

Technologies for Pollution Control Industry

CHEMICAL INDUSTRIES

Fertiliser Industry

The fertiliser industry occupies a place of pride in the chemical industries sector. This industry can be classified into three categories, i.e. phosphatic fertiliser, nitrogenous fertiliser and complex fertiliser. The main pollutants from the phosphatic fertiliser plants are sulphur dioxide from the captive sulphuric acid plants and fluoride and particulate matter from the processing units (phosphate rock grinding, granulation & bagging sections). The scrubbing liquid for control of gaseous emission results in the generation of wastewater. Besides, there may be some wastewater (spillage/washings) generated from sulphuric acid plant.

The existing pollution control systems in these sectors and the scope for making them more efficient are tabulated below:

Phosphatic Fertiliser Plant :

Technologies/Current Practices	Requirements
The double conversion double absorption (DCDA) process has been recommended and adopted to minimise generation of SO ₂ from sulphuric acid plants. Some plants have scrubbing system to control excessive SO ₂ during start-up and shut-down of the plant.	Scrubbing systems with proper treatment for reuse / recovery of the scrubbing liquid should be provided by all the plants.
Scrubbing system (two or three stages) or venturi scrubbing system has been adopted to control fluoride emitted from	Venturi scrubbers with reuse/recovery of scrubbing liquid or fluoride recovery plant need to be provided

acidulation of rock phosphate	
Bag filters and cyclones have been provided for control of SPM.	Proper collection and disposal of collected particulate matter through cyclone, bag filters etc. Pneumatic systems can be used for collection and transportation of dust in large plants.
Neutralisation for acidic wastewater and fluoride and phosphate removal through chemical precipitation for fluoride & phosphate bearing effluent have been adopted.	Automatic feeding system for chemical dosing with pH indicator and alarm system need to be installed.

Nitrogenous Fertiliser Plant :

The pollutants from nitrogenous fertiliser plants are SO₂ & NO_x from fuel burning in reformers, emission of ammonia from ammonia & urea plants, ammonia & oil bearing effluents from ammonia & urea plants, beside urea in effluent from urea plant, NO_x from nitric acid plant and ammonia & nitrates in effluent from ammonium nitrate plants. The arsenic bearing effluent is also generated from the plants where Vetrocoke system of CO₂ absorption is followed. The cyanide bearing effluent is generated from ammonia plants where partial oxidation process is followed (having fuel oil as feed stock).

Technologies/Current Practices	Requirements
API separator for oil removal	Oil removed is to be properly stored and transported for reuse/recovery

The technologies adopted for effluent are (i) air stripping, (ii) stream stripping with recovery of ammonia for ammonia bearing effluents from ammonia and urea plants, and (iii) hydrolyser stripper for urea bearing effluent.	High-pressure hydrolyser strippers with recovery of ammonia and condensate. Retrofitting of hydrolyser stripper in old plants.
Nitrification and denitrification system for ammonia, urea and nitrate bearing effluent	For proper operation of the denitrification system, availability of carbon source has to be ensured.
Cyanide treatment by alkaline chlorination	Cyanide destruction by thermal/oxidation system.
Arsenic bearing effluent is evaporated or chemically treated. The sludge generated is either stored or encapsulated	Few plants which are still having Vetrocoke system of CO ₂ absorption using arsenic as medium, should change over to the non-arsenic system

Complex Fertiliser Plant :

The pollutants from complex fertiliser plants could be generated from nitrogenous or phosphatic fertiliser plants, or both, depending upon the captive units. Generally, fluoride and suspended particulate matter are generated in emission through stacks and effluent generated can be recycled due to negative water balance in the process.

Technologies/Current Practices	Requirements
Venturi scrubbing system for fluoride control in emission from phosphoric	Fluoride recovery plant where phosphoric acid is produced

acid and complex fertiliser plants	
Treatment of fluoride and phosphate bearing effluent	Improved treatment using alum where receiving environment cannot accept Fluoride above 2 mg/l
Recycle and reuse of effluent from NPK and DAP plants	Zero discharge should be aimed from the complex fertiliser plants
Phosphogypsum generated from phosphoric acid plant is generally stacked and partly used for mixing in cement and for making gypsum board	Technology (such as to produce ammonium sulphate) to use entire phosphogypsum generated from phosphoric acid production

[Index](#)

Bulk Drug Manufacturing Industry

Environmental pollution control in bulk-drug manufacturing industry requires high skilled manpower due to its nature of pollutants. In general, it has been observed that the final product's purity is of major concern to the industry. Thus, the rejects (unreacted/ converted portion of raw materials) contribute to the major pollution load from the industry. The industry involves several batch reactors to get required product and each reaction yields different kinds of pollutants depending upon particular reactants and process. There are number of streams with different characteristics which emanate from the various sections of the industry, requiring segregation and corresponding treatment instead of the conventional end-of-pipe treatment system for combined effluent. The air pollution potential is also significant, though quantity of air pollutants may not be much. However, the toxic emissions (fugitive and channelised) are required to be properly collected and treated. The solid waste generated from the industry falls under hazardous categories, thus the compliance as per hazardous waste management rules is required.

Technologies/Current Practices	Requirements
<p data-bbox="235 310 553 346"><u>Wastewater treatment</u></p> <p data-bbox="235 405 784 552">Collection of all the streams and providing collective treatment (end-of-the-pipe treatment) as follows:</p> <ul data-bbox="284 611 784 1308" style="list-style-type: none"> <li data-bbox="284 611 784 810">• Collection tanks - For separation of carbon black (usually used for the colour removal of the final product). <li data-bbox="284 831 784 919">• Oil & Grease trap - conventional separator <li data-bbox="284 940 578 976">• Equalisation tank <li data-bbox="284 997 529 1033">• Neutralisation <li data-bbox="284 1054 613 1089">• Primary clarification <li data-bbox="284 1110 784 1257">• Biological treatment (mostly activated sludge process and lagoons) <li data-bbox="284 1278 599 1314">• Secondary clarifier 	<p data-bbox="812 310 1130 346"><u>Wastewater treatment</u></p> <ul data-bbox="860 405 1390 1272" style="list-style-type: none"> <li data-bbox="860 405 1390 493">• In-plant pollution control measures <li data-bbox="860 514 1390 714">• Process optimisation/modifications to avoid untreatable pollutants generation <li data-bbox="860 735 1390 934">• Segregation of effluent streams and characterisation for separate treatment as necessary is shown on next page. <li data-bbox="860 955 1390 1155">• Salt recovery from high TDS (inorganic) containing streams through forced evaporation system. <li data-bbox="860 1176 1390 1272">• Efficient solvent recovery systems.
<p data-bbox="235 1394 651 1430"><u>Air Pollution Control Systems</u></p> <ul data-bbox="284 1488 784 1749" style="list-style-type: none"> <li data-bbox="284 1488 784 1577">• Scrubbers for point source emissions <li data-bbox="284 1598 724 1633">• Cyclone to control emission <li data-bbox="284 1654 784 1749">• Suitable stack height for appropriate dispersion 	<p data-bbox="909 1394 1325 1430"><u>Air Pollution Control Systems</u></p> <ul data-bbox="860 1488 1390 1854" style="list-style-type: none"> <li data-bbox="860 1488 1390 1635">• Properly designed chlorine storage facility with automatic control equipment <li data-bbox="860 1656 1390 1854">• Collection of fugitive emissions from the processing sections and loading/unloading sections through hoods & ducts and

	<p>providing control equipment such as absorption/ adsorption systems</p> <ul style="list-style-type: none"> • Multi-cyclones or bag filters for control of emissions from boilers • Continuous monitoring equipment/ sensors to be provided
<p><u>Solid/ hazardous waste management</u></p> <ul style="list-style-type: none"> • Empty drums are sold to third party for reuse. • Process residues are stored in drums • ETP primary sludge is sent sludge drying beds • Oil & grease is collected & burnt in boilers 	<p><u>Solid/hazardouswaste management</u></p> <ul style="list-style-type: none"> • The process residues and other hazardous wastes generated in the industry should be stored/treated/ disposed as per the Hazardous Waste Management & Handling Rules , 1989 • Proper incineration of organic residues, instead of burning in boiler, which leads to air pollution problem • Detoxification of empty drums/bags etc, before selling and to maintain good manifest system.

Combination	Quality of Effluent	Treatment Options
1	Waste is not easily biodegradable but toxic	1. Thermal decomposition (based on calorific value) 2. Chemical oxidation by hydrogen peroxide, ozone etc. 3. Evaporation + Secure land-fill
2	May be toxic; not suitable for biological treatment; mostly inorganic salts	1. Chemical treatment (recovery, precipitation etc.) 2. Evaporation + Secure land-fill of evaporated residue
3	Highly organic effluent fully biodegradable	1. Anaerobic + Aerobic treatment 2. If quantity is less, incineration (based on calorific value) + Secure land-fill of incineration ash
4	Only inorganic salts, no need for biological treatment	1. Solar evaporation 2. Forced evaporation (after separation of volatile organic matter) 3. Reverse osmosis
5	Highly organic effluent, may not be easily biodegradable	1. Thermal decomposition 2. Chemical oxidation by hydrogen peroxide or ozone or sodium, hypochlorite etc. 3. Chemical + biological treatment
6	Highly inorganic effluent, not suitable for biological treatment	1. Chemical recovery 2. Chemical oxidation + biological treatment
7	Organic effluent. fullv	Anaerobic + aerobic treatment

	biodegradable	
8	Low organic and low inorganic effluent	Recycle and reuse (after preliminary treatment)

Combination Exercise for Treatment of Individual Effluent Streams in Bulk-Drug Industry

Index

Pesticides Industries

Pesticides manufacturing involves various toxic chemicals as raw materials and a number of unit operations to get required technical grade product. In a unit process, due to impurities in raw materials, variations in operational parameters of the reactor vessels and thermodynamic limitations, 100% conversion of raw materials into products is impracticable. Hence, excess chemicals are fed into the reactor to get the required efficiency and quantity of final product. The unconverted reactants from each unit process generate wastes in the form of effluents, emissions and solids.

Technologies/Current Practices	Requirements
<u>Wastewater Treatment</u> <ul style="list-style-type: none"> pH correction Solar evaporation ponds for high TDS/inorganic 	<u>Wastewater Treatment</u> <ul style="list-style-type: none"> In-plant pollution control measures Process optimisation/automation to avoid discarded products, and to reduce pollutants generation Segregation of streams and providing treatment as follows:

<p>effluent</p> <ul style="list-style-type: none"> • Incinerator for high organic waste 	<ul style="list-style-type: none"> • Inorganic streams - recovery of salts through forced evaporation or membrane separation • Highly organic streams (toxic effluents) which cannot be treated biologically are to be chemically treated or incinerated, depending on calorific value. • medium organic streams are to be biologically treated (preferably extended aeration). • Efficient solvent recovery systems. • Identification of compatible streams for neutralisation to avoid chemical closing and formation of additional total dissolved solids concentrations. • Homogenisation of effluent, before feeding into biological systems • Usage of pure oxygen, ozonation, chemical wherever necessary.
<p><u>Air Pollution</u> Scrubbers</p>	<p><u>Air Pollution</u></p> <ul style="list-style-type: none"> • Stack gas scrubbing and /or carbon adsorption (for toxic organics) and baghouses (for particulate removal) are applicable and effective technologies for minimizing the release of significant pollutants to air combustion devices (Incinerator) should be used to destroy toxic organics. Combustion devices should be operated at temperature above 1100°C with a residence time of atleast 0.5 second to achieve acceptable destruction efficiency of toxics.

	<ul style="list-style-type: none"> • Handling of mercaptans needs special attention in terms of proper collection, and incineration. • Open flaring of any gas should be avoided. Instead, incinerator (with pollution control equipment) needs to be provided. • All the fugitive emissions from various sources need to be collected through ducts & hoods and treated (may be alongwith channelised emissions). • Continuous monitoring equipment in the stack and minimum height of the stacks needs to be ensured. • The boilers should be provided with multicyclones or bag filters depending on size and local conditions.
<p><u>Solid/Hazardous Waste Management</u></p> <ul style="list-style-type: none"> • Incineration 	<p><u>Solid/Hazardous Waste Management</u></p> <ul style="list-style-type: none"> • Proper handling of hazardous waste as per the Hazardous Waste Management & Handling Rules, 1989 need to be followed. • The waste should be incinerated or disposed at authorised secured land fills identified by the State Government with the prior authorisation from the local regulatory authorities and should follow the guidelines framed under the Rules.

Index

Oil refinery

In a refinery, crude oil is processed in Crude Distillation Unit, consisting of atmospheric distillation and vacuum distillation columns. In addition, various chemical conversion processes viz. catalytic cracking, hydrocracking, thermal cracking, viz., breaking, etc.; purification processes viz. hydrodesulphurisation, desalting, sulphur recovery, etc.; and utilities & auxiliary facilities viz. water, power, steam, hydrocarbon slop treatment, etc. are also in use in refineries.

Various unit processes in the refining of petroleum oil cause significant amount of air and water pollution and also generate solid wastes. The type and quantum of the pollutants, generated from an oil refinery, will depend on type of crude and processes in use. The major pollutants emanated are emissions of Oxides of Sulphur (SO_x) and Hydrocarbons (HC); liquid effluent containing oil, phenol, sulphide with significant concentration of BOD and COD; and solid waste including oily sludge.

The available pollution control technologies and the requirements are tabulated hereunder:

Technologies/Current Practices	Requirements
Effluent treatment comprising primary (physico-chemical), secondary (biological) and tertiary (e.g. activated carbon) systems.	Possibilities (implant measures) for reducing water consumption and effluent generation; and better management practices for reuse/recycle of the treated effluent.
To minimise emissions of SO _x , Sulphur Recovery Units (SRU) based on Claus/modified Claus process. are installed.	Super Claus process with greater sulphur removal efficiencies and SCOT process for off-gas treatment. Catalytic cracking units should be provided with

Besides this, scrubbers are also installed for controlling the emissions.	particulate removal devices.
To minimise fugitive emissions of HC, floating and fixed roof tanks are provided for storage of lighter products and crude oil respectively.	Better practices are needed for maintenance of flanges/valves, handling and transport of material etc., to reduce the fugitive emissions. Steam injection in flaring stacks to reduce particulate emission, vapour recovery system to be installed to control losses of volatile organic compounds (VOC's) from storage tanks and loading areas and it should achieve 90-100% recovery.
Part of the oil is recovered from oily sludge and the sludge is disposed off through a secured landfill.	Technology is required for minimising the generation of oily sludge and proper handling of oily sludge and more efficient recovery of oil from sludge using improved adsorbent.

Index

Dyes and Dye Intermediates

Dyes and Dye Intermediates industry is an important sector of the Indian Chemical Industry. This sector has grown at a very fast pace after independence and nearly half of its production is being exported today. A remarkable feature of the Indian dyestuff industry is the co-existence of units in the small, medium and large sectors, actively involved in the manufacture of dyestuffs and their intermediates. The pollution that accompanies this industry in its nature and extents, particularly, because of the non-biodegradable nature of the dyes as well as due to the presence of acid/ alkali/ toxic trace metals/ carcinogenic aromatic amines in the effluents. In addition to effluent, gaseous emissions such as SO₂,

NO_x, NH₃ & HCl and solid wastes in the form of iron sludge, gypsum and sludge from treatment facilities are generated.

The available pollution control systems and the requirements are tabulated below:

Technologies/Current Practices	Requirements
<p>Effluent treatment comprising primary (physico-chemical) and secondary (biological) systems are in practice. Some of the units have also provided tertiary treatment and incinerators for non-biodegradable waste.</p>	<p>Possibilities for adaptation of cleaner process options for reducing the water consumption and effluent generation; better management practices for segregation and reuse/ recycle of the treated effluent; effective utilisation of raw materials; improvement in efficiency of process; and recovery of by-products.</p> <p>The effluent generated from manufacturing of some of the dyes and intermediates such as H-acid is not biodegradable, which requires process change.</p>
<p>Gaseous emissions such as SO_x, NO_x, HCl and NH₃ are generally scrubbed.</p>	<p>Properly designed scrubber with recovery reuse of scrubbed liquid is required.</p>
<p>Gypsum, iron sludge and sludge from ETP are generated as solid waste. The gypsum and iron sludge can be used in the cement and niament industries. The sludae is</p>	<p>Cleaner process technologies e.g. catalytic hydrogenation, use of spent acid after nitration for acidification of fusion mass, which can eliminate generation of iron and gypsum sludge.</p>

either disposed off on land/secured landfill or sent to other user industries.	
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Index

Caustic Soda Industry

There are 40 units manufacturing caustic soda in India with an installed capacity of 2.27 million tonnes per annum, and the actual production in the year 1998 has been about 1.49 million tonnes. 34% of the capacity is based on the mercury cell process, and 66% on the membrane process. The major environmental problems posed by this industrial sector is from the mercury cell process and although this metal is not supposed to get consumed as per the chemistry of the production, it gets entrapped into the circulating brine solution and all the product and by-product streams. This leads to contamination of the water, wastewater, air and solid wastes generated from the production activities. Also, since the quantity of mercury involved in the production is very large, its leakage, spillage and even evaporation of the spilled mercury are observed to be very common and require proper and timely attention. A limit of 0.01 mg/l has been prescribed for the levels of mercury in the effluent alongwith a limitation of a maximum of 10 cum effluent per tonne of product. The CPCB experience gathered through visits and in-depth studies of the mercury cell based chlor-alkali plants confirm that a major part of mercury escaping into the environment is due to the lack of good housekeeping practices specially in the cell house and related activities. It has also to be noted here that the efficiency of any of the control measures which mostly involve the end-of-pipe treatment technology, can be affected by the lack of attention in attending the mercury leakage/ spillage or even floor washings in the cell room. Special attention needs to be given to all the mercury cell-based chlor-alkali plants looking at the manner in which the return brine from the electrolysis cells is treated soon after the power failures. This is because the mercury concentration

in the return brine after power failures may go upto even 200 mg/l as against a concentration of about 7 mg/l in the brine in the normal running of the plant. There has been a practice of adding Sodium Sulphide to the brine after power failures for avoiding the chlorine nuisance but this addition of Sodium Sulphide results into a bigger nuisance as the high level of mercury present in the brine gets precipitated as Mercury Sulphide and the subsequent brine sludge from the clarifier may contain upto over 1000 mg/kg of mercury [Chemical Age of India 35 (9):1984]. The escape of mercury in the brine sludge in a single power failure can be as much as 10 times the loss in the sludge produced in a day under the normal running of the plant.

The commissioning/expansion of caustic soda units based on mercury cell process has already been banned by the Government and the existing mercury cell based plants are also in the process of switching over to the membrane process. However, there is no mandatory target existing for this conversion and the mercury cell based units need to take proper attention for their mercury bearing wastes including the disposal of the brine sludge. The pollution control measures, existing as well as waiting to be incorporated, are given below.

Technologies/Current Practices	Requirements
Caustic Soda production through Mercury Cell as well as Membrane Cell Process	Conversion of Mercury Cells into Membrane Cells in a phased manner
Addition of sodium sulphide to the brine to avoid chlorine nuisance after power failures	Stand-by Power supply for dechlorination of the return brine in the existing mercury cell plants after power failures, instead of adding sodium sulphide to eliminate chlorine. This dechlorinated brine should be stored and recycled directly to the cells

	<p>in a controlled manner to ensure conversion of the high amount of the dissolved mercury back into the elemental mercury.</p>
<p>Rejection of the cell cleaning water as effluent for treatment with final effluent</p>	<p>Collection of the washings immediately after the start of the cell cleaning operation and recycle of the washings into the brine system.</p>
<p>Floor Washings with fresh water</p>	<p>Collection of the wastewater from cell house in a amply dimensioned sedimentation tank, providing a pump with nipple and hose pipe arrangements in the discharge line and use of this collected water for floor washings as well as its recycle into the brine system as and when possible with the help of same pumping arrangements (Chemical Age of India 37 (11) : 1986). Also, the floor should be preferably swept and the wet washings should be avoided as far as possible.</p>
<p>The collection and washing of the solid wastes generated from the cell house for mercury recovery</p>	<p>The solid wastes resulting from the cell room should be heated in a closed system and the mercury should be recovered through condensation (indirect cooling).</p>
<p>Scrubbing of the uncondensed gases from the HCl production system.</p>	<p>The hydrogen gas should be treated at source with the help of activated carbon adsorption technique (Chemical Age of</p>

	<p>India 37 (12):1986). This will eliminate the involvement of the mercury in the HCl production system. The hydrogen produced can also be used for hydrogenation of the oils and the mercury free HCl produced from this hydrogen will be useful even for the food and pharmaceuticals sector.</p>
<p>Utilisation of excess chlorine with caustic soda or lime slurry</p>	<p>The production of caustic soda should be optimised on the basis of the demand, and the chlorine neutralisation should be minimised as far as possible. If at all required, the use of caustic soda or lime slurry should be made on the basis of the use of resulting Calcium hypochlorite or Sodium hypochlorite.</p>
<p>Disposal of sludge cake from the brine recovery drum filter into authorised landfills</p>	<p>Each of the mercury cell chlor- alkali plant need to study the level of excess chlorine which can be maintained in the circulating brine of the production system as the presence of chlorine in brine avoids precipitation of mercury into the brine sludge. Also, the disposal of brine sludge should be made in a secured landfill with proper arrangements for the collection and recycle of the leachate.</p>
<p>Sodium sulphide precipitation, filtration followed by ion exchange</p>	<p>The mercury bearing streams should be segregated at the source itself in the plant</p>

or activated carbon adsorption method of the mercury from the final effluent

and recycled into the brine system. This will result into minimisation of mercury input load to the final treatment system, and the steps like precipitation, ion exchange etc. can be decided by individual plants depending upon the level of mercury control that can be achieved at source.