

## Tanning Industry Tanning Process

### Sources of Waste Water and their Characteristics

Skins of cows and buffalos are called "Hides". Skins of goats and sheeps are called "Skins". Tanning is the art of converting animal skins into leather. The tannery wastes are characterized by strong color, high BOD, high pH and high dissolved salts. The tanning process consumes large quantities of water. Most of this water used is finally discharged as waste water carrying high amounts of suspended solids, dissolved solids, BOD, COD, strong colour, bad smell. Depending upon the type of process 30-40 litres of water is used to process each kilogram of raw hides or skin into finished leather.

### Tanning Process:

The tanning process consists of three basic stages

1. Preparation of the hides for tanning.
2. Tanning proper.
3. Finishing.

Tannery wastes originate from the beam house and the tanyard.

In the beam house curing, fleshing, washing, soaking, dehairing, lime splitting, bating, pickling and degreasing operations are carried out. In the tanyard, the final leather is prepared by several processes. These include vegetable or chrome tanning, shaving and finishing. The finishing operation includes bleaching, stiffing and fat liquoring and coloring.

Protective treatment administered soon after the hides and skins are flayed is called curing. Curing involves dehydration of the hide by drying it with salt or air in order to stop proteolytic enzyme degradation. Curing creates an environment for the hides and skins in which the protein destroying organism cannot function. Its sole purpose is to ensure that the hides and the skins are protected during transit from slaughter house to the tanneries which are generally located some good distance away. It also facilitates storing.

Fleshing removes the fatty tissues from the skin by mechanical means. Cured hides and skins arriving at tannery are trimmed to remove long shanks and other unwanted areas.

Washing and soaking remove the dirt, salts, blood, manure and nonfibrous proteins and restore the moisture lost during preservation and storage.

Unhairing is accomplished by the use of lime, with or without sodium sulfide, this makes the skin more attractive and more amenable to the removal of trace protein impurities.

Lime splitting separates the skin into two layers, one is more valuable grain layer the other the lower or flesh side is called the split.

Bating prepares the hide for tanning by reducing the pH, reducing the swelling, peptizing the fibres and removing the protein degradation products.

Bating is generally accomplished with ammonium salts and a mixture of commercially prepared enzymes, the bating bath renders the grain sticky, slippery, smoother and more porous increases its width and decreases its wrinkles.

Pickling generally precedes chrome tanning and involves treatment of the skin with salt and acid to prevent precipitation of the chromium salts on the skin fibers.

Degreasing removes natural grease, thus preventing formation of metallic soaps and allowing the skin to be more evenly penetrated by tanning liquors. Chrome tanning is used primarily for light leathers while vegetable tanning is preferred for most heavy leather products. The process of chrome tanning is of shorter duration and produces more resistant leather.

The second stage of leather making, the tanning proper, involves the treatment of the hides to make them non putrescible and even soft when dried.

In chrome tanning process the tanning is done in the same vat after one day of pickling by adding a solution of chromium sulphate. After 4 hours of tanning, the leather is bleached with a dilute solution sodium thiosulphate and sodium carbonate in the same bath. The third stage of finishing consists of stuffing and fat liquoring followed by dyeing. In the former process the tanned leather incorporates oil and grease and thus becomes soft and resistant to tearing. Dyeing can be done using synthetic dye stuffs.

Depending on the type of product, either vegetable substances containing natural tanning eg. the extract of barks, wood etc. or inorganic chromium salts.

Vegetable tanning produces leathers which are fuller, plumper, more easily tooled and embossed and less effected by body perspiration or changes in humidity. Dyeing to produce the final colored leather product is usually done with basic dyestuffs.

#### **Sources of waste water and their characteristics :**

The waste may be classified as continuous flow waste and intermittent flow waste. Continuous flow waste consists of wash wastes after various processes and comprise of a large portion of the total waste, and are relatively less polluted than the other one. Spent liquors belonging to soaking, liming, bating, pickling, tanning and finishing operations are discharged intermittently.

Although these are relatively small in volume, they are highly polluted and contain varieties of soluble organic and inorganic substances. The waste water from beam house process viz. soaking, liming, deliming etc. are highly alkaline, containing decomposing organic matter, hair, lime, sulphide and organic nitrogen with high BOD and COD.

The spent soak liquor contains soluble proteins of the hides, dirt and a large amount of common salt when salted hides are processed. The spent liquor undergoes putrefaction very rapidly as it offers a good amount of nutrients and favourable environments for bacterial growth.

The spent bate liquor contains high amount of organic and ammonia-nitrogen due to the presence of soluble skin proteins and ammonia salts.

The vegetable tan extract contains tannins and also non tannins and high organic matter. Tannins are of high COD but relatively low BOD, while non tannins including inorganic salts, organic acids and salts and sugar are high both in COD and BOD. The waste water from tanyard process viz. pickling, chrome tanning are acidic and coloured.

The spent pickling and chrome tanning waste comprise a small volume, have a low BOD and contains trace of proteinic impurities, sodium chloride, mineral acids and chromium salts, mostly in the trivalent form.

The spent lime liquor contains dissolved and suspended lime and colloidal proteins and their degradation products, sulphides, emulsified fatty matters and also carry a sludge composed of unreacted lime, calcium sulphide and calcium carbonate. The spent liquor has a high alkalinity, moderate BOD and a high ammonia-nitrogen content.

#### **Effects of waste on receiving water and sewers :**

Tannery wastes are characterized by high BOD, high-suspended solids and strong color. These wastes when discharge as such deplete the dissolved oxygen of the stream very rapidly, due to both chemical and biological oxidation of sulfur and organic compounds.

A secondary pollution of the stream may occur due to the deposition of the solids near the discharge point and its subsequent putrefication. Presence of tannins in the raw water renders it unsuitable for use in certain industries.

The tannery waste when discharged into a sewer only chokes the sewer due to the deposition of solids, but also reduces the cross-section of the sewer arising out of the lime encrustation.

#### **Treatment of waste :**

The method of treatment of waste may be classified as physical, chemical, and biological. The physical treatment includes mainly screening and primary sedimentation. Screens are required to

remove fleshings, hairs and other floating substances. About 98% of the chromium is precipitated in the primary sedimentation tanks and is removed along with the sludge.

Chemical coagulation, with or without prior neutralization followed by biological treatment is necessary for better quality of the effluent. Ferrous sulfate is reported to be the best coagulant for the removal of the sulfides and may be used for the effective removal of color, chromium, sulfides, BOD and suspended solids from chrome tan wastes.

Biological treatment of the tannery waste, in activated sludge process, after mixing with municipal waste water in a suitable proportion, and using acclimatized micro organisms capable to reduce the BOD, COD and tannin by about 90%. Trickling filters may also be used for effective removal of BOD, COD and color.

The low cost biological methods of treatment may effectively be used for the treatment of tannery wastes. Both oxidation pond and anaerobic lagoons are recommended for small and isolated tanners. For further improvement of the effluent quality the anaerobic lagoons may be followed by an aerated lagoon.

Composition of composite waste water	
pH	9.8 - 11.8
Organic solids	1500 mg/l
Hardness	1600 mg/l
BOD	1000 mg/l
Sulfides	1000 mg/l
Total solids	6170 mg/l
Chromium	40 mg/l

### **Textiles Mills Waste**

The Fibres used in the Textile Industry may be broadly classified into four groups : cotton, wool, regenerated and synthetics.

#### **Cotton textile mill waste:**

An integrated cotton textile mill produces its own yarn from the raw cotton. Production of yarn from raw cotton includes steps like opening and cleaning, picking, carding, drawing, spinning,

winding and warping. All these sequences are dry operations and as such do not contribute to the liquid waste of the mill.

**Carding :** It is a process in the manufacture of spun yarns whereby the staple is opened, cleaned, aligned and formed into a continuous untwisted strand called sliver.

**Drawing :** It is the process of increasing the length per unit weight of sliver.

**Combing :** A method to remove short fibers, foreign matter from cotton stock by pressing it through a series of needles or combs.

**Spinning :** It is a process by which a long strand of fibres is drawn out to a short strand and converted into a yarn. After drawing out, it is subjected to twisting and the resulting yarn is wound into a bobbin.

**Winding :** It is the process of transfer of a yarn or thread from one type of package to another.

**Weaving :** It is the process of interlocking two yarns of similar materials so that they cross each other at right angles to produce a woven fabric.

The entire liquid waste from the textile mills comes from the following operation of slashing (or sizing), scouring and desizing, bleaching, mercerizing, dyeing and finishing.

In slashing, (to give it the tensile strength and smoothness necessary for subsequent weaving) the yarn is strengthened by loading it with starch or other sizing substances. Waste originates from this section due to spills, and the floor washings at the weak end.

After slashing the yarn goes for weaving, the prepared cloth now requires scouring and desizing to remove natural impurities and the slashing compounds.

Enzymes are usually used in India to hydrolyze the starch ; acids may also be used for this purpose. Caustic soda, soda ash, detergents etc. are used in scouring in kier boilers. To remove the natural impurities such as greases, waxes, fats and other impurities, the desized cloth is subjected to kier boiling i.e. they are boiled with the aid of steam in an alkaline solution containing caustic soda. After boiling the spent liquor is discharged as waste. This is a strong waste, dark brown in colour, and highly alkaline. Temperature of the effluent is high. BOD of the liquor is also high, contributing 35% of the total waste. Replacement of soap used in scouring by low B.O.D detergents may reduce B.O.D load by 35% about 50% of the total pollution load of the mill is contributed by this section.

Bleaching operations use oxidizing chemicals like peroxides and hypochlorites to remove natural colouring materials and to render the clothes white. The bleaching process is necessary where fabrics are to be given a full white or where they are to be dyed in specific shades. In this process

the natural colouring matter in the textile material is removed by the use of oxidising chemicals like peroxides and hypochlorites.

Mercerizing consists of passing the cloth through 20% caustic soda solution. The process improves the strength, elasticity, lustre and dye affinity. Waste from this section is recycled after sodium hydroxide recovery. Dyeing may be done in various ways, using different types of dyes and auxiliary chemicals. Classes of dyes used include vat dyes, developing dyes, naphthol dyes, sulfur dyes, basic dyes, direct dyes etc.

Direct Dyes (Neutral Dyes) are used as they are easy to apply and no auxiliary chemicals are needed.

Basic Dyes : This class of dyes give bright colours. They are applied along with weak organic acids.

Sulphur Dyes : For dark colours, these dyes employed. These are sulphur compounds applied usually with sodium sulphide followed oxidation with chromate. Vat dyes require caustic soda and sodium hydrosulfite to reduce the dye into a soluble form. Sulfur dyes are reduced by sodium sulfide and oxidized by chromate. Indigo dyes are also similar to vat dyes, but require only air oxidation. Colour from the dyes vary widely and although those are not usually toxic, they are esthetically objectional when they impart colour in the drinking water supplies. Thickened dyes, along with printing gums and necessary auxiliaries, are used for printing and subsequent fixation. After fixation of the prints, the fabric is given a thorough wash to remove unfixed dyes. The finishing section of the mill imparts various finishes to the fabrics. Various types of chemicals are used for various objectives

Composition of composite cotton textile mill waste	
pH	9.8 - 11.8
Total alkalinity	17.35 mg/l as CaCO <sub>3</sub>
BOD	760 mg/l
COD	1418 mg/l
Total solids	6170 mg/l
Total Chromium	12.5 mg/l

#### **Woolen Textile Mills waste :**

Wool wastes originate from scouring, carbonizing, bleaching, dyeing, oiling, fulling and finishing operations.

Impurities of raw wool, consisting mainly of wool grease and other foreign matter are removed by scouring the wool in hot detergent alkali solution. Some wool are scoured by organic solvents.

Wool grease may be recovered from the scouring waste by centrifuging , coagulation or floating and may be processed further for the production of lanoline and potash.

Carbonizing is a process in which hot concentrated acids are used to convert vegetable matter in the wool into loose charred particles, followed by mechanical dusting of the same.

Wool may be dyed at any stage, either as raw stock, or after spinning and weaving . Normally hot dye solutions are circulated through the wool, packed in a metal container.

In oiling, usually olive oil or a barg-oil-mineral-oil mixture is sprayed over the wool to aid in the spinning. Fulling is an operation where the loosely woven wool from the loom is shrunk into a tight closely woven cloth. To aid this process, chemicals like soda ash, soap etc are used. Excess fulling chemicals , all of the oil etc are washed out of the fabric in a finishing process.

Waste from a dyeing and finishing process are contributed by the spent liquors and by subsequent washing of wool after bleaching , dyeing and finishing.

<b>Characteristics of a typical wool waste :</b>	
pH	9-10.5
Total alkalinity	600 mg/l
BOD	900 mg/l
Colour	<del>1000</del> Brown
Total solids	<del>30000</del> 3000 mg/l
Suspended solids	100 mg/l
Total Chromium	4 mg/l

#### **Effects of the cotton textile and woolen textile mill wastes on receiving streams / sewers :**

The crude waste, if discharged into the streams, causes rapid depletion of the dissolved oxygen of the streams. The condition aggravates due to the settlement of the suspended substances and subsequent decomposition of the deposited sludges in anaerobic condition. The alkalinity and the toxic substances like sulphides and chromium affect the aquatic life; and also interfere with the biological treatment process; some of the dyes are also found toxic.

### **Treatment of Cotton and Woolen Textile Mill Waste :**

The pollution load of the waste is dealt with in the operations like segregation , equalization , neutralization, chemical precipitation , chemical oxidation and biological oxidation. Several chemicals are used to reduce the BOD by chemical coagulation. These are alum, ferrous sulfate , ferric sulfate, ferric chloride etc., lime or sulfuric acid is used to adjust the pH in this process. Calcium chloride is found to be effective in treating wool-scouring waste.

The dye wastes may be treated economically by biological methods, with prior equalization , neutralization and chemical oxidation for certain wastes.

A composite waste, when free from toxic substances may be treated as efficiently as domestic sewage, as most of the textile mill wastes contain sufficient nutrients like nitrogen and phosphorus. Trickling filters, Activated Sludge Process , Waste Stabilization ponds, all these types of biological treatment have been tried for the treatment of textile mill wastes and all of them are found to be very effective. Excellent results were also obtained with Extended Aeration in treating a strong waste , even without any equalization and pre-treatment; this method eliminates the necessity of sludge digestion as well.

### **Synthetic Textile Mill Waste :**

The most prominent man made synthetic fibers are Rayon, nylon and polyester. These fabrics require no processing for the removal of natural impurities as they are man made.

Manufacture of synthetic fabrics involve two steps:

- (i) manufacture of the synthetic fibre and
- (ii) preparation of the cloth.

These two steps may be carried out either in one integrated plant, or may be separated in two different plants.

Wastes from the manufacture of the synthetic fibre resembles chemical manufacturing wastes, and depends entirely on the raw materials used and the process adopted. A typical synthetic fibre Nylon-6 is obtained through polymerization of caprolactum and subsequent pelletization , drying , remelting in extruders , spinning and twisting.

The wastes from this manufacture are usually characterized by a colloidal type turbidity , a typical colour , a low alkalinity (pH around 7.5) , high amount of total solids in the order of 2500 mg/l and comparatively small amount of suspended solids. The waste usually contains a large amount of nitrogen, entirely of organic origin. The waste is also characterized by a high COD value (in the order of 500 mg/l) though the BOD is found to be very low (around 50 mg/l)

**Treatment of Wastes from Synthetic Textile Mills**



## **Dairy Wastes**

### **Units Operation in a Dairy :**

#### **Receiving Stations**

The receiving station serves as a collection point for raw milk from the farmers. When milk is delivered to the dairy in cans and these cans are emptied, rinsed and washed and in some cases sterilized before returning.

#### **Bottling**

Raw milk received is weighed and classified (generally based on the fat content), it is preheated, pasteurized, cooled and then filled into bottles, polythene bags, cardboard packets etc.

#### **Product Making**

Dry milk, milk powder, cheese, butter and other products as ice cream, condensed milk are prepared out of milk.

#### **Sources of wastes:**

Waste producing operations are washing of bottles, cases, cans, tanks, cooling equipment, Processing equipment and floors.

Dripping, leaks, spillages and overflows due to improper equipment or inefficient operation.

Discharges from evaporators.

Wasted buttermilk and whey (watery liquid left when milk forms curds).

Spoiled raw or treated products.

#### **Classification of Waste:**

- ☐ Spent waters: Water used for condensing and free from milk solids. These are easily disposed off.
- ☐ Waste waters produced during handling and manufacturing of dairy products as :
  - ☐ (i) Spoiled products of skim milk, whey and buttermilk.
  - ☐ (ii) Drips, leaks, first rinses and alkaline wash waters. Whey and buttermilk have high BOD.

#### **Characteristics of wastes:**

They are wholly organic with high oxygen demand (Milk is a balanced food for bacteria, therefore it is consumed at a faster rate depleting the oxygen)

1kg of whole milk produces about 10kg of BOD

BOD= 300 to 3000mg/l and BOD/COD very high (0.68) indicating degradability of the waste.

Heavy black sludge and strong butyric acid odors because of decomposition of casein are common. Also, these wastes contain nitrogen and phosphorous which are excellent nutrients for algae and other aquatic plants, which on death add to the taste and odour of the waste water.

Composition: Parameter	Value
pH	7.2
C.O.D mg/	
B.O.D mg/l	1240mg/l
Alkalinity	600 mg/l as CaCO <sub>3</sub>
Total Dissolved Solids	1060mg/l
Chlorides	105mg/l
Nitrogen	80mg/l
Phosphates	10mg/l
Organic Grease	290mg/l
Suspended Solids	760mg/l

#### **Treatment of Waste:**

As evident from the high BOD/COD ratio, the dairy wastes can be treated efficiently by biological processes.

Reduction of volume and strength of the wastes by:

- Prevention of spills, leakages and dropping of milk from cans.
- By reducing the amount of water for washes
- By segregating the uncontaminated cooling water and recycling the same.

Due to the intermittent nature of the waste discharge, it is desirable to provide, Equalization tank with or without aeration before the same is sent for biological treatment. A provision of grease trap is also necessary as a pretreatment to remove fat and other greasy substances from the waste. An aeration for a day not only prevents the formation of lactic acid, but also reduces the BOD by about 50%. Both high rate trickling filters and activated sludge plants can be employed very effectively for a complete treatment of the dairy waste. On the other hand the low cost treatment methods like oxidation ditch, aerated lagoon, waste stabilization pond etc can be employed with simpler type of equipments and less maintenance.

Waste Equalization □ Aerator □ grease Trap □ Biological Treatment ASP/TF low cost □ Effluent

Use of dairy waste for irrigation after primary treatment in an aerated lagoon.

## **Breweries Wineries Distilleries**

### **Introduction :**

While Breweries and Wineries produce beer and wine respectively, a large number of products of varying origin are obtained in Distilleries. The range of products from distilleries includes industrial alcohols, rectified spirit, silent spirit, absolute alcohol, beverage alcohol etc.

But two things are common all the products:

1. All the products are obtained through the bio-chemical process of fermentation by yeast, using carbo-hydrates as raw materials
2. All the products contain ethyl alcohol in different proportions.

### **Origin and Characteristics of Breweries Wastes**

Making of beer essentially consists of two stages:

1. Preparation of malt from grains like barley and
2. Brewing (boiling and fermentation) the Barely.

In malt making, the barely grains are steeped (soaked in liquid) to bleach out colour, and then made to sprout (appear or begin to grow) under aerobic conditions. The grain malt is then dried and stored after screening the sprouts out.

The malt from the malt house is then transported to the brewing section, where the wort (infusion of malt before it is fermented into beer), the medium of fermentation is prepared by making a mash of coarse grained malt with hot water, and by transforming the starch to sugar by boiling with hops (which are used to give a bitter flavour to beer.).

The wort is then filtered and cooled. The filtered wort is then inoculated with a prepared suspension of yeast, which ferments the sugar to alcohol.

When the fermentation is complete the yeast and malt residue is filtered out and finally the beer is carbonated before packing for sale.

Brewery Wastes Originate in both these stages. One being the spent water from the steeping process from the malt house. The waste includes the water soluble substances of the grain that are diffused into it. Characteristically it contains a large amount of organic soluble solids indicated by a high B.O.D in the order of 400-800mg/l and low suspended solids.

In the brewing plant, the major potential pollutant is the fermentation residue or the spent grains. Wastes also originate in the preparation of yeast suspension, from washing of containers, equipments and floors. Large volume of almost on polluted water also comes out as waste cooling water.

The waste from the brewing plant contains high-suspended solids and also a high B.O.D

### Origin And Characteristics of Distilleries Waste:

The beverage alcohol industries utilize different grains, malted barley and molasses as raw materials. on the other hand the molasses (black strap type) are exclusively used as raw materials in the industrial alcohol industry.

In beverage alcohol industry, the preparation of mash consists of:

1. Preparation of green malt
2. Preparation of cooked slurries of the grains
3. Mixing of the above two followed by pH adjustment and nutrient (ammonium salts and phosphates) supplementation.

On the other hand in molasses distilleries, the preparation of mash consists of:

1. Dilution by water to a sugar content of about 15%
2. pH adjustment to 4.0 - 4.5 to prohibit bacterial activities and
3. Nutrient addition.

The yeast suspension is prepared separately in the laboratory with art of the diluted molasses and then inoculated into the mash for fermentation under controlled conditions. The fermented liquor containing alcohol is then sent to an overhead tank without separation of the solid materials. The same is then degasified, and then the alcohol is stripped leaving a spent wash. The crude alcohol is then redistilled and stored in vats. The spent wash is the major polluting component of the distilleries and it is reported to be ten to fifteen times the final product in volume. The other pollutants include yeast sludge, which deposits at the bottom of fermentation vats. Malt house wastes also contribute towards pollution in beverage alcohol distilleries. In addition to these major B.O.D and solids contributing wastes, floor washes, waste cooling water, and wastes from the operations of yeast recovery or by-products recovery process also contribute to the volume of these wastes.

Characteristics of Composited Combined Waste	
Parameter	Value
pH	3.9 - 4.3
C.O.D mg/	27900 - 73000
B.O.D mg/l	12230 - 40000
Total Solids mg/l	16640 - 26000
Suspended Solids mg/l	4500 - 12000
Alkalinity	3 80 - 510

**Composition of Malt House & Combined brewery wastes:**

Parameter	Malt House Waste	Brewery Waste
pH	6.9- 9.5	4.0 - 7.0
Total solids, mg/l	428 -700	272 - 2724
Total Nitrogen(N)mg/l	14 -56	7 - 42
C.O.D , mg/l	31 - 175	30 - 1225
B.O.D, mg/l	20 - 204	70 - 3000
Suspended solids ,mg/l	22 -339	16 - 516

**Origin And Characteristics of Wineries Waste:**

The wineries utilize the fruit juices as the raw materials. So the first operation in any winery is the pressing of fermentable juice from the fruits like grape etc. The waste from this operation includes the spent fruits or pomace, wastage of fermentable juices and floor wastes etc. The second stage in any winery consists of fermentation of this juice employing the method described earlier.

The wine attains its final form at this stage and requires only decantation, blending and bottling for sale.

The waste from this stage comes from fermentation, decanting spillages, floor washes etc.

**Characteristics of Combined Wastes from Brewery, Winery and Food Processing Units:**

Parameter	Value
pH	4.0
C.O.D mg/	1800 - 3000
B.O.D mg/l	1500 - 2000
Colour	brownish yellow
Dissolved Solids mg/l	6800 - 9400

### **Effects on Receiving Streams/Sewers:**

While Breweries and Wineries produce beer and wine respectively, a large number of products of varying origin are obtained in Distilleries. The range of products from distilleries includes industrial alcohols, rectified spirit, silent spirit, absolute alcohol, beverage alcohol etc.

But two things are common all the products:

1. All the products are obtained through the bio-chemical process of fermentation by yeast, using carbo-hydrates as raw materials
2. All the products contain ethyl alcohol in different proportions.

### **Treatment of the Wastes:**

Brewery wastes being comparatively less strong can be treated by aerobic biological treatment, after screening and neutralization. The biological treatment is accomplished by two-stage process for 90 - 94% B.O.D reductions.

The yeast sludge from the distilleries which contains very high suspended solids and B.O.D and is rich in proteins, carbo hydrates, vitamins may be treated separately for by product recovery.

The raw spent wash with low pH, high dissolved solids, high temperature, high sulphates, and high B.O.D is not amenable to aerobic biological; treatment. Two-stage biological methods of treatment consisting of an aerobic treatment have been widely accepted as the only methods of treatment of the wastes from the distilleries.

A single stage digester is usually adopted for the anaerobic treatment when land available is limited. Anaerobic lagooning is a low cost alternative to the digesters when land is available in plenty. The only disadvantage of anaerobic lagoons is the evolution of volatile gases and obnoxious odour from the ponds.

Effluent of the digesters an the anaerobic lagoons still contain a high B.O.D, which cannot be discharged into the receiving streams. These effluents can successfully be treated either in aerated lagoons, or in oxidation ponds.

### **By-Product Recovery:**

The yeast sludge from the distilleries contains the degradation product of the dead yeasts and organic debris from the malt s like proteins, fats, vitamins and carbo-hydrates. On the other hand the spent wash contains al, the above nutrients plus unfermented sugars, amino acids, ammonium phosphates etc. So two types of by products viz. the nutrient rich animal feed, and the potassium rich fertilizers may be recovered in a distillery. The segregation of yeast sludge for processing

for animal feed is practiced in some distilleries, which in turn reduces the insoluble B.O.D load of the waste.

### **Pulp and Paper Mill Waste**

The paper mills use the 'pulp' as the raw material, which is again produced utilizing different cellulosic materials like wood, bamboo, jute, straw mainly of rice and wheat, waste paper, bagasse etc in the pulp mills.

#### **Manufacturing Process :**

The Process of manufacturing of paper may be divided into two phases - Pulp making and then making of final product of paper.

The major portion of the pollution from papermaking originates in the pulping processes.

Raw materials are reduced to a fibrous pulp by either mechanical or chemical means.

The bark is mechanically or hydraulically removed from wood before it is reduced to chips for cooking.

Mechanically prepared (groundwood) pulp is made by grinding the wood on large emery (very hard mineral) or sand stone wheels and then carrying it by water through screens.

This type of pulp is low-grade, usually highly colored, and contains relatively short fibers, it is mainly used to manufacture non durable paper products such as newspaper. The screened bark effluent contains fine particles of bark and wood and some dissolved solids.

Chemically prepared pulps, as compared with mechanically prepared ones, are made by the soda, sulfate (Kraft) or sulfite process. In all these methods the wood is prepared, as in the making of groundwood, by reduction to chips and screening to remove dust. The chemical processes differ from one another only in the chemical used to digest the chips.

Pulping is the process in which wood or other cellulosic raw materials are digested with chemicals under high temperature and pressure so that cellulosic fibres of wood are relieved from its binders such as lignin, resin etc

To a digester holding about four cords (128 cft) of chips, a mixture of soda ash ( $\text{Na}_2\text{CO}_3$ ) and Lime ( $\text{Ca}(\text{OH})_2$ ) (alkali process) is added and the total contents are boiled under steam pressure for about ten hours. This digestion decomposes or separates the binding, non cellulosic materials, such as lignins and resins from the fiber. During digestion most of the lignins are hydrolysed to alcohol and acids.

The spent liquor produced by the above process of digestion is known as black liquor. Black liquor very rich in lignin content but also contains a large amount of unutilised chemicals. The

black liquor of the Kraft process is concentrated by evaporation, and then incinerated with the addition of sodium sulphate. The organics like lignin, resin etc are burnt out, and the spent is dissolved in water. The resulting liquid is known as green liquor. Lime is added to this liquor, resulting in the formation of white liquor and lime mud containing chiefly calcium carbonate. White liquor contains desired cooking (digestion) chemicals and is sent for use in digester.

The sulfate process calls for a shorter digestion period of about five or six hours, with a mixture of sodium sulfide, hydroxide, sulfate and carbonate. The lignin and non cellulosic materials are dissolved, leaving a stronger fiber for paper formation.

After digestion, chemically prepared wood pulps are blown into a closed blow pit, where the black liquor is allowed to drain to the sewer or to the recovery processes.

The drained pulp is then washed. These wash waters may then be wasted, reused or sent through recovery operations while the washed pulp is passed through some type of refining machine to remove knots and other non disintegrated matter.

A cylindrical screen, called a Decker, revolving across the path of the pulp partially dewater it, after which it is passed to bleach tanks, where it is mixed in a warm, dilute solution of calcium hypochlorite or hydrogen peroxide. The dried, bleached pulp is then ready for sale or delivery to the paper mill.

The washed cellulosic fibres are sent for the bleaching in 3 stages, where chlorine, caustic and hypochlorite are used in successive stages. Waste waters from first and last stages are light yellow in colour, while that from caustic highly coloured.

In the paper mill, the pulp mixture is disintegrated and mixed in a Beater to which are added various fillers like alum, talc etc and dyes, to improve the quality of the final paper product, and sizing to fill the pores of the paper.

The Beater is essentially an oblong tank equipped with a rotating cylinder, to which are attached dull knives to break up the knotted or bunched fibers and cause a thorough mixing of the entire contents of the tank.

Sometimes the pulps are washed in the 'breaker beater' prior to the addition of chemicals. After beating, the pulp is usually refined in a Jordan, machine that consists of a stationary hollow cone with projecting knives on its interior surface, fitted over a rapidly rotating adjustable cone having similar knives on its outside surface. This machine cuts the fibers to the final size desired.

The pulp then passes to stuffing boxes, where it is stored, mixed and adjusted to the proper uniform consistency for papermaking.



Finally the pulp is screened to remove lumps or slime spots, which would lower the quality of the final paper.

The pulp is evenly distributed from a head box over a travelling belt of fine wire screening , known as fourdrivein weir , and carried to rolls . A small portion of the water contained in the pulp passed through the screen while the longer fibers are laid down as a mat on the wire . A considerable portion of the fine fibers and some fillers also pass through the screen wire with the water. Because of its colour, this waste water is called white water. The paper mat passes through a series of rolls as follows ; a screen roll to eliminate inequalities at the end of the wire, a suction roll to draw out more water, press and drying rolls to rid of the paper of most of the remaining water and finally finishing rolls(Calenders) which produce the final shape of the paper.

#### **Characteristics of pulp and paper mill wastes :**

The volume depends mainly on the manufacturing procedure, and the water economy adopted in the plant. It has been observed that a well operated and well managed integrated pulp and paper mill employing Kraft process for pulping , produces a waste volume in the range of 225 to 320 m<sup>3</sup> per tone of paper manufactured. The mills manufacturing special quality of paper produce larger amount of water for washing and bleaching.

Like the volume of waste, the chemical composition of the waste will also depend on the size of the plant, manufacturing process. In most of the small paper mills in India, the chemical recovery is not practiced due to economical reasons.

The pulp and paper mill wastes are characterized by very strong colour, high BOD , high suspended solids and high COD/BOD ratio.

Small Mill - (<20 t of paper/day)		Large Mill - (2000 t of paper/day)
pH	8.2 - 8.5	8.5 - 9.5
Total solids, mg/l	----	4410
Suspended solids , mg/l	900-2000	3300
COD , mg/l	3400-5780	716
BOD, mg/l	680-1250	155
Colour	Dark Brown	Dark Brown
COD/BOD	3.9-5	4.6

**The effect of wastes on receiving water courses or sewers:**

Crude pulp and paper mill wastes, or insufficiently treated wastes cause very serious pollution problems, when discharged into the streams.

The fine fibers often clog the water intake screens in the down stream side. A toxic effect may also be induced upon the flora and fauna of the stream due to sulfites and phenols in the waste.

The bottom deposit of Lignin - Cellulosic materials near the point of the discharge of the waste in a stream undergo slow decomposition and may lead to the dissolved oxygen depletion followed by the creation of anaerobic condition and destruction of the aquatic life.

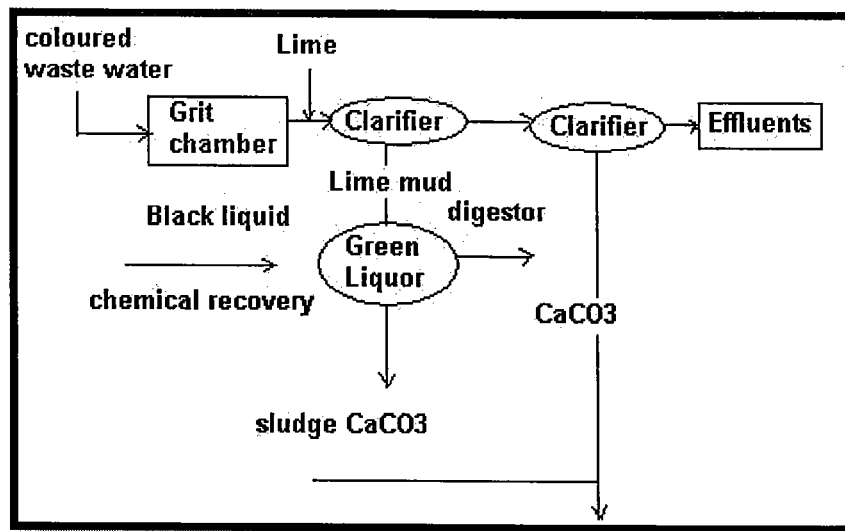
**The treatment of the waste may consist of all or a combination of some of the following processes :**

**Recovery :** The recovery of the process chemicals and the fibres reduces the pollution load to a great extent. Where the economy permits the colour bearing black liquor is treated for the chemical recovery. In this process the lignin is destroyed. The same may also be recovered from the black liquor, by precipitation by acidulation with either carbon dioxide or sulphuric acid. The fibres in the white water from the paper mills are recovered either by sedimentation or by floatation using dissolved air in the tank.

**Chemical treatment for colour removal :** Massive lime treatment capable of removing 90% of colour and 40 to 60% of BOD from the waste. In this process, entire quantity of lime, normally required for the recaustisation of green liquor into white liquor, is taken and allowed to react first with the coloured waste effluent. The colour is absorbed by lime and the sludge after settling is used in recaustifying the green liquor.

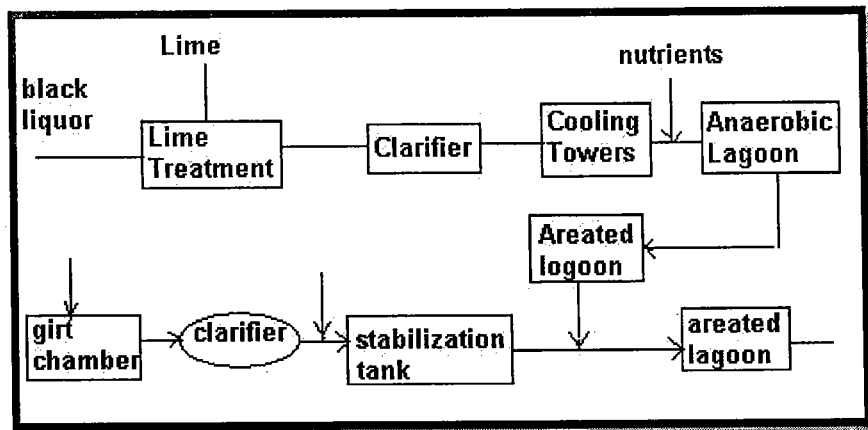
**Activated carbon for colour removal:** In a study conducted by NEERI, it has been observed that acidic activated carbon can remove 94% colour from the pulp mill waste

**Physical treatment for clarification:** Mechanically cleaned circular clarifiers alone are found to be capable of 70-80% removal of the suspended solids from the combined mill effluent. About 95 to 99% removal of settleable solids can be accomplished in the clarifiers. However the BOD reduction is comparatively small and of the order of 25-40% only.



Biological treatment of the waste: Considerable reduction of BOD from the waste can be accomplished in both conventional and low cost biological treatment processes. If sufficient area is available, the waste stabilization ponds offer the cheapest means for treatment. A minimum of 85% removal of BOD is found to be achievable. Aerated lagoons are the improved forms of the stabilization ponds. It may be noted that the pulp and paper mill wastes do not contain necessary nutrients for the bacterial growth, and hence Nitrogen and Phosphorous are to be added into the lagoons in the form of Urea or Ammonia and Phosphoric acid in BOD: N: P ratio of 100:5:1. Activated sludge process is the most satisfactory and sophisticated system for the effluent treatment. Trickling filter has got a limited use in the treatment of the pulp and paper mill effluent, due to the greater chances of clogging of the media with fibrous material. Also the trickling filter system is incapable to provide a high degree of treatment -even with the new plastic media with greater specific surface area the BOD removal is found to be only 40-50%.

**Lagooning :** In small mills , where the black liquor is not treated separately for the chemical recovery, the strong black liquor must be segregated from the other wastes and stored in a lagoon.



## **Steel Plant Wastes**

### **Introduction**

Integrated steel plants usually consist of five main units, Viz; Coal washery, Coke oven blast furnace, steel melting shop and rolling mills. In addition to the above the plants may have auxiliary units like oxygen plant and power plant for their own uses.

**Coal washery and its wastewater:** The coal needs some processing to make it suitable for use in coke ovens. The main objective of such treatment is the removal of solid foreign matter present in the coal. Generally the process in a coal washery include crushing, screening and wet washing of coal. In the wet process the coal is separated from the impurities using the principal of differential settling. Water used for washing is recycled and reused after sedimentation. But in spite of all care taken to ensure maximum reuse, appreciable quantity of wash water containing coal fines, and other impurities like clay and small amounts of other minerals like calcite, gypsum, pyrite etc, comes out as waste, normally in a thickened form as the under- flow of the sedimentation tank.

### **Coke Ovens and their Water Waste**

The production of coke involves the carbonization of bituminous coal by heating in the absence of air at a temperature range of 900 - 1100 degrees centigrade in an oven, which drives off all volatile portions in the coal. The gas which is evolved containing the volatile matters is collected through the stand pipes and is cooled in stages. In the first stage the gas is cooled to about 80 degrees centigrade by spraying cold liquor over the gas, there by producing mainly tar as

condensate. In the second stage by a further cooling to about 30 degrees centigrade, condensate containing additional tar and ammonia liquor is produced. These two condensate liquors after the separation of tar in a tar-decanter are recycled as sprays in the first stage.

The excess liquor known as 'Ammonia-liquor' containing mainly ammonia and various other compounds is subjected to distillation for the recovery of ammonia; the waste is sent for further treatment or other chemical recovery. After the second stage of cooling i.e in the third stage, the gas is compressed and cooled for further recovery of chemicals. Besides the arrangement for separation of tar and ammonia, this stage may include a benzol washer for the recovery of light oils. The remaining gas may be used or sold as fuel. The coal after being carbonized is removed from the oven and quenched by cold water.

About 30% of the quenching water is evaporated while the remaining water containing coke fines comes out as waste. This wastewater is usually re-circulated through breeze settling ponds and does not present any pollution problem. The largest single source of wastewater from coke oven plant, having the highest pollution potential in an integrated steel plant is the ammonia still from where the waste ammoniacal liquor comes out. The second source of wastewater is the benzol plant, the pollution potential and the volume of waste from which are much smaller compared to the first.

#### Characteristics of Coal Washeries

Parameter	Value
Total Solids	1000 - 25000 mg/l
Suspended Solids	800 - 24700 mg/l
Dissolved Solids	200 - 300 mg/l
Hardness	230 mg/l as CaCo <sub>3</sub>
Alkalinity	86 mg/l as Ca Co <sub>3</sub>
Ph	7.4 - 7.8

#### Characteristics of a typical spent ammoniacal liquor

Parameter	Value
Ph	7.5-8.0
Total free ammonia	300-350mg/l

Total phenol	900-1000mg/l
Cyanides	10-50mg/l
Thio-cynates as CNS	50-100mg/l
Thio-sulphates	110-220mg/l
Sulphides	10-20mg/l
Chlorides	4000-4200mg/l

#### Typical benzol plant waste

Parameter	Value
Ph	6.0 - 8.5
ammonia	5 - 30mg/l
phenol	30 - 150mg/l
5day BOD	300 - 800mg/l

#### Treatment of Coke Owen Waste

All the pollutants of the spent ammonical liquor, affect the ecology of the waste receiving water course, the phenol is considered to be the most objectionable pollutant. The other objectionable substances include thio-cynate, thio-sulphate, cyanide etc. In some plants spent ammonical liquor is utilised for quenching of hot coke, this practice destroys the toxic matters like phenols in the liquor, But as this causes heavy corrosion in the quenching cars and in other quenching equipments , the method is not generally favoured. Phenol being a valuable chemical by-product, may be recovered instead of destroying it. Several techniques have been developed for the recovery of phenol by liquid extraction methods Most of these processes use Benzene as solvent, to extract phenol from the crude ammonical liquor , before it enters the Ammonia still for ammonia stripping . Other solvents used include light oil, petroleum oil etc. The extracted phenols from all absorption process can be recovered by washing with sodium hydroxide solution; the phenol reacts with the caustic solution to produce sodium phenolate. The crude phenol is then liberated from it using gases containing carbon dioxide.

Certain microorganisms both bacteria and yeast, are identified which can oxidise biologically phenols, thio cynates , thio sulphates and ammonia. When optimum pH and temperature are maintained, sufficient nutrients are added, and the reactor is suitably seeded, the proper loading

of this phenolic substrate to the reactor may result in the desirable reduction of the pollution load of the waste. Phenol in concentrations as high as 800 mg/l may be treated biologically.

In all practical cases, the phenol concentration in the waste ammoniacal liquor is too high to be treated directly by biological means. So these are either pretreated by physical or chemical methods, or are diluted using other waste to reduce the concentration of phenols.

When coal washeries waste is available it has been shown that considerable reduction in the strength of ammoniacal liquor can be accomplished when equal volumes of coal washeries waste and ammoniacal liquor is mixed and flocculated with lime in a clariflocculator. Effluent of the clariflocculator may then be sent for Activated Sludge Process.

The biological treatment of the coke oven effluents can be carried out economically in a three stage process, with isolated or cultured bacteria, appropriate in each stage. In the first stage the phenol is oxidised, in the second stage the thio sulphate and thio cyanate are reduced, and in the third stage the ammonia is oxidised.

### **Treatment of Coal Washery Waste**

The major pollutant of the coal washery is the suspended solids. As such this waste is usually treated in a Clarifier with or without coagulation. However the addition of Coagulant reduces both the detention time and surface area of the tank. Several coagulants like lime, starch and indigenous coagulants like Nirmali seed extracts can be used effectively for the clarification of coal washery wastes. The clarified effluent is either recycled or discharged as waste.

### **Blast Furnace and its Wastewater**

Blast furnace is a basic unit in an integrated steel plant. Essentially the blast furnace process consists of charging iron ore and coke as fuel limestone and dolomite as fluxing material into the top of the furnace and blowing heated air (blast) into the bottom. Pig iron is the metallic product of this unit. Appreciable quantity of water is used in blast furnace for the purpose of cooling and gas cleaning operations. However, the cooling water normally remains un-contaminated and is reused after cooling.

The entire quantum of wastewater originates from the gas cleaning operations. The blast furnace gas, which is heavily loaded with flue dust, is cleaned in a three stage process.

The major portion of the flue dust which comes out along with blast furnace gas is recovered by the dry dust catchers. The remaining is removed by washing with water by "Wes Scrubbing".

The portion which escapes wet scrubber may be removed by electrostatic precipitator. In wet

scrubber the down flow water sprays clean the dust from the up flowing gases and the wastewater contains 1000-10000 mg/l of suspended solids.

#### **Characteristics of Typical Blast Furnace Waste**

Parameter	Value
Total Dissolved Solids	346 - 500mg/l
Total Suspended Solids	1000 - 10500 mg/l
Dissolved Solids	80 - 118 mg/l as CaCo <sub>3</sub>
Total Hardness	230 mg/l as CaCo <sub>3</sub>
Total Alkalinity	380 mg/l as CaCo <sub>3</sub>
Chlorides	210 - 250 mg/l
Ph	7.3 - 8.2

#### **Treatment of Blast Furnace Waste**

The blast furnace waste contains about 40% of the total dust coming out of the blast furnace along with the flue gas. Iron oxide and silica comprise about 70% and 12% respectively of the flue dust content. The waste can be treated in a clariflocculator even without the addition of coagulant. However the flocculation time can be reduced to a great extent when certain coagulants like alum or lime is added. The efficiency of the clariflocculator can be increased alternatively by a judicious mixing of this waste with the other wastes of the steel plant. The oxygen plant waste containing sodium hydroxide, may be used for this purpose.

#### **Steel Melting Shop and its Wastes**

In the steel melting shop, the pig iron obtained from the blast furnace is further treated to produce ingots. The basic principle involved is the oxidation of unwanted impurities in the pig iron which lead to the production of steel ingots. Water requirement in the steel melting process lies in keeping the furnace body cool. And as such this water remains uncontaminated and is reused.

#### **Rolling mills and their wastes :**

The steel ingots obtained from the steel melting shop are rolled to different products in the rolling mills however, the ingots are treated first in the soaking pits until these are plastic enough



for economic reduction by rolling. Ingots are usually rolled into bloomes, billets or slabs depending upon the final product. These rolled bloomes, billets and slabs are then cooled and stored and subsequently sent to another mill, where these are re-rolled to produce finer products. During the process of rolling of ingots, blooms, billets and slabs, lots of scales are given off and are collected in the scale flume, below the roll tables. These scales are flushed down with high-pressure water and are collected at the scale pit.

The rolls also get heated during the process and are cooled with liberal supply of water. Naturally it carries lot of oil and grease used in different bearings.

When ever finer products like sheets, strips etc are required the products from hot rolling mills are normally subjected to cold rolling. For the production of cold reduced steel sheets it is essential however to remove the surface oxides of the steel slabs before they are subjected to rolling. The removal of oxides is essentially done by a process known as 'pickling' at an earlier stage.

#### **Bloom - intermediate stage of manufacture of iron.**

#### **Billets – Short cyclinders**

The pickling is essentially a process in which the hard black oxides formed on the surface of the products during the hot rolling is removed by immersion in acid. Normally either sulfuric acid or hydrochloric acid is used for this purpose. The acid react with the iron oxide scales, and forms ferrous sulfates. Where sulfuric acid is used for pickling the process can be continued until the build up of ferrous sulfate reaches to strength of 25% and the free acid content reduces to less than 5%. The used pickling liquor is then discharged and a fresh batch of acid is taken up.

After pickling and cold rolling the finer products are subjected to various finishing operations viz tinning, plating, Galvanizing, wire drawing etc. the waste generated in these operations may be contaminated with chromate, cyanide, fluoride, zinc, tin, copper acids and alkalies.

#### **Characteristics of a typical hot rolling mill waste**

Parameter	Value
Total Suspended Solids	320 - 600 mg/l
Total Hardness	80 - 118 mg/l as CaCo <sub>3</sub>
Oil and Grease	60-80 mg/l
Ph	7.8 - 8.1

### **Treatment of Scale-Pit Effluents**

The primary treatment of the scale bearing waste from the rolling mills are offered by the scale pits associated with the different sections of the mill. The scales produced in primary mills, like blooming mills etc are coarse and mostly settle in the scale pit itself. The substantial quantity of finer scales produced in the process of rolling the billets, slabs etc are also settled in the associated scale pits.

The effluent from the scale pits still contains considerable amount of fine scales, oil and grease and requires secondary treatment.

The above effluent contains about 170 to 440 mg/l of suspended solids, and can be treated well in the clariflocculators using either sodium hydroxide or the oxygen plant waste as coagulant.

The iron content of the Clarifier sludge is as high as 46% . As such the sludge is thickened, dewatered using vacuum filters and then sent to the sintering plant, so that it can be fed back to blast furnace.

## **Oil Refineries Waste**

### **Sources of Waste Water**

#### **Manufacturing Process :**

Crude oils are complex mixtures of hydrocarbons of varying molecular weight and structure. These hydrocarbons range from simply highly volatile substances to complex waxes and asphaltic compounds. The final petroleum products are obtained from the crude oil through a series of operations viz. topping , thermal cracking , catalytic cracking , catalytic reforming etc.

In general , the crude oil is first subjected to fractional distillation in the process known as " topping " . The products obtained are called raw products and include raw gasoline, raw naptha , raw kerosene , gas oil, fuel oil etc.

Now these intermediate refinery products are again treated to yield various finished market products as per the requirements. The operations practiced include "catalytic cracking" or "thermal cracking" and further purification processes like "acid treatment" , "sweetening treatment" , "hydrodesulphurization" etc.

The decomposition of heavy or high boiling petroleum distillates like gas oil and fuel oil to lighter products like gasoline is called cracking. These operations take place practically at the atmospheric pressure and at a high temperature. In catalytic cracking, however, an acid type solid catalyst (such as synthetic silica alumina) is introduced into the reactor.

A residue of heavy black material known as coke, is obtained out of the process of cracking. In the catalytic cracking process, however, the asphaltic or tar-like products get adsorbed on to the surface of the catalysts in the form of coke.

When "high octane" fuels are in demand, much of the naphtha is "catalytically reformed" into high octane gasoline; the process involved is another form of cracking.

The wax distillates of the crude oil may be used as raw material for the manufacture of light lubricating oils. The process of their manufacture consists of chilling the distillates and filtering the wax from the oil.

The products thus obtained either as final product or as feedstock for further processing may contain certain undesirable constituents which must be either removed or converted into less harmful compounds by further refining processes. Such refining processes include (i) removal of hydrogen sulfide gas and mercaptans by washing with strong caustic soda solution, or (ii) absorption of hydrogen sulfide gas in an alkaline absorber liquid followed by the recovery of the hydrogen sulfide gas, in the process known as regenerative process (iii) conversion of mercaptans to less harmful desulphide, employing solutions like lead oxide in caustic soda together with sulphur, or sodium hypochlorite or copper chloride, in a process known as "sweatening" and (iv) conversion of alkylsulphides and thiophenes and practically all other sulphur compounds into hydrogen sulfide in a catalytic process known as "hydrodesulphurization" - hydrogen sulfide thus formed is recovered by the regenerative process.

## **Fertilizer Plant Waste**

### **Introduction :**

**Fertilizer industry can be divided into three main categories depending upon**

1. Fertilizer raw materials
2. Fertilizer intermediates
3. Fertilizer products

### **Fertilizer Intermediates:**

1. Sulphuric acid
2. Phosphoric acid
3. Nitric acid

### **Fertilizer products:**

#### **SOLID**

**N - Fertilizers**

1. Ammonium nitrate

2. Urea

3. Ammonium sulfate

P - Fertilizers

1. Super phosphates NPK fertilizers

**LIQUID:**

Ammonia fertilizers produced in India can be classified broadly into two groups viz., nitrogenous fertilizers, and phosphatic fertilizer. Plants may be producing only nitrogenous fertilizers like urea, Ammonium sulphate, Ammonium Nitrate, Ammonium chloride or only phosphatic fertilizers like super phosphates; there are plants where complex fertilizers containing both nitrogen and phosphates like Ammonium phosphate and Ammonium sulphate phosphate are produced

**Manufacturing Process :**

Ammonia is the principal intermediate in the manufacture of all nitrogenous fertilizers. So, except when the byproduct ammonia will be available from a coke oven, raw materials for nitrogenous fertilizer production is the carbonaceous materials, which are required for making ammonia. So all the nitrogenous fertilizer plants will have essentially an Ammonia production unit and a reactor where the synthetic ammonia will be reacted with other chemicals to produce the final product. The plant may have auxiliary units to produce the reacting chemicals also. Basic process steps in the manufacture of urea, from carbonaceous raw materials

like naphtha are as follows:

- (i) reaction of the carbonaceous materials with steam and air to form a mixture of hydrogen and carbon monoxide, known as synthesis gas.
- (ii) Reaction of the carbon monoxide with steam over a catalyst to form more hydrogen and carbon dioxide.
- (iii) Separation and purification of carbon dioxide.
- (iv) Removal of residual carbon monoxide from gas mixture
- (v) Synthesis of ammonia by reacting hydrogen and nitrogen over a catalyst (Nitrogen is supplied as air in an earlier step) and
- (vi) Synthesis of urea by treating ammonia with carbon dioxide in a reactor at higher temperature and pressure

□ plants using by product Ammonia from other manufacturing plants (coke oven) have to produce carbon dioxide separately for the production of urea

□ Ammonia sulphate may be produced by reacting Anhydrous Ammonia with Sulphuric Acid, usually obtained as by-product sulphuric acid from other manufacturing plants

□ Ammonia sulphate may also be manufactured from Gypsum or from Calcium sulphate sludge obtained from the phosphatic fertiliser plant using Ammonia and  $\text{CO}_2$  obtained from Ammonia plant. In this process calcium sulphate is reacted with Ammonia carbonate solution to produce ammonium sulphate.

□ Ammonium nitrate is produced when ammonia is reacted with nitric acid. Normally the required quantity of nitric acid is produced in the same plant, by oxidizing the ammonia.

□ Super phosphate is produced by merely mixing the phosphate ore (commonly known as phosphatic rock) with sulfuric acid to convert the phosphate to 'Monocalcium' phosphate. The by-product calcium sulphate of this process may be used in the manufacture of Ammonium sulphate.

□ Ammonium phosphate is made by treating phosphoric acid with Ammonia, the phosphoric acid production process involves the following steps

1. Dissolving phosphate rock in enough sulphuric acid
2. Holding the mixture until the calcium sulphate crystals grow to adequate size.
3. Separating the phosphoric acid and calcium sulfate by filtration and Concentration of acid to the desired level.

#### **Treatment of Fertilizer Waste Water :**

Major pollutants in the fertilizers waste water for which the treatment is necessary include oil, arsenic, ammonia, urea, phosphate and fluoride.

The effluent streams can be characterized as either a phosphoric effluent or an ammonia effluent. The phosphoric acid effluent is high in fluoride concentration, low in pH, High in phosphate and high in suspended solids. Standard practice has been contain the water for reuse, allowing enough time for solids sedimentation.

Oil is removed in a gravity separator

Arsenic containing waste is segregated and after its concentration the solid waste is disposed off in a safe place.

Phosphate and fluoride bearing wastes are also segregated and chemically coagulated by lime; clarified effluent which still contains some amount of phosphate and fluoride is diluted by mixing with other wastes.

The other effluent type is characteristic of ammonia production and ammonia containing products. Most of the contamination comes from ammonia production itself. It is characteristically high in ammonia from effluent gas scrubbing and gas cleaning operations and high in sodium hydroxide or carbonate from gas cleaning process.

Several alternatives are there for the treatment of Ammonia bearing wastes

1. Steam stripping
2. Air stripping in towers
3. Lagooning after pH adjustment
4. Biological nitrification and denitrification

For all practical purposes, steam stripping for the ammonia removal from fertilizer wastes have been found to be uneconomical.

Removal of Ammonia gas from the solution in an air stripping tower, packed with red wood stakes, is found to be very efficient method. Very encouraging results are obtained from some laboratory and pilot plant studies conducted by NEERI in the removal of Ammonia by simply lagooning the waste. It was found that considerable reduction in the Ammonia content can be accomplished just by retaining the Ammoniacal waste in an Earthen tank about 1m deep, for a day or two after a pretreatment of the waste by lime increase the pH to 11.0. Of course with urea containing waste, no reduction in urea content is observed within this period' Thus waste containing both urea and Ammonia required to be retained in the Lagoon for a longer period, to allow urea to decompose to ammonia first.

Biological nitrification involves oxidation of Ammonia to nitrate via nitrite under aerobic condition; this followed by the denitrification of the nitrified effluent under anaerobic condition; in which gaseous  $N_2$  and  $N_2O$  is the end product and is released to the atmosphere. The denitrification requires addition of some quantity of carbonaceous matter in the reactor.

In all the Ammonia removal method described above, urea remain as untouched. If urea removal is required the urea containing wastes must be retained for a sufficiently long time in an earthen lagoon to allow it to decompose first to ammonia.

#### **Waste Water from Fertilizer Plant:**

A variety of wastes are discharged from the Fertilizer plant as water pollutants in the form of

1. Processing chemicals like Sulphuric acid
2. Process intermediate like Ammonium, Phosphoric and etc.
3. Final products like urea, Ammonium sulphate, Ammonium phosphate etc.

In addition to the above, oil bearing wastes from compressor houses of ammonia and urea plants, some portion of the cooling water and the wash water from the scrubbing towers, for the purification of gases, also come as waste.

Wash water from the scrubbing towers may contain toxic substances like Arsenic, Monoethanolamine, Potassium carbonate etc. in a Nitrogenous fertilizer plant, while that in a phosphatic fertilizer plant may contain a mixture of carbonic acid, hydrofluoric acid. Both alkaline and acidic wastes are also expected from the boiler feed water treatment plant, the wastes being generated during the regeneration of anion and cat ion exchanger units.

Additional pollutants like phenol and cyanide will be introduced in the list of pollutants in the fertilizer plant where ammonia is derived from the waste ammonia cal liquor of the coke ovens.

Average characteristics of the waste water from a typical Indian fertilizer plant producing both nitrogenous and phosphatic fertilizer is given below.

pH	7.5to 9.5
Total solids, mg/l	5400 mg/l
Ammonia Nitrogen	700 mg/l
Urea Nitrogen	600 mg/l
Phosphate	75 mg/l
Arsenic	1.5 mg/l
Fluoride	15 mg/l

#### **Effects of Wastes on receiving streams:**

All the components of the waste from the fertilizer plants induced adverse effects in the stream. Acids and Alkalis can destroy the normal aquatic life in the stream. Arsenic, Fluorides and Ammonium salts are found to be toxic to the fishes. Presence of different types of salts renders the stream unfit for use as a source of drinking water in the downstream side. Nitrogen and other nutrient content of the waste encourages growth of aquatic plants in the stream.

## **Suger Mill Wastes**

### **Introduction & Manufacturing Process**

#### **Introduction**

In Countries like India, Cuba and Jamaica, the sugar is produced from sugar canes, while in many other places beetroots are used as the raw materials for the sugar production. In India most of the sugar mills operate for about 4 to 8 months just after the harvesting of the sugar canes

## **Manufacturing Process**

The sugar canes are cut into pieces and crushed in a series of rollers to extract the juice, in the mill house. Juice is extracted from the sugar cane, leaving a fibrous residue called bagasse, which can be used as a fuel for the boilers or can be disposed of as solid waste. The milk of lime is then added to the juice and heated, when all the colloidal and suspended impurities are coagulated; much of the colour is also removed during this lime treatment. Lime is added to the extracted juice to raise its pH and to prevent the inversion of the sucrose molecule to glucose and fructose. The coagulated juice is then clarified to remove the sludge. The clarifier is further filtered through filter presses, and then disposed off as solid waste. The filterate is recycled to the process, and the entire quantity of clarified juice is treated by passing sulphur dioxide gas through it. The process is known as "sulphitation process"; colour of the juice is completely bleached out due to this process.

The clarified juice is then preheated and concentrated in evaporators and vacuum pans. The partially crystallized syrup from the vacuum pan, known as "massecuite" is then transferred to the crystallizers, where complete crystallization of sugar occurs.

The massecuite is then centrifuged, to separate the sugar crystals from the mother liquor. The spent liquor is discarded as "black strap molasses". The sugar is then dried and bagged for transport. The black strap molasses may be used in the distilleries.

## **Sources of Waste Water and the Characteristics of the Waste**

Wastes from the mill house include the water used as splashes to extract maximum amount of juice, and those used to cool the rolling bearings. As such the mill house waste contains high B.O.D due to the presence of sugar, and oil from the machineries.

The filter clothes, used for filtering the juice, need occasional cleaning. The wastewater thus produced through small in volume, contains high B.O.D and suspended solids. A large volume of water is required in the barometric condensers of the multiple effect evaporators and vacuum pans. The water is usually partially or fully recirculated, after cooling through a spray pond. This cooling water gets polluted as it picks up some organic substances from the vapour of boiling syrup in evaporators and vacuum pans.

The water from spray pond when overflows, becomes a part of the wastewater, and usually of low B.O.D in a properly operated sugar mill. Additional waste originates due to the leakages and spillages of juice, syrup and molasses in different sections, and also due to the handling of molasses.



### Characteristics of Sugar Mill Waste

Parameter	Value
pH	4.6- 7.1
C.O.D mg/	600 - 4380
B.O.D mg/l	300 - 2000
Total Solids	870 - 3500
Total Volatile Solids	400 - 2200
Total SuspendedSolids	220 - 800
Total Nitrogen	10 - 40
C.O.D /B.O.D ratio	1.3 - 2.0

The fresh effluent from the sugar mill decomposes rapidly after few hours of stagnation. It has been found to cause considerable difficulties when their effluent gets an access to the watercourse. The rapid depletion of oxygen due to biological oxidation followed by anaerobic stabilization of the waste causes a secondary pollution of offensive odour and black colour.

#### Treatment :

Disposal of the effluent on land as irrigation water is practical in many sugar mills, but it is associated with odour problem. The reasonable C.O.D/B.O.D ratio of the mill effluents indicate that the waste is amenable to biological treatment. However, generally it is found that, the aerobic treatment with conventional activated sludge process and trickling filter is not too efficient, even at a low organic loading rate. A max B.O.D reduction of 51% is observed in a pilot plant study at Kanpur, where both trickling filter and activated sludge process were tried. In view of the high cost of installation and supervision of the treatment units, and the seasonal nature of the operation of this industry, it is generally observed that the conventional aerobic treatment will not be economical in this country. Anaerobic treatment of the effluent, using both digesters and lagoons, have been found to be more effective and economical.

A B.O.D reduction of about 70% was observed in a pilot plant study with an anaerobic digester. The effluents of the anaerobic treatment units are found to contain sufficient nutrients (nitrogen and phosphorous). As such further reduction of B.O.D can be accomplished in aerobic waste stabilization ponds. Where sufficient land is available, a two stage biological treatment, with anaerobic lagoons followed by aerobic waste stabilization ponds, is recommended for Indian conditions. The mill effluent however is to be pretreated primarily in bar screens and grease trap. It is expected that the B.O.D reduction in the anaerobic process will be in the order of 60%, while overall B.O.D reduction may be in the order of 90%.

