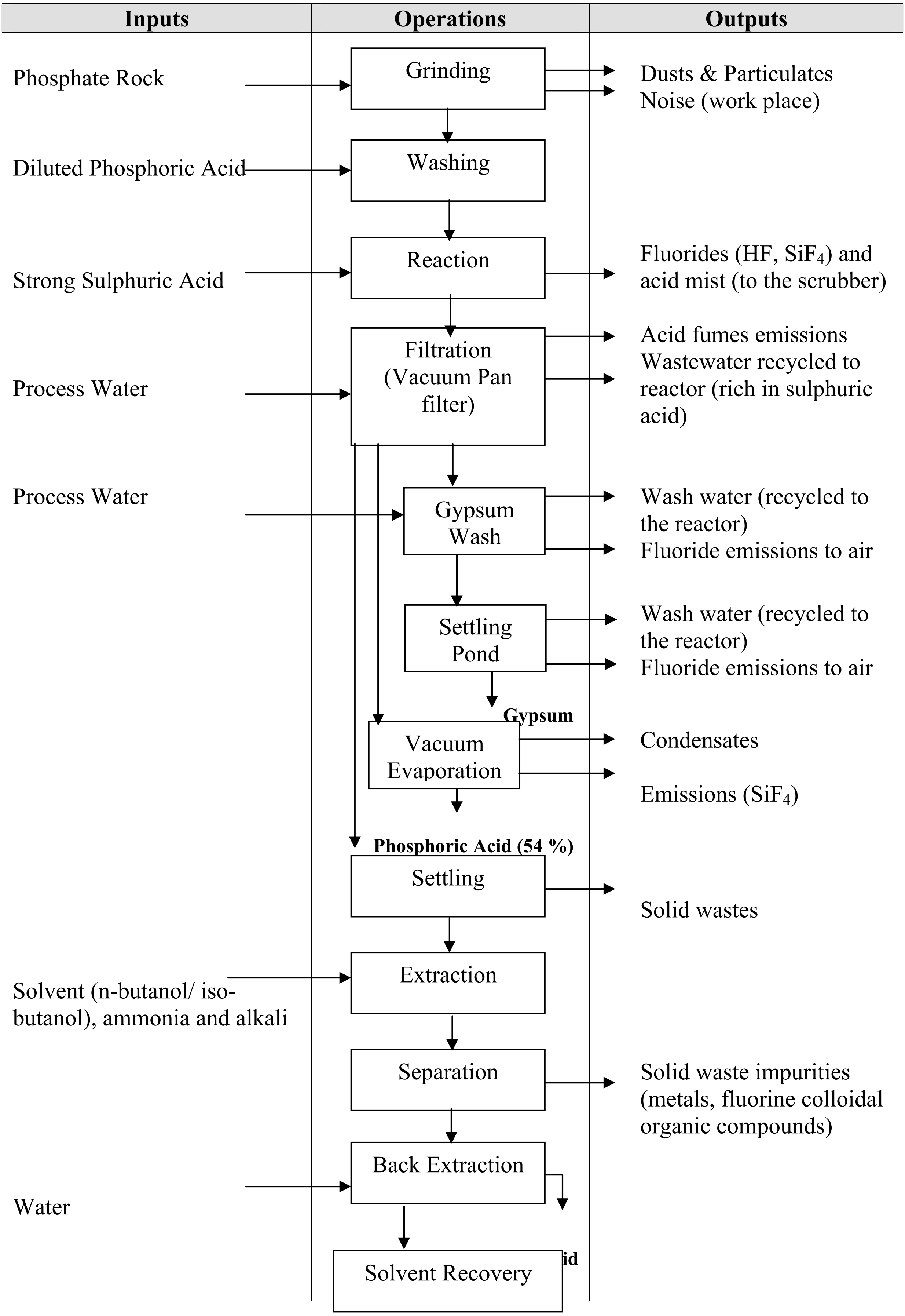
This process produces 28 to 32 % acid which must be concentrated in an evaporator, to meet phosphate feed material specifications for fertilizer production. The crude acid is often black and contains dissolved metals and fluorine, and dissolved and colloidal organic compounds. Suspended solid impurities are usually removed by settling. Solvent extraction or solvent precipitation is used to remove the dissolved impurities. Solvent extraction uses a partially miscible solvent, such as n-butanol, iso-butanol, or n-heptanol. The phosphoric acid is extracted and the impurities are left behind. Back-extraction with water recovers the purified phosphoric acid. Solvent precipitation uses a completely miscible solvent plus alkalis or ammonia to precipitate the impurities as phosphate salts. After filtration, the solvent is separated by distillation and recycled.

Major Hazards

The chance of an acid spill from storage tanks is very small, with the highest risk being a leak from the tank because of corrosion. Corrosion with Phosphoric acid is a relatively slow process and starts with a small hole in the tank. Normally the leak will be seen and the tank emptied before a significant spillage can take place. There is also a risk of the loading pipe cracking during acid loading and this could lead to a significant uncontrolled spillage. Pumping equipment should be available for emptying the pipes.

The more important considerations in the design and construction of phosphogypsum disposal areas are: site selection, cooling ponds and percolation control. The height of the stack depends on the engineering properties of the underlying soil and its load bearing strength, if there are no legal restrictions. The cooling pond surfaces will have to be adapted to local climatic conditions and the water balance in the plant. The process water associated with phosphogypsum is highly acidic and contains high levels of contaminants. some of the following options may be necessary to prevent this water reaching the surrounding ground water system: seepage collection ditches, intercept wells, natural barriers, lining systems (natural or synthetic) and fixing of soluble P_2O_5 and trace elements by neutralization.

Fig (5) Process Flow Diagram for Phosphoric Acid Manufacturing (Wet Process)



d) Sulphuric Acid Manufacturing Process:

The process used is the contact process. Fig (6) presents the raw materials, products and expected pollutants. Elemental sulphur is usually used as raw material and is oxidized to sulphur dioxide. The sulphur dioxide is then oxidized to sulphur trioxide using vanadium pentoxide catalyst. The chemical reactions taking place can be expressed by the following equations:

$$S + O_2 \rightarrow SO_2$$

$$SO_2 + \tfrac{1}{2}\ O_2 \overset{V_2O_5}{\rightleftarrows} SO_3$$

$$SO_3 + H_2O \rightarrow H_2SO_4$$

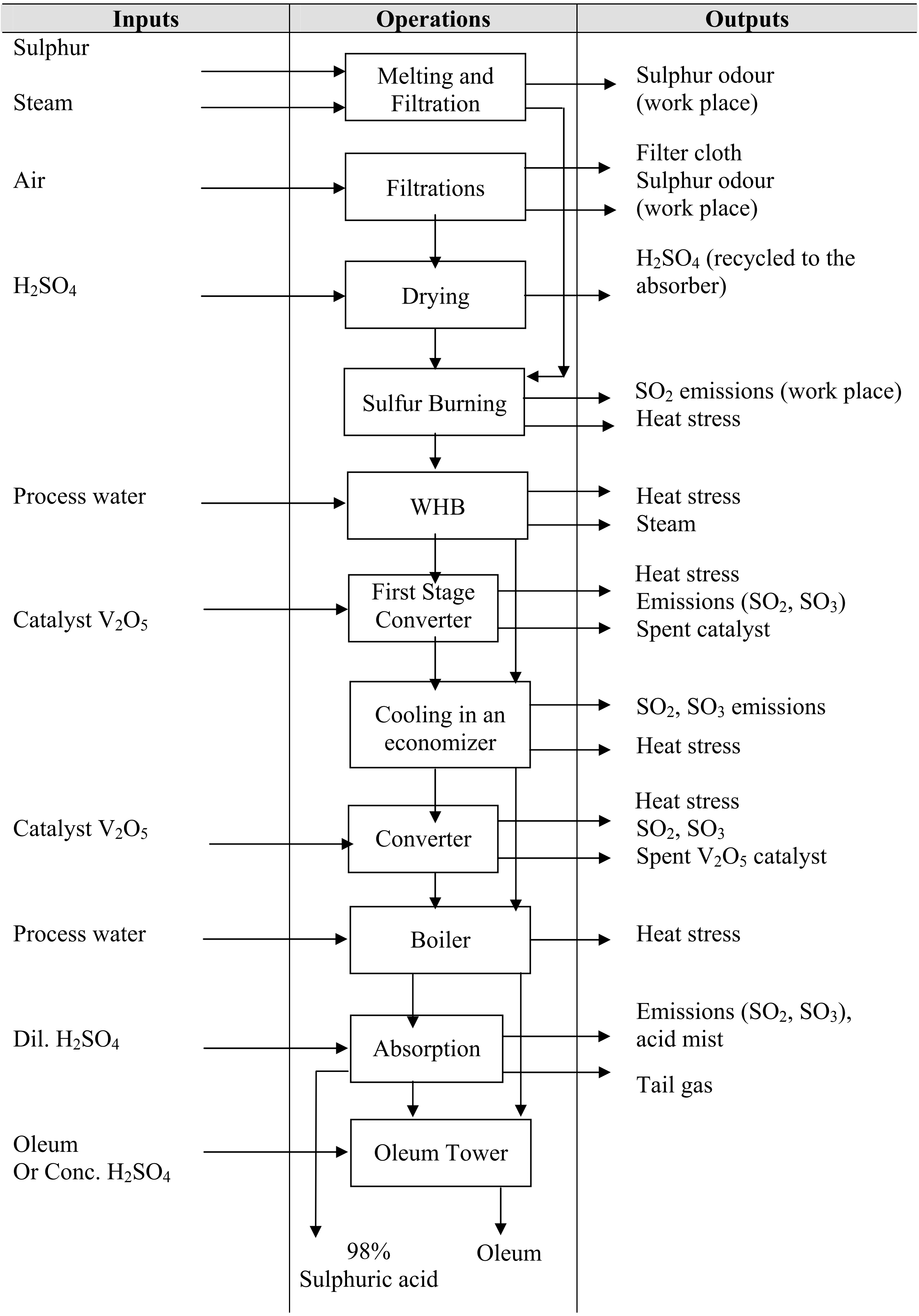
Sulphur is first melted using steam and then filtered to remove contaminants that might poison the catalyst. The liquid sulphur is burned in a sulphur burner using filtered dry air. The air has been dried using concentrated sulphuric acid. The result of burning is a gas containing 8-11% SO_2 and 8-13% oxygen, which is cooled in a waste-heat boiler to about 420° C. The specific inlet temperature of the gas entering the converter is dependent upon the quantity and quality of the catalyst and the composition and flow rate of the sulphur dioxide gas, but it is usually in excess of 426ºC. The converter contains layers of catalyst, usually vanadium pentoxide, placed in horizontal trays or beds arranged so that the gas containing SO_2 and an excess of oxygen passes through two, three, or four stages of catalyst. As the gas passes through the converter, approximately 95 to 98% of SO_2 is converted to sulphur trioxide, with the evolution of considerable heat. Maximum conversion cannot be obtained if the temperature in any stage becomes too high. Therefore, gas coolers are employed between converter stages. The concentration of sulphur trioxide leaving the converter at 426 - 454ºC is approximately the same as that of the entering sulphur dioxide.

The converter gas is cooled to 232 to 260° C in an economizer or tubular heat exchanger. The cooled gas enters the absorption tower where the sulphur trioxide is absorbed with high efficiency in circulating stream of 98 to 99 % sulphuric acid. The sulphur trioxide combines with the excess water in the acid to form more concentrated sulphuric acid. To reduce the emission of sulphur trioxide in the exit gases, a second absorption stage is added where exit gases from the absorption tower are introduced into a second absorption tower. The gases leaving the absorbing tower may pass through a heat exchanger, in which they are reheated to about 426° C before reentering the converter. They are then passed through the catalyst, cooled, and flow through the absorption towers and then to the atmosphere. A great source of pollution in this process is due to the emission of SO_2, SO_3 gas with acid mist from the absorption tower and leaks from heat exchangers.

Major Hazards

the highest risk hazard for accidental pollution exists during the storage and transportation of the sulphuric acid. Plants have different systems to collect leaks and spillages. Gas leaks are not normally a problem as they are handled by various monitoring and control systems, which measure the SO_2 content in air.

Fig (6) Process Flow Diagram for Sulphuric Acid Manufacturing



2.2.2 Nitrogenous Fertilizers

Nitrogenous fertilizers are considered the major type widely produced and used in Egypt. It includes many fertilizers such as ammonium nitrate (NH_4 NO_3), ammonium sulphate $(NH_4)_2$ SO_4, calcium nitrate Ca $(NO_3)_2$ and urea $CO(NH_2)_2$. Ammonia, which is the essential raw material for nitrogen base fertilizers, is produced inside the facility itself. Ammonia is produced by catalytic reaction of H_2 and N_2. Hydrogen can be produced by electrolysis of water (very limited), from steam reforming of natural gas and partial oxidation of naphtha and fuel oil. Nitrogen is obtained from air.

a) Synthetic Ammonia (NH_3)

As illustrated in fig (7), synthetic ammonia, from natural gas, is produced by reacting hydrogen with nitrogen. Six processing steps are required to produce synthetic ammonia using the catalytic steam reforming method as follows:

1. Natural gas desulfurization

In this operation, the sulfur content (mainly as H_2S) is reduced to below 280 micrograms/ m^3 to prevent poisoning of the catalyst used in steam reforming step. Desulfurization takes place by adsorption of H_2S gas on the surface of zinc oxide or active carbon. The adsorbent is reactivated by stripping with super heated steam. The feed gas is preheated to 350-400° C and then treated in a desulphurisation vessel where the sulphur compounds are hydrogenated to H2S using cobalt molybdenum catalyst (CoO and MgO_3) and then adsorbed on palletized zinc oxide.

2. Catalytic steam reforming

The desulfurized natural gas is preheated by mixing with superheated steam (to 500-600° C) then enters the primary reformer and passes over the Ni catalyst where it is converted to hydrogen, CO and CO_2 according to the following equation:

$$CH_4 + H_2O \underset{790\text{-}820^{\circ}\,C}{\overset{Ni}{\rightleftarrows}} CO + 3H_2$$

$$CO + H_2O \leftrightarrow CO_2 + H_2$$

The reaction is highly endothermic and additional heat is required to raise the temperature to 780- 830° C at the reformer outlet. Only 30- 40 % of the methane feed is reformed in the primary reformer. The gas from the primary reformer is then sent to the secondary reformer, where it is mixed with compressed hot air at around 600° C and passed over nickel catalyst. Sufficient air is added to produce a final synthesis gas having a hydrogen to nitrogen mole ratio of three to one. The gas leaving the secondary reformer (H_2, N_2, CO, CO_2 and H_2O) is cooled to 360ºC in a waste heat boiler before being sent to carbon monoxide shift.

$$CH_4 + \frac{1}{2}\ O_2 + 2N_2 \xrightarrow[900 - 1200^\circ\ C]{\text{Ni Catalyst}} CO + 2H_2 + 2N_2$$

3. *Carbon monoxide shift*

After cooling, the gas, which contains 12-15 % CO dry gas base, enters high temperature CO shift converter (350-400ºC) where CO converts to CO_2 using iron oxide catalyst and chromium oxide initiator. The following reaction takes place:

$$CO + H_2O \rightarrow CO_2 + H_2$$

The exit gas is then cooled in a heat exchanger before being sent to a low temperature shift converter, where CO is converted to CO_2 by a copper oxide/ zinc oxide catalyst. The residual CO content in the converter gas is about 0.2-0.4 % (dry gas base) CO content is important for the efficiency of the process.

4. *Carbon dioxide removal*

The gas from the shift is cooled from 210 to 110° C and steam is condensed and separated from the gas. The shift gas is purified from CO_2 in a chemical or a physical absorption process. The solvents used in chemical absorption are mainly aqueous amine solutions (Mono Ethanolamine (MEA), Di Ethanolamine (aMDEA) or hot potassium carbonate solutions. Physical solvents are glycol dimethylethers, propylene carbonate and others. V_2O_5 is used as a corrosion inhibitor. The MEA process has a high regeneration energy consumption and is not regarded as a BAT process. The condensed steam contains ammonia and methanol, and small amount of amines, formic acid, acetic acid, sodium, iron, copper, zinc, aluminum and calcium. This condensate is sent to the stripper. Trace metals remaining in the process condensate can be removed in waste water treatment plant by ion exchange. The solvent is regenerated by preheating and steam stripping. In the BAT processes the stripped condensate is recycled.

5. *Methanation*

Residual CO_2 and CO, in the synthesis gas, must be removed by catalytic methanation by using Ni catalyst at 400-600ºC according to the following reaction:

$$CO_2 + H_2 \rightarrow CO + H_2O$$

$$CO + 3H_2 \rightarrow CH_4 + H_2O$$

Methane is an inert gas with respect to ammonia catalyst, while CO_2 and CO can poison the catalyst.

6. *Ammonia Synthesis*

Exit gas from the methanator is almost a pure. Three to one mole ratio of hydrogen to nitrogen is converted to ammonia according to the following reaction

$$N_2 + 3H_2 \rightarrow 2NH_3$$

First the gas is compressed from 30 atm to a pressure 200 atm, heated against exit gas from converter and entered the converter containing iron promoted catalyst. This results in a portion of the gas being converted to ammonia (15 %), which is condensed and separated in a liquid vapor separator and sent to a let-down separator. The unconverted synthesis gas is further compressed and heated to 180ºC before entering the converter containing an iron oxide catalyst. A newly developed ammonia synthesis catalyst containing ruthenium on a graphite support has a much higher activity per unit of volume and has a potential to increase conversion and lower operating pressures. Ammonia gas from the converter is condensed and separated then sent to the let-down separator where a small portion of the overhead gas is purged to prevent buildup of inert gases such as argon in the circulating gas system. Ammonia is flashed to get rid of dissolved gas. These gases are scrubbed to remove the traces of NH_3 in the form of ammonium hydroxide and the gases are used as part of the primary reformer fuel. The liquid ammonia can be either stored in pressure storage or in atmospheric double insulated refrigerated tank.

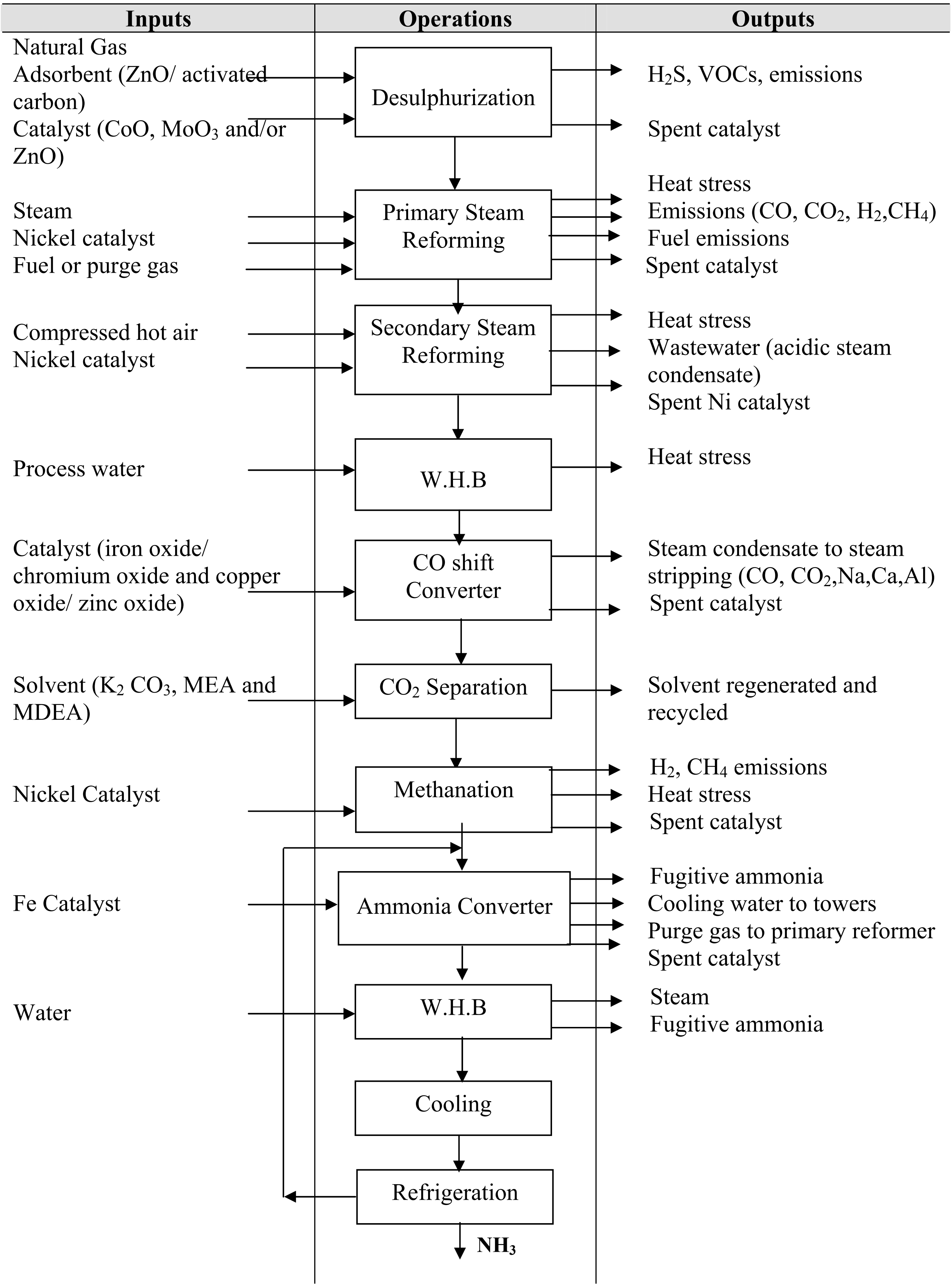
Major Hazards

The major accidents in ammonia plants are explosions and fires. In addition, there is also the potential for toxic hazard due to the handling and storage of liquid ammonia. The credible major hazards identified in an ammonia production plant are:

- fire/explosion hazard due to leaks from the hydrocarbon feed system,
- fire/explosion hazard due to leaks of synthesis gas in the CO removal/synthesis gas compression areas (75 % hydrogen)
- toxic hazard from the release of liquid ammonia from the synthesis loop.

In ammonia storage the release of liquid ammonia (by sabotage) is a credible major hazard event. Fires and explosions are usually not a hazard or only a minor hazard to the local population although potentially most severe for the plant operators. Appropriate precautions to protect both the operators and the local population are considered in the design and operation of the plants. The toxic hazard of a potential large release of liquid ammonia (i.e. from a storage tank) may be much more serious for the local population. An emergency plan for this event, covering the operators and the local population must be maintained.

Fig (7) Process Flow Diagram for Ammonia Manufacturing



Inputs	Operations	Outputs
Natural Gas Adsorbent (ZnO/ activated carbon) Catalyst (CoO, MoO_3 and/or ZnO)	Desulphurization	H_2S, VOCs, emissions Spent catalyst
Steam Nickel catalyst Fuel or purge gas	Primary Steam Reforming	Heat stress Emissions (CO, CO_2, H_2,CH_4) Fuel emissions Spent catalyst
Compressed hot air Nickel catalyst	Secondary Steam Reforming	Heat stress Wastewater (acidic steam condensate) Spent Ni catalyst
Process water	W.H.B	Heat stress
Catalyst (iron oxide/ chromium oxide and copper oxide/ zinc oxide)	CO shift Converter	Steam condensate to steam stripping (CO, CO_2,Na,Ca,Al) Spent catalyst
Solvent (K_2CO_3, MEA and MDEA)	CO_2 Separation	Solvent regenerated and recycled
Nickel Catalyst	Methanation	H_2, CH_4 emissions Heat stress Spent catalyst
Fe Catalyst	Ammonia Converter	Fugitive ammonia Cooling water to towers Purge gas to primary reformer Spent catalyst
Water	W.H.B	Steam Fugitive ammonia
	Cooling	
	Refrigeration	
	NH_3	

b) Preparation of Nitric Acid

All plants for the production of nitric acid are currently based on the same basic chemical operations: Oxidation of ammonia with air to give nitric oxide and oxidation of the nitric oxide to nitrogen dioxide and absorption in water to give a solution of nitric acid. The efficiency of the first step is favoured by low pressure whereas that of the second is favoured by high pressure. These considerations, combined with economic reasons give rise to two types of nitric acid plant, single pressure plants and dual pressure plants. In the single pressure plant, the oxidation and absorption steps take place at essentially the same pressure. In dual pressure plants absorption takes place at a higher pressure than the oxidation stage.

The oxidation and absorption steps can be classified as: low pressure (pressure below 1,7 bar), medium pressure (1,7 - 6,5 bar) and high pressure (6,5 - 13 bar). Except for some very old plants, single pressure plants operate at medium or high pressure and dual pressure plants operate at medium pressure for the oxidation stage and high pressure for the absorption.

The main unit operation involved in the nitric acid process are the same for all types of plant and in sequential order these are: air filtration, air compression, air/ammonia mixing, air/ammonia oxidation over catalytic gauzes, energy recovery by steam generation and/or gas re-heating, gas cooling, gas compression, energy recovery and cooling (dual pressure plants only), absorption with the production of nitric acid, waste gas (tail gas) heating and energy recovery by expansion of the waste gas to atmosphere in a gas turbine.

Although there are three main processes in the nitric acid production (mono, dual and atmospheric pressure) but the routes are more or less the same as follows:

1- Primary air filtration

Feed air contains, beside nitrogen and oxygen, some inert gases, carbon monoxide and some dust and impurities. Dust and impurities harmfully affect the platinum catalyst efficiency, therefore air must be filtered through a series of filters. Air is sucked (by Nox turbo- compressor set in case of atmospheric or by an air compressor in case of mono or dual pressure processes) through a filter (usually candle felt filter elements in case of atmospheric or special paper filter elements) and then heated.

2- ***Air Preheating:***
In this step filtered air is introduced through a series of steel pipes, in which fledges are provided on its outer surface to increase the heating surface area. Steam, at 3 kgm/cm^2, 140ºC is passed through the pipes and air outside. The steam condensate is collected by steam traps and recycled to the boilers.

3- ***Ammonia evaporation and filtration***
Anhydrous liquid ammonia is evaporated, superheated and its pressure is maintained according to the process (whether atmospheric or pressure). The ammonia is filtered (usually across ceramic candle filters that are cleaned every now and then).

4- ***Mixture Filtration***
The purpose of this operation is to increase purification of (air/ammonia) mixture. Cylindrical filters of large diameters are used, each one contains a porous ceramic candle hanged on a disc with openings. These candles permit the mixture to pass leaving the impurities on their surfaces. After a certain level of impurities, the filters needed to be opened and washed with water then dried by hot air. The generated wastewater from washing the filters generate a pollution problem.

5- ***Ammonia Oxidation (converters)***
Ammonia is reacted with air on platinum/ rhodium alloy catalysts in the oxidation section of nitric acid plants. Nitric oxide and water are formed in this process. The yield of nitric oxide depend on pressure and temperature:

- Pressure below 1,7 bar, temperature 810-850^{o}C -> NO yield 97%
- Pressure 1,7-6,5 bar, temperature 850-900^{o}C -> NO yield 96%
- Pressure above 6,5 bar, temperature 900-940^{o}C -> NO yield 95%

In this operation combustion takes place with the aid of platinum rhodium catalyst.

It consists of several woven or knitted gauzes formed from wire containing about 90 % platinum alloyed with rhodium for greater strength and sometimes containing palladium. Heated ammonia (60° C) is mixed with air (at 80° C) in a pipe with a big diameter. The ammonia/ air mixture is introduced to the converter. The converter contains two parts, the upper part (of a conical shape) has a pierced disc fitted on its entrance to distribute the mixture on the platinum net equally. The lower part of the converter is a bottom pierced pot filled with pottery rings to distribute the hot gases (evolving from the reaction) on to the coils of the bottom boiler. The ammonia air ratio should be strictly maintained at 12 % in case of atmospheric process or 13 % in case of dual pressure process.

Ammonia goes through oxidation according to the following reaction

$$4NH_3 + 5O_2 \xrightarrow[\text{cat}]{\text{Pt + Rh}} 4NO + 6H_2O + Q$$

$$2NO + O_2 \rightarrow 2NO_2 + Q$$

Temperature is adjusted in a range 800°-900°C, because above 900 nitrogen oxide will decompose to N_2 and O_2, and below 800° C nitrogen oxide will be formed which does not produce nitric acid when dissolved in water. The heat released from those highly exothermic reactions is mostly recovered by the waste heat boiler (WHB) fitted in the ammonia reaction (burners) in the form of superheated steam for running the NO_x and air compressors.

Air pollution and contamination from the ammonia can poison the catalyst. This effect, as well as poor ammonia-air mixing and poor gas distribution across the catalyst, may reduce the yield by 10 %. Maintenance of the catalyst operating temperature is very important for the NO yield. This is achieved by adjusting the air/ammonia ratio and ensuring that the lower explosive limit for ammonia in air is not exceeded. The preheated ammonia is thoroughly mixed with preheated air and subjected to further filtration to avoid contaminants from entering to the catalyst. The ratio of ammonia air mixture is controlled by a high precision ratio controller which is considered as the safeguard for protecting arising from:

- Catalyst temperature exceeds 850^o C
- Ammonia/ air ratio exceeds 12.5 % (in atmospheric oxidation) or 10 % (in case of pressure oxidation)
- Failure of air compressor or No_x compressor …etc

The water produced in oxidation is then condensed in a cooler-condenser and transferred to the absorption column. Nitric oxide is oxidized to nitrogen dioxide as the combustion gases are cooled. For this purpose secondary air is added to the gas mixture obtained from the ammonia oxidation to increase the oxygen content to such a level that the waste gas leaving the plant has a normal oxygen content of between 2 - 4 %.

6- Energy Recovery

The hot reaction gases are used to produce steam and/or to preheat the waste gas (tail gas). The heated waste gas is discharged to the atmosphere through a gas turbine for energy recovery. The combustion gas after this heat transfer for energy recovery, has a temperature of 100 to 200^o C, depending on the process and it is then further cooled with water.

7- Cooling

Exit gases (NOx, excess air and water vapour) are cooled through a water cooler in two stages, where nitrogen oxides are then dissolved in the water condensate to form a very diluted nitric acid (about 2% conc.) which is collected in a tank. The collected diluted acid is withdrawn by pumps and discharged to the bottom of the absorption tower. The remaining gases are withdrawn, together with excess air, by compressing turbines to the absorption towers.

8- Absorption:

The absorber is operated with a counter-current flow of water. the absorption of the nitrogen dioxide and its reaction to nitric acid and nitric oxide take place simultaneously in the gaseous and liquid phases. The main reaction taking place is as follows:

$2NO + O_2 \rightarrow 2NO_2$

$3NO_2 + H_2O \rightarrow 2HNO_3 + NO$

$2NO_2 \rightarrow N_2O_4$

These reactions depend on pressure and temperature to a large extent and are favored by higher pressure and lower temperature.

Series of towers with 3.5m diameter and 24m height are used in this stage. The absorber-reactor is a sieve plate or bubble cap unit with cooling coils on each of the 20 to 50 trays. Gas enters at the bottom, dilute nitric acid part way up the column, with cold water entering at the top. In the first tower most of the oxidation operation takes place where NO is converted to nitrogen dioxide. Diluted Nitric acid is then formed, collected in a level tank and discharged to the bleaching operation. Chlorine impurities presents a unique problem in the absorber, they cannot be transferred through the bottom neither can they leave in the top gas. Therefore, they must be excluded from entry or provision made for their purging as the reaction of nitric oxide proceeds during gas flow. Consequently the gases are cooled (remove heat of reaction and promote oxidation reactions to go to completion), against the cold tail gases coming out of the absorption tower to preheat them before entering the tail gas turbine. The preheated tail gas passes through the expansion turbine (part of the NO_x compressor drives) to recover the energy and reduce tail gas temperature. Then further cooled before passing through the series of counter-current packed towers.

9- Bleaching

The acid leaving the bottom of the column contains some NO_x, mostly as N_2O_4 (colorless) but some as red NO_2. It is therefore sent to a bleaching tower to eliminate its colour. In bleaching operation the acid is sprayed at the top of the tower (about 5.5m height and 90 cm diameter), which is filled with a Raschig rings at the bottom. A counter current air stream is introduced at the bottom of the tower through a screen, to absorb the gases from the acid then withdrawn from the top of the tower. The acid, free from gases, is collected at the bottom of the tower and then cooled in cooling plates and sent to storage tanks. Cooling plates are essential, especially at the first tower, where the highest quantity of heat is released because most of the oxidation and absorption reactions take place in that tower.

Fig (8) illustrates the block diagram for nitric acid production.

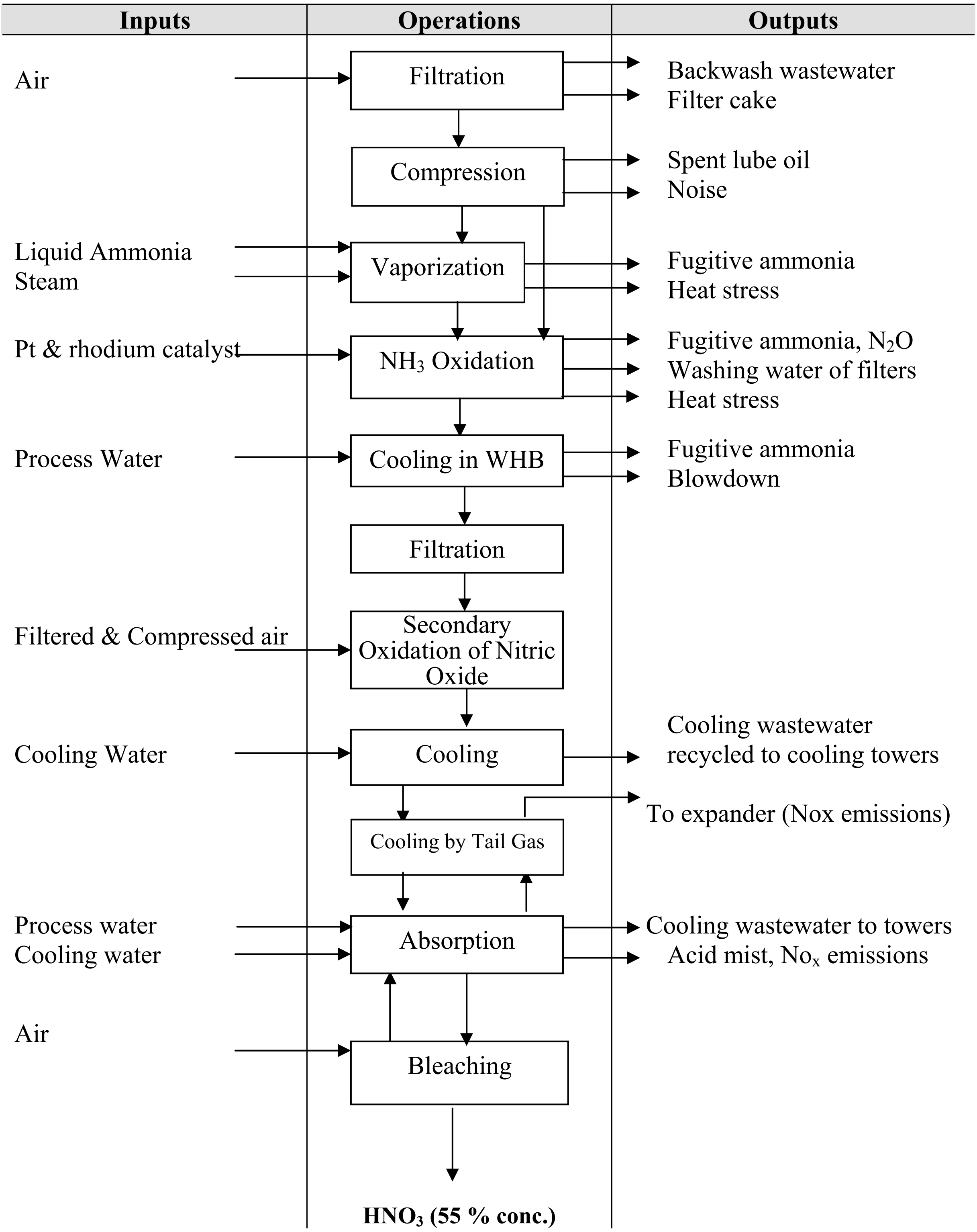
Major Hazards

The following hazards may arise during nitric acid production:

- equipment/piping failure because of corrosion
- explosion hazard due to the air ammonia mixture
- explosion of nitrite/nitrate salts.

Corrosion protection is achieved by the well proven use of suitable austenitic stainless steel where condensation can occur and by regular monitoring of conditions. Safety is ensured by the automatic closure of the ammonia control valve and separate shutdown trip valve when too high an air ammonia ratio is measured, either from each individual flow meter or indirectly from the catalyst gauze temperature. The air ammonia ratio should be continuously controlled and kept below the hazardous range. Any free ammonia present in the nitrous gas will have a deposit of nitrite/nitrate in a cold spot. Local washing and well proven operating practices will prevent the hazard.

Fig (8) Process Flow Diagram for Nitric Acid Manufacturing



c) Methanol Production

This unit replaced the copper liquor (ammoniacal copper formate or acetate) section which was used for the removal of CO from synthesis. The liquor pollutes water streams as it contains copper, ammonia and carbonic acid. The copper liquor reacts with CO which later released when the solution is regenerated.

Methanol is formed by the reaction of CO and CO_2 with H_2 according to the reaction:

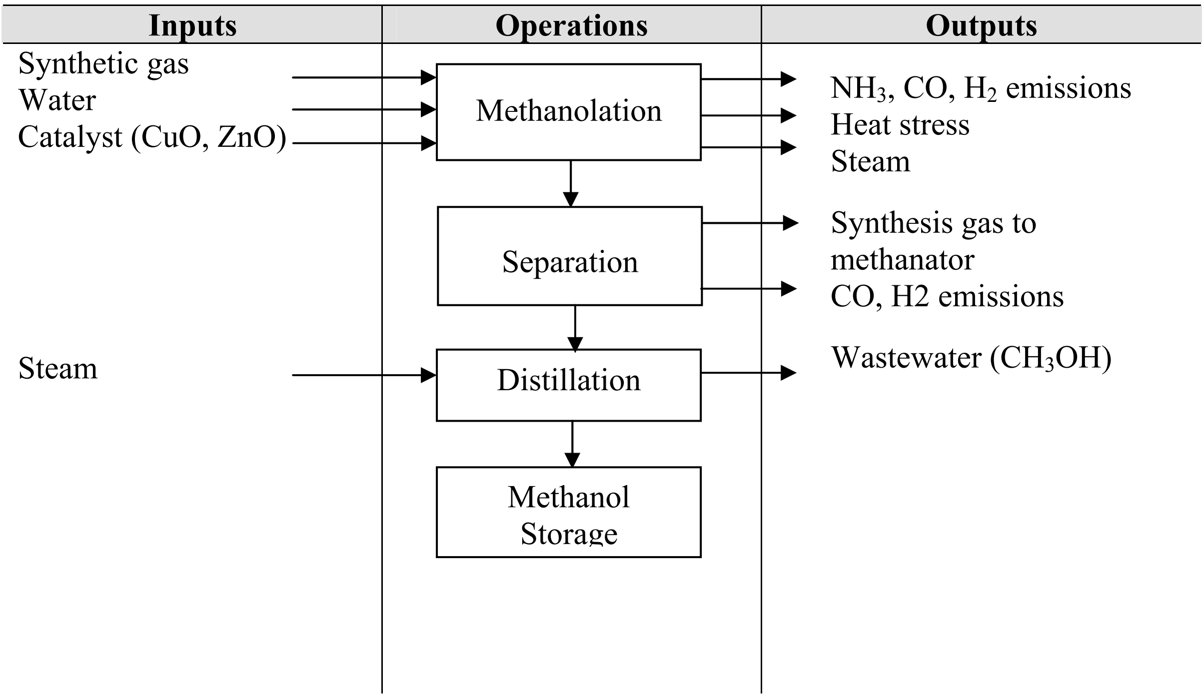
$CO + 2H_2 \rightarrow CH_3OH$

$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O$

This reaction takes place at 210^o C and 220 atmosphere in presence of Cu O and ZnO catalyst. The product is raw methanol which is purified by distillation to 99 % concentration.

Fig (9) shows the process flow diagram for methanol production.

Fig (9) Process Flow Diagram for Methanol Production



d) Ammonium Nitrate Production

Ammonium Nitrate is in the first place a nitrogenous fertilizer representing. 12.4% of the total nitrogen consumption worldwide. It is more readily available to crops than urea. In the second place, due to its powerful oxidizing properties is used with proper additives as commercial explosive.

The production process comprises three main unit operations: neutralization, evaporation, solidification (prilling and granulation). Individual plants vary widely in process detail.

1. Neutralization:

Anhydrous liquid ammonia is evaporated in an evaporator using cooling water. The stoichiometic quantities of nitric acid (55% concentration wt/ wt) and gaseous ammonia are introduced by an automatic ratio controller to a neutralizer. The reaction between Ammonia and nitric acid produces ammonium nitrate solution according to the following exothermic reaction.

$$NH_3 + HNO_3 \longrightarrow NH_4\,NO_3$$

Neutralization can be performed in a single stage or in two stages. The neutralizer can be carried out at atmospheric (either normal or low emission neutralizers where the temperature does not exceed 105°C and pH will be 6 and 3 respectively) or at elevated pressure of almost 4 atmospheres. The normal neutralizers are usually followed by flash evaporation in order to in crease the out let A.N concentration to 70%. In case of pressure neutralizers the temperature will be in the range of 178°C and the steam generated from the heat of reaction will be utilized in the subsequent step namely concentration of A.N solution.

During evaporation some ammonia is lost from the solution. The steam which is boiled off is contaminated. The control of the neutralizer is important. The pH and the temperature must both be strictly controlled to limit the losses from the neutralizer. All installations must include pH and temperature controls. At the operating temperature of the neutralizer, impurity control is of great importance because a safety incident will also be a significant environmental incident. The ammonium nitrate solution from neutralizer may be fed to storage without further processing but, if it is used in the manufacture of solid ammonium nitrate, it is concentrated by evaporation.

2. *Evaporation to Concentrate the A.N*

The outlet from the neutralizer is received in an intermediate tank. The solution should be made alkaline before being pumped (no need for pumps in case of pressure neutralizers since the pressure will maintain the flow) to the evaporation section (multi-effect) running under vacuum. The solution will be steam heated in the multi effect evaporation section. The solution will be concentrated up to 97.5-99.5% (normally over 99 %) depending on whether ammonium nitrate will be granulated or prilled.

3. *Mixing the Filling Material:*

In order to reduce the nitrogen content of A.N from 35% to 33.5%, the proper filling material is added (about 4% by weight of powdered limestone or dolomite or even kaolin)

4. *Prilling or Granulation*

The hot concentrated melt is either granulated (fluidize bed granulation, drum granulation … etc) or prilled. Ammonium nitrate is formed into droplets which then fall down a fall tower (prill tower) where they cool and solidify. Granulation requires more complicated plant than prilling and variety of equipment. The main advantage of granulation with respect of environment is that the quantity of air to be treated is much smaller and abatement equipment is cheaper.

5. *Drying, Screening*

The ammonium nitrate (prills or granules) is dried (usually in drums) using hot air (steam heated), then screened to separate the correct product size. The oversize and undersize will be recycled either in the mixing tank (in case of prilling) or to the granulator.

6. ***Final Cooling***

The hot proper size granules, are then cooled (against cooled and humid free air) down to 40°C and treated with anti-caking (usually amines) and then coated with an inert material (usually, kaolin, limestone or dolomite) and then conveyed to the storage.

Fig (10) illustrates the block flow diagram for ammonium nitrate production process.

Major Hazards

Ammonia, nitric acid and ammonium nitrate are the hazardous chemicals present in ammonium nitrate plants. A.N is an oxidizing agent and precautions must be taken in manufacturing, transport and storage.

The main chemical hazards associated with ammonium nitrate are fire, decomposition and explosion. Burns caused by hot AN solution should also be considered from a safety point of view.

Ammonium nitrate itself does not burn. Being an oxidizing agent, it can facilitate the initiation of a fire and intensify fires in combustible materials. Hot AN solution can initiate a fire in rags, wooden articles ets., on coming into contact with them. Similarly, fertilizer products or dust contaminated with oil or other combustible materials can also start fires when left on hot surfaces.

Pure solid A.N melts at 169^o C. On further heating it decomposes by way of a complex series of reactions. Up to about 250^o C it decomposes primarily into N_2O and H_2O. Above 300^o C reactions producing N2, NO, NO_2 etc., become significant. These reactions are exothermic and irreversible. They are accompanied by the vapour pressure dependent endothermic dissociation into HNO_3 and NH_3 vapours which can provide a temperature limiting mechanism, provided the gases can escape freely. If they cannot, the endothermic dissociation is suppressed and a run-away decomposition can develop, leading to explosive behavior. A number of materials have a strong catalytic effect on the thermal decomposition of A.N. These include acids, chlorides, organic materials, chromates, dichromate, salts of manganese, copper and nickel and certain metals such as zinc, copper and lead. The decomposition of AN is suppressed or prevented by an alkaline condition. Thus the addition of ammonia offers a major safeguard against the decomposition hazard. The release of toxic fumes is one of the main hazards associated with the decomposition of AN.

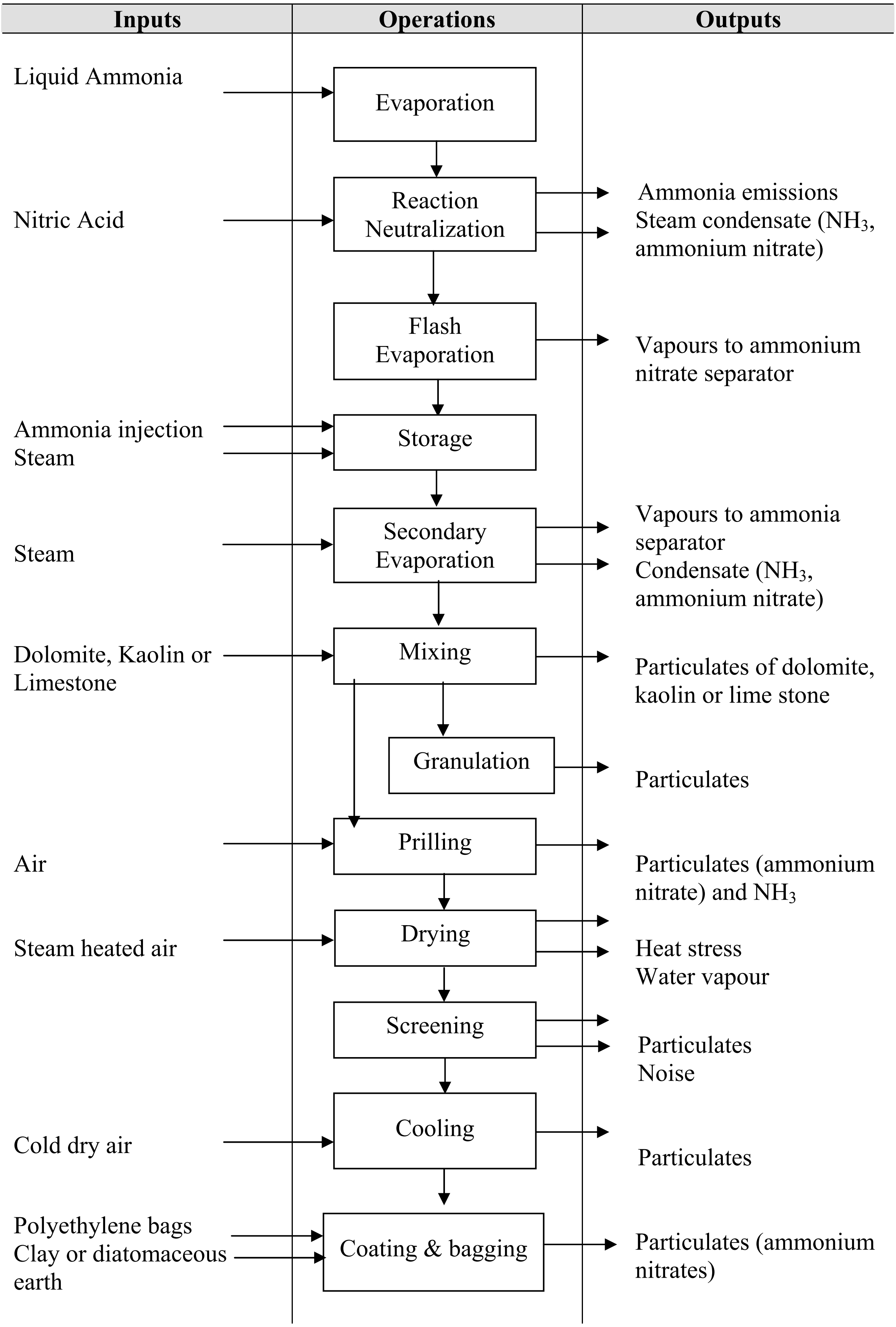
Strongly acidic conditions and the presence of contaminants should be avoided to counter the explosion hazard in AN solutions. Explosions can occur when ammonium nitrate is heated under confinement in pumps. Reasons for pump explosions include:

1) No (or insufficient) flow through the pump.
2) incorrect design (design may incorporate low flow and/or high temperature trips).
3) poor maintenance practices.
4) contamination.

It is more common for the major storage of these chemicals to be located within their own manufacturing plants. Possible requirements for storage

- materials of construction used in the building of the store, other buildings in the locality, storage of other product in the same building, absence of drains, fire detection and fire fighting systems, layout and size of stacks

Fig (10) Process Flow Diagram for Ammonium Nitrate Manufacturing



e) Ammonium Sulphate

Ammonium sulphate (A.S) is a nitrogenous fertilizer with an additional source of soluble sulphur which is a secondary plant nutrient. The majority of its production is coming from coking of coal as a byproduct. Ammonium sulphate is produced by the direct reaction of concentrated sulphuric acid and gaseous ammonia and proceeds according to the following steps.

1. ***Reaction of Ammonia and Sulphuric Acid:***

   Liquid ammonia is evaporated in an evaporator using 16 bar steam and preheated using low pressure steam.

   The stiochiometric quantities of preheated gaseous ammonia and concentrated sulphuric acid (98.5% wt/wt) are introduced to the evaporator – crystalliser (operating under vacuum). These quantities are maintained by a flow recorder controller and properly mixed by a circulating pump (from upper part of the crystalliser to the evaporator)

2. ***Crystallization***

   The reaction takes place in the crystallizer where the generated heat of reaction causes evaporation of water making the solution supersaturated. The supersaturated solution settles down to the bottom of crystalliser where it is pumped to vacuum metallic filter where the A. S crystals are separated, while the mother liquor is recycled to the crystalliser.

3. ***Drying of the wet Ammonium Sulphate Crystals***

   The wet A.S crystals are conveyed (by belt conveyors) to the rotary dryer to be dried against hot air (steam heated) and then conveyed to the storage area where it naturally cooled and bagged.

Fig (12) presents the process block diagram for ammonium sulphate production.

f) Ammonium Phosphate

There are two types of ammonium phosphate, namely: mono-ammonium phosphate and di-ammonium phosphate. Mono-ammonium phosphate is made by reacting ammonia with phosphoric acid, centrifuging and drying in a rotary dryer. Di-ammonium phosphate requires a two-stage reactor system in order to prevent loss of ammonia. A granulation process follows with completion of the reaction in a rotary dryer which is heated by a furnace using fuel.

To produce mono-ammonium phosphate, ammonia to phosphoric acid ratio is 0.6 in the pre-neutralizer and then 1.0 in the granulator. For production of di-ammonium phosphate, the ratios are 1.4 and 1.0 in the pre-neutralizer and granulator respectively.
The resulting ammonium phosphate is then screened. The undersize particles are recycled back to the granulation operation, while the oversized particles are grinded first before recycling to the granulator. After screening the fertilizer granules are coated with specific material in order to regulate its dissolving process in the soil when used.

Fig (13) illustrates the process block diagram for the manufacturing of ammonium phosphate fertilizer.

Fig (12) Process Flow Diagram for Ammonium Sulphate Manufacturing

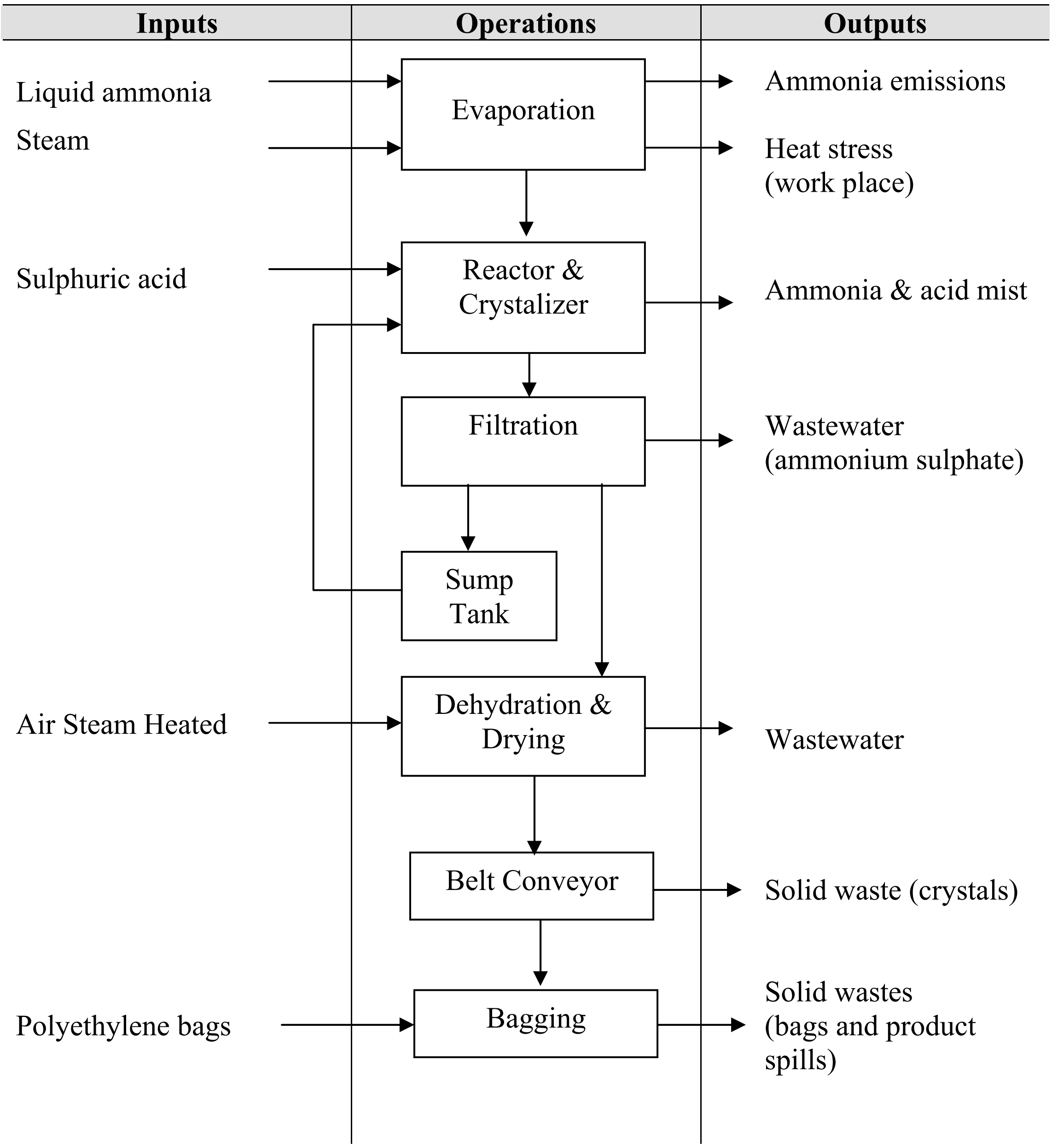
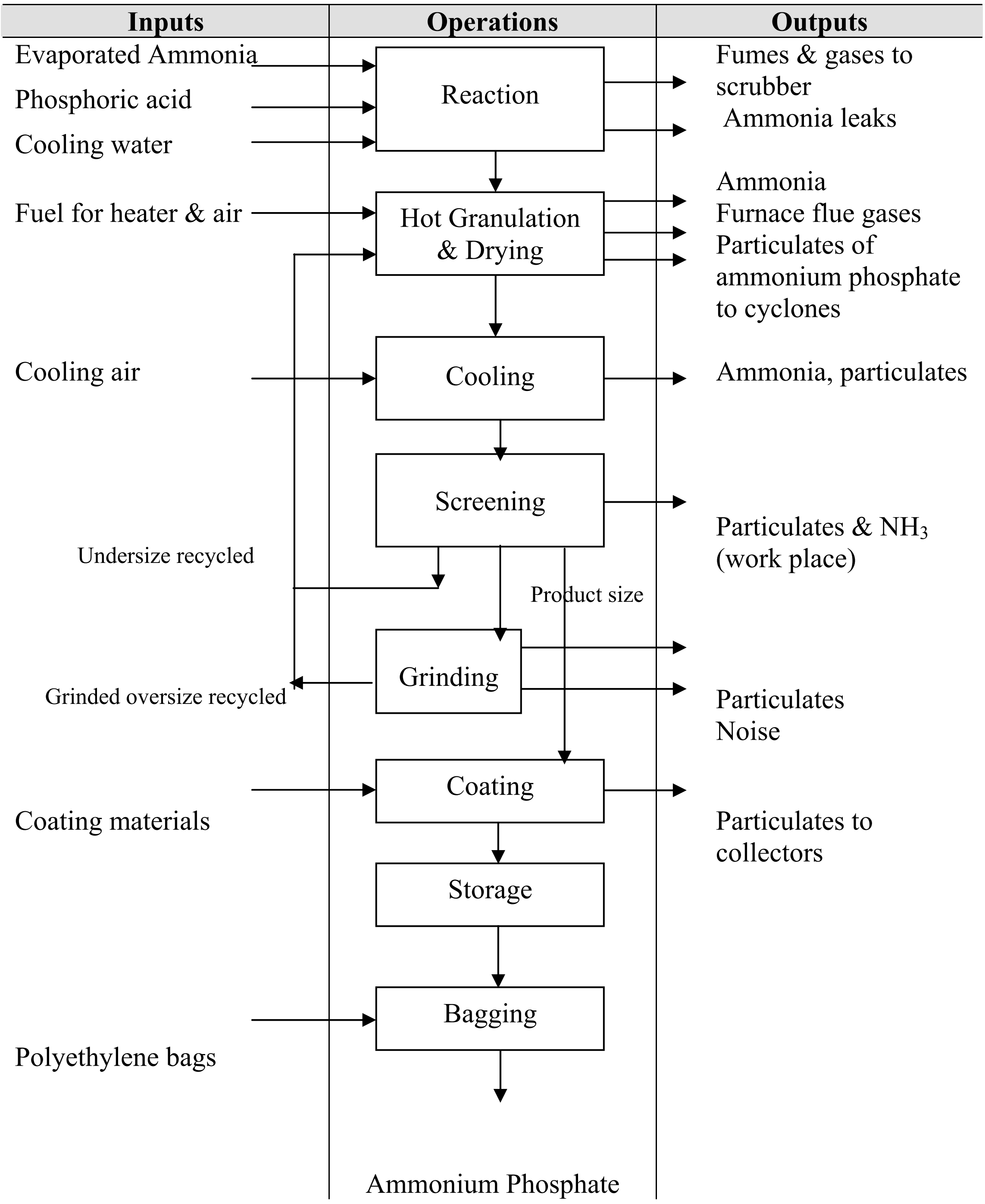


Fig (13) Process Flow Diagram for Ammonium Phosphate Manufacturing



g) Calcium Nitrate

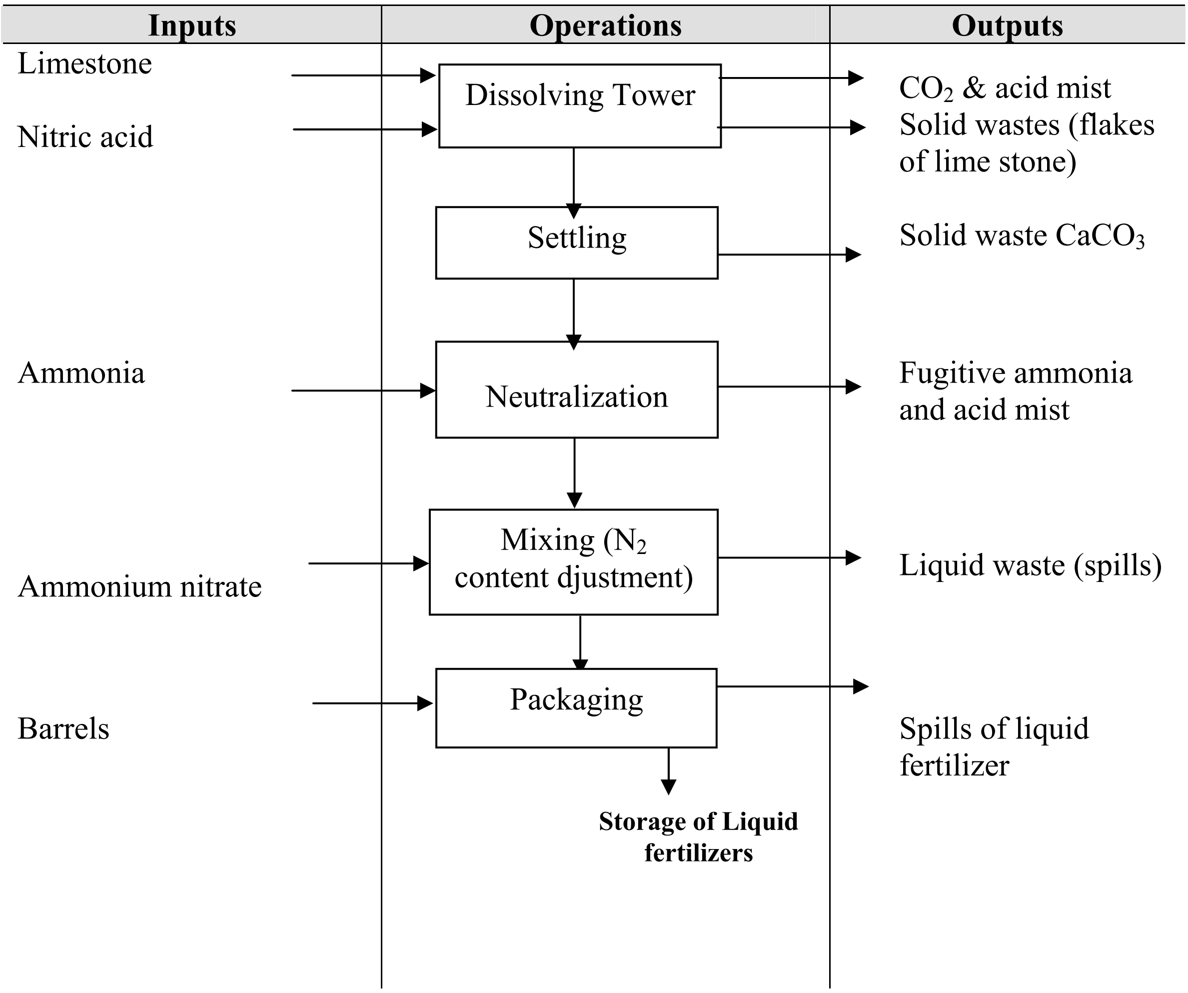
Calcium nitrate is produced by dissolving the calcium carbonate (lime stone) with nitric acid, according to the following reaction:

$$CaCO_3 + 2HNO_3 \rightarrow Ca(NO_3)_2 + CO_2 + H_2O$$

The lime stone is transported to the site as small size stones and lifted to the dissolving tower. The nitric acid is fed to the bottom of the dissolving tower and the formed calcium nitrate is fed to the settling tank. After settling, the excess acid is neutralized with ammonia. The nitrogen content is adjusted with ammonium nitrate. The fertilizer is produced in the liquid state and the nitrogen content of the final product is adjusted to the required specifications using ammonium nitrate.

Fig (14) illustrates the process flow diagram for the production of calcium nitrate fertilizers.

Fig (14) Process Flow Diagram for Calcium Nitrate



h) Urea

Urea (carbamide) is a high-concentration nitrogenous fertilizer, with a 46 % nitrogen content. It is produced from liquid ammonia and gaseous carbon dioxide at about 170- 190° C and 135- 145 bar, according to the following reactions:

$$CO_2 + 2NH_3 \rightarrow NH_2COONH_4 \qquad (1)$$

$$NH_2COONH_4 \leftrightarrow NH_2CONH_2 + H_2O \qquad (2)$$

The second reaction is dehydration of the carbamate to produce liquid phase urea.

The urea plant consists of high and low pressure sections. The high pressure section is composed of:

- Urea synthesis including the high stripper and condenser.
- Urea rectifying operation.

Whereas, the low pressure section is composed of:

- Evaporation.
- Recovery.
- Prilling.

Carbon dioxide is supplied from the ammonia plant and compressed in the centrifugal CO_2 compressor then introduced into the bottom of the high pressure stripper, which is a part of urea synthesis section. Liquid ammonia is pumped from the storage tank to the urea plant and is preheated to a temperature around 10° C. The high pressure NH_3 pump raises the pressure to 165 bars and delivers it to the high pressure carbamate condenser. NH_3 and CO_2 are fed to the synthesis section in the molar ratio of 2 for NH_3/ CO_2.

In the urea reactor most of the condensate carbamate is converted to urea and water. The reaction mixture, leaving the reactor from the overflow through internal down comer, is distributed over the top of the stripper tubes. CO_2 gas is introduced in counter flow. The gases leaving the top of the stripper are led into the high pressure carbamate condenser. Major parts of the stripper off-gases are condensed gases and non-condensed NH_3, CO_2. They are introduced into the bottom of the reactor where the conversion of carbamate into urea takes place. Non-converted NH_3 and CO_2 leave the reactor to the high pressure scrubber, where major parts of NH_3 and CO_2 are recovered and mixed with fresh NH_3 feed through the high pressure ejector.

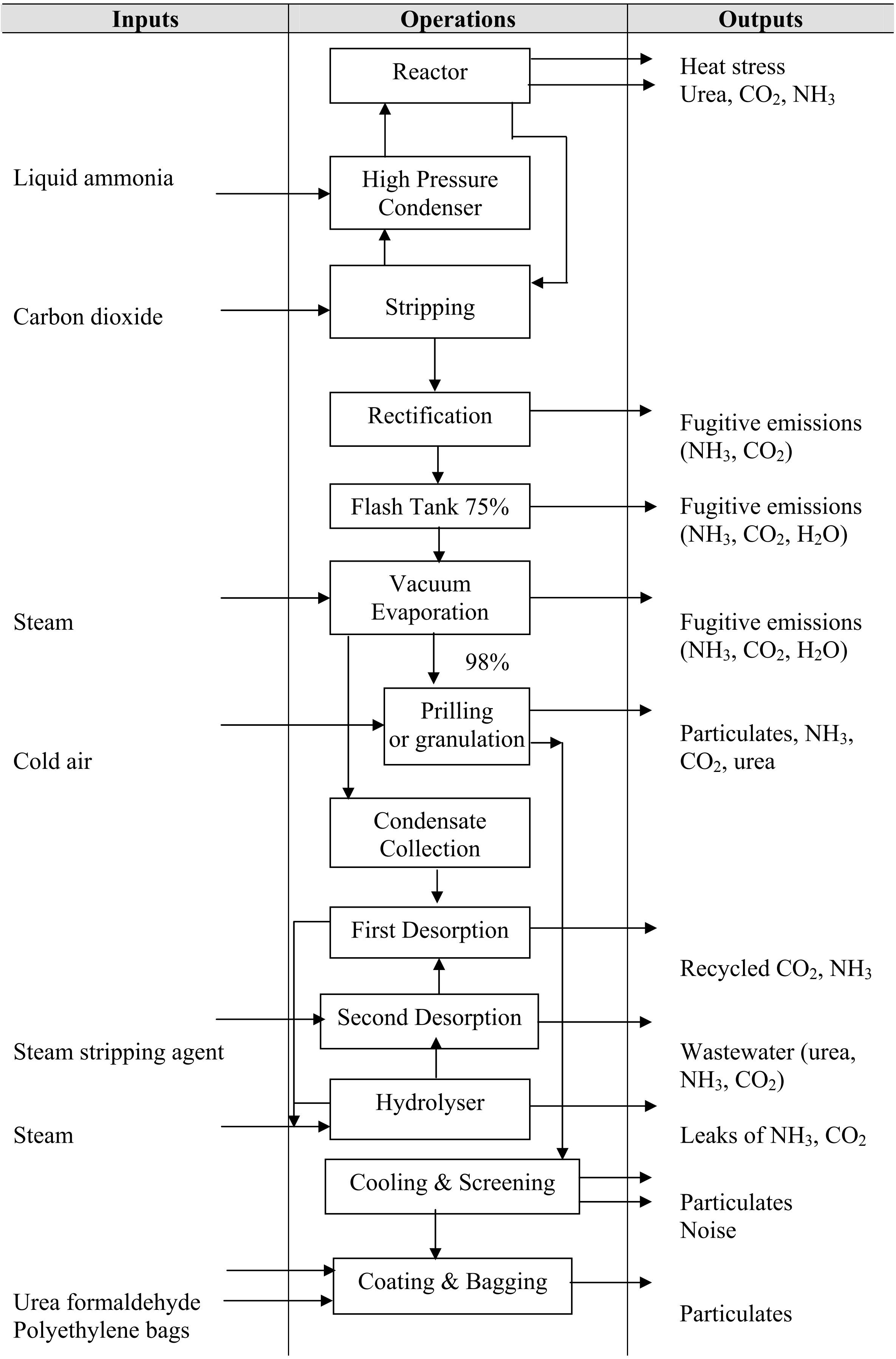
The urea carbamate solution leaving the bottom part of the stripper is sprayed on a bed of ball rings in a rectifying column. The urea solution leaving the bottom part flows to a flash tank and then to the urea solution storage tank (about 70- 80 % concentration). This solution is further concentrated to a melt (98 % urea) by evaporation under vacuum in two stages. The urea melt is pumped to the prilling tower. The prills are received on conveyors and transported to the bagging section.

The condensate containing NH_3, CO_2 and urea is pumped from the NH_3- water tank to the upper part of the first desorber, which is stripped by the overhead vapours of the second desorber. The bottom effluent of the first desorber is pumped to the hydrolyser column. In the hydrolyser the urea is decomposed into NH_3 and CO_2 and fed to the first desorber after separation in the second desorber. The process condensate is discharged from the bottom of the second desorber to the sewer system of the plant.

The desired temperature of the prills ranges from 60° C to 65° C. If the temperature is 80° C- 85° C then the residual heat in the prills causes some stretching and bursting for the polyethylene bags after the bagging operation.

Fig (15) shows the process flow diagram for the production of urea.

Fig (15) Process Flow Diagram for Urea Production



i) Bagging Section

The produced fertilizers are sent to the bagging section by belt conveyors. Fertilizers are piled in this section and withdrawn by rail scrapers which moves on a rail bars. By using forks the fertilizers slide down to the feed network then to a sliding car with small bunker which ensure constant feeding. The car slides along the section to transport the product to an inclined belt conveyor or then to bucket elevators and hammer mill. By a screw conveyor, the product is discharged to the final product and packed.

In the packaging stage a balance exist between the conveyor and the packaging bunker at which a level meter is fixed. The bunkers feed the balance which consequently feed packaging operation in which polyethylene bags are filled and transported by belt conveyors to the trucks.

2.3 Service Units and Related Pollution Sources

Medium and large size plants will have some/all of the following service and auxiliary units. These units can be pollution sources and therefore should be inspected and monitored. Fig (16) shows the various units with their corresponding raw materials and potential pollution sources.

2.3.1 Boilers

Boilers are used to produce steam for:

- heat supply to the processes, reaction (steam reforming) and CO shift converter (in ammonia production and other processes utilizing steam).
- electric power generation.

Conventional steam-producing thermal power plants generate electricity through a series of energy conversion stages. Fuel is burned in boilers to convert water to high-pressure steam, which is then used to drive the turbine to generate electricity.

The gaseous emissions generated by boilers are typical of those from combustion processes. The exhaust gases from burning fuel oil (Mazot) or diesel oil (solar) contain primarily particulates (including heavy metals if they are present in significant concentrations in the fuel), sulfur and nitrogen oxides (SOx and NOx) and volatile organic compounds (VOCs).

The concentration of these pollutants in the exhaust gases is a function of firing configuration (nozzle design, chimney height), operating practices and fuel composition.

Gas-fired boilers generally produce negligible quantities of particulates and pollutants.

Wastewater is generated as blowdown purged from boilers to keep the concentration of dissolved salts at a level that prevents salt precipitation and consequently scale formation. The blowdown will be high in TDS.

In the case of power plants, water is used for cooling the turbines and is also generated as steam condensate. The amount of wastewater generated depends on whether cooling is performed in open or closed cycle and on the recycling of steam condensate. Contamination may arise from lubricating and fuel oil.

2.3.2 Water Treatment Units

There are different types of water used in industry. Depending on the application and the water source, different treatment processes are applied.

a. Water Softening for medium hardness water

Calcium and magnesium ions are removed from hard water by cation exchange for sodium ions. When the exchange resin has removed the ions to the limits of its capacity, it is regenerated to the sodium form with a salt solution (sodium chloride) in the pH range of 6-8. This is performed by taking the softener out of service, backwashing with the salt solution, rinsing to eliminate excess salt, then returning it to service. The treated water has a hardness level of less than 1 ppm expressed as calcium carbonate.

b. ***Water softening for very high bicarbonate hardness***

Water from wells and canals is pre-treated before softening. Water is treated first by the lime process, then by cation exchange. The lime process reduces dissolved solids by precipitating calcium carbonate and magnesium hydroxide from the water. It can reduce calcium hardness to 35 ppm if proper opportunity is given for precipitation. A coagulant such as aluminum sulfate (alum) or ferric sulfate is added to aid magnesium hydroxide precipitation. Calcium hypochlorite is added in some cases. Currently the use of organic poly-electrolytes is replacing many of the traditional inorganic coagulant aid. Sludge precipitates and is discharged to disposal sites whereas the overflowing water is fed to a sand filer followed by an activated carbon filter that removes any substances causing odor and taste. A micro filter can then be used to remove remaining traces. A successful method to accelerate precipitation is contacting previously precipitated sludge with the raw water and chemicals. The sludge particles act as seeds for further precipitation. The result is a more rapid and more complete reaction with larger and more easily settled particles.

c. ***Water Demineralization***

Water demineralization units are indispensable units in industrial plants. These units provide the relevant water, after removing the soluble salts, for pressure boilers and dematerialized necessary for process (as process water for nitric acid, sulphuric acid .. etc). The removal of salts in the raw water is carried out by special resins through ion exchange. The raw water is pumped to cation, anion (and mixed bed) exchangers. The resins when exhausted (saturated with salts) are regenerated using various chemicals such as sodium chloride, hydrochloric acid or sulphuric acids and sodium hydroxide. The effluents during these regeneration processes (twice a day) represent a considerable source of pollution.

2.3.3 Cooling Towers

Cooling water is used extensively in industry. During the cooling process, water heats up and can only be reused if cooled. Cooling towers provide the means for recycling water and thus minimizing its consumption. The cooling effect is performed through partial evaporation. This causes an increase in the concentration of dissolved salts which is controlled by purifying some water (blowdown). The blowdown will be high in TDS.

2.3.4 Compressors

Several types of compressors are needed in the fertilizers plants, including the ammonia, steam, gas and air compressors. Compressors consume a considerable quantities of lube oils for lubrication and cooling purposes, in addition to electricity. The major resulting pollutants are noise affecting workers and the spent oils.

Lube oils are essential for several parts of the compressors. It utilizes as a pillow which facilitate the revolving motion, in addition to the absorption of resulted heat due to friction. When the compressor is started-up a pump drafts the oil from its storage tank, to a filter and an oil cooler. The lube oil, after passes through different parts of the compressor, is collected back in the oil tank.

Ammonia compressing is composed of two stages, the first includes two cylinders and the second four. No greasing is applied inside the cylinders, but only the other parts are being greased in order to lower the friction. The temperature of a gas arises by compression, hence it needs to be cooled before any further compression. Compressing is done by the piston inside the cylinder, in which the gases in front of the piston are being pressed until their pressure equalize the repelling pipe pressure. This opens the discharging valve and compressed gases exit into their path. The suction valve is consequently opened and gases introduce the cylinder behind the piston. These types are named the frequency compressors. Gaseous leaks may result from the compressors, which generate a pollution problem in the work place of the unit. A good check should be implemented for the equipment in order to avoid operating problems, such as clogging in the filter of oil suction pump, leaks from the non-return valve, broken pipelines of any other parts, temperature increasing than usual, decreasing in cooling efficiency …etc. The compressor' motor is cooled by cold air.

2.3.5 Laboratories

There are several laboratories in the fertilizers plants which are responsible for different activities, as follows:

- Research laboratory, responsible for developing, through research and analysis, new types of fertilizers as well as studying the different effects on soil and plant.
- Quality control laboratory, responsible for the analysis of the different products and comparing the findings with the standard specifications. It also analyze the raw materials inputs to the different units of the plant.
- Environmental laboratory, responsible for the collection of periodical routine and sudden random samples to control air and water pollution. It is also responsible for the performance of water and wastewater treatment units, through periodic analysis for the inlet and outlet streams.

Different types and quantities of hazardous chemicals are used for different testing and analysis. Proper handling and storage are required for compliance with environmental law.

2.3.6 Workshops and Garage

Large facilities have electrical and mechanical workshops for maintenance and repair purposes. Environmental violations could be due to:

- Noise
- Rinse water contaminated with lube oil

Pollution in the garage area will depend upon the services offered. The presence of a gasoline or diesel station implies fuel storage in underground or over the ground tanks that require leak and spill control plans.

Replacing lube oil implies discharge of spent oil to the sewer lines or selling it to recycling stations. Washing agents and solvents may be used.

2.3.7 Storage Facilities

The specifications for the storage facilities depend on the stored material. Fuel is used for the boilers, cars and delivery trucks. It is stored in underground or over ground lined tanks. Usually, fuel oil (Mazot), gas oil (solar) or natural gas are used as fuel. Acids such as sulphuric or nitric or phosphoric acids are stored in large capacities tanks.

2.3.8 Wastewater Treatment Plants

Although a WWTP is a pollution abatement measure, it has to be inspected and monitored for potential pollution. Pollution may be due to malfunctioning or improper management. Disregarding treatment of boilers and cooling towers blowdown, which is by far the largest wastewater problem in the industry, several treatment schemes have been used. Most approaches have been based on the origin of the product, that is phosphate or nitrogenous fertilizer.

The effluent streams can be characterized as either a phosphoric acid effluent or an ammonia effluent. The phosphoric acid effluent is high in fluoride concentration, low in pH, high in phosphate and in suspended solids. Standard practice has been to contain the water for reuse, allowing enough time for solids sedimentation. The problem is that fresh water addition may result in overflow of the retained water. The retention ponds should be carefully designed. If overflow is evident, it must be treated with lime and clarified.

A slightly more sophisticated method for discharging overflow water is with a two-stage liming process. The first lime treatment brings the pH up to 3 or 4 and reduces the fluoride concentration to 20- 25 mg/ l and the P concentration to 50- 60 mg/ l. The $CaF2$ precipitate is settled out and the effluent is treated again with lime to raise the pH to 6 or 7. The F and P concentrations are reduced to about 10 mg/ l. the water is clarified and released to a receiving stream. The two-stage fluoride removal process of lime precipitation followed by alum-polyelectrolytes flocculation and sedimentation was found to be workable. Maximum precipitation of fluoride with lime occurs at a pH greater than or equal to 12 and optimum coagulation with the alum-polyelectrolyte occurred at a pH of about 6 to 7.

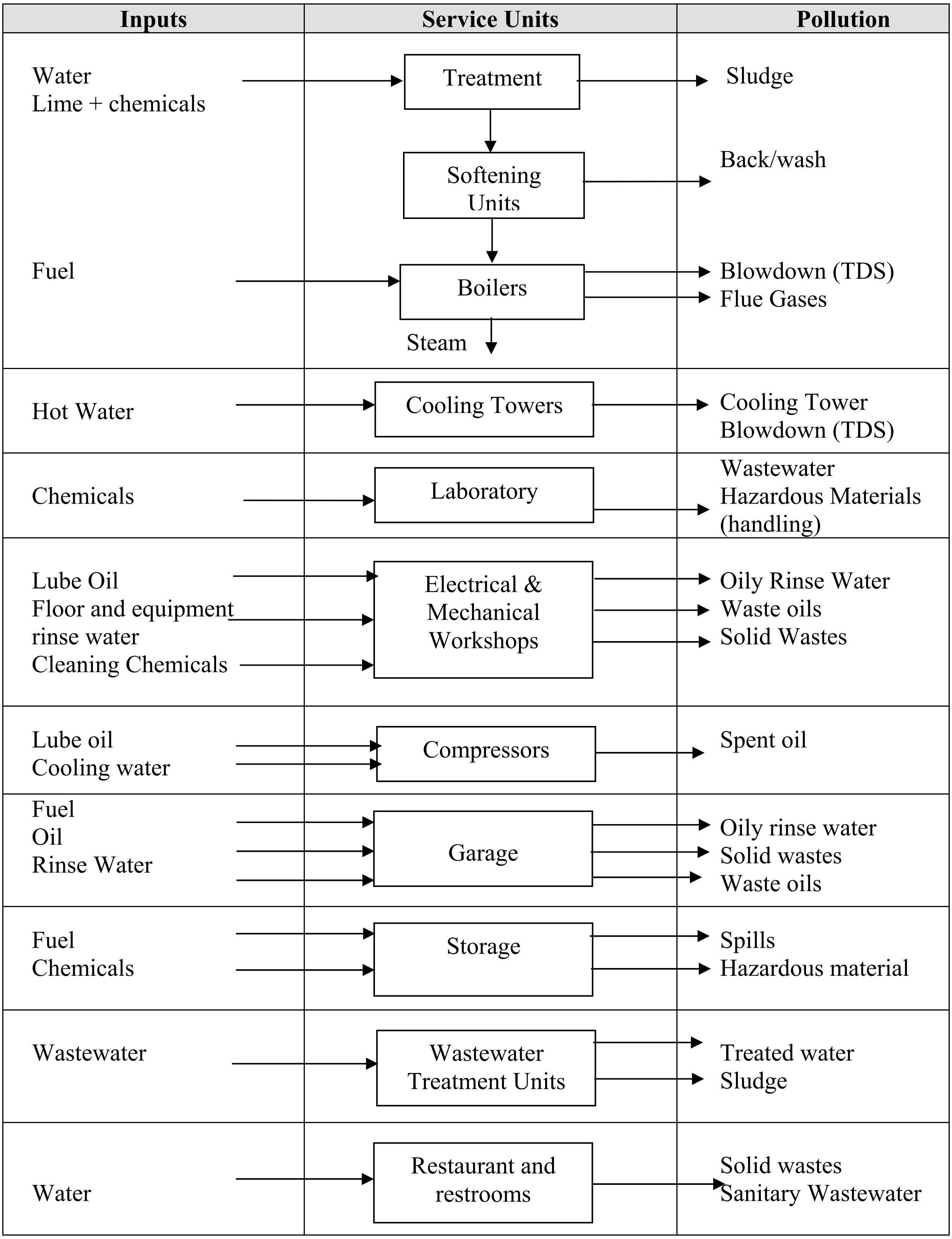
The other effluent type is characteristic of ammonia production and ammonia containing products. Most of the contamination comes from the production of the ammonia itself. It is characteristically high in ammonia from effluent gas scrubbing operation and high in ammonia, total suspended solids and carbamate. These effluents require a pH adjustment and settling.

The treated effluent is discharged to the receiving media and a final sludge is remained. Safe sludge disposal should be implemented, due its high content of hazardous constituents such as heavy metals, phosphorous, ammonia and silicates.

2.3.9 Restaurants, Washrooms and Housing Complex

These facilities will generate domestic wastewater as well as domestic solid waste.

Fig (16) Service Units and their Related Pollution Sources



Inputs	Service Units	Pollution
Water Lime + chemicals Fuel	Treatment Softening Units Boilers Steam	Sludge Back/wash Blowdown (TDS) Flue Gases
Hot Water	Cooling Towers	Cooling Tower Blowdown (TDS)
Chemicals	Laboratory	Wastewater Hazardous Materials (handling)
Lube Oil Floor and equipment rinse water Cleaning Chemicals	Electrical & Mechanical Workshops	Oily Rinse Water Waste oils Solid Wastes
Lube oil Cooling water	Compressors	Spent oil
Fuel Oil Rinse Water	Garage	Oily rinse water Solid wastes Waste oils
Fuel Chemicals	Storage	Spills Hazardous material
Wastewater	Wastewater Treatment Units	Treated water Sludge
Water	Restaurant and restrooms	Solid wastes Sanitary Wastewater

2.4 Emissions, Effluents and Solid Wastes

Fertilizers industry manufacturing processes originate is gas, contaminated liquid effluents in addition to dust and solid by-products. These wastes pollute air, water as well as impair soil. Pollution problems arise from low processes efficiency and/or inefficient dust collecting systems, gas scrubbing (if it does exist) and most important is the lack of a proven recycle of such recovered contaminants to the process streams.

2.4.1 Air Emissions

The major emission in phosphoric and nitrogenous fertilizers cited here below includes particulates, sulphur oxides, hydrogen fluoride (and compounds Ca F_2 SiF_4) phosphogypsum, phosphoric acid, ammonia, NO_x, ammonium nitrate, sulphate, carbon oxides … etc. Detailed are as follows:

a. Phosphate Fertilizers

Fluoride emissions are considered the major air pollutants from phosphate fertilizers plants.

- ***Single Superphosphate Production***

  Sources of emissions at a single superphosphate plant include rock unloading and feeding, mixing operations (in the reactor), storage (in the curing building), and fertilizer handling operations. Rock unloading, crushing, screening, handling and feeding generate particulate emissions of phosphate rock dust. The mixer, den and curing building emit gases in the form of silicon tetrafluoride (SiF_4), hydrogen fluoride (HF) and particulates composed of fluoride and phosphate material.

  The major polluting parameters are total suspended particulates, fluorides, sulphuric acid mist, dust fall and inhaled dust.

- ***Triple Superphosphate Production***

  Emissions of fluorine compounds and dust particles occur during the production of granulated triple superphosphate. Silicon tetrafluoride (SiF_4) and hydrogen fluoride (HF) are released by the acidulation reaction and they evolve from the reactors, granulator, and dryer. Evolution of fluoride is essentially finished in the dryer and there is little fluoride evolved from the storage pile in the curing building.

  Sources of particulate emissions include the reactor, granulator, dryer, screens, mills, and transfer conveyors. Additional emissions of particulate result from the unloading, grinding, storage, and transfer of ground phosphate rock. Facilities may also receive limestone in granulated form which does not require additional milling.

The major emissions result from phosphate rock preparation operations, reaction and granulation.

- ***Phosphoric Acid Production***
  The main emissions are gaseous fluorides and dust. Gaseous fluorides such as silicon tetra-fluoride (SiF_4) and hydrogen fluoride (HF) can be major emissions from wet process acid production. Phosphate rock contains 3.5 to 4.0 percent fluorine. Fluorine is liberated during acidulation initially as HF, but later in the presence of silica as H_2SiF_6. A proportion of F is evolved as vapour. Part of the fluorine from the rock is precipitated with the gypsum, another part is leached out with the phosphoric acid product, and the remaining portion is vaporized in the reactor or evaporator. The relative quantities of fluorides in the filter acid and gypsum depend on the type of rock and the operating conditions. Final disposition of the volatilized fluoride depends on the design and operation of the plant. Another group of impurities are As, Cd, Cu,Pb, Ni,Zn an Hg which are present in most phosphate rocks and may pass into acid during acidulation.

  The reactor in which phosphate rock is reacted with sulfuric acid is the main source of emissions. Fluoride emissions accompany the air used to cool the reactor slurry. Vacuum flash cooling has replaced the air cooling method to a large extent, since emissions are minimized in the closed system. Acid concentration by evaporation is another source of fluoride emissions. Approximately 20 to 40 percent of the fluorine originally present in the rock vaporizes in this operation. Particulate matter containing fluorides can be emitted directly from process equipment. About three to six percent of the particulates can be fluorides, as measured at one facility. Hence the major detected parameters in air emissions are fluorides compounds measured as (F).

- ***Sulphuric Acid Production***
  The major polluting parameters are sulphur dioxide , sulphur trioxide and acid mist. Emissions occur during sulphur burning, in converters and absorption.
  Sulphuric acid production is one of the few chemical processes where more energy is produced than is used in the process. In many cases sulphuric acid plants are used as the energy source for the production processes for other chemicals.

Tables (4) show some typical air emissions measurements in a phosphate fertilizers plant.

Table (4) Typical Air Emissions Measurements for Phosphatic Fertilizers Plant

Location	A	B	C	D
TSP Conc. (µg/ m^3)	527.7	458.8	512.2	396.6
Gaseous Fluorides (µg/ m^3)	527.7	458.8	512.2	396.6
Particulate fluorides (µg/ m^3)	10.18	12.98	11096	16.40
Sulphur Dioxide (ppm)	0.028	0.022	0.018	0.038
Dust Fall (g/ m$_2$/ month)	527.7	458.8	512.2	396.6
Sulphuric Acid Mist (µg/ m^3)	1100	800	960	880

A, B, C and D are locations 150 m outside the plant in directions East, West, North and South respectively.

b. Nitrogenous Fertilizers

- ***Ammonia Production***

  Air pollutants from the manufacture of synthetic ammonia are emitted primarily from four process steps:

  - regeneration of the desulfurization bed,
  - heating of the catalytic steam (flue gases from primary reformer),
  - flue gases from CO_2 removal and regeneration of carbon dioxide scrubbing solution,
  - steam stripping of process condensate.

  The major gaseous emissions include sulphur dioxide, carbon monoxide, carbon dioxide, hydrogen sulfide (which is generated from natural gas), volatile organic compounds (VOCs), methane and the leakage of ammonia from the converter or liquefaction process.

  Vented regeneration steam contains sulfur oxides (SO_x) and hydrogen sulfide (H_2S), depending on the amount of oxygen in the steam. Regeneration may also emit hydrocarbons and carbon monoxide (CO). The reformer, heated with natural gas or fuel oil, may emit combustion products such as NO_x, CO, SO_x, hydrocarbons, and particulates. Carbon dioxide (CO_2) is removed from the synthesis gas by scrubbing with monoethanolamine ($C_2H_4NH_2OH$) or hot potassium carbonate solution. Regeneration of this CO_2 scrubbing solution with steam produces emissions of water, NH_3, CO, CO_2 and monoethanolamine. Purge and flash gases from synthesis section are usually washed to remove ammonia and purge gas may be treated in a recovery unit before being returned to primary reformer.

- ***Nitric Acid Production***

  Emissions from nitric acid manufacturing consist primarily of NO and NO_2 (which account for visible emissions), and trace amounts of HNO_3 mist and NH_3. The major source of nitrogen oxides is the tail gas from the acid absorption tower. In general, the quantity of nitrogen oxides (NO_x) emissions is directly related to the kinetics of the nitric acid formation reaction and absorption tower design. NO_x emissions can increase when there is:

- Insufficient air supply to the oxidizer and absorber,
- Low pressure, especially in the absorber,
- High temperatures in the cooler/condenser and absorber,
- Production of an excessively high-strength product acid,
- Operation at high throughput rates,
- Faulty equipment such as compressors or pumps which lead to lower pressures, leaks, and reduced plant efficiency.

Comparatively small amounts of nitrogen oxides are also lost from acid concentrating plants. These losses (mostly NO_2) are from the condenser system, but the emissions are small enough to be controlled easily by absorbers.

Acid mist emissions do not occur from the tail gas of a properly operated plant. The small amounts that may be present in the absorber exit gas streams are typically removed by a separator or collector prior to entering the catalytic reduction unit or expander. The acid production system and storage tanks can be a significant source of visible NOx emissions at nitric acid plants. Emissions from acid storage tanks are most likely to occur during tank filling. Therefore, the major polluting parameters to be detected are Nox and any visible emissions.
Air pollution problem are created because it is too expensive to try to absorb more than 97- 98 % of the NO leaving the gauze. Three methods are currently used to meet the environmental requirements. First, stack gas (containing NO) is reheated and reacts with natural gas, the combustion reaction increases the gas temperature and this increases the power recovered in the expander. Second, reheated stack gas can be treated with ammonia or hydrogen (if available) in a catalytic reactor to reduce the NO to N_2. Third, additional absorption capacity operating at low temperature can increase absorption sufficiently to meet the requirements.

- ***Ammonium Nitrate Production***
  The primary air emissions from ammonium nitrate production plants are particulate matter (ammonium nitrate and coating materials), ammonia and nitric acid. Ammonia and nitric acid are emitted primarily from solution formation and granulators. Particulate matter (largely as ammonium nitrate) can be emitted from most of the process operations.

The emission sources in solution formation and concentration processes are neutralizers and evaporators, emitting droplets of ammonium nitrate and ammonia. The vapor stream off the top of the neutralization reactor is primarily steam with some ammonia and NH_4NO_3 particulates present. Specific plant operating characteristics, however, make these emissions vary depending upon use of excess ammonia or acid in the neutralizer. Particulate emissions from these operations tend to be smaller in size than those from solids production and handling processes and generally are recycled back to the process. Emissions of very fine particles are very difficult to remove. A combination of droplet separators and scrubbers can be used.
Contaminated steam from evaporator should be purified before discharge to the environment.

Emissions from solids formation processes are ammonium nitrate particulate matter and ammonia. The sources of primary importance are prill towers (for high density and low density prills) and granulators (rotary drum and pan). Ammonia is normally removed by neutralization in a wet scrubber. Most conventional scrubbers are less efficient for the removal of particles below 1 micron of prill tower fume. Candle filters are normally required. Gases from granulator and drier may be cleaned by combination of dry cyclones or bag filters and wet scrubbers.

Emissions from prilling towers result from carryover of fine particles and fume by the prill cooling air flowing through the tower. These fine particles are from microprill formation, attrition of prills colliding with the tower or one another, and rapid transition of the ammonia nitrate between crystal states.

Microprill formation resulting from partially plugged orifices of melt spray devices can increase fine dust loading and emissions. Certain designs (spinning buckets) and practices (vibration of spray plates) help reduce plugged orifices and thus microprill formation. High ambient air temperatures can cause increased emissions because of entrainment as a result of higher air flow required to cool prills and because of increased fume formation at the higher temperatures.

Emissions from screening operations are generated by the attrition of the ammonium nitrate solids against the screens and against one another. Almost all screening operations used in the ammonium nitrate manufacturing industry are enclosed or have a cover over the uppermost screen. Emissions are ducted from the process for recovery or reuse.

Bagging and bulk loading operations are also a source of particulate emissions. Dust is emitted from each type of bagging process during final filling when dust laden air is displaced from the bag by the ammonium nitrate. The potential for emissions during bagging is greater for coated than for uncoated material. It is expected that emissions from bagging operations are primarily the kaolin, talc or diatomaceous earth coating matter. About 90 percent of solid ammonium nitrate produced domestically is bulk loaded. While particulate emissions from bulk loading are not generally controlled, visible emissions are within typical state regulatory requirements (below 20 percent opacity).

- ***Methanol Production***
  Ammonia, carbon monoxide and hydrogen are considered the major air emissions from this production line. Usually these emissions are scrubbed through efficient scrubbers, but in some cases facilities do not utilize scrubbers.

- ***Ammonium Sulphate Production***
  Several air emissions are generated during the production of ammonium sulphate fertilizer, they include ammonia and sulphuric acid mist. Some facilities directs these emissions to scrubbers. In case of the absence of scrubbing operation it is expected to find these emissions in the atmosphere.

- ***Di-Ammonium Phosphate Production***
  Phosphoric acid and ammonia are used in the production of ammonium phosphate fertilizer. Emissions of ammonia, fumes and particulates are also emitted to the atmosphere if no cyclones or scrubbers exist in these facilities. Furnace flue gases from drier.

- ***Calcium Nitrate***
  Limestone is used in this production line, therefore particulates emissions are generated during preparation, transportation and handling of the stone. On the other hand ammonia, acid mist and particulates are also generated during the process.

- ***Urea Production***
  Emissions from urea manufacture are mainly ammonia particulate matter.

Formaldehyde and methanol, hazardous air pollutants, may be emitted if additives are used. Formalin TM, used as a formaldehyde additive, may contain up to 15 percent methanol. Ammonia is emitted during the solution synthesis and solids production processes. Particulate matter is emitted during all urea processes. In the synthesis process, some emission control is inherent in the recycle process where carbamate gases and/or liquids are recovered and recycled. Typical emission sources from the solution synthesis process are noncondensable vent streams from ammonium carbamate decomposers and separators. Emissions from synthesis processes are generally combined with emissions from the solution concentration process and are vented through a common stack. Combined particulate emissions from urea synthesis and concentration operations are small compared to particulate emissions from a typical solids-producing urea plant. The synthesis and concentration operations are usually uncontrolled except for recycle provisions to recover ammonia.

Uncontrolled emission rates from prill towers may be affected by the following factors:

- Product grade being produced
- Air flow rate through the tower
- Type of tower bed
- Ambient temperature and humidity

The total of mass emissions per unit is usually lower for feed grade prill production than for agricultural grade prills, due to lower airflows. Uncontrolled particulate emission rates for fluidized bed prill towers are higher than those for non-fluidized bed prill towers making agricultural grade prills, and are approximately equal to those for non-fluidized bed feed grade prills.

Ambient air conditions can affect prill tower emissions. Available data indicate that colder temperatures promote the formation of smaller particles in the prill tower exhaust. Since smaller particles are more difficult to remove, the efficiency of prill tower control devices tends to decrease with ambient temperatures. This can lead to higher emission levels for prill towers operated during cold weather. Ambient humidity can also affect prill tower emissions. Air flow rates must be increased with high humidity, and higher air flow rates usually cause higher emissions. In the solids screening process, dust is generated by abrasion of urea particles and the vibration of the screening mechanisms. Therefore, almost all screening operations used in the urea manufacturing industry are enclosed or are covered over the uppermost screen. Emissions attributable to coating include entrained clay dust from loading, in-plant transfer, and leaks from the seals of the coater.

2.4.2 Effluents

Wastewater from the fertilizer industry can be classified into four groups:

- Process effluents resulting from contact with gas, liquids, or solids
- Dedicated effluents which may be separated for use in one process or for recycling at a controlled rate
- Effluents from general services such as cleaning or pretreatment
- Occasional effluents such as leaks or spills

Wastewater is generated in any fertilizer production facility by leaks, spills, cleaning, maintenance, and laboratory tests. Cooling water may contain ammonia, sulfate, chloride, phosphate, chromate, and dissolved solids which become concentrated through evaporation.

a. Phosphate Fertilizers

Effluents include wastewater from water treatment unit, cooling towers and boilers blowdown, spills and leaks, surface run-off. Cooling water is not significantly contaminated in most cases. Another contaminated stream may result from condensers, heat exchangers and gas scrubbers. It was found that the main sources of pollution are attributed to the washing water of the scrubbing towers.

Primary parameters for wastewater are phosphorous, fluorides, silicate, suspended solids and pH.

Phosphoric acid production creates large quantities of pond water for cooling of the process, concentration of the product and for processing and storage of the gypsum byproduct. Gypsum slurry water is decanted from the top of the gypsum stacks and sent to the cooling pond through collection ditches

Through evaporation and recycling, contaminant concentrations in pond water can reach several grams per liter of phosphates and fluoride. Additional elemental contaminants in pond water which originate in phosphate rock are arsenic, cadmium, uranium, vanadium, and radium.

Tables (5 and 6) give typical characterization of wastewater from superphosphate fertilizer and phosphoric acid production units, respectively.

Table (5) Characterization of wastewater from Superphosphate Production Unit

Parameters	Units	Source (1)	Source (2)	Source (3)	Source (4)
pH		1.17	2.3	7.67	1.1

Parameters	Units	Source (1)	Source (2)	Source (3)	Source (4)
COD	mg/ l	-	-	15.56	-
BOD	mg/ l	-	-	5	-
Total nitrogen	mg/ l	-	-	14	-
Settleable solids	mg/ l	2	-	-	0.5
Total residue at 105° C	mg/ l	11834	1029	332	7889
Total volatile residue at 550° C	mg/ l	5368	447	71	4429
Total suspended solids	mg/ l	2422	108	4303	980
Total dissolved solids	mg/ l	9412	921	288.7	6909
Total phosphate	mg/ l	340	20	1.2	304
Hydrogen sulfide	mg/ l	-	-	-	-
Sulphate	mg/ l	270	120	34	260
Total hardness	mg/ l	-	-	160	302
Calcium hardness	mg/ l	-	-	98	149
Fluoride	mg/ l	16400	1550	1.2	14750
Soluble silicate	mg/ l	6000	2700	6.5	6400
Iron	mg/ l	65	3.6	0.4	7.5

Source (1): washing water of scrubbing towers in the single superphosphate unit.
Source (2): Washing water from scrubbing tower in the triple superphosphate unit.
Source (3): cooling water from the dilution of sulphuric acid unit.
Source (4): final effluent.

Table (6) Characterization of wastewater from Phosphoric Acid Production Unit

Parameters	Units	Source (1)	Source (2)
pH		2.07	1.01
COD	mg/ l	22.3	86.4
BOD	mg/ l	11.3	57
Total nitrogen	mg/ l	1	6.5
Settleable solids	mg/ l	-	0.4
Total residue at 105° C	mg/ l	873	34291
Total volatile residue at 550° C	mg/ l	246	10766
Total suspended solids	mg/ l	15	816
Total dissolved solids	mg/ l	858	33475
Total phosphate	mg/ l	6.8	940
Sulphate	mg/ l	52	2500
Total hardness	mg/ l	65	-
Calcium hardness	mg/ l	32.5	-
Fluoride	mg/ l	1400	15200
Soluble silicate	mg/ l	210	180
Iron	mg/ l	1.1	115

Source (1): cooling water.
Source (2): process water (washing water).

b. Nitrogenous Fertilizers

Wastewater is considered the major pollution problem in such plants. A number of process wastewater streams from the nitrogenous fertilizer industry have been identified. Wastewater is analyzed in terms of ammonia, nitrates, organic nitrogen and hydrogen ions concentration (pH).

- ***Ammonia Production***

  In ammonia production, wastewater is generated from process condensate stripping. Cooling the synthesis gas after low temperature shift conversion forms a condensate containing NH_3, CO_2, methanol (CH_3OH), and trace metals. Condensate steam strippers are used to remove NH_3 and methanol from the water. Stripped condensate can be reused as boiler feed water after treatment of ion exchange. In some cases, the process condensate is used for feed gas saturation and thus recycled.

  Wastewater is contaminated with traces of ammonia and oils from compressing gas unit. Emissions to water may also occur due to the scrubbing of waste gases containing ammonia if gases are not recovered in a closed loop so that no aqueous ammonia emissions occur.

- ***Nitric Acid Production***
  Nitric acid production generates relatively little wastewater since there is no process wastewater source. Steam condensate generated in nitrogenous fertilizer processing is characterized by dissolved and suspended solids, alkalinity, and hardness. The ammonia vaporizer blow-down should have the ammonia vaporized and recovered into the process. The waste oil should be reprocessed.

- ***Ammonium Nitrate Production***
  Wastewater effluent is discharged from cooling tower blowdown, backwash from multi-media filters and from equipment and floor washing. Loss of ammonium nitrate to drain from a large number of sources is a potential problem for all ammonium nitrate plants. Causes are different kinds of leaks and washings.

  Ammonium nitrate manufacturing produces process wastewater in the neutralization process, the evaporation unit, and air cooling equipment. The vacuum condenser in ammonium nitrate plants is a source of wastewater. Most scrubbing operations are also a source of wastewater. The steam condensate leaving the neutralizer can be purified. Purification can be achieved by stripping, distillation and membrane separation processes as reverse osmosis. Ion exchange can also be considered but ther are some safety concerns which must be addressed. The steam can be used in the evaporator or to preheat and evaporate ammonia and to preheat nitric acid. The solution from wet scrubbers is normally recycled.

- ***Urea Production***
  Steam is used in considerable amounts in this production line, therefore, steam condensate is the major effluent. Fugitive ammonia, carbamate and particulates are dissolved in the steam condensate forming a pollution source for this effluent if not recycled.

- ***Ammonium Sulphate Production***
  Wastewater includes the blowdown from boilers, water from the wet scrubbers and floor drains is redirected to the process for recapture of ammonium sulphate. Wastewater contains traces of ammonia, sulphate and acidity.

  Floor drains collect liquid spills and bleed line discharges from circulating pumps and directs the liquids to the sump tank from which it is pumped back to the crystalizer. The sump tank also collects the bottom drain line discharges from the crystalizer. Overflow, if exist, from the sump tank could generate another source of pollution. Steam condensate is another source of pollution to the wastewater.

- ***Di-Ammonium Phosphate Production***
  Spills of acids (sulphuric and phosphoric acids) and ammonia leaks are dissolved in floor washing wastewater and polluting the effluent stream from this unit. Also contaminated wastewater from scrubbers is generated.

- ***Calcium Nitrate***
  Nitric acid is used in this unit, hence spills of this acid highly pollute the effluent stream. Moreover, spills of liquid fertilizer and particulates from the solid fertilizer and fugitive ammonia are dissolved in the floor washing water generating another pollution source.

- ***Methanol Production***
  Wastewater contaminated with alcohol produced from distillation of the product is considered the major polluting source in this unit.

2.4.3 Solid Wastes

For all fertilizers plants, solid materials may be found in storage piles, settled dust and other similar forms. The following are the major solid wastes in different production lines of fertilizers.

a. Phosphate Fertilizers

- ***Single Superphosphate Production***

Off-specification product, products spills, and dusts collected in emission control systems are potential sources of residual wastes. Products are occasionally suspended or canceled, leaving stockpiles of residual product.

- ***Triple Superphosphate Production***
  Sources of solid wastes in this production line are spent containers, wastewater treatment sludges, and spent filters. Many of these wastes are transported offsite for disposal. However, with good housekeeping techniques and dedicated systems, some of these wastes may be recycled back into the process instead of being wasted.

- ***Phosphoric Acid Production***
  One of the largest solid wastes in this production unit is phosphogypsum. Approximately 1.5 tons of phosphogypsum is produced per ton of phosphate rock fed, or 5 tons per ton of phosphoric acid produced (expressed as P_2O_5). Gypsum (calcium sulphate dihydrate) is a mineral which also occurs in nature. Phosphogypsum is produced by the reaction of phosphate rock with sulphuric acid during the process of producing phosphoric acid.

  The use of waste phosphogypsum for other purposes has been widely encouraged, but economic and/or quality problems and/or the demand for the resulting products frequently inhibit or prevent this. These problems relate not only to the impurities in the gypsum, but also to its relatively high moisture content. Plasterboard, plaster, and cement are the main possibilities. It is also possible to recycle phosphogypsum in sulphuric acid production.
  Dumping gypsum on land is not possible everywhere because the material settles and dries slowly and requires an adequate land area and certain climatic and soil conditions where the stack is situated. Gypsum stacks are being increasingly

regulated in terms of lining and cap systems to prevent contaminated leaching or runoff .

Cadmium is a heavy metal which accumulates in living systems and can become toxic above certain limits. The quantity of cadmium contained in a phosphatic fertilizer depends on the source of the rock or waste material from which it was made. The cadmium content of phosphate rocks varies from almost zero to over 300 mg/kg P_2O_5. The acidulation of phosphate rock partitions the cadmium between the fertilizer product and the by-products, mainly the phosphogypsum arising from phosphoric acid production.

- ***Sulphuric Acid Production***
  Spent catalyst is generated from this production line and usually returned to the licensor. The vanadium content of the V_2O_2 catalysts can be reclaimed for further use. This service is usually provided by the catalyst manufacturer. The metal can be recycled as vanadium salts or ferrovanadium for steel production.

b. Nitrogenous Fertilizers

- ***Ammonia Production***
  Solid wastes are generated due to the usage of many catalysts types and quantities. The spent catalysts can not be purified or recycled, hence, they create a disposal problem which should be checked. These catalysts are considered hazardous, due to their heavy metals content (chromium and nickel). Another solid waste problem is the filling material for absorption tower. They are consumed and disposed off-site.

  Catalysts used in the steam reforming process need to be replaced every two to six years. Spent catalysts contain oxides of hexavalent chromium, zinc, iron, and nickel. They are typically returned to the manufacturer or other metal recovery companies for recycling and reclamation of valuable materials.

- ***Nitric Acid Production***
  Spent catalyst from the reactor and filter cake and cloth generated from the filter are considered the major solid wastes generated from this unit. Usually spent catalyst is sent to the suppliers and it must not be disposed in dumping sites due to its hazardous nature.

- ***Ammonium Nitrate Production***
  Dolomite and clay from the mixing and coating operations are the major solid wastes from this unit as well dump product.

- ***Ammonium Sulphate Production***
  Ammonium sulphate crystals during conveying and bagging are collected and recycled.

- ***Ammonium Phosphate Production***
  Spills of the fertilizers in the bagging section are collected and recycled.

- ***Urea Production***
  Prills coating material in the bagging section are collected and recycled.

2.4.4 Work Environment

Several pollutants are generated in the work environment within the fertilizers plants, these include the following:

- Fugitive gases and vapours inside the production units, which vary according to the production line. In phosphatic fertilizers plants, these emissions include fluoride compounds (HF, SiF_4 and H_2SiF_6) and NO_x ammonium nitrate and sulphur oxides. Whereas, in the nitrogenous fertilizers plants ammonia, VOCs, carbon dioxide and urea are considered the major emissions concerning workplace.
- Dust and particulates are also emitted inside the work environment from several sources including; crushing and grinding of phosphate rock, granulation and screening operations for fertilizers and also from bagging section. Also belt and screw conveyors are considered another source for particulates emissions in the workplace.
- Heat is evolved from several sources inside the fertilizers plant including; acidulation, methanation, exothermic

reactions, drying and prilling of fertilizers. Heat is also evolved in the boilers house and bagging section.

- Noise is another problem of concern inside workplace. It can occur in several production and service units, such as; compressors pumping units, boilers house, towers pump water for cooling, granulation and screening of fertilizers. Also transportation of fertilizers by belt conveyors generates high noise.

In general workers in the fertilizers plants are exposed to numerous hazards including; sulphur vapours, high temperature from molten sulphur, burns from the corrosive sulphuric acid, noise from turbines, phosphates as powdered fertilizer, fluorine gases during concentration operations and exposure to phosphoric acid, fugitive ammonia, methane gas and nitrogen oxides.

Table (7) gives some typical measurement for noise in some places in a fertilizers plant.

Table (7) Typical Noise Measurements in a Fertilizer Plant

Place	Noise Intensity, dB
Water intake pumps	96
Boilers pumps	106
Air liquification	90- 105
Cooling towers pumps	99- 100
compressors	101- 109
Ammonia production section	100- 99
Urea production section	86- 100

Table (8) gives some typical measurement for emissions in some places in a fertilizers plant.

Table (8) Typical Emissions Measurements in Workplace for a Fertilizers Plant

Parameters	1	2	3	4	5	6	7	8
TSP (µg/ m^3)	7524	893.3	2109	6336	1266	697.3	9241	527.7
Fluoride mg/ m^3	53.2	24.7	23.4	73	14	18	-	13.9
Particulates (µg/ m^3)	87.6	61.2	15.2	24.7	23.6	22.7	-	13.8
SO_2	0.04	0.06	0.03	0.05	0.02	0.03	0.04	0.02

(1): Superphosphate plant.
(2): Phosphoric acid plant.
(3): Phosphoric acid plant.
(4): polish water station.
(5): old administrative building.
(6): near the phosphate port.
(7): 150 m far from the phosphoric acid gate.
(8): near the fertilizer concentration plant.

Table (9) gives the summary of production lines in the fertilizers industry and the related inputs and the pollution sources and types.

Table (9) Inputs and Pollution Sources and Types in the Fertilizers Industry

Operation	Inputs	Air Emissions	Liquid Wastes	Solid Wastes	Work Environment
Single Super Phosphate					
Crushing and grinding	Phosphate rock	Dust and particulates to the air	-	-	Noise and particulates
Acidulation	Sulphuric acid, phosphate rock	Hydrogen fluoride, acid mist and SiO_2	-	-	Acid mist, heat stress
Reaction den	-	Hydrogen fluoride and SiF_4 and SiO_2	-	-	-
Scrubbing towers	Gases from the den and mixer water		Wastewater containing H_2SiF_6 and S.S	-	-
Conveying and storage for curing	-	-	-	-	Particulates, HF and SiF_4
Granulation	Water	Dust & fumes to the scrubber	-	-	Particulates
Screening	-	-	-	-	Particulates
Bagging	Polyethylene or polypropylene bags	-	-	Spills of product and spent bags	Particulates
Triple Superphosphate					
Crushing and grinding	Phosphate rock	Dust and particulates to the air	-	-	Noise, dust and particulates
Two-stage reaction	Ground phosphate rock and phosphoric acid	Hydrogen fluoride and SiF_4	-	-	-
Granulation	Water and recycled over & under sired products	Hydrogen fluoride and SiF_4	-	-	- Water vapors, - Fluoro compounds particulates
Screening	-	-	-	-	Particulates
Cooling	Cold air	-		-	-
Scrubbers	Water		Wastewater containing H_2SiF_6 and S.S		
Storage and bagging	Polyethylene bags	Emissions from stored product piles containing HF, SiF_4	-	Spills of product and spent bags	Particulates & emissions of fluoro compounds
Phosphoric Acid Production					
Crushing & grinding	Phosphate rock	Dust and particulates	-	-	Dust & particulates
Washing	Diluted phosphoric acid	-	-	-	-

Operation	Inputs	Air Emissions	Liquid Wastes	Solid Wastes	Work Environment
Reaction	Strong sulphuric acid	Hydrogen fluoride, SiF_4 and acid mist to scrubber	-	-	HF, SiF_4 and acid mist
Filtration	Water	-	Wastewater recycled to the reactor (rich in H_3PO_4)	-	Acid fumes
Scrubbers	Water	-	Waste water containing fluoride phosphate and sulphate	-	-
Gypsum washing	Water	Fluoride emissions	Wash wastewater recycled to the reactor	-	-
Settling pond	-	Fluoride emissions	Separated water recycled to the reactor (rich in fluorides and trace metals)	-	-
Vacuum Evaporator	-	SiF_4	Condensate	-	-
Sulphuric Acid Production					
Melting	Sulphur, steam	Fugitive sulphur emissions	-	-	- Heat stress - Sulphur odour
Filtration	Air	-	-	Filter cloth	Sulphur odour
Drying	H_2SO_4	-	H_2SO_4 spills	-	-
Sulphur burning	Air	- SO_2 emissions	-	-	Heat stress
Waste heat boiler	Water	-	Steam condensate	-	Heat stress
First stage converter		SO_2, SO_3 emissions	-	-	Leaks of SO_2SO_3 and heat stress
Cooling boilers	Water	-	-	-	Heat stress
Absorption	Diluted H_2SO_4	SO_2, SO_3 and acid mist and tail gas	-	-	Leaks of SO_2SO_3
Oleum tower	Oleum Conc. $H_2 SO_4$	-	Leaks and spills of $H_2 SO_4$	-	-
Synthetic Ammonia Production					
Desulphurization	Natural gas, adsorbent (ZnO), and catalyst (CoO and MoO_3	H_2 S, volatiles and SO_x emissions during regeneration	-	Spent adsorbent and catalyst	VOCs, H_2S leaks
Primary steam reforming	Steam, fuel or purge gas and catalyst (Ni)	Hydrogen and flue gases CO_2, NO_x, SO_2, CO and particulates	-	Spent Ni catalyst	Heat stress
Secondary reforming	Compressed hot air and Ni	-	Acidic steam condensate	Spent Ni catalyst	Heat stress

Operation	Inputs	Air Emissions	Liquid Wastes	Solid Wastes	Work Environment
	catalyst				
CO converter	Catalyst (iron oxide/chromium oxide, copper oxide/zinc oxide)	-	Condensate to steam traps	Spent Ni Catalyst	-
CO_2 separation	Solvent (MEA, DMEA or potassium carbonate)	SO_2, H_2S, CO from solvent regeneration	Solvent recycled after regeneration	-	-
Steam condensate stripping	Steam condensate	NH_3, CO, CO_2 and MEA	Wastewater (ammonia and methanol)	-	-
Methanation	Ni catalyst	CH_4 and Hydrogen	-	Spent Ni catalyst	Heat stress
Ammonia converter	Cooling water and Fe catalyst	Purge and flash gases to primary converter	Waste cooling water to cooling tower	Spent catalyst	Ammonia leaks
Ammonia Condensation	-	-	-	-	Ammonia leaks
Nitric Acid Production					
Air filtration	Air	-	Backwash water	Filter cake	-
Ammonia vaporization.	Liquid ammonia and steam	Fugitive ammonia	-	-	Heat stress ammonia
Cooling in W.H.B	Water	Fugitive ammonia	-		Heat stress leaks
Catalytic oxidation	-	NOx and fugitive ammonia	Washing water from filters	Pt catalyst is very expensive and it never considered a solid waste	Ammonia leaks and heat stress
Cooling	Cooling water	-	Cooling water to cooling towers	-	-
Absorptions	Cooling water and process water	No_x, acid mist emissions	Cooling water to cooling towers	-	-
Bleaching	Air	-	-	-	-
Tail gas expander	Tail gas from absorption	NOx emissions	-	-	-
Ammonium Nitrate Production					
Preheating	Liquid ammonia	-	-	-	Heat stress, ammonia leak
Reaction (neutralization)	Nitric acid	Vapours of ammonia and ammonium nitrate	Wastewater (NH_3 and ammonium nitrate)	-	Ammonia leaks

Operation	Inputs	Air Emissions	Liquid Wastes	Solid Wastes	Work Environment
Flash evaporator	-	Vapours of ammonia and ammonium nitrate	-	-	Ammonia vapours
Secondary evaporator	Steam	Vapours of ammonia	Condensate (NH_3 and ammonium nitrate)	-	Ammonia vapours
Mixing	Dolomite, kaolin or limestone	Particulates	-	-	Particulates
Prilling or granulation	Ammonium nitrate	Particulates	-	-	Particulates
Drying	Steam heated air and ammonium nitrate	Water vapour	-	-	Heat stress
Screening	Ammonium nitrate	-	-	-	Particulates and noise
Cooling	Ammonium nitrate and cold dry air	Particulates	-	-	Particulates
Coating	Clay or diatomaceous earth	Particulates	-	-	particulates
Bagging	Polyethylene or polypropylene bags	-	-	Spills of product and spent bags	Particulates
Ammonium Sulphate Production					
Evaporation	Liquid ammonia and steam	Ammonia emissions	-	-	Heat stress
Reactor & crystallization	Sulphuric acid	Ammonia and acid mist	-	-	Fugitive ammonia and acid
Filtration	Ammonium sulphate	-	Wastewater (ammonium sulphate)	-	-
Dehydration & drying	Steam heated air and ammonium sulphate	-	Wastewater (ammonium sulphate)	-	-
Conveying	Ammonium sulphate	-	-	Spills of ammonium sulphate crystals	
Bagging	Polyethylene or polypropylene bags	-	-	Spills of product and spent bags	Particulates
Ammonium Phosphate Production					
Reaction	Phosphoric acid, NH_3 and cooling water	Fumes and gases to scrubber and ammonia leaks	-	-	Leaks of ammonia
Scrubbers	Water, fumes and gases from several operations	-	Wastewater containing ammonia and phosphoric acid	-	-
Hot granulation and	Fuel and air	Flue gases from furnace	-	Dust and part from	Particulates

Operation	Inputs	Air Emissions	Liquid Wastes	Solid Wastes	Work Environment
drying		and particulates to collectors		collectors	
Cooling	Air	Ammonia and particulates	-	Dust & particulates from collectors	Dust & particulates
Screening	Ammonium phosphate	-	-	-	Particulates and ammonia
Grinding	Oversize ammonium phosphate	-	-	-	Particulates and noise
Coating	Coating material	-	-	-	Particulates
Bagging	Polyethylene or polypropylene bags	-	-	Spills of product and spent bags	Particulates
Urea Production					
Synthesis	Liquid ammonia and carbon dioxide	CO_2, urea and ammonia	-	Dust & particulates from collectors	Heat stress
Rectification		Ammonia and CO_2	-	-	Ammonia leaks
Vacuum evaporation	Steam and carbamate	Ammonia, CO_2 and water vapour		-	Ammonia leaks
Prilling or granulation	Cold air and urea	Urea particulates	-	-	Particulates of urea
Desorption of condensate	Steam stripping agent and condensate	-	Wastewater (urea, NH_3 and CO_2	-	-
Screening	Urea	-	-	Collected particulates	Particulates and noise
Coating	Urea formaldehyde	-	-	-	Particulates
Bagging	Polyethylene or polypropylene bags	-	-	Spills of product and spent bags	Particulates
Liquid Calcium Nitrate Production					
Dissolving tower	Limestone and HNO_3	CO_2 and acid mist	-	Flakes of limestone	-
Settling	-	-	-	Calcium carbonate	-
Neutralization	Ammonia and calcium nitrate	Fugitive ammonia and acid mist	-	-	Fugitive ammonia and acid mist
Mixing	Ammonium nitrate and calcium nitrate	-	Spills of liquid fertilizer	-	-
Packaging	Barrels and calcium nitrate	-	Spills of calcium nitrate	-	-

3. Impacts of Pollutants on Health and Environment

3.1 Impact of Air Emissions

Ammonia

Ammonia is a colorless gas at atmospheric pressure, but is shipped as a liquefied compressed gas. It is soluble to about 34 percent in water and has a boiling point of –15.5^o C. Ammonia is corrosive and has a pungent odor.
Ammonia is the primary nitrogen source for all nitrogenous fertilizers and ammonium phosphatic fertilizers.

Anhydrous ammonia is irritating to the skin, eyes, nose, throat, and upper respiratory system. Ecologically, ammonia is a source of nitrogen (an essential element for aquatic plant growth), and may therefore contribute to eutrophication of standing or slow-moving surface water, particularly in nitrogen-limited waters. In addition, aqueous ammonia is moderately toxic to aquatic organisms.
There is currently no evidence to suggest that ammonia is carcinogenic.

Ammonia's ability to dissolve in water and its tendency to escape quickly as a gas make it a potential environmental problem. It can hurt wild-life and fish when absorbed by water streams, it has a harmful effect on cold-water fish. Ammonia combines with sulfate ions in the atmosphere and is washed out by rainfall, resulting in rapid return of ammonia to the soil and surface waters. Ammonia is a central compound in the environmental cycling of nitrogen. Ammonia in lakes, rivers, and streams is converted to nitrate.

Phosphoric Acid

Phosphoric acid is a thick, colorless, and odorless crystalline solid, often used in an aqueous solution. Its boiling point is 230.5° C and it is soluble in water.
Phosphoric acid is the primary phosphorous source used for phosphatic fertilizers.

Phosphoric acid is toxic by ingestion and inhalation, and is an irritant to skin and eyes. The toxicity of phosphoric acid is related to its corrosivity as an acid, with ulceration of membranes and tissues with which it comes in contact. Because it is a source of phosphorous, an essential element for aquatic plant growth, phosphoric acid may contribute to eutrophication of standing or slow-moving surface water, particularly in phosphorous-limited.
There is currently no evidence to suggest that phosphoric acid is carcinogenic.

The acidity of phosphoric acid may be reduced readily by natural water hardness minerals. The phosphate will persist until used by plants as a nutrient.

Nitrate compounds

Many different nitrate compounds are formed during nitrogenous fertilizer production.
Nitrate compounds that are soluble in water release nitrate ions which can cause both human health and environmental effects. Human infants exposed to aqueous solutions of nitrate ion can develop a condition in which the blood's ability to carry oxygen is reduced. This reduced supply of oxygen can lead to damaged organs and death. Because it is a source of nitrogen, an essential element for aquatic plant growth, nitrate ion may contribute to eutrophication of standing or slow-moving surface water, particularly in nitrogen-limited waters.
There is currently no evidence to suggest that nitrate compounds are carcinogenic.

Nitrogen in nitrate is the form of nitrogen most available to plants. In the environment, nitrate ion is taken up by plants and becomes part of the natural nitrogen cycle. Excess nitrate can stimulate primary production in plants and can produce changes in the dominant species of plants, leading to cultural eutrophication and ultimately to deterioration of water quality.

Urea

Urea is a colorless to white, prismatic crystals or white crystalline powder. It is almost odorless, may gradually develop slight odour of ammonia, especially in the presence of moisture. It has a saline cooling taste. Its melting point reaches 132.7° C.

Urea causes redness and irritation of skin and eyes. Adverse reactions include headache, nausea, vomiting, syncope, disorientation, transient confusion and electrolyte depletion (hyponatremia and hypokalemia). Because the eye is permeable to urea, rebound elevation in intraocular pressure and vitreous volume may occur after ocular hypotensive effect has terminated. Urea is irritating to tissues, it causes pain at site of infusion and necrosis may result if extravasations occurs.

Urea is artificially released to the environment through direct application to soil as a nitrogen-released fertilizer. If released to the atmosphere, urea will degrade rapidly in the vapour phase by reaction with photo-chemically produced hydroxyl radicals. If released to soil, urea is hydrolyzed to ammonium through soil urease activity. The rate of hydrolysis can be fast (24 hrs), however, a number of variables (such as increasing the pellet size of the fertilizer) can decrease the degradation rate from days to weeks. If released to water, urea can degrade readily through biotic hydrolysis. The presence of naturally- occurring phytoplankton increases the degradation rate because phytoplankton use urea as a nitrogen source and because urea is decomposed by phytoplankton photosynthesis. Degradation of urea occurs much faster in sunlight than in dark water. Addition of urea appeared to have adverse effects on the uptake of phosphorous. Biodegradation is expected to be the major fate process in the aquatic ecosystem. Urea can biodegrade readily with the release of CO_2 and ammonia. The rate of degradation generally decreases with decreasing temperature. In aqueous solution, urea is in equilibrium with ammonia and isocyanate ions; in the absence of microorganisms, urea hydrolyzes very slowly to yield ammonium carbamate which decomposes to form ammonia and carbon dioxide. The hydrolysis is catalyzed by increasing temperatures and alkalinity.

Occupational exposure to urea occurs through dermal contact and inhalation of dust.

Methanol

Methanol is a colorless liquid with a characteristic pungent odor. It is miscible with water, and its boiling point is 81.6°C.

Methanol is generated in ammonia production. It is also used as a solvent and for equipment cleaning in pesticide formulations.

Methanol is readily absorbed from the gastrointestinal tract and the respiratory tract and is toxic to humans in moderate to high doses. In the body, methanol is converted into formaldehyde and formic acid. Methanol is excreted as formic acid. Observed toxic effects at high dose levels generally include central nervous system damage and blindness. Long-term exposure to high levels of methanol via inhalation cause liver and blood damage in animals.
Ecologically, methanol is expected to have low toxicity to aquatic organisms. Concentrations lethal to half the organisms of a test population are expected to exceed one mg methanol per liter water. Methanol is not likely to persist in water or to bioaccumulate in aquatic organisms.
There is currently no evidence to suggest that methanol is carcinogenic.

Methanol is highly volatile and flammable. Liquid methanol is likely to evaporate when left exposed. Methanol reacts in air to produce formaldehyde which contributes to the formation of air pollutants. In the atmosphere it can react with other atmospheric chemicals or be washed out by rain. Methanol is readily degraded by microorganisms in soils and surface waters.

Sulfuric Acid

Sulfuric acid is an oily, odorless liquid which can be colorless to dark-brown. It is miscible, and its boiling point is 307.7°C. Sulfuric acid reacts violently with water with evolution of heat and is corrosive to metals. Pure sulfuric acid is a solid below 28°C.
Sulfuric acid is a raw material of most fertilizer products. Concentrated sulfuric acid is corrosive. In its aerosol form, sulfuric acid has been implicated in causing and exacerbating a variety of respiratory ailments.

Ecologically, accidental releases of solution forms of sulfuric acid may adversely affect aquatic life by inducing a transient lowering of the pH (i.e., increasing the acidity) of surface waters. In addition, sulfuric acid in its aerosol form is also a component of acid rain. Acid rain can cause serious damage to crops and forests. Releases of sulfuric acid to surface waters and soils will be neutralized to an extent due to the buffering capacities of both systems. The extent of these reactions will depend on the characteristics of the specific environment.

There is sufficient evidence that occupational exposure to strong-inorganic acid mists containing sulphuric acid is carcinogenic. Sulphuric acid causes irritation of the mucous membranes, eye irritation and a pronounced reflex cough. In addition it results in corrosion of mucous membranes of mouth, throat and esophagus with immediate pain and dysphagia.

Particulate matters

Much of the health damage caused by exposure to particulates is associated with particulate matters smaller than 10µm (PM_{10}). These particles penetrate most deeply into the lungs, causing a large spectrum of illnesses including asthma attack, cough, chronic bronchitis and may lead to obstructive lung diseases, skin irritation.

Emissions of particulates include ash, soot and carbon compounds, which are often the result of incomplete combustion. Dust fall concentration is considered another sensitizing factor in fertilizers plants. It can be visualized in many places inside the plants, causing skin eczema and chronic bronchitis and bronchial asthma.

Sulfur Oxides

Air pollution by sulfur oxides is a major environmental problem. This compound is harmful to plant and animal life, as well as many building materials. Sulphur oxides are harmful for human health. They cause mild respiratory irritation. Inhalation of low concentrations causes burning pain in chest.

Another problem of great concern is acid rain which is caused by the dissolution of sulfur oxides in atmospheric water droplets to form acidic solutions that can be very damaging when distributed in the form of rain. Acid rain is corrosive to metals, limestone, and other materials, also deteriorates the agriculture land.

Nitrogen Oxides

Nitrogen oxides also dissolve in atmospheric water droplets to form acid rain. They cause severe irritation of eyes and respiratory tract. High concentrations can cause immediate asphyxia.

Carbon dioxide

Combustion of fossil fuels to produce electricity and heat contribute to the green house effect caused by the formation of carbon dioxide. The greenhouse phenomenon occurs when heat radiation from earth is absorbed by the gases causing a surface temperature increase. High concentrations of carbon dioxide can cause immediate asphyxia.

Carbon monoxide

It is absorbed through lungs and in addition to its reaction with hemoglobin, it combines with myglobin, cytochromes, and metalloenzymes.

The binding of CO with hemoglobin producing decreasing the oxygen carrying capacity of blood, this is appear to be the principle mechanism of the toxic action of low-level carbon monoxide exposure. Carbon monoxide reduces blood oxygen- carrying capacity, causing dizziness, weakness, headache. Concentrations above 1000 ppm can be fatal within one hour.

Water Vapor (Humidity)

Humidity in workplace is regulated by law 4/1994 due to its effect on the respiratory system especially for people suffering from asthma.

Hydrogen Fluoride

Hydrogen fluoride is a colorless gas or fuming liquid. It has a strong irritating odour. It corrodes most substances except lead, wax, polyethylene, Teflon and platinum.

It is non combustible substance, but it may decompose upon heating to produce corrosive and/ or toxic fumes.

Inhalation or ingestion of this gas may cause fluorosis, symptoms, weight losses, malaise, anemia, leucopoenia and discoloration of teeth. In addition it may cause eyes injury, severe skin burns, respiratory diseases and in extreme cases it may cause death. All forms diluted or concentrated solution or vapour of hydrofluoric acid cause severe burns. Inhalation of anhydrous HF or its mists or vapours can cause severe respiratory irritation that may be fatal. Severe irritation to eyes resulting in visual defects. Skin contact results in pungent irritation odour. Concentrated aqueous solution also cause early sensation of pain. Ingestion of large quantities of the acid cause sudden death without gross pathologic damage. On the other hand repeated ingestion of small amounts of the acid resulted in moderately advanced osteosclerosis. Thus HF is capable of inducing system manifestations of both acute & chronic poisoning additional hazard. It was found that hydrogen fluoride in liquid or vapour phases produces tissue dehydration and necrosis similarly to other mineral acids. It can also penetrate deeply into tissues. Its toxicity occurs after ingestion, inhalation or ocular or dermal contact. Ingestion of this gas produces pan and corrosion of the oral mucous membranes, esophagus and stomach. Inhalation of the concentrated fumes of this gas results in irritation, coughing and retrosternal burning.

Its corrosive action on metals can result in formation of hydrogen in containers and piping to create fire hazard. Therefore, potential sources of ignition should be excluded from areas around equipment containing the acid.

It reacts with water releasing corrosive toxic gases and heat which increases the concentration of its fumes in the air. Fluoride concentration in groundwater fluctuate within wide limits. Its concentrations are higher in sea water than in fresh water.

Fluoride in the air may accumulate to vegetation and may lead even to damage the vegetation. Conifers are especially sensitive to fluoride.

Silicon compounds

These compounds are emitted during the production of phosphate fertilizers.

There is sufficient evidence in humans for the carcinogenicity of inhaled crystalline silica or contribute from occupational sources. Carcinogenicity may be dependent on inherent characteristics of the inhaled silica or on external factors affecting is biological activities or distribution of its polymorphs.

There is inadequate evidence for the carcinogenicity of uncalcined diatomaceous earth.

The action of crystalline silica on the lungs results in the production of a diffuse, nodular fibrosis in which the parenchyma and the lymphatic system are involved. This fibrosis is, to a certain extent, progressive, and may continue to increase for several years after exposure is terminated.

The most physical; sign of silicosis is a limitation of expansion of the chest. There may be a dry cough and shortness of breath. Further progress of the disease results in marked fatigue, extreme dyspnea and cyanosis, loss of appetite, pleuritic pain and total incapacity to work.

Ammonium sulfate

It is emitted during the production of ammonium sulfate fertilizer, its bagging and storage. It is transferred into human body by inhalation, which cause breathing passages to contract and decrease air flow. Dust also may irritate the skin, eyes, digestive tract and respiratory tract. Ammonium sulfate is not considered a carcinogenic.

Burning ammonium sulfate releases toxic gases such as ammonia, sulphur oxides, sulphuric acid and nitrogen oxides.

Sulphur and hydrogen sulfide

It is used during the production of sulphuric acid, during the combining of elemental sulphur and water. Combining elemental sulphur with oxygen creates sulphur dioxide. Sulphur causes physical burns and exposure to hydrogen sulphide with its powerful rotten eggs odor, can irritate breathing passages, temporarily destroy sense of smell, and even crowd out air in the lungs to suffocate those who breathe it in concentrations above 550 ppm. Exposure to hydrogen sulphide may cause nausea, cough, headache, dizziness, extreme eye irritation and bronchitis. Although liquid sulphur is only a slight fire hazard, the hydrogen sulphide gas can give off explodes or burns relatively does

	burn, it gives off poisonous gases such as sulphur dioxide, sulphuric acid and other sulphur compounds. If molten sulphur spills, it causes hazardous vapours emissions. Sulphur dioxide, which is a colourless gas, can cause irritating odour that is toxic by inhalation and is a strong irritant to eyes and mucous membranes.
Gypsum	Gypsum dust has an irritant action on mucous membranes of the respiratory tract and eyes. It also causes chronic rhinitis, laryngitis, pharyngitis, impaired sense of smell and taste, bleeding from the nose, reactions of tracheal bronchial membranes in exposed workers. Waste gypsum contains also fluoride and trace metals.
Dolomite	Calcium carbonate is considered the main component of dolomite. This compound causes systemic and renal effects, slight to moderate metabolic alkalosis, hypercalciuria and alkaluria predispose to nephrolithiasis, admin and hypophosphatemia. Large doses of calcium carbonate increase gastric secretion for a period of time that considerably outlasts elevation of pH.
Kaolin	The use of kaolin causes innocuous, granuloma of the stomach. Occupationally inhaled kaolin produced chronic pulmonary fibrosis, sites of action: lung parenchyma and lymph nodes.

3.2 Impact of Effluents

Wastewater from fertilizer industry generates from several sources including; process effluents resulting from scrubbers, condensers and stripping operations, effluents from service units and occasional effluents such as leaks or spills. In addition wastewater from equipment and floor washing constituents is considered a major polluting source for the effluents.

Concerning the nitrogenous fertilizers effluents, the most polluting parameters are ammonia, nitrates and organic nitrogen as well as organic load and suspended solids. On the other hand phosphate fertilizers industry generate wastewater which is highly contaminated with phosphate, fluoride, heavy metals and organic load as well as suspended solids. Fluorine, a gaseous halogen does not exist in free state, but occurs in combination without elements. Fluoride becomes toxic to animals and human beings when present at a concentration of about 1 mg/ l in drinking water. It was found by several investigators that industrial effluents containing fluorides up to 10 mg/ l have injurious effect to some crops when present in soil solution. On the other hand, fluoride could affect skeletal components due to the natural affinity of fluoride ions for calcium.

The organic material in wastewater stimulates the growth of bacteria and fungi naturally present in water which then consume dissolved oxygen. Spent lube oil from lubricating equipments, garage and workshops could be a cause for concern if discharged into the sewer system. There can be also heavy metals and other hazardous components in wastewater.

The environmental impact of wastewater depends on the receiving water body. Polluting parameters from fertilizers industry could affect the plants and aquatic life. Discharging polluted wastewater high in BOD, O&G, and COD into lakes and sea can cause eutrophication and impact bio-diversity. Eutrophication is a natural aging process in which the water becomes organically enriched, leading to increasing domination by aquatic weeds, transformation to marsh land and eventually to dry land. It can be accelerated by human input of nutrients, its effects are compounded by large day-night excursions in dissolved oxygen due to photosynthesis and respiration.

Sudden discharge of high O&G, BOD, and COD loads to the public sewer system will have an indirect environmental impact. Shock loads can cause malfunction of the domestic wastewater treatment plant. In addition, spent solvent and caustic wash wastewater make corrosion of the internal sewer system of the plant, if discharged.

3.3 Impact of Solid Wastes

One of the largest solid wastes in the fertilizers industry is phosphogypsum which is produced during phosphoric acid production. It contains traces of many mineral impurities that accompany phosphate rock. It is considered a hazardous solid waste due to its content of radium, nickel, cadmium, lead, aluminum, fluoride and phosphoric acid. Cadmium is a heavy metal which accumulates in living systems and can become toxic above certain limits. The cadmium content in the phosphate rocks varies from almost zero to over 300 mg/kg P_2O_5. It takes large areas to pile phosphogypsum. Waste waters from storage areas should be treated. Fluoride and particulates can be emitted in air around the storage area. Phosphogypsum ponds and leaks from other storage areas may contaminate surface and ground water.

Catalysts used in the steam reforming process need to be replaced every several years depending on the operating conditions, type and the life time for the catalyst. These catalysts are considered hazardous and should not disposed on land. Spent catalysts in general should be returned for regeneration, if not possible they should be disposed in the safe landfill.

Sludge generated from WWTP contaminates the soil, surface water and underground water, if disposed on them. Therefore this sludge must be dried first and safely dumped in special dumping sites.

Ashes may contain heavy metals depending on the burned fuel. Also other solid wastes from industry and service units may contaminate surface and ground waters and soil if not disposed safety.

4. Egyptian Laws

There are numbers of laws and regulations that address the different environmental violations. The following are the laws applicable to the fertilizers industry.

4.1 Concerning Air Emissions

Article 40 of Law 4/1994, article 42 of the executive regulations and annex 6 deal with gaseous emissions from combustion of fuel. The statutes relevant to the fuel combustion are:

- The use of fuel oil (mazot) and other heavy oil products, as well crude oil shall be prohibited in dwelling zones.
- The sulfur percentage in fuel used in urban zones and near the dwelling zones shall not exceed 1.5%.
- The design of the burner and fire-house shall allow for complete mixing of fuel with the required amount of air, and for the uniform temperature distribution that ensure complete combustion and minimize gas emissions caused by incomplete combustion..
- Gases containing sulfur dioxide shall be emitted through chimneys rising sufficiently high in order that these gases become lighter before reaching the ground surface, or using fuel that contains high proportions of sulfur in power generating stations, as well as in industry and other regions lying away from inhabited urban areas, providing that atmospheric factors and adequate distances to prevent these gases from reaching the dwelling and agricultural zones and regions, as well as the water courses shall be observed.
- Chimneys from which a total emission of wastes reaches 7000 – 15000 kg/hr, shall have heights ranging between 18 – 36 meters.
- Chimneys from which a total emission of gaseous wastes reaches more than 15000 kg/hour, shall have heights exceeding at least two and a half times the height of surrounding buildings, including the building served by the chimney.

The permissible limits of emissions from sources of fuel combustion in boilers and other equipments are given in tables (10 and 11) (Ministerial decree no. 495, 2001).

Table (10) Maximum Limits of Emissions from Sources of Fuel Combustion in Boilers

Pollution	Maximum limit mg/m^3 of Exhaust
Sulfur Dioxide.	3400
Carbon Monoxide.	250
Smoke.	50

Table (11) Maximum Limits of Emission from Fuel Burning Sources

Pollutant	Maximum Permissible Limit, mg/ m^3
Smoke	250
Suspended Ashes	250 (sources existing in urban regions, or close to residential areas)
	500 (sources far from inhabited urban areas)
	500 (burning of wastes)
Sulfur Dioxide	4000 (Existing) 2500 (New)
Aldehydes	Burning of waste 20
Carbon Monoxide	4000 (Existing) 2500 (New)

4.2 Concerning Effluents

Limits for pollutants in wastewater vary depending on the type of receiving water body. The parameters that should be monitored and/or inspected are BOD, COD, pH, temperature, total phosphorous, phosphates, nitrates, fluorides, ammonia, sulphates, nickel, iron, zinc, nitrogen, TSS, TDS, Oil and Grease.

Table (12) presents the permissible limits for discharges to the different recipients (sea, Nile, canals, agricultural drains, public sewer) according to the different relevant laws.

Spent lube oil has a negative impact on water and soil and therefore its disposal should be monitored/inspected. A record should be kept for this purpose.

Table (12) Egyptian Environmental Legal Requirements for Industrial Wastewater

Parameter (mg/1 unless otherwise noted)	**Law 4/94: Discharge Coastal Environment**	**Law 93/62 Discharge to Sewer System (as modified by Decree 44/2000)**	**Law 48/82: Discharge into :**			
			Underground Reservoir & Nile Branches/Canals	**Nile (Main Stream)**	**Drains**	
					Municipal	**Industrial**
BOD (5day,20 deg.)	60	<600	20	30	60	60
COD	100	<1100	30	40	80	100
pH	6-9	6-9.5	6-9	6-9	6-9	6-9
Oil & Grease	15	<100	5	5	10	10
Temperature (deg.)	10C>avg. temp of receiving body	<43	35	35	35	35
Total Suspended Solids	60	<800	30	30	50	60
Settable Solids	—	8 cm^3/ l (10 min) 15 cm^3/ l (30 min)	—	20	—	—
PO$_4$	5	—	—	1	—	10
Total phosphorus	—	25	—	—	—	—
Fluoride	1	—	0.5	0.5	—	0.5
Total Dissolved Solids	2000	—	800	1200	2000	2000
Ammonia	3	—	—	—	—	—
Nitrates	40	—	30	30	50	40
Sulphides	1	10	1	1	1	1

Parameter (mg/1 unless otherwise noted)	**Law 4/94: Discharge Coastal Environment**	**Law 93/62 Discharge to Sewer System (as modified by Decree 44/2000)**	**Law 48/82: Discharge into :**			
			Underground Reservoir & Nile Branches/Canals	**Nile (Main Stream)**	**Drains**	
					Municipal	**Industrial**
Nitrogen	—	100	—	—	—	—
Iron	1.5	—	1	1	—	—
Zinc	5	—	1	1	—	—
Nickel	0.1	1	0.1	0.1	—	—

4.3 Concerning Solid Wastes

A number of laws addresses solid wastes management. The following laws are applied to solid wastes and sludge from the WWTP:

- Law 38/1967 which addresses public cleanliness, regulates the collection and disposal of solid wastes from houses, public places, commercial and industrial establishments.
- Ministry of Housing, Utilities and Urban Communities (MHUUC) decree No. 134 of 1968, which provides guidelines from domestic and industrial sources, including specifications for collection, transportation, composting, incineration and land disposal.
- Law 31/1976, which amended law 38/1967
- Law 43/1979, the Law of Local administration, which provided that city councils are responsible for "physical and social infrastructure", effectively delegating responsibility for infrastructure functions.
- Law 4/1994 regulates incineration of solid waste

4.4 Concerning Work Environment

The following summarizes the laws and articles concerning work place conditions:

- Gas emissions are regulated by article 43 of Law 4/1994, article 45 of the executive regulations and annex (8). The limits for the relevant gaseous pollutants are presented in table (13).
- Heat stress is regulated by article 44 of Law 4/1994, article 46 of the executive regulations and annex (9). Table (14) shows the maximum limits for heat stress.
- Near heavy machinery, noise is regulated by article 42 of Law 4/1994, article 44 of the executive regulations and table (1) in annex (7). These limits are given in the tables (15, 16 and 17).
- Ventilation is regulated by article 45 of Law 4/1994 and article 47 of the executive regulations.
- Work environment conditions are addressed in Law 137/1981 for Labor, Minister of Housing Decree 380/1983, Minister of Industry Decree 380/1982.

Table (13) Permissible Limits as Mean Time Exposure and for Short Periods

Substance	Exposure limits				
	Mean time		Short term		Remarks
	ppm	mg/m^3	ppm	mg/m^3	
Ammonia	25	18	35	27	-
Calcium carbonate	-	-	-	20	-
Carbon dioxide	5,000	9,000	15,000	27,000	-
Carbon monoxide	50	55	400	440	-
Copper fumes	-	0.2	-	-	-
Capper dust and mists	-	1	-	2	-
Fluorine	-	2	2	4	Ceiling
Hydrogen fluoride	3	2.5	6	5	-
Hydrogen sulfide	10	14	15	21	-
Nickel*	-	1	-	-	-
Nitric acid	2	5	4	10	-
NO	25	30	35	45	-
NO_2	3	6	5	10	-
Phosphoric acid	-	1	-	3	-
Yellow phosphorus	-	0.1	-	0.3	-
Platinum metal	-	1	-	-	-
Silicon	-	-	-	20	-
SO_2	2	5	5	10	-
Sulfuric acid	-	1	-	-	-
Zinc oxide fumes	-	5	-	10	-

[*] Limit of Nickel dusts and fumes is 0.1mg/m^3 (as nickel). Nickel is a carcinogenic substance.

Table (14) Maximum Permissible Limits for Heat Stress (law 4/1994)

Type of Work	Low Air Velocity	High Air Velocity
Light work	30° C	32.2 ° C
Moderate work	27.8 ° C	30.5 ° C
Severe work	26.1 ° C	28.9 ° C

Table (15) Maximum Permissible Noise Levels (law 4/1994)

No	Type of Place and Activity	Maximum Permissible Noise Decibel (A)
1	Work place with up to 8 hour and aiming to limit noise hazards on sense of hearing	90 dB
2	Work place where acoustic signals and good audibility are required	80 dB
3	Work rooms for the follow up, measurement and adjustment of high performance operations	65 dB
4	Work rooms for computers, typewriters or similar equipment	70 d.B
5	Work rooms for activities requiring routine mental concentration	60 dB

Table (16) Noise Intensity Level Related to the Exposure Period

Noise Intensity Level Decibel (A)	95	100	105	110	115
Period of Exposure (hour)	4	2	1	½	¼

Table (17) Noise Intensity Level In Intermittent Knocking Places

Noise Intensity db	Max Allowable Knocks During Daily Work Period
135	300
130	1000
125	3000
120	10,000
115	30,000

4.5 Concerning Hazardous Material and Wastes

Law 4/1994 introduced the control of hazardous materials and wastes. The fertilizers industry generate some hazardous solid wastes (such as spent catalyst and phosphogypsum). Hazardous materials (sulphuric nitric and phosphoric acids) are produced on-site, therefore articles 29 and 33 of law 4/1994 ought to be performed. Also the hazardous chemicals used in the lab and the fuel for the boilers, fall under the provisions of Law 4/1994. Articles 29 and 33 of the law makes it mandatory for those who produce or handle dangerous materials in gaseous, liquid or solid form, to take precautions to ensure that no environmental damage shall occur. Articles 25, 31 and 32 of the executive regulations (decree 338/1995) specify the necessary precautions for handling hazardous materials. Storing of fuel for the boilers is covered by the Law 4 as hazardous material There is no explicit articles in Law 4/1994 or in decree 338/1995 (executive regulations), regarding holding a register for the hazardous materials; article 33 is concerned with hazardous wastes. However, keeping the register for the hazardous materials is implicit in article 25 of the executive regulations regarding the application for a license.

4.6 The Environmental Register

Article 22 of Law 4/1994 states that the owner of the establishment shall keep a register showing the impact of the establishment activity on the environment. Article 17 and Annex (3) of the executive regulations specify the type of data recorded in the register.

The emergency response plan and the hazardous materials register will also be part of the environmental register as stated in law 4/ 1994.

5. Pollution Abatement Measures

This section deals with pollution abatement (preventions) in the three media air, water and soil. Three types of interventions will be considered:

- In-plant modifications, which are changes that are performed in the plant to reduce pollutant concentrations in streams through recovery of materials, segregation and/or integration of streams, reducing the flow rate of the wastewater streams that need further treatment to reduce the hold-up of the required WWTP.
- In-Process modifications, which are changes performed on the process such as the introduction of cleaner technology, substitution of a hazardous raw material, performing process optimization and control.
- End-of-pipe (EoP) measures, which involve treatment of the pollutant or its separation for further disposal. Whereas in-plant and in-process modifications usually have an economic return on investment, end-of-pipe measures will be performed for the sole purpose of compliance with the laws without economic.

Egyptian Environmental Laws do not require water and energy conservation measures. These measures have been considered in this manual since resource depletion and hence conservation is a worldwide-recognized environmental issue that could be implemented in Egypt in the near future. Water conservation measures can lead to higher concentrations of pollutants in the effluent streams. Both energy and water conservation measures will provide both financial and economic benefits.

5.1 Air pollution Abatement Measures

Flue gases Particulate matter in flue (exhaust) gases are due the ash and heavy metal content of the fuel, low combustion temperature, insufficient excess air, high flow rate of flue gases. Sulfur dioxide is due to the sulfur content of the fuel. Nitrogen oxides are formed when maximum combustion temperature and high excess air. Carbon monoxide is formed when incomplete combustion occurs at low air to fuel ratio.

The following measures can be adopted to minimize air pollution from flue (exhaust) gases:

- Replace fuel oil (mazot) by solar (diesel oil) or natural gas. Fuel oil (mazot) is high in sulfur content.
- Regulate the fuel to air ratio for an optimum excess air that ensures complete combustion of carbon monoxide to dioxide.
- Keep the combustion temperature at a moderate value to minimize particulate matter and nitrogen oxides formation.
- Emissions from the boilers can also be reduced by the

installation of low NO_x gas burners (staged at combustion air inlet) and by substituting fuel oil by natural gas.

- Continuous boilers tuning using gas analyzer can also lead to the reduction in the contents of stack flue gases.
- Use sulphur removal techniques to prevent SO_2 formation.

Particulates & Dust

- Fertilizers manufacturing plants often produce large quantities of particulates which are collected from numerous sources. Since most of the streams were mixed, none of the waste could be recycled to the process that generated them. By installing separate dedicated bag houses for each production line, all of the collected particulates could be recycled.
- Plants may also use wet scrubbers to control air emissions. Some facilities may only need a wet scrubber on one particular process (i.e., a dedicated scrubber). These facilities have been able to reuse the scrubber blowdown or changed-out scrubber water as make-up water in the formulation of that particular product. Some facilities with no dedicated scrubbers have been able to use the scrubber blowdown or changed-out scrubber water for floor or equipment exterior cleaning.
- In ammonium nitrate plants, use of fabric filters, with injection of absorbent as necessary, is the preferable mean for particulates emissions.
- Cyclones are also necessary for the collection of particulates which are emitted from several operations such as granulation, preparation of raw phosphate rocks, prilling and bagging of fertilizers.

Microbrill formation

- Microprill formation resulting from partially plugged orifices of melt spray devices can increase fine dust loading and emissions. Certain designs (spinning buckets) and practices (vibration of spray plates) help reduce microprill formation. Reducing the ambient air temperature reduces emissions because the air flow required to cool prills and the formation of fumes are decreased at lower temperatures.
- Use a collection system such as cyclones is essential for the reduction of particulates emissions. The result collected solid waste is then disposed off-site in dumping sites.
- Use a fattening of prills in order to reduce fines.

Ammonia Synthesis Modifications

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

- Addition of Process Computer A dedicated process computer can be installed along with other on-line analysis and control systems to monitor and control key variables. With this system, continuous set point changes are possible to optimize the operation of several plant areas such as hydrogen/nitrogen ratio, steam/carbon ratio, synthesis loop purge, methane leakage, converter control, and refrigeration purge. Hydrogen Recovery from the Purge Gas Inert gases must be pumped from the plant to avoid their buildup in the system. This purge is carried out by removing a side stream of synthesis gas after recovering the ammonia. By installing the proper recovery system, the hydrogen in this gas mixture can be recovered decreasing the energy requirements of the process by about five percent or permitting an increase of about five percent in production capacity.
- Use natural gas as the feed stock for the ammonia plant, to minimize the gaseous air emissions.
- Use hot process gas from the secondary reformer to heat the primary reformer tubes, thus reducing the need for natural gas.
- Consider using purge gases from the synthesis process to fire the reformer; strip condensate to reduce the ammonia and methanol.
- Use carbon dioxide removal process that do not release toxics to the environment.

Wet scrubbing recovery unit

Scrubbers are used to remove fluorides, silicon tetra-fluoride and acid mist from air emissions of phosphate fertilizer plants.

Sulphur oxides and acid mist removal

The discharge of sulphur dioxide from sulphuric acid plant should be minimized by using the double-contact, double-absorption process, with high efficiency mist eliminator. A Lime-solution scrubbing system is implemented in some fertilizers plants to remove sulphur oxides from the absorber off-gas of sulphuric acid plant. In this process the tail gas (containing SO_2, SO_3 and acid mist) is directed to a venturi absorber (scrubber), in which a solution of calcium hydroxide is charged into the scrubber. Sulphur oxides are absorbed in the solution producing clean gas which is discharged to the atmosphere. The resulted effluent from the bottom of the absorber is subjected to a clarifier from which a slurry and mother liquor are separated. The mother liquor is recycled to the absorber and the slurry is further dried in a centrifuge. The resulted dry sludge constitute mainly calcium sulphate and calcium hydroxide.

Tail gas processing in nitric acid plant

In this process, tail gas (containing NO_x) from the absorber is preheated and fed to a catalytic afterburner (reduction) in which natural gas is fed as fuel. In this operation large heat is evolved, it is recovered by entering the effluent through a waste heat boiler and then a power recovery turbine.

Nitrogen Oxides

- Extended absorption system could reduce tail gas emissions.
- NO_2 is removed from the gas stream by reaction, but is not recovered for use.
- Use cooler water in the upper trays of the absorption tower.

Neutralization Scrubber of ammonia and nitric acid

- Gases release from neutralization operation of these units, containing ammonia and ammonium nitrate. These gases can be controlled by scrubbers (using water in packed towers).

5.2 Water Pollution Abatement Measures

The Fertilizer Industry uses many pollution prevention (P2), recycle and reuse, and water conservation practices. Wastewaters are primarily generated not by the production or formulating processes themselves but by cleaning operations of the process areas and associated equipment. There are many P2, recycle and reuse, and water conservation practices that are widely accepted and practiced by the Fertilizer Industry today. Some of these practices and equipment conserve water, others reduce the amount of fertilizer product in the wastewater, and still others may prevent the generation of a wastewater altogether. A number of common P2 practices are listed below. Production practices include:

- scheduling production to minimize cleanouts
- performing preventive maintenance on all valves, fittings, and pumps
- placing drip pans under leaky valves and fittings or under any valves or fittings where hoses or lines are routinely connected and disconnected
- cleaning up spills or leaks in outdoor bulk containment areas to prevent contamination of storm water

The following are some ways for liquid waste control measures:

In-plant modifications

- In all cases, it is recommended the industrial liquid waste discharged separately from domestic wastes as they differ in the pollutant nature.
- Collect spent lube oils and lubricants they do not discharge to drain or soil. They can be reprocessed.
- The installation of product-capture systems for bagging

machines can reduce product losses.

- Implementation of a quality control system such as HACCP (Hazard Analysis & Critical Control Point) is recommended to minimize waste.
- During processing and packaging operations, the exteriors of equipment may become soiled from drips, spills, and dust (especially equipment located near dry lines). The floors in the area become dirty in the same manner and also from normal traffic. Facility workers clean the equipment exteriors and floors for general housekeeping purposes, and to keep sources of product contamination to a minimum. When water is used, these cleaning procedures become a source of wastewater.
- Wastewater can again be minimized through the use of high-pressure, low-volume washers rather than ordinary water hoses. Squeegees are also used to clean equipment exteriors and floors, and are not disposed of after single uses. It may be possible to dedicate squeegees to a certain line or piece of equipment, but using squeegees may still require using some water. Some facilities use automated floor scrubbers, which replace the practice of hosing down floors. Floor scrubbers are mechanical devices that continually recirculate cleaning water to clean flat, smooth surfaces with circulating brushes. During operation, the scrubber collects the cleaning water in a small tank that is easily emptied after the cleaning process, or at a later date. Using a floor scrubbing machine can require as little as five to fifteen gallons of cleaning solution (typically water) per use. A mop and a single bucket of water can also be used in place of a hose. Floor mopping can generate as little as ten gallons of water per cleaning depending on the size of the surface to be cleaned. A number of facilities reuse their floor wash water with and without filtering.
- Dry products that have leaked or spilled can be vacuumed or swept without generating any wastewater. Liquid leaks and spills can be collected into a trench or sump (for reuse, discharge, or disposal) with a squeegee, leaving only a residue to be mopped up or hosed down if further water cleanup is required. Liquid leaks and spills can also be cleaned up using absorbent material, such as absorbent pads or soda ash. For an acidic product, soda ash or a similar base material will also serve to neutralize the spill. If a residue remains, some water may be used for mopping up or hosing the area down, but methods to reduce floor wash should be implemented whenever possible.
- Precipitation runoff includes all precipitation that falls

on facility surfaces that are believed to be contaminated. Contaminated precipitation runoff can be prevented by bringing all operations indoors, as many facilities have done, or by covering outdoor storage tanks and dikes with roofs, which has also been done at many facilities.

- In phosphoric acid plant, neither the evaporators nor the reactor can operate without the barometric condensers associated with them, therefore, the condensers are process equipment even though a large portion of the gaseous fluorides evolved are absorbed in them. Fluoride and gypsum ponds are necessary to prevent fluoride water pollution. The gases from miscellaneous vents are scrubbed and discharged to the cooling pond to combine with the effluents from the gypsum ponds (free from gypsum). If the fluoride content of the pond water is high enough fluoride may be vaporized and emitted to air.

In-process modifications

- Fertilizer mixing plants sometimes produce large quantities of formulated fertilizer products and receive large quantities of raw materials used to produce those products. Those products and raw materials are stored on site in bulk tanks. The tanks are typically rinsed only when it becomes necessary to use the tank to store a different material. Product changeover cleaning can be eliminated or greatly reduced by dedicating equipment to specific products or groups of products.
- For minimizing the discharge of copper from ammonia plant, copper can be precipitated as copper hydroxide or can be removed by ion- exchange. Also copper can be recovered by electrolysis.
- One method to reduce the amount of wastewater from ammonium nitrate production is to incorporate a wastewater evaporator system which reduces the amount of contaminated cooling water discharge. The wastewater passes through a series of evaporation steps whereby the vapors are used as wash water in the calcium carbonate filters and the concentrated solution is pumped to the neutralizers where it is mixed with the acidic nitrogen-phosphate solution and used to regulate the nitrogen-phosphate nutrient ratio of the fertilizer. Through this modified technology, steam and electric energy consumption increases somewhat, but such increases are balanced by the more effective utilization of nitrogen and the reduction of wastewater.
- Replacement of cupper liquor operation by using a catalytic unit for the removal of carbon dioxide in the ammonia production. This will avoid the pollution of cupper liquor completely.

- Oil losses can be reduced through the installation of a collecting sump tank overflow and treated biologically.

End-of-pipe treatment

Wastewater treatment is essential for effluents of fertilizers plants. It includes several treatment stages depending on the product type. Wastewater from phosphate fertilizers plants contains H_2SiF_6, suspended solids, fluoride, silicates and phosphates. This wastewater can be neutralized by using limestone. This process is not cost effective due to the large quantities of lime consumed in one day. Another alternative for this treatment is the production of AlF_3 from the wastewater generated from phosphate fertilizers plants. In this process wastewater is treated with Al2O3 according to the following reaction:

$Al_2O_3 . 3H_2O + H_2SiF_6 \rightarrow AlF_3 + SiO_2 + H_2O$

SiO_2 precipitate and then removed and disposed off-site. The metastable AlF_3 filtrate flows into crystallizer in which AlF_3 trihydrate precipitate out. The crystallization process requires about 5 hours, then the crystals are removed by filtration and calcined to produce AlF_3 which is sold for the aluminum industry to be used as flux. Chemical treatment is necessary for the pH adjustment and for the reduction of suspended matter and fluoride concentrations.

The resulted H_2SiF_6 from the scrubber is concentrated, sodium chloride is then added to produce Na_2SiF_6 which is a sellable product.

In the nitrogenous fertilizers plants the nitrates are removed by the use of biological action in aerated ponds or basins. Ion exchange units have also been used successfully to remove ammonia and nitrates from the wastewater. At ammonium nitrate plants condensates (containing ammonia, ammonium nitrate and some oxides of nitrogen) need to be treated before discharging to the environment.

5.3 Abatement Measures for Work Environment

Workers in the fertilizers industry are exposed to chemical hazards due to the presence of various emissions in the work place from numerous operations. Also they are exposed to noise and heat stress hazard. These hazards can be controlled through the following measures:

- Using control equipment such as; Fabric filters or cyclones should be used to mitigate particulates and dust emissions.
- For noise effect, ear plugs could be used.
- For eye diseases prevention, wearing safety glasses is essential.
- Performing efficient ventilation system in the different production units reduces the various emissions in work place.

5.4 Abatement Measures for Hazardous and Solid Waste Pollution

The aim should be to decrease wastes be formed. Economical consumption of raw materials and good operating practice can help to minimize the amount the wastes. The use of non-hazardous raw materials whenever it is possible enable to reduce the amount of hazardous waste.

Scrap

- Scrap metals are collected from workshops and garage and sold.

Hazardous Solid wastes

Hazardous solid wastes sources includes catalysts, chemicals sacs, packs, empty barrels, filters cartridge, materials spills, and precipitates from liquid wastes (caustic solutions and solvents) clarification by settling or distillation. The following are some ways for reducing solid waste pollution:

- Planning of packaging systems to avoid solid waste and/or to facilitate recycling of packages or packaging wastes.
- Label and store toxic and hazardous materials in secure, bounded areas.
- Separating hazardous solid waste from non-hazardous ones. This means separating sacs or packs containing hazardous materials such as lead or chromium compounds, from that free from such compounds.
- Handling of solid materials spills, by dry cleaning methods such as; vacuum cleaner. Also the personnel should be trained to close the grills of the internal sewer system, when leaks or spills occur, to reduce the pollution load discharged to the sewer.
- Solid wastes, generated from spent solvent distillation or pretreatment of alkali solutions, used in cleaning and washing, could be safely disposed into a landfill or burned.
- Generally, recycling of incoming raw materials packaging like steel barrels, plastic barrels, paper bags, shrink plastic (PE) and transition to storage of raw materials in tanks. The reuse of these packages is a measure to reduce costs and amounts of waste.
- Spent catalysts are considered hazardous solid wastes, therefore they should be carefully returned to the suppliers. Platinum catalyst is very expensive, hence it is recycled (after several years of use) by the supplier, which recharge it and return it to the fertilizer plant.

Sludge from water and wastewater

- Effluent treatment processes generate sludge. It can also be hazardous to health by absorbing pathogens that

treatment

multiply in this favorable medium and toxins. It also contain traces of heavy metals and phosphates and nitrates. Raw sludge is saturated with water, should be de-watered and disposed off to safe landfills. Safe landfill: Safe landfill is supposed to be tight at bottom so that any liquid leaks to groundwater is not possible. Contaminated water from landfill should be collected and treated.

- Sludge also generated from water treatment unit due to addition of lime and chemicals to water.

Gypsum reuse

- Opportunities to use gypsum wastes as soil conditioner should be implemented to minimize the volume of gypsum results from the manufacturing of phosphoric acid.

Phosphogypsum

- The management of phosphogypsum is a major problem because of the large volumes and large area required and because of the potential release of dust, fluorides and cadmium in seepage. The following measures will help to minimize the impacts:
    - Maintain a water cover to reduce radon gas release and dust emissions.
    - Where water cover cannot be maintained, keep the tailings wet.
    - Line the tailings storage area to prevent contamination of groundwater by fluoride. (tight bottom and preventing leakage and overflow to the environment)
    - Where contamination of groundwater is a concern, a management and monitoring plan should be implemented.

  Phosphogypsum may find a use in the production of gypsum board for the construction industry.

5.5 Water and Energy Conservation

Water and sewer service costs have been rising, and these increases can cut into profits. Using water more efficiently can help counter these increases.

Water Conservation

- Fertilizers plants use large quantities of water for cooling purposes, therefore recycling cooling water by means of cooling towers is a good practice for water conservation.
- Install water meters and monitor water use
- Use automatic shut-off nozzles and mark hand-operated valves so that open, close and directed-flow positions are easily identified.
- Install liquid level controls with automatic pump stops

where overflow is likely to occur.
- Repair leaks.
- Handle solid waste dry.
- Recycle steam condensate whenever economically viable.

Energy conservation measures

- Installation of steam traps.
- Repair or replace steam valves.
- Use the optimum excess air to perform efficient combustion process
- Install pressure regulators on steam lines.
- Installation of condensate recovery system to utilize the steam condensate collected from the different plant sections to be used as boilers feed water. This lowers the steam requirement for heating the needed water.
- Improvement of power factor.
- Proper insulation of all hot pipes and equipment in order to minimize heat losses.
- A mixture of steam and natural gas with a volumetric ratio of steam to carbon of about 3.5:1 is reacted in the primary reformer in the ammonia plant. Most of the steam is generated from heat sources within the plant, but the balance of the steam has to be produced in auxiliary boilers.
- The traditional systems used for removal of carbon dioxide from the process steam uses hot potassium carbonate which requires heat for regeneration. This heat comes from process heat but needs to be supplemented with external steam. A new low-heat removal system is now available, which uses flashing for part of the regeneration process, and requires less external heat.
- Heat evolved from the carbamate condensers can be recovered and utilized to convert condensed water to low pressure steam.

6. Industrial Inspection

The environmental inspection of the fertilizers manufacturing industry is to follow the procedures described in the General Inspection Manual (GIM EPAP 2002). This chapter summarizes the inspection process regarding objective, different inspection types and the suggested inspection procedures concerning fertilizers industry.

The overall purpose of inspection is to enforce compliance with the environmental laws. Table (18) lists the various types of inspections and the objectives that have to be fulfilled for each type.

Table (18) Various Types of Inspections and Relative Objectives

Inspection type	Inspection Objectives
Site Inspection	
1. Comprehensive	- Checking compliance with the aspects of the law4.
2.Specific site inspection	- Checking compliance with some specific aspects of the law4/1994. - Checking special conditions set by EEAA in EIA studies. Investigate complaints.
2. follow up	- Checking environmental register and implementation of compliance measures.
Inspection Campaigns	- Checking specific pollution sources to specific receiving media
1. Geographically oriented	
2. sector oriented	- Checking the environmental aspects related to the specific sector

As evident from the above table, comprehensive inspection deals with all aspects of environmental laws, and therefore is considered in this manual. Other inspection types can be tailored accordingly.

Developing an inspection strategy and quarterly and/or monthly plans are the responsibilities of the inspectorate management. Developing site-specific inspection plans for carrying out the scope of work that fulfills inspection objectives is the responsibility of the inspection team. Planning for inspections is presented in more detail in the General Inspection Manual, (GIM EPAP-2002).

The following chapters describe the application of the general guideline of the inspection team to the fertilizers industry, taking into account the specific features of the fertilizers industry as described in section 2. It is important to note that the check-list must be tailored to the specific facility depending on the existing production lines and service units.

7. Inspection Planning at the Inspectorate Level

7.1 Defining the Objectives

Taking the comprehensive inspection as an example, the objectives stated in table (18) dictate the activities required for covering all aspects of compliance with environmental laws and regulations. The required personnel, equipment and logistics are determined accordingly.

Fertilizers facilities form integrates which contain several facilities and the inspection requires more than one inspector so it is important to determine the targeted sampling and the order of inspection before proceeding with the inspection. It is probably needed a great many different kinds of samples and measurements.

7.2 Providing Information About the Facility

Chapter 2 presents the technical aspects regarding the fertilizers industry and its pollution sources. Information regarding compliance history related to other inspection parties (irrigation inspectors, occupational health inspectors, etc) can be helpful in anticipating potential violations and preparing necessary equipment.

Compliance action plans for the facilities, environmental impact assessment and block flow diagrams are considered the main information sources, which provide the necessary data base for inspection before the field visit.

Addition information can be provided from the following sites on the Internet:

- TOXNET.
- http://wbln0018.worldbank.org/essd/essd.nsf
- http://www.emcentre.com/unepweb/tec_case/chemical_24/house/h7.htm
- http://www.epa.gov/oeca/sector
- http://www.cleanerproduction.com/industries/fertilizer.html
- http://eippcb.jrc.es/pages/factivities.htm

7.3 Providing Required Personnel, Tools and Equipment

The required tools, personnel and equipment depend on the size of the facility to be inspected. The team leader, in coordination with inspectorate, should assess the number of needed inspectors relevant to the size of facility.

The team is divided into groups of different tasks, which guarantees that inspection is implemented in a synchronous way. Large facilities require several inspectors including a laboratory technician, sampling equipment and measuring devices. The inspectorate should provide inspection checklists to be used during field visits. A typical checklist is shown in annex (1) of this manual.

8. Preparation of the On-Site Visit

As presented in the General Inspection Manual (GIM EPAP-2002). Tasks for preparation for on-site visit are:

- Gathering information about the specific facility to be inspected
- Preparing the inspection plan
- Preparing the checklists and providing the measuring devices.

8.1 Collecting and Reviewing Information

The inspection team should review the general information prepared for the fertilizers industry (chapter 2) and then check- if possible- what production lines and what service units are present in the targeted facility. In addition to the required information listed in the Annex (C) of the General Inspection Manual (GIM EPAP 2002), it is important at this stage to determine the following:

- The type of receiving body for the industrial wastewater and review relevant Egyptian laws (chapter 4).
- The scope of inspection and related activities based on the type and objectives of inspection required by the inspectorate management.
- The potential pollution hazards as addressed in section 2-4, and accordingly, define measurements and analyses needs.
- The characteristics of the fertilizers industry as presented in section 2-5, and their implications on the inspection process of the targeted facility.

8.2 Preparation of the Inspection Plan

An example of the inspection plan is included in Annex (E) of the General Inspection Manual, (GIM EPAP-2002). The plan should take into account the following:

- For fertilizers facilities, the inspection team could be divided into smaller groups. Each group will be responsible for inspecting a specific number of production lines and service units.
- At the beginning of on-site visit the inspection team should check the environmental register for its completeness using the checklist provided in Annex (G) of the General Inspection Manual (GIM EPAP-2002).
- The results of the analyses included in the environmental register should be checked at the end of the on-site visit (if suspicion arises about them) and copies of these results should be obtained.
- Planning for stacks measurement, should be taken as well as the noise and heat stress measurements. This means that inspection team should provide the mobile measuring equipment.
- Planning for taking samples from the final discharge points of the industrial wastewater.

8.3 Preparation of the Required Checklists

The inspection checklist for a fertilizer plant is presented in Annex (1) of this manual. The checklist has been prepared in such a way that it starts with general information about the facility and its operation. Separate check-lists are then filled for each production unit or service unit independently for relevant environmental aspects and media.

- Prepare the block flow diagrams for the production lines with their pollution sources.
- Identify the areas of possible non-compliance and the parameters that need checking.
- Identify the aspects to be observe, ask about that can convey information about pollutants.

8.4 Legal Aspects

Section (2.4) of this manual gives a detailed description of emissions and wastes generated from this industry. This enables the inspectors to identify the violations in these facilities.

The inspection team should be prepared for legally establishing such a violation.

General Inspection Manual describes in details the procedures should be taken in case of violating the environmental laws.

Note to inspector:

The information about the nature and cause of violation must be well and the evidence sound. The case could be contested in court and the inspector will be asked to defend his technical judgment

9. On-Site Visit

9.1 Starting the Field Visit

The General Inspection Manual (GIM EPAP-2002) describes the procedures involved for entering an industrial facility. The inspectors’ attitude and behavior are very important from the start and will dictate the factory’s personnel response to the inspection tasks. If entry is denied to the team, the team leader must document the circumstances and actions taken. This includes recording the name, title and telephone number of the person(s) denying entry.

Note to the inspector:

- *It is preferable, in the first phase of the inspection visit, not to ask direct questions about pollutants. It is better to conclude some information during the interview with the workers.*
- *Inspectors should check the results of air emissions measurements and wastewater analysis, as well as the sampling date and place. They should also take their own samples and measurements, if necessary.*
- *Inspectors should take a copy for the facility’ map, which shows the points of gaseous emissions (stacks), sewage system, the final wastewater discharge points and hazardous wastes disposal/ storage areas.*

9.2 Proceeding with the On-Site Visit

Information gathered during the facility tour is dependent on interviews of facility personnel and visual observation. Annex (H) in the General Inspection Manual (GIM EPAP- 2002) presents some useful interviewing techniques.
Using the facility layout, start by checking the final disposal points and the various plants and/or service units connected to each point. Inspection of the production lines should start with the feeding of raw materials and end with the product storage. This will determine where and how to take effluent and emissions samples.

The following are the important aspects that should be inspected carefully in the different fertilizers production facilities:

Production Units

Super phosphate production line	- Check the noise resulted from phosphate rock crushing. - Check particulates emissions from crushing, grinding, and weighing of the phosphate rock. - Check any gaseous and liquid leakage of HF and SiF_4 beside the reaction den and the scrubber. - Check the disposal of H_2SiF_6 from scrubber. - Check whether belt conveyers to transport the

	material are covered (measure particulate emissions). - Check whether the facility produce Na_2SiF_6 from H_2SiF_6 or not. - Check particulate and HF emissions in storage area. - Check wastewater management from scrubbers and disposal of the sludge. - Check particulate during granulation of powdered product, screening, and bagging. Check disposal/ recycling of residual product (spills and dusts).
Triple super phosphate production line	- Check the particulates emissions during crushing and grinding of phosphate rock. - Check the noise during rock crushing. - Check the leakage of HF, SiF_4 from the reactor and the scrubber. - Check the disposal of H_2SiF_6 or Na_2 SiF_6 production. Check the particulates emissions during granulation, screening, and bagging of fertilizers. - Check waste water management from scrubbers and disposal of sludge Check disposal of solid wastes (spent containers, wastewater treatment sludge, spent filters)
Phosphoric acid production line	Check the particulates emissions during phosphate rock crushing and grinding. Check the noise from crushers. Check the SiF_4, HF emissions from the reactor. Check the acid fumes emissions during filtration. Check the cooling technique of reactor slurry Check the gaseous emissions in vacuum evaporators. Check how the facility deals with the resulted gypsum from the filtration operation and its disposal method. Check the cooling water ponds and the gypsum ponds. Check disposal of solid wastes and wastewater treatment sludge
Sulfuric acid production line	Check the sulfur vapours, odour during sulfur melting and filtration. Check the disposal of filter cloth and V_2O_5 catalyst. Check heat stress in sulfur burning operation. Check the flue gases leakage from waste heat boiler. Check the analysis of exhaust gases from boiler and converters, as well as the noise and heat stress in the boilers house.

Check the SO_2, SO_3, and acid mist near the absorber.

Check wastewater treatment.

Check disposal of solid wastes.

Ammonia production line

Check H_2S and VOCs emissions during desulphurization.

emissions of steam forming processes.

Check the heat stress near the secondary steam reformer.

Check steam condensate handling.

Check the wastewater parameters.

Check the heat stress near the methanator.

Check the ammonia leakage from the separator.

Check the disposal of spent catalyst.

Nitric acid production line

Check the disposal of filter cake from air and ammonia filtration.

Check the noise from the compressors.

Check the disposal of spent lube oil.

Check the fugitive ammonia during vaporization, oxidation and cooling of liquid ammonia.

Check the disposal method of spent catalyst.

Check the parameters of the final wastewater stream.

Check the treatment of blowdown from vaporization.

Check the gaseous NO_x emissions and acid mist near the absorber.

Check the gaseous emissions near the expander and storage tanks.

Ammonium nitrate production line

Check the heat stress in preheating of ammonia.

Check the gaseous emissions of ammonia, and ammonium nitrate near the absorber.

Check the prevention system for the ammonium nitrate leakages.

Check condensates of neutralization and evaporation.

Check vapors in the primary evaporator.

Check the particulates emissions resulted from dolomite mixing and prilling.

Check heat stress from drying.

Check the particulates emissions generated from screening, coating and bagging of fertilizers.

Check the disposal of solid wastes.

Ammonium phosphate production line

Check gaseous, fumes emissions generated from mixing operation and the reactor.

Check gases and particulates from hot granulation,

	cooling, and screening operations. Check noise from grinding. Check particulates emissions generated from coating and bagging.
Urea production line	Check the heat stress, gaseous emission from synthesis operation. Check the gaseous emissions and particulates from rectification, flash tank, vacuum evaporator, prilling, hydrolyser and packaging. Check wastewater parameters (HH_3)
Ammonium sulfate production line	Check NH_3 emission, heat stress from evaporate. Check NH_3, and acid mist from reactor crystallizer. Check the wastewater parameters. Check particulate emission during conveying of solid material. Check reuse of solid waste from belt conveyor.
Methanol production line	Check heat stress, NH_3, CO, H_2 and steam from methantor and separator. Check wastewater parameter from distiller.

Service Units

compressor	Check the noise level, exposure line. Check the oily wastewater disposal from compressor.
Water treatment units	Check the chemicals used and method applied (ion exchange –lime process – other). Check the amount of wastewater from backwash. Check for recording of results.
Boilers	Check the chimney's height and amount of gases emission kg/hr. Perform exhaust gases analysis and compare with limitation in law 4, 1994. Check fuel storage regulations and spill prevention. Check noise in boiler area. Check the blow-down as wastewater from boiler.
Cooling towers	Check the amount of blowdown from cooling tower. Check the tower basin for algae and contamination. Check the temperature difference across the tower.
Garage, and Workshops	Check for noise. Check for used oil collection system.

	Check for classification of scraps from workshop from source.
Storage facilities	Check storage and handling of hazardous materials according to instructions described in law 4, 1994. Check the spill prevention and storage classification (liquids flammable, explosive, volatiles compounds … etc).
WWTP	Check for efficiency of wastewater treatment unit by analyzing the outputs from the unit. Check for sludge disposal
Restaurant	Check the domestic waste disposal.

Effluent analysis

Receiving body	The nature of the receiving body determines the applicable laws. Check if effluent discharge is to public sewer, canals and Nile branches, agricultural drains, sea or main River Nile. Accordingly, define applicable laws, relevant parameters (BOD, COD, TDS, TSS, S.S, pH, O&G and temp.) and their limits.
Sampling	A composite sample must be taken from each final disposal point over the duration of the shift or a grab sample at peak discharge. Each sample will be analyzed independently. According to legal procedures in Egypt, the effluent sample is spilt and one of them is sealed and kept untouched.

9.3 Ending the On-Site Visit

At the end of the inspection visit, a closing meeting with the facility management can be held to discuss the inspection findings and complete any missing data and documents and also to compare the team observations with the data recorded in the environmental register. During this meeting a legal minutes of meeting should be written and signed by the facility' representative (see annex-J in the General Inspection Manual GIM EPAP 2002).This minutes of meeting includes information about the inspection team, the inspected places in the plant, place and time of measurements and the samples were taken by the inspection team. The emphatic violations should be recorded in the minutes of meeting, these include the violations concerning work environment, solid wastes accumulation, handling and storage of hazardous materials and wastes. In addition, a record for the documents were taken by the inspectors should also be registered in the minutes of meeting. On the other hand, violation that are less certain (due to their need for a laboratory analysis such as those concerning wastewater) should not be recorded in the minutes of meeting.

> ***Note:***
> *The less certain violations, should not be discussed during the closing meeting.*

10. Conclusion of the On-Site Visit

The activities performed during the site inspection are essential for the preparation of the inspection report, assessing the seriousness of violation, pursuing a civil action against the facility, presenting the legal case and making it stand in court without being contested, and for further follow up of the compliance status of the facility.

10.1 Preparing the Report

An example of an inspection report is included in Annex (K) of the General Inspection Manual (GIM EPAP, 2002). The inspection report presents the findings, conclusions, recommendations and supporting information in an organized manner.

10.2 Supporting the Enforcement Case

Many issues may be raised and disputed in typical enforcement action. Enforcement officials should always be prepared to:

- Prove that a violation has occurred. The inspector must provide information that can be used as evidence in the court of law.
- Establish that the procedures were fairly followed.
- Demonstrate the environmental and health effects of the violating cases.

10.3 Following-Up Compliance Status of the Violating Facility

After performing the comprehensive inspection and detecting the violations, the inspectorate management should:

- Decide on the sanctions and send the legal report to the judicial authority.
- Plan routine follow-up inspection. This type of inspection focuses on the violation sources and its related pollution abatement measures. Self-monitoring results are reviewed during the visit.
- Follow-up the enforcement case.

List of References

1) SEMMADCO's Environmental Action Plan
2) Pollution Abatement Action Plan for El Nasr Company for Fertilizers and Chemical Industries SEMADCI.
3) Pollution Control of Industrial Effluents In Rosetta Branch Water course (Vol. 1,2)
4) Suez Fertilizer Manufacturing Industrial Wastewater Treatment Plant.
5) Talkha Fertilizer Plant
6) Audit of Kafr El Zayaat for Pesticides and Chemicals Company
7) Concept Evaluation and Comprehensive Pollution Abatement Plant for El Nasr Company of or Fertilizers and Chemicals.
8) Profile of the Agricultural Chemical, Pesticides and Fertilizer Industry, (EPA , Sept. 2000)
9) Best Available Techniques for Producing Large Volume Gaseous and Liquid Inorganic Chemicals, UIC – Union Des Industries Chimiques Jan. 2000.
10) The Environmental Audit of The Abu Zaabal Co. for Fertilizers and Chemicals.
11) تكنولوجيا صناعة الأسمدة ، التقرير السنوى لمصانع الأسمدة الآزوتية بحلوان، الكتاب الثانى الإدارة العامة للتدريب.

ANNEX 1

Inspection Checklist for a Fertilizers Production Facility

Annex (1- A)

Basic Data Sheet

(To be fed to the database of the inspection units)

Date of visit:…………………………………… Visit number:…………………………

Facility name:……………………………………

Commercial name:………………………………………………………………………

Licensed Activity:……………………………... Days off:………………………

Legal status:……………………………………………………………………………

Address of facility

Area of facility:………………………………… Governorate:…………………………

City:…………………………………………… Zone:………………………………

Phone no. :………………………………… Fax no.:………………………………

……………………………….. …………………………………

Year of operation :…………………………….. Postal code:……………………………

The Facility Representative:…………………………………………………………..

Environmental management representative:…………………………………………………

Chairman/Owner:………………………………………………………………………

Address of Administration

e-mail:……………………………………………..

Phone no. :………………………………… Fax no.:………………………………

……………………………….. …………………………………

The industrial sector:…………………………………………………

No. of male employees: …………………… No. of female employees:…………………

Do they work in production ……………………………

Total no. of employees: ………………………….

Number of shifts/day:…………………shifts/day

Duration of shift:………………….…hrs/shift

Environmental register:………………………….. Hazardous waste register:……………

EIA:…………………………………………….. Self monitoring:………………………

Nature of Surrounding Environment

Industrial ☐ Coastal ☐ Coastal/ Residential ☐

Industrial/ Residential ☐ Residential ☐ Agricultural ☐

Agricultural/ Industrial ☐ Agricultural/ Residential ☐ Desert ☐

Power Consumption

Electricity ☐ Fuel ☐

Electric power: ……………...kWh/(day-month-year)

Type of fuel	Fuel consumption	
Mazot	………………………	Ton/(day-month-year)
Solar	………………………	Ton/(day-month-year)
Natural gas	………………………	Ton/(day-month-year)
Butagas	………………………	Ton/(day-month-year)
Other ….	………………………	Ton/(day-month-year)

The GPS (Global Positioning System) reading for Gaseous Emissions

1-	LAT(Latitude):..…….	LONG(Longitude):…….
2-	LAT(Latitude):………	LONG(Longitude):…….
3-	LAT(Latitude):………	LONG(Longitude):…….

Production

Product	Quantity/ (day-month-year)
……………………………………………	……………………………………………………
……………………………………………	……………………………………………………
……………………………………………	……………………………………………………
……………………………………………	……………………………………………………
……………………………………………	……………………………………………………
……………………………………………	……………………………………………………
……………………………………………	……………………………………………………
……………………………………………	……………………………………………………
……………………………………………	……………………………………………………
……………………………………………	……………………………………………………
……………………………………………	……………………………………………………

Water Supply

Artesian well ☐ Municipal water ☐ Treated water ☐ Nile water ☐

Canal water ☐ Other………….. ☐

Water Consumption

Amount of water consumed in operation (day-month-year):

Process ……..m^3/ Boilers…………………..m^3/

Domestic usage……….....m^3/ Cooling………………....m^3/

Other…….. …………….m^3 /

Total amount of water consumed (day-month-year)……… …………..m^3/

Type of waste water:
Industrial ☐ Domestic ☐ Mixed ☐

Wastewater Treatment:
Treated ☐ Untreated ☐

Type of Treatment:
Septic tanks ☐ pH adjustment ☐ Biological treatment ☐
Chemical treatment ☐ Tertiary treatment ☐

Amount of treated water/ (day-month-year)……………..m^3 /
Amount of waste water/(day-month-year)……………………….m^3 /

Final wastewater receiving body:
Nile ☐ Lakes (fresh water) ☐ Drain ☐

Groundwater ☐ Public sewer system ☐ Canals☐

Agricultural Land ☐ Desert Land ☐ Other……………………..☐

The Global Positioning System(GPS) reading for final disposal
1-LAT(Latitude):……. LONG(Longitude):…….
2-LAT(Latitude):……. LONG(Longitude):…….
Engineering Drawings for the Facility
Gaseous emissions map Yes ☐ No ☐

Sewer map: Domestic ☐
Industrial ☐
Mixed ☐
Factory Layout ☐
Production process flow diagram ☐

Raw material consumption

No.	Trade name	Scientific name	CAS no.	UN no.	Physical state	Type of container	Amount	Classification	
								Hazardous	Non-Hazardous

Inspection Team Member:

Team member	**Position**

Date: Inspector signature:

Annex (1- B)

Inspection Checklist for Hazardous Materials and Wastes

Annex (F-2)
Inspection checklists for hazardous materials and wastes for a facility

1. Hazardous materials (to be filled in case the facility uses hazardous materials) (1)

Fill the following table according to the codes below

Hazardous material	Amount	Field of utilization	Storage method(2)	Method of disposal of the containers	Conformity of containers to specifications(3)	Presence of MSDS(4)

(1) To be filled from the list of used raw material and chemicals according to the hazardous material list issued by the Ministry of Industry, checking the presence of a valid license for handling

(2) According to law 4/1994, does the storage area have:
S_1: alarm, precaution and fire fighting system? S_2: first aid procedures?

(3) Check containers' compliance with law4/1994:
C_1: sealed and don't cause any threats while handling C_2: unaffected with along storing period
C_3: labeled with hazard and toxicity signs C_4: labeled in Arabic (production, origin, utilization instruction)
C_5: labeled with its content, the effective substance and its concentration

(4) Material safety data sheet

2. Hazardous wastes (to be filled in case the facility generates hazardous wastes)(1)

Fill the following table according to the codes below

Hazardous waste	Source	Amount generated/ year	Storing method			On-site treatment and disposal			Transportation method	Presence of documents indicating off-site disposal(6)
			Method of storage inside the facility	Compliance of containers' specifications and labels with law 4/1994(2)	Compliance of storage areas with law 4/1994(3)	Treatment(4)	Final disposal(5)	Compliance of treatment and disposal with law 4/1994		

(1) Hazardous wastes can be identified according to law 4/1994 and by using the hazardous wastes list of the Ministerial decree no.65 for 2002 as refrence

Is there a hazardous wastes register? Yes ☐ No ☐

(2)Does the facility take into consideration that the storage containers should be:
C_1: with sealed covers to protect the container from rain water and dust and to prevent any wastes leakage during storage and/or transportation
C_2: constructed or lined by impermeable material which doesn't react with the contained material
C_3: of suitable capacity C_4: labeled

(3 Specification of storage area: determining specified locations for storage of hazardous wastes where safety conditions are set up to prevent the occurrence of any harm to the public or to those persons exposed to the wastes

(4) Which of the following methods are used by the facility for the treatment of hazardous wastes?
N_1: biodegradation N_2: incineration N_3: physical or chemical treatment

(5) Which of the following methods are used by the facility for the hazardous wastes final disposal?
F_1: land filling in specially engineered landfill F_3: other (specify)……………….

(6) Contracts with wastes' contractors and receipts.

Annex (1- C)

Inspection Checklist for Production Lines and Service Units

Inspection Checklist for Superphosphate Production

1. General	
1.1 The status of housekeeping Floor condition Spills of raw materials/ products Pilling of solid wastes	-------------------------- -------------------------- --------------------------
Check that all operations are working	
1.2 Check the storage and handling conditions of the used hazardous materials (sulphuric acid). - Do they comply with the restrictions of law 4/ 1994?	-------------------------- Yes ☐ No ☐
2. Status of Ambient Air	
2.1 Check the measurements of gaseous emissions from the scrubber. - Do they include particulates, HF, H_2SiF_6, CO_2, SiF_4 and SiO_2. - Are there measurements at the facility fence? Are they included in the environmental register? - In case of suspecting these measurements, the inspector can make his own measurements for checking.	Yes☐ No ☐ Yes ☐ No ☐
2.2 Are there any measurements for the particulates resulting from crushing and grinding of phosphate rock? Are these measurements included in the environmental register?	Exist☐ Does not exist ☐ Yes ☐ No ☐
2.3 Identify the stacks lengths with respect to the building height.	--------------------------
2.4 Identify the presence and efficiency of the control equipments for gaseous emissions and particulates in the unit.	-------------------------- --------------------------
2.5 Are there any measurements from the Nuclear Power Authority for radio activity of phosphate rock and the produced superphosphate? - Take a copy from these measurements, if applicable.	Yes ☐ No ☐
3. Status of Effluents	
3.1 Identify the disposal point for the effluent from the scrubber	--------------------------
3.2 Do the facility clean the raw materials and product spills by using water?	Yes ☐ No ☐
3.3 Identify the amount of effluent wastewater from this unit.	--------------------------
4. Status of Work Environment	
4.1 Identify the safety supplies for the workers in this unit concerning the protection during handling of sulphuric acid and crushing and grinding of phosphate rock.	-------------------------- --------------------------
4.2 Are there any measurements for the following: - Total and inhaled particulates during crushing and grinding of phosphate rock, handling and bagging of the product. - HF, SiF4 and sulphuric acid emissions beside the reaction den and scrubber.	Yes ☐ No ☐ Yes ☐ No ☐
4.3 Identify the pollution abatement measures in work environment and there efficiency.	------------------------
4.4 Check the efficiency of ventilation system in the unit	--------------------------
4.5 Do you notice high levels of noise in certain places in the unit?	Yes ☐ No ☐
4.6 Check the noise levels in the environmental register at these places: - Crushing and grinding of phosphate rock. - Belt conveyors of the product. - Bagging of the product.	-------------------------- -------------------------- --------------------------
In case of suspecting any measurements, the inspector can make his own measurements for checking.	
5. Status of Solid wastes	
5.1 Identify the amount and disposal method for the waste polyethylene bags.	--------------------------
5.2 What is the disposal method for the superphosphate spills?	--------------------------
5.3 In case of using cyclones for collecting the particulates and dust, identify the disposal method for there wastes.	--------------------------

6. Emergency Plan and Spill Prevention	
6.1 Is there an emergency plan deals with the hazardous accidents?	Yes ☐ No ☐
6.2 Identify the plan' s procedures for dealing with spills of sulphuric acid.	--------------------------
6.3 Do the plan include the procedures followed in case of hazardous operating conditions in the reactor?	Yes ☐ No ☐
6.4 Identify the existing fire protection measures.	--------------------------

Inspection Checklist for Triple Superphosphate Production

1. General	
1.1 The status of housekeeping Floor condition Spills of raw materials/ products Pilling of solid wastes Penetrative odours	 -------------------------- -------------------------- -------------------------- --------------------------
Check that all operations are working	
1.2 Check the storage and handling conditions of the used hazardous materials (sulphuric acid). - Do they comply with the restrictions of law 4/ 1994?	-------------------------- Yes ☐ No ☐
2. Status of Ambient Air	
2.1 Check the measurements of the following gaseous emissions: - HF and SiF_4 from the scrubber. - Flue gases from burning fuel for the granulation operation. - Are these measurements included in the environmental register? - In case of suspecting these measurements, the inspector can make his own measurements for checking.	 Yes ☐ No ☐ Yes ☐ No ☐ Yes ☐ No ☐
2.2 Identify the existence of measurements of particulates resulting from crushing and grinding of phosphate rock. Are these measurements registered in the environmental register?	Yes ☐ No ☐ Yes ☐ No ☐
2.3 Type of the burned fuel.	Mazout ☐ Solar ☐ Natural Gas ☐
2.4 Identify the stacks lengths with respect to the building height.	--------------------------
2.5 Identify the presence and efficiency of the control equipments for gaseous emissions and particulates in the unit.	-------------------------- --------------------------
2.5 Are there any measurements from the Nuclear Power Authority for radio activity of phosphate rock and the produced superphosphate? - Take a copy from these measurements, if applicable.	Yes ☐ No ☐
Note: Mazout usage is fobidden in residential areas by law 4/ 1994.	
3. Status of Effluents	
3.1 Identify the disposal point of the effluent from the scrubber.	--------------------------
3.2 Do the facility clean the raw materials and product spills by using water?	Yes ☐ No ☐
3.3 Identify the amount of effluent wastewater from this unit.	--------------------------
4. Status of Work Environment	
4.1 Identify the safety supplies in this unit concerning the protection during handling of phosphoric acid and crushing and grinding of phosphate rock.	-------------------------- --------------------------
4.2 Do you notice any high noise levels beside crushing and grinding of phosphate rock and in bagging section? - Are there any measurements for these levels? - Are these measurements included in the environmental register?	Yes ☐ No ☐ Yes ☐ No ☐ Yes ☐ No ☐
4.3 Do the following measurements exist in the environmental register: - Total and inhaled particulates beside crushing and grinding of phosphate rock, granulation, screening and handling and bagging of the product. - HF, SiF4 and phosphoric acid beside the reaction, scrubber and storage and bagging of the product.	 Yes ☐ No ☐ Yes ☐ No ☐
4.4 Do you notice any heat stress beside granulation operation? - Are there any measurements included in the environmental register concerning heat stress?	Yes ☐ No ☐ Yes ☐ No ☐
In case of suspecting any measurements, the inspector can make his own measurements for checking.	
4.5 Identify the pollution abatement measures in work environment and there efficiency.	------------------------

4.6 Check the efficiency of ventilation system in the unit	
5. Status of Solid Wastes	
5.1 Identify the disposal method for the waste polyethylene bags.	---------------------------
5.2 What is the dealing method with the spills of triple superphosphate.	---------------------------
5.3 In case of using cyclones for collecting particulates, identify the disposal method for the collected dust and particulates.	---------------------------
6. Emergency Plan and Spill Prevention	
6.1 Is there an emergency plan deals with the hazardous accidents?	Yes ☐ No ☐
6.2 Do the plan include the procedures followed in case of hazardous operating conditions in the reactor?	Yes ☐ No ☐
6.3 Do the plan include the necessary procedures for dealing with phosphoric acid spills?	Yes ☐ No ☐
6.4 Identify the existing fire protection measures.	--------------------------

Inspection Checklist for Phosphoric Acid Production

1. General	
1.1 The status of housekeeping Floor condition Spills of raw materials/ products Pilling of solid wastes Penetrative odours	------------------------- ------------------------- ------------------------- -------------------------
Check that all operations are working	
1.2 Check the storage and handling conditions of the used hazardous materials (sulphuric acid and solvents) as well as the produced phosphoric acid. - Do they comply with the restrictions of law 4/ 1994?	------------------------- Yes ☐ No ☐
2. Status of Ambient Air	
2.1 Check the measurements of gaseous emissions from the scrubber. - Do they include particulates, HF and SiF_4. - Are there measurements at the facility fence? Are they included in the environmental register? - In case of suspecting these measurements, the inspector can make his own measurements for checking.	Yes ☐ No ☐ Yes ☐ No ☐
2.2 Identify the existence of measurements for the resulting particulates from crushing and grinding of phosphate rock. - Are they included in the environmental register?	Yes ☐ No ☐ Yes ☐ No ☐
2.3 Are there any measurements, included in the environmental register, for the fluoride emissions resulting from washing and settling of Gypsum?	Yes ☐ No ☐
2.4 Identify the presence and efficiency of the control equipments for gaseous emissions and particulates in the unit.	-------------------------
2.6 Are there any measurements from the Nuclear Power Authority for radio activity of phosphate rock and the produced superphosphate? - Take a copy from these measurements, if applicable.	Yes ☐ No ☐
3. Status of Effluents	
3.1 Is there any recycling for the Gypsum washing water to the reactor?	Yes ☐ No ☐
3.2 In case of no recycling, where do this water disposed off?	-------------------------
3.3 Is there any condensate recycling from vacuum evaporation operation, or is it disposed on the sewage system?	-------------------------
4. Status of Work Environment	
4.1 Identify the safety supplies concerning protection during handling of acids and solvents and during crushing and grinding of the rocks.	-------------------------
4.2 Do you notice high noise levels beside the crushing and grinding of rock? - Are there any measurements for these levels. - Are they included in the environmental register?	Yes ☐ No ☐ Yes ☐ No ☐
4.3 Are there measurements for the following included in the environmental register: - Total and inhaled particulates at crushing and grinding operation. - Fluoride emissions (HF and SiF4) and phosphoric acid at the reactor, scrubbers and storage of the product. - Vapours of sulphuric acid at filtration operation. - Solvents (N-Butanol/ Iso-Butanol) and ammonia emissions at solvent extraction operation.	Yes ☐ No ☐ Yes ☐ No ☐ Yes ☐ No ☐ Yes ☐ No ☐
4.4 Do you notice any heat stress beside the granulation operation? If yes, are there any measurements included in the environmental register?	Yes ☐ No ☐ Yes ☐ No ☐
In case of suspecting any measurements, the inspector can make his own measurements for checking.	
4.5 Identify the pollution abatement measures in work environment and there efficiency.	-------------------------
4.6 Check the efficiency of ventilation system in the unit	

5. Status of Solid Wastes	
5.1 Identify the quantities and disposal method for each of the following: - The slurry resulting from the filtration of the reaction product. - Phosphorous gypsum resulting from the settling ponds. - The product of residual settling operation before solvent extraction. - Resulting residues from separation operation.	 ------------------------- ------------------------- ------------------------- -------------------------
5.2 Are these solid wastes included in the environmental register?	Yes ☐ No ☐
5.3 Do the handling, storage and disposal conditions comply with law 4/ 1994?	Yes ☐ No ☐
6. Emergency Plan and Spill Prevention	
6.1 Is there an emergency plan deals with the hazardous accidents?	Yes ☐ No ☐
6.2 Identify the protection procedures for dealing with acids (sulphuric and phosphoric) and solvents spills.	-------------------------
6.3 Do the plan include the procedures followed in case of hazardous operating conditions in the reactor?	Yes ☐ No ☐
6.4 Identify the existing fire protection measures.	-------------------------

Inspection Checklist for Sulphuric Acid Production

1. General	
1.1 The status of housekeeping Floor condition Spills of raw materials/ produced sulphuric acid Steam leakage Penetrative odours	 -------------------------- -------------------------- -------------------------- --------------------------
Check that all operations are working	
1.2 Check the storage and handling conditions of the used hazardous materials (sulphur) as well as the produced sulphuric acid. - Do they comply with the restrictions of law 4/ 1994?	Yes ☐ No ☐
2. Status of Ambient Air	
2.1 Check the measurements for sulphur, sulphur di and tri oxides resulting from sulphur melting and burning as well as from the reactor and absorption tower. - Are these measurements included in the environmental register? - In case of suspecting these measurements, the inspector can make his own measurements for checking.	Yes ☐ No ☐
2.2 Identify the stacks lengths with respect to the building height.	--------------------------
2.3 Identify the presence and efficiency of the control equipments for gaseous emissions and particulates in the unit.	--------------------------
3. Status of Effluents	
3.1 Is there any recycling for steam condensate?	Yes ☐ No ☐
3.2 Identify the quantity of effluent wastewater from the unit.	--------------------------
3.3 Identify the disposal point of this effluent.	--------------------------
4. Status of Work Environment	
4.1 Check the following measurements: - Sulphur (during handling and melting) - Sulphur di and tri oxides (at burning, reaction and absorption) - Sulphuric acid vapours and mist (at the absorption tower) Are these measurements included in the environmental register?	Yes ☐ No ☐
4.2 Identify the safety supplies concerning handling of raw sulphur.	--------------------------
4.3 Identify the safety measures concerning protection from gaseous emissions in the unit.	--------------------------
4.4 Identify the pollution abatement measures and there efficiency concerning work environment.	------------------------
4.5 Check the efficiency of ventilation system in the unit	--------------------------
4.6 Do you notice any heat stress beside the sulphur burning and reactors? - Are there any measurements for heat stress included in the environmental register?	Yes ☐ No ☐ Yes ☐ No ☐
In case of suspecting any measurements, the inspector can make his own measurements for checking.	
5. Status of Solid Waste	
5.1 Identify the quantity and disposal method for the waste filters bags.	--------------------------
5.2 Identify the quantity and disposal method for the waste resulting from air filtration for burning sulphur.	--------------------------
6. Status of Hazardous Wastes	
6.1 Identify the amount and disposal method for the residue resulting from melted sulphur filtration.	--------------------------
6.2 Identify the method and period of catalyst regeneration (Vanadium pentoxide)	--------------------------
6.3 Identify the disposal method for the spent catalyst (vanadium pentoxide)	--------------------------
7. Emergency Plan and Spill Prevention	
7.1 Is there an emergency plan deals with the hazardous accidents?	Yes ☐ No ☐
7.2 Identify the protection procedures for dealing with acids (sulphuric and phosphoric) and solvents spills.	--------------------------

7.3 Do the plan include the procedures followed in case of hazardous operating conditions in the reactor?	Yes ☐ No ☐
7.4 Identify the existing fire protection measures.	--------------------------

Inspection Checklist for Ammonia Production

1. General	
1.1 The status of housekeeping Floor condition Spills of raw materials Steam leakage Penetrative odours	 ------------------------- ------------------------- ------------------------- -------------------------
Check that all operations are working	
1.2 Check the storage and handling conditions of the used hazardous materials (Catalysts and solvents) as well as the produced ammonia. - Do they comply with the restrictions of law 4/ 1994?	Yes ☐ No ☐
2. Status of Ambient Air	
2.1 Check the gaseous emissions measurements H_2S, VOCs, CO, CO_2, H_2, CH_4 and NH_3. - Are these measurements included in the environmental register? - In case of suspecting these measurements, the inspector can make his own measurements for checking.	Yes ☐ No ☐
2.2 Identify the stacks lengths with respect to the building height.	-------------------------
2.3 Identify the presence and efficiency of the control equipments for gaseous emissions and particulates in the unit.	-------------------------
3. Status of Effluents	
3.1 What are the pollution sources for wastewater in this unit.	-------------------------
3.2 Identify the quantity of effluent wastewater from the unit.	-------------------------
3.3 Identify the disposal point of this effluent.	-------------------------
3.4 Are there any steam condensate recycling from the CO converter and WHB?	Yes ☐ No ☐
3.5 Is the cooling circuit open or closed?	-------------------------
4. Status of Work Environment	
4.1 Identify the safety supplies concerning protection from emissions and heat stress.	------------------------
4.2 Do you notice any heat stress beside desulphurization, steam reforming, methanation and ammonia converter? - Are there any measurements for the heat stress? - Are these measurements included in the environmental register?	Yes ☐ No ☐ Yes ☐ No ☐ Yes ☐ No ☐
4.3 Are the following measurements included in the environmental register: - H_2S and VOCs beside desulphurization. - CO and CO_2 beside steam reforming. - MEA and MDEA beside CO_2 separation. - H_2 and CH_4 beside methanation. - NH_3 beside ammonia converter and cooler. - Particulates from catalyst regeneration.	Yes ☐ No ☐ Yes ☐ No ☐ Yes ☐ No ☐ Yes ☐ No ☐ Yes ☐ No ☐ Yes ☐ No ☐
4.4 Identify the safety measures concerning protection during catalyst regeneration operation	------------------------
In case of suspecting any measurements, the inspector can make his own measurements for checking.	
4.5 Identify the pollution abatement measures and there efficiency concerning work environment.	------------------------
4.6 Check the efficiency of ventilation system in the unit	
5. Status of Hazardous Wastes	
5.1 Identify the amounts and management for the following hazardous wastes: - Spent catalyst (Ni) in steam reforming operation. - Spent catalyst (FeO/ CrO and CuO/ ZnO) in CO converter.	 ------------------------- -------------------------

- Spent catalyst (Ni) in methanation. - Spent catalyst (Fe) in ammonia converter.	-------------------------- --------------------------
5.2 Identify the regeneration period for the catalysts.	--------------------------
5.3 Are the data for these hazardous wastes included in the environmental register?	Yes ☐ No ☐
6. Emergency Plan and Spill Prevention	
6.1 Is there an emergency plan deals with the hazardous accidents?	Yes ☐ No ☐
6.2 Identify the protection procedures for ammonia leakage.	--------------------------
6.3 Do the plan include the followed procedures in case of equipment failure	Yes ☐ No ☐
6.4 Do the plan include the procedures followed in case of hazardous operating conditions in the converter?	Yes ☐ No ☐
6.5 Identify the existing fire protection measures.	--------------------------

Inspection Checklist for Nitric Acid Production (Wet Process)

1. General	
1.1 The status of housekeeping	
Floor condition	-------------------------
Spills of raw materials/ product	-------------------------
Steam leakage	-------------------------
Penetrative odours	-------------------------
Check that all operations are working	
1.2 Check the storage and handling conditions of the used hazardous materials (ammonia) as well as the produced nitric acid. - Do they comply with the restrictions of law 4/ 1994?	Yes ☐ No ☐
2. Status of Ambient Air	
2.1 Check the measurements for resulting gaseous emissions (ammonia and NOx). - Are there any measurement at the facility fence? Are they included in the environmental register? - In case of suspecting these measurements, the inspector can make his own measurements for checking.	Yes ☐ No ☐
2.2 Identify the presence and efficiency of the control equipments for gaseous emissions and particulates in the unit.	-------------------------
3. Status of Effluents	
3.1 What are the pollution sources for wastewater in this unit.	-------------------------
3.2 Identify the quantity of effluent wastewater from the unit.	-------------------------
3.3 Identify the disposal point of this effluent.	-------------------------
3.4 Is there any steam condensate recycling?	Yes ☐ No ☐
3.5 Is the cooling circuit closed or open?	-------------------------
3.6 Identify the disposal method for spent lube oils.	-------------------------
3.7 Identify the disposal point for filters backwash wastewater.	-------------------------
4. Status of Work Environment	
4.1 Identify the safety supplies for protection from emissions, noise and heat stress.	------------------------ ------------------------
4.2 Do you notice any heat stress beside ammonia evaporation and oxidation?	Yes ☐ No ☐
- Are there any measurements for heat stress?	Yes ☐ No ☐
- Are they included in the environmental register?	Yes ☐ No ☐
4.3 Are the following measurements included in the environmental register:	
- Ammonia beside ammonia evaporation, oxidation and cooling in boilers.	Yes ☐ No ☐
- NOx beside oxidation and the tail gas expander.	Yes ☐ No ☐
- Nitric acid mist beside the absorption tower.	Yes ☐ No ☐
3.4 Do you notice high noise levels beside the ammonia compressors?	Yes ☐ No ☐
- Are these measurements included in the environmental register?	Yes ☐ No ☐
In case of suspecting any measurements, the inspector can make his own measurements for checking.	
4.4 Identify the pollution abatement measures and there efficiency concerning work environment.	------------------------ ------------------------
4.5 Check the efficiency of ventilation system in the unit	
5. Status of Solid Wastes	
5.1 Identify the disposal method for the filters cake.	-------------------------

6. Emergency Plan and Spill Prevention	
6.1 Is there an emergency plan deals with the hazardous accidents?	Yes ☐ No ☐
6.2 Identify the protection procedures for ammonia leakage.	--------------------------
6.3 Do the plan include the followed procedures in case of equipment failure	Yes ☐ No ☐
6.4 Do the plan include the necessary precautions for nitric acid spills?	Yes ☐ No ☐
6.5 Identify the existing fire protection measures.	--------------------------

Inspection Checklist for Methane Production

1. General	
1.1 The status of housekeeping Floor condition Spills of raw materials/ product Steam leakage Penetrative odours	 ------------------------- ------------------------- -------------------------
Check that all operations are working	
1.2 Check the storage and handling conditions of the used hazardous materials (Catalysts and ammonia) as well as the produced methanol. - Do they comply with the restrictions of law 4/ 1994?	Yes ☐ No ☐
2. Status of Ambient Air	
2.1 Check the measurements of resulted emissions (ammonia, hydrogen, CO and CO_2). - Are there measurements at the facility fence? Are these measurements included in the environmental register? - In case of suspecting these measurements, the inspector can make his own measurements for checking.	Yes ☐ No ☐
2.2 Identify the presence and efficiency of the control equipments for gaseous emissions and particulates in the unit.	-------------------------
3. Status of Effluents	
3.1 Is there any recovery for the wastewater generated from distillation?	-------------------------
3.2 Identify the quantity of wastewater generated from this unit.	-------------------------
3.3 What is the disposal point of this wastewater?	-------------------------
3.4 Is there any recycling for steam condensate?	Yes ☐ No ☐
4. Status of Work Environment	
4.1 Identify the safety supplies concerning the protection from emissions and heat stress.	------------------------ ------------------------
4.2 Do you notice any heat stress beside the methanolation operation? - Are there any measurements for heat stress? - Are they included in the environmental register?	Yes ☐ No ☐ Yes ☐ No ☐ Yes ☐ No ☐
4.3 Check the presence of the following measurements in the environmental register: - Ammonia beside methanolation. - Methanol beside the separation, distillation and methanol storage. - Hydrogen and CO .	Yes ☐ No ☐ Yes ☐ No ☐ Yes ☐ No ☐
In case of suspecting any measurements, the inspector can make his own measurements for checking.	
4.4 Identify the pollution abatement measures and there efficiency concerning work environment.	------------------------
4.5 Check the efficiency of ventilation system in the unit	
5. Status of Hazardous Wastes	
5.1 Identify the amounts and management system for the spent catalyst (CuO and ZnO) used in methanolation.	-------------------------
5.2 Identify the regeneration period for the catalysts.	Yes ☐ No ☐
5.3 Are the data for these hazardous wastes included in the environmental register?	-------------------------
6. Emergency Plan and Spill Prevention	
6.1 Is there an emergency plan deals with the hazardous accidents?	Yes ☐ No ☐
6.2 Identify the protection procedures for ammonia leakage.	-------------------------
6.3 Do the plan include the followed procedures in case of equipment failure	Yes ☐ No ☐
6.4 Do the plan include the necessary precautions for methanol spills?	Yes ☐ No ☐
6.5 Identify the existing fire protection measures.	-------------------------

Inspection Checklist for Ammonium Nitrate Production

1. General	
1.1 The status of housekeeping Floor condition Spills of raw materials or the produced ammonium nitrate Steam leakage Penetrative odours	 ------------------------- ------------------------- ------------------------- -------------------------
Check that all operations are working	
1.2 Check the storage and handling conditions of the used hazardous materials (ammonia and nitric acid) as well as the produced ammonium nitrate. - Do they comply with the restrictions of law 4/ 1994?	Yes ☐ No ☐
2. Status of Ambient Air	
2.1 Check the measurements of the resulted emissions (ammonia and ammonium nitrate). - Are there measurements at the facility fence? Are they included in the environmental register? - In case of suspecting these measurements, the inspector can make his own measurements for checking.	Yes ☐ No ☐
2.2 Identify the presence and efficiency of the control equipments for gaseous emissions and particulates in the unit.	-------------------------
3. Status of Effluents	
3.1 What are the sources of wastewater pollution from this unit?	-------------------------
3.2 Identify the quantity of wastewater generated from this unit.	-------------------------
3.3 What is the disposal point of this wastewater?	-------------------------
3.4 Is there any recycling for steam condensate?	Yes ☐ No ☐
4. Status of Work Environment	
4.1 Identify the safety supplies concerning protection from emissions, noise and heat stress.	------------------------
4.2 Do you notice any heat stress beside ammonia evaporation and oxidation? - Are their any measurements for heat stress? - Are they included in the environmental register?	Yes ☐ No ☐ Yes ☐ No ☐ Yes ☐ No ☐
4.3 Are the following measurements available in the environmental register: - Ammonia beside reaction and granulation. - Ammonium nitrate beside the reaction, evaporation, granulation and screening. - Nitric acid beside the reaction. - Ammonium nitrate beside prilling tower, screening, coating.	 Yes ☐ No ☐ Yes ☐ No ☐ Yes ☐ No ☐ Yes ☐ No ☐
In case of suspecting any measurements, the inspector can make his own measurements for checking.	
4.4 Identify the pollution abatement measures and there efficiency concerning work environment.	------------------------
4.5 Check the efficiency of ventilation system in the unit	
5. Status of Solid Wastes	
5.1 In case of using cyclones for dust collection, what is the disposal method for the collected particulates and dust?	-------------------------
5.2 Identify the disposal method for the rejected polyethylene bags.	-------------------------
5.3 What is the disposal method for the spilled product on floors?	-------------------------
6. Emergency Plan and Spill Prevention	
6.1 Is there an emergency plan deals with the hazardous accidents?	Yes ☐ No ☐
6.2 Identify the protection procedures for ammonia leakage.	-------------------------
6.3 Do the plan include the procedures taken for the reactor safe operation?	Yes ☐ No ☐

6.4 Do the plan include the followed procedures in case of equipment failure	Yes ☐ No ☐
6.5 Do the plan include the necessary precautions for nitric acid spills?	Yes ☐ No ☐
6.6 Identify the existing fire or explosion protection measures.	--------------------------

Inspection Checklist for Ammonium Sulphate Production

1. General	
1.1 The status of housekeeping Floor condition Spills of raw materials or the produced ammonium sulphate Steam leakage Penetrative odours	 ------------------------- ------------------------- ------------------------- -------------------------
Check that all operations are working	
1.2 Check the storage and handling conditions of the used hazardous materials (ammonia and sulphuric acid) as well as the produced ammonium sulphate. - Do they comply with the restrictions of law 4/ 1994?	Yes ☐ No ☐
2. Status of Ambient Air	
2.1 Check the measurements for the resulted emissions (ammonia, acid mist and ammonium nitrate) - Are there measurements at the facility fence? Are they included in the environmental register? - In case of suspecting these measurements, the inspector can make his own measurements for checking.	Yes ☐ No ☐
2.2 Identify the presence and efficiency of the control equipments for gaseous emissions and particulates in the unit.	-------------------------
3. Status of Effluents	
3.1 What are the sources of wastewater pollution in this unit?	-------------------------
3.2 Identify the quantity of wastewater generated from this unit.	-------------------------
3.3 What is the disposal point of this wastewater?	-------------------------
3.4 Is there any recycling for steam condensate?	Yes ☐ No ☐
4. Status of Work Environment	
4.1 Identify the safety supplies concerning protection from emissions and heat stress.	------------------------- -------------------------
4.2 Do you notice any heat stress beside ammonia evaporation? - Are their any measurements for heat stress? - Are they included in the environmental register?	Yes ☐ No ☐ Yes ☐ No ☐ Yes ☐ No ☐
4.3 Are the following measurements available in the environmental register: - Ammonia beside reaction and evaporation. - Sulphuric acid beside the reaction. - Ammonium sulphate beside filtration, belt conveyors and bagging.	Yes ☐ No ☐ Yes ☐ No ☐ Yes ☐ No ☐
In case of suspecting any measurements, the inspector can make his own measurements for checking.	
4.4 Identify the pollution abatement measures and there efficiency concerning work environment.	-------------------------
4.5 Check the efficiency of ventilation system in the unit	
5. Status of Solid Wastes	
5.1 Identify the disposal method for the rejected polyethylene bags.	-------------------------
5.2 Identify the disposal method for the spills of ammonium sulphate.	-------------------------
6. Emergency Plan and Spill Prevention	
6.1 Is there an emergency plan deals with the hazardous accidents?	Yes ☐ No ☐
6.2 Identify the protection procedures for ammonia leakage.	-------------------------
6.3 Do the plan include the followed procedures in case of equipment failure	Yes ☐ No ☐
6.4 Do the plan include the necessary precautions for sulphuric acid spills?	Yes ☐ No ☐
6.5 Identify the existing fire or explosion protection measures.	-------------------------

Inspection Checklist for Ammonium Phosphate

1. General	
1.1 The status of housekeeping Floor condition Spills of ammonium phosphate Penetrative odours	 ------------------------- ------------------------- -------------------------
Check that all operations are working	
1.2 Check the storage and handling conditions of the used hazardous materials (ammonia and phosphoric acid) as well as the produced ammonium sulphate. - Do they comply with the restrictions of law 4/ 1994?	 Yes ☐ No ☐
2. Status of Ambient Air	
2.1 Check the measurement of the following emissions: - Ammonia, phosphoric acid mist and ammonium phosphate from the reaction. - Flue gases from fuel burning for dryer. - Are they included in the environmental register? - In case of suspecting these measurements, the inspector can make his own measurements for checking.	 Yes ☐ No ☐ Yes ☐ No ☐ Yes ☐ No ☐
2.2 Identify the furnace' stack length with respect to the building height.	-------------------------
2.3 Identify the presence and efficiency of the control equipments for gaseous emissions and particulates in the unit.	-------------------------
3. Status of Effluents	
3.1 Identify the quantity of wastewater generated from the unit.	-------------------------
3.2 Identify the disposal point for this wastewater.	-------------------------
4. Status of Work Environment	
4.1 Identify the safety supplies concerning protection from emissions, particulates and heat stress.	------------------------ ------------------------
4.2 Do you notice high noise levels beside screening and grinding of phosphate rock? - Are their any measurements included in the environmental register?	Yes ☐ No ☐ Yes ☐ No ☐
4.3 Are there any measurements for the following emissions available in the environmental register: - Ammonia beside the reactor. - Phosphoric acid beside the reactor. - Ammonium phosphate particulates beside screening, grinding, coating and bagging.	 Yes ☐ No ☐ Yes ☐ No ☐ Yes ☐ No ☐
In case of suspecting any measurements, the inspector can make his own measurements for checking.	
4.4 Identify the pollution abatement measures and there efficiency concerning work environment.	------------------------ ------------------------
4.5 Check the efficiency of ventilation system in the unit	
5. Status of Solid Wastes	
5.1 Identify the disposal method for the rejected polyethylene bags	-------------------------
5.2 Identify the disposal method for the spilled product.	-------------------------
5.3 Identify the disposal method for the ammonium phosphate which is collected by the cyclones.	-------------------------
6. Emergency Plan and Spill Prevention	
6.1 Is there an emergency plan deals with the hazardous accidents?	Yes ☐ No ☐
6.2 Identify the protection procedures for ammonia leakage.	-------------------------
6.3 Do the plan include the followed procedures in case of equipment failure	Yes ☐ No ☐
6.4 Do the plan include the necessary precautions for sulphuric acid spills?	Yes ☐ No ☐
6.5 Identify the existing fire or explosion protection measures.	-------------------------

Inspection Checklist for Calcium Nitrate Production

1. General	
1.1 The status of housekeeping Floor condition Spills of raw materials/ produced calcium nitrate Penetrative odours	 ------------------------- ------------------------- -------------------------
Check that all operations are working	
1.2 Check the storage and handling conditions of the used hazardous materials (ammonia and nitric acid) as well as the produced calcium nitrate. - Do they comply with the restrictions of law 4/ 1994?	Yes ☐ No ☐
2. Status of Ambient Air	
2.1 Check the measurement of the following emissions: - CO_2, nitric and acid mist from the scrubber. - Are there measurements at the facility fence? Are they included in the environmental register? - In case of suspecting these measurements, the inspector can make his own measurements for checking.	Yes ☐ No ☐
2.2 Identify the presence and efficiency of the control equipments for gaseous emissions and particulates in the unit.	-------------------------
3. Status of Effluents	
3.1 Identify the wastewater generated from this unit.	-------------------------
3.2 Identify the disposal point for this wastewater.	-------------------------
3.3 Identify the disposal method for the spills from mixing and filling the liquid fertilizer.	-------------------------
4. Status of Work Environment	
4.1 Identify the safety supplies concerning protection from emissions and particulates	------------------------ ------------------------
4.2 Are the measurements for the following emissions available in the environmental register: - Ammonia beside the neutralization. - Nitric acid beside absorption tower. - Particulates of lime stone during handling for feeding the absorption tower.	Yes ☐ No ☐ Yes ☐ No ☐ Yes ☐ No ☐
In case of suspecting any measurements, the inspector can make his own measurements for checking.	
4.4 Identify the pollution abatement measures and there efficiency concerning work environment.	------------------------
4.5 Check the efficiency of ventilation system in the unit	
5. Status of Solid Wastes	
5.1 Identify the disposal method for the spills of lime stones.	-------------------------
5.2 Identify the disposal method for calcium carbonate generated from settling	-------------------------
6. Emergency Plan and Spill Prevention	
6.1 Is there an emergency plan deals with the hazardous accidents?	Yes ☐ No ☐
6.2 Identify the protection procedures for ammonia leakage.	-------------------------
6.3 Do the plan include the followed procedures in case of equipment failure	Yes ☐ No ☐
6.4 Do the plan include the necessary precautions for nitric acid spills?	Yes ☐ No ☐
6.5 Identify the existing fire protection measures.	-------------------------

Inspection Checklist for Urea Production

1. General	
1.1 The status of housekeeping	
Floor condition	-------------------------
Spills of raw materials/ produced calcium nitrate	-------------------------
Penetrative odours	-------------------------
Check that all operations are working	
1.2 Check the storage and handling conditions of the used hazardous materials (ammonia and urea formaldehyde) as well as the produced Urea. - Do they comply with the restrictions of law 4/ 1994?	Yes ☐ No ☐
2. Status of Ambient Air	
2.1 Check the CO_2 measurements from the scrubber. - Are there measurements at the facility fence? Are they included in the environmental register? - In case of suspecting these measurements, the inspector can take his own measurements for checking, at the facility fence.	Yes ☐ No ☐
2.2 Identify the presence and efficiency of the control equipments for gaseous emissions and particulates in the unit.	-------------------------
3. Status of Effluents	
3.1 Identify the quantity of wastewater generated from the scrubber and the secondary absorption tower	-------------------------
3.2 Identify the disposal point for this wastewater.	-------------------------
3.3 Is there any steam condensate recycling in this unit?	Yes ☐ No ☐
4. Status of Work Environment	
4.1 Identify the safety supplies concerning protection from emissions, particulates, heat stress and noise.	------------------------ ------------------------
4.2 Are the measurements for the following emissions available in the environmental register:	
- Ammonia beside the reactor, purification, evaporation, absorption towers and hydrolyzer.	Yes ☐ No ☐
- CO_2 beside the extraction, reactor and filtration.	Yes ☐ No ☐
- Urea emissions beside the reactor.	Yes ☐ No ☐
- Urea particulates beside the evaporation, granulation, screening and bagging.	Yes ☐ No ☐
- Urea formaldehyde beside coating and bagging.	Yes ☐ No ☐
4.3 Do you notice any heat stress beside the reactor?	Yes ☐ No ☐
- Are ere any measurements available in the environmental register?	Yes ☐ No ☐
4.4 Do you notice any noise beside screening?	Yes ☐ No ☐
- Are there any measurements available in the environmental register?	Yes ☐ No ☐
In case of suspecting any measurements, the inspector can make his own measurements for checking.	
4.5 Identify the pollution abatement measures and there efficiency concerning work environment.	------------------------ ------------------------
4.6 Check the efficiency of ventilation system in the unit	
5. Status of Solid Wastes	
5.1 In case of using cyclones for collecting the particulates generated from prilling and granulation and screening operations, identify the disposal method for the collected particulates.	------------------------- -------------------------
6. Status of Hazardous Wastes	
6.1 Identify the disposal method for urea formaldehyde spills in the bagging section	-------------------------
7. Emergency Plan and Spill Prevention	
7.1 Is there an emergency plan deals with the hazardous accidents?	Yes ☐ No ☐
7.2 Identify the protection procedures for ammonia leakage.	-------------------------
7.3 Do the plan include the followed procedures in case of hazardous operating conditions in the reactor.	Yes ☐ No ☐

7.4 Do the plan include the necessary precautions for CO_2?	Yes ☐ No ☐
7.5 Identify the existing fire protection measures.	--------------------------

Inspection Checklist for Boilers and Water Treatment Unit

1. General	
1.1 Number of boilers and their capacities	---------------------------- ----------------------------
1.2 Identify the type of used fuel in the boilers. In case of using Mazout, is the surrounding region residential?	Mazout ☐ Solar ☐ Natural gas ☐ Yes ☐ No ☐
Note: Using mazout in the residential areas is forbidden according to law 4/ 1994.	
1.3 Identify the used method for water treatment.	Lime process ☐ Ion exchange ☐
2. Status of Ambient Air	
2.1 Identify the boilers' stacks height	----------------------------
Note: Stack height must be 2.5 as the height of the building.	
2.1 Check the stacks measurements (CO, SO2 and particulates). - Are these measurements included in the environmental register?	Yes ☐ No ☐
Note: In case of suspicious, the inspector can make his own measurements for checking.	
3. Status of Work Environment	
3.1 Do you notice any heat stress beside the boilers?	Yes ☐ No ☐
3.2 Do you notice any noise beside the boilers?	Yes ☐ No ☐
3.3 Are there any measurements of noise and heat stress included in the environmental register?	--------------------
4. Status of Effluents	
4.1 Quantity of boilers blow-down.	------------------------ m_3/ d
4.2 Quantity of backwash water generated from the water treatment unit	------------------------ m_3/ d ------------------------ m_3/ d
4.3 Steam condensate.	Recycled to the boiler ☐ Disposed to sewers ☐
5. Status of Solid Wastes	
5.1 Sludge generates when using lime process for water treatment. - Identify the amount of generated sludge/ day.	----------------------------
5.2 Identify the sludge disposal method.	----------------------------
6. Handling and Storage of Hazardous Materials	
6.1 Check the handling and storage measures for the used chemicals. Do they comply with law 4/ 1994?	No ☐ ☐ Yes
6.2 Is there any fuel leakage from its storage tanks?	No ☐ ☐ Yes
6.3 Is there a plan for fire protection.	No ☐ ☐ Yes
6.4 Is there a spill prevention	No ☐ ☐ Yes
6.5 Is there any source for fire ignition, such as the presence of a pump below the fuel storage tank? (start operating the pump may cause a spark ignition)	Yes ☐ No ☐ **Notes:** ---------------------------- ----------------------------

Checklist for Cooling Towers

1.General	
1.1 Number and capacity of cooling towers	--- --- ---
1.2 Cooling tower make-up rate Note : Blow-down = 10-15% of make-up	**Rate ---** Blow-down ---------------------------------------
2. Status of Effluent	
2.1 Cooling water for the compressors is performed in	☐ Open Cycle ☐ Closed Cycle
Note : If performed in open cycle it will dilute the final effluent	
2.2 Record the amount of open cycle cooling	---

Checklist for Garage

1. General	
1.2 Is there any detergent or solvent used for washing equipment parts, trucks, floor,….etc	☐ Yes ☐ No
1.3 What is the amount of oil and grease used per day?	--
1.4 What is the amount of spent lube oil generated per day ?	--
1.5 How does the facility dispose of the spent oil ?	--
2. Status of Effluent	
2.1 What is the amount of wastewater generated ?	--
2.2 Do you observe any oil / foams / solid matter in the inspection manhole ?	☐ Yes ☐ No

Checklist for Workshops

1. Status for Effluent	
1.1 What is the amount of wastewater genertaed?	---
1.2 What is your visual observation for the inspection manhole of the workshop ?	---
2. Status of Solid Wastes	
2.1 What is the amount of solid waste generated?	---
2.2 How does the facility get rid of the solid waste produced?	---
3. Status Of Work Environment	
3.1 Are there any noise in work place If yes 3.2 Are there any measurements for noise If not Perform measurements 3.3 Check the exposure time	☐ Yes ☐ No ☐ Yes ☐ No ☐ Yes ☐ No ---

Check list for Laboratories

1. General	
1.1 What is the amount of wastewater generated per day?	---
1.2 List the chemicals and materials used in the laboratories	--- --- ---
2. Status of Work Environment	
2.1 Are there any odor/ gases/ noise in the work environment? 2.2 Check the exposure time	☐ Yes ☐ No ---
3. Handling of Hazardous Material	
3.1 Inspect storage of hazardous material. Is it in compliance with the requirements of law 4.	☐ Yes ☐ No
3.2 Are there any first aid measures in place	☐ Yes ☐ No

Inspection Checklist for Wastewater Treatment Plant

1. General	
1.1 What is the capacity of WWTP	---
1.2 Specify the units included in WWTP :	
Pumping station	☐ Found ☐ Not found
Equalization tank	☐ Found ☐ Not found
Neutralization	☐ Found ☐ Not found
Sedimentation tank	☐ Found ☐ Not found
Sludge thickening tank	☐ Found ☐ Not found
Sludge drying	☐ Found ☐ Not found
Others	---
1.3 List any chemical and their quantity used for wastewater treatment (coagulants,…..)	--- --- ---
2. Status of Effluent	
2.1 Are there analyses for the effluent If not Make your own	☐ Yes ☐ No
2.2 Are the results of the analysis included in the environmental register	☐ Yes ☐ No
3. Status of Solid Wastes	
3.1 Determine the sludge disposal	---
Note : It can be use in liquid or dry form, in agriculture	
If a third party is involved in disposal, get documents for proof	☐ Found ☐ Not found Comment --- ---

Inspection Checklist for Compressors

1. General	
1.1 number of compressors	-------------------------
1.2 Type of compressors (air, ammonia or gases)	-------------------------
2. Status of Effluents	
2.1 Identify the type of the used lube oil.	-------------------------
2.2 Identify the amount of generated spent lube oil and its disposal method.	-------------------------
2.3 Check the documents confirming selling of lube oils in the environmental register.	-------------------------
2.4 What is the quantity of spent cooling water discharged from the compressors?	-------------------------
2.5 Identify the disposal point of this wastewater.	-------------------------
3. Status of Work Environment	
3.1 Do you notice high noise levels beside the compressors?	-------------------------
3.2 Is there any measurement for this noise included in the environmental register?	Yes ☐ No ☐
3.3 Do you notice any ammonia leaks at the ammonia compressors?	Yes ☐ No ☐
Check the emergency procedures concerning the ammonia compressor.	