## Unit-II

## Chemical oxygen demand (COD)

COD is defined as the amount of oxygen required for the chemical oxidation of biodegradable and nonbiodegradable organic matter.

non-biodegradable because they are toxic to organisms, organic pesticides, plastics, etc.

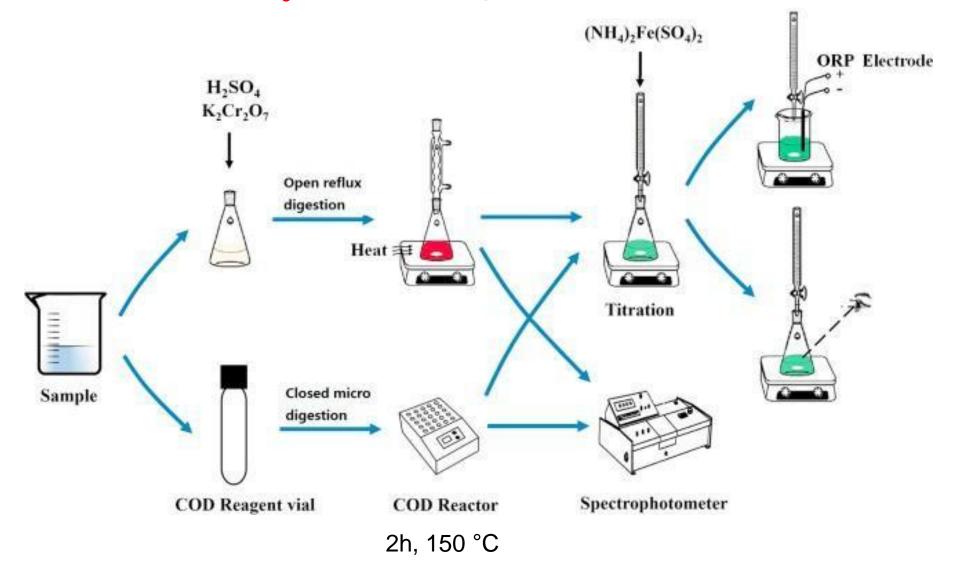
$$[COD] = mg O_2/L$$

total organic matter  $\longrightarrow$   $CO_2 + H_2O$ 

It is a rapid test and only required 2h of incubation time.

Therefore, it is an rough estimation.

## COD test by K2Cr2O7



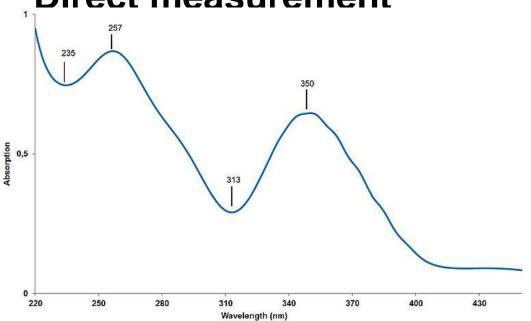
organic matter + 
$$K_2Cr_2O_7$$
 +  $H_2SO_4$  + cat.  

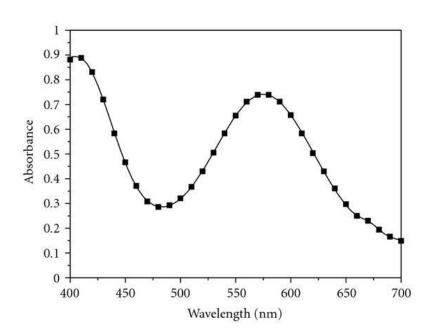
$$CO_2 + H_2O + Cr^{3+}$$

#### **Titration**

$$K_2Cr_2O_7 \longrightarrow Cr^{3+}$$

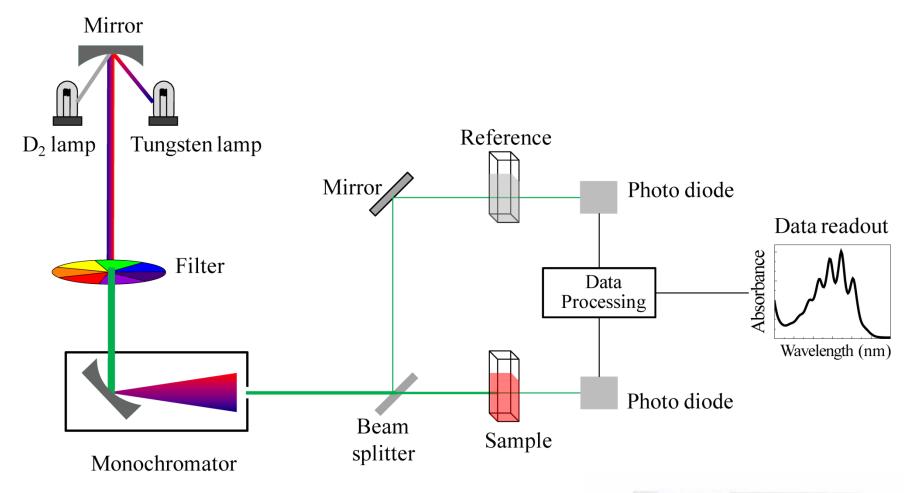
### **Direct measurement**





 $A = \varepsilon c I$ 

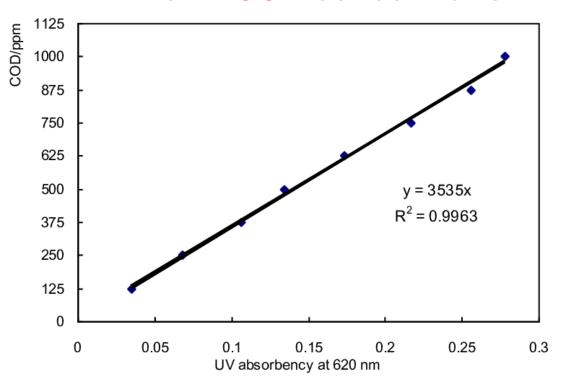
# $\epsilon$ is molar absorbance, c is concentration, I is length

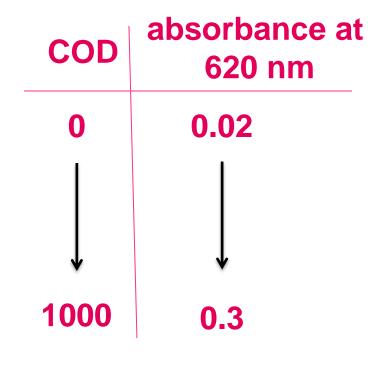




### **Calibration**







y = mx + c y = [COD] x is absorption at 620 nm For an unknown sample you can get the COD just incorporating x value

$$y = 50x + 2 (mg O_2/L)$$

application range: 1-1000 mg O<sub>2</sub>/L

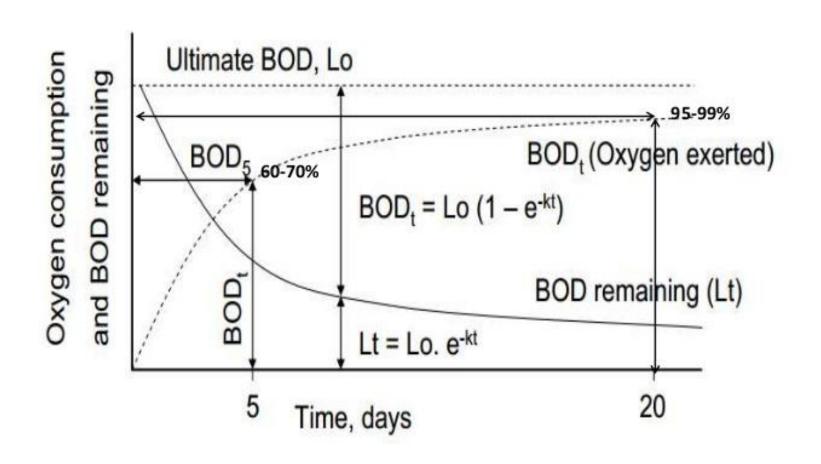
Biochemical/biological oxygen demand (BOD) is the amount of dissolved oxygen needed (i.e., demanded) by aerobic biological organisms to break down organic material present in a given water sample at certain temperature over a specific time period.

BOD test was first developed in 1930.

## **Importance**

- ❖ The goal of sewage treatment is to stabilize organic matter, convert it into an effluent of acceptable standard of purity and dispose it safety.
- The standard test which is an indicator of organic content of the sewage is biochemical oxygen demand.

- The BOD value is most commonly expressed in mg O<sub>2</sub>/L
- Incubation time: 5 days
- > temperature: 20°C
- $\triangleright$  [BOD] = [DO]<sub>t=0</sub> [DO]<sub>t=5</sub> where DO is dissolve oxygen



BOD reaction is a first order reaction

Rate of change in reactant concentration CAmount of reactant present at any time

$$-\frac{dL}{dt} \propto L$$
 L= Oxygen equivalent of biodegradable organics present at time t, mg/L 
$$-\frac{dL}{dt} = kL$$
 
$$\frac{dL}{L} = -kdt$$
 k = BOD rate constant, day -1 
$$\ln L = -kt + C$$
 Integrating we get, 
$$\int \frac{dL}{L} = -k \int dt$$
 
$$\ln L = -kt + C$$

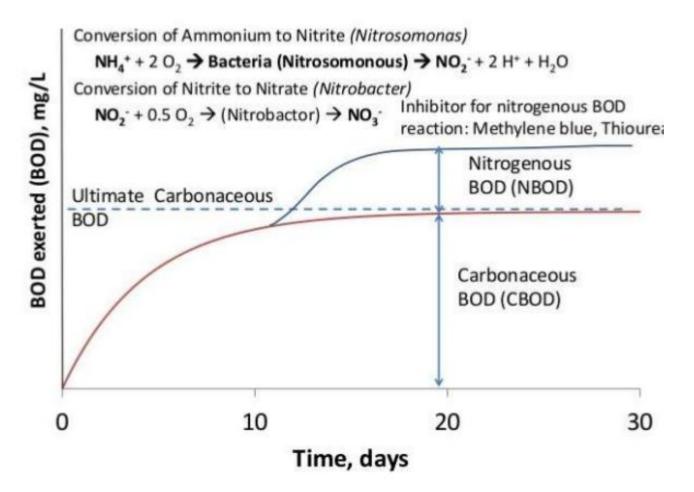
At time t = 0,  $L = L_0$ 

L<sub>0</sub>= Oxygen equivalent of biodegradable organics present at t=0, mg/L

$$\ln \frac{L}{L_0} = -kt \qquad \qquad L = L_0 e^{-kt} \quad \text{or,} \quad L_t = L_0 e^{-kt}$$

Lor L is often known as BOD remaining at time t

## Types (BOD)



Started late stage, after 10 days, requires more energy Amount is less hence attention is not given.

## Methods to find DO

Two methods for DO analysis are

- The Winkler or iodometric method and its modifications -titrimetric procedure based on the oxidizing property of DO
- Electrometric method using membrane electrodes-rate of diffusion of molecular oxygen across a membrane
- The choice of procedure depends on the interferences present, the accuracy desired, and, in some cases, convenience or expedience.

## **Determination of DO (Winkler's method)**

Can be measured by Winkler's method (lodometric method)

- □ DO measurement is based on the fact that dissolved oxygen oxidizes KI and liberate I<sub>2</sub>. The liberated iodine is titrated against thiosulphate solution using starch as an indicator.
- ☐ Since dissolved O₂ in water is in molecular state, it as such cannot oxidize the KI. Hence manganese hydroxide is used as an oxygen carrier.
- Manganese hydroxide in turn is obtained by the action of KOH on MnSO<sub>4</sub>

$$MnSO_4 + 2KOH \longrightarrow Mn(OH)_2 + K_2SO_4$$

$$2Mn(OH)_2 + O_2 \longrightarrow 2MnO_2 + 2H_2O$$

☐ The brown precipitate dissolves on acidification liberates nascent oxygen

$$2MnO_2 + H_2SO_4 \longrightarrow MnSO_4 + 2H_2O + [O]$$

☐ When treated with iodide ions liberates iodine in an amount equivalent to the initial DO.

$$2KI + H_2SO_4 + [O] \longrightarrow K_2SO_4 + I_2 + H_2O$$

The liberated iodine is finally estimated by titration with sodium thiosulphate

$$Na_2S_2O_3 + I_2 \longrightarrow S_2O_6^{2-} + 2I^{-}$$

During the titration starch solution is used as indicator which changes color from blue to colorless.

The stoichiometric expression relating DO and sodium thiosulfate is given below

I mole of O<sub>2</sub> reacts with 4 moles of thiosulphate.

## BOD

## COD

Organic matter oxidised to CO<sub>2</sub> and H<sub>2</sub>O by microorganisms

Organic matter oxidised to CO<sub>2</sub> and H<sub>2</sub>O by a chemical oxidising agent [usually potassium dichromate(VI) K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>]

other (often inorganic) substances oxidised as well, e.g. Fe(II) → Fe(III) SO<sub>3</sub><sup>2-</sup> → SO<sub>4</sub><sup>2-</sup>

## ADVANTAGES OF COD TEST

- COD result are available much sooner than BOD test results.
- The COD test requires fewer manipulations of the sample.
- The COD test oxidizes a wide range of chemical compounds.
- It can be standardize more easily.

## What is it TDS

**Total dissolved solids** is the term used to describe the inorganic salts and small amounts of organic matter present in solution in water. The principal constituents are usually calcium, magnesium sodium and potassium cations and carbonate, hydrogen carbonate, chloride, sulphate and nitrate anion.

## Acceptable level

The presence of dissolved solids in water may affects its taste. The palatability of drinking water has been rated by panels of tasters in relation to its TDS level as follows: excellent, less than 300mg/litre; good between 300 and 600 mg/litre; fair between 600-900 mg/litre; poor, between 900 and 1200 mg/litre and unacceptable, greater than 1200 mg/litre. Water with extremely low concentrations of TDS may also be unacceptable because of its flat, insipid taste

## **Determination of TDS**

- Lab wet method
- take 1L water sample
- evaporate water
- measure the quantity

#### Instrumental methods

Measure conductivity assuming most of then can conduct electricity, potentiometer

## **Determination of TDS**

AAS (Atomic Absorption Spectrometry)

 ICP-AES (Inductively Coupled Plasma atomic Emission spectroscopy)

## Soil Pollution

## **SOIL POLLUTION**

## **Definition**

The contamination of soil by human and natural activities, which may cause harmful effects to living things.

Human and animals activities generate many wastes that are discarded as useless. They are solid and generally termed as soil or land pollution

## **Composition of soil**

Inorganic mineral-45%

Organic matter-5%

Soil water-25%

Soil air-25%

The Term solid waste incorporates the highly heterogeneous mass of discarded materials from urban community as well as the homogeneous of waste generated by agricultural and industrial activities

### **Types of solid wastes**

- Municipal solid waste
- Organic waste
- Biodegradable waste
- Bulky waste
- > Combustible waste
- > Hazardous waste
- Medical waste
- > Chemicals
- > Radioactive pollutants
- > Pathological waste





#### **Effect of solid wastes**

- Increase the disease- causing organisms such as mosquitoes, flies
- ➤ Biodegradable waste decompose under uncontrolled and unhygienic conditions-produce smell and various types of insects and infections organism.
- > Huge quantity of fertilizer, pesticides etc. alter the soil quality
- The solid wastes run off with rainwater resulting water pollution.
- > Burning of solid wastes casus air pollution
- Radioactive elements due to explosions of nuclear bomb, unspent fuel etc. accumulate in the soil cause disease in human beings
- ➤ Industrial wastes alter the chemical and biological properties of soil.
- hazardous chemicals affect the human food chain leading to serious effects on living organisms.

# Types, effects and sources of soil pollution

- 1.Industrial wastes
- 2.Urban wastes
- 3.Agricultural practices
- 4. Radio active pollutants
- 5.Biological agents





## 1. Industrial wastes

Disposal of industrial wastes such as ash, slag, corroded metal on land

## **Sources**

- i) Pulp and paper mills
- ii) Chemical industries, oil refineries, Sugar factories,
- iii) Manufacturing and construction industries
- iii) Coal, Mining industries,
- iv) Chemical, glass, cement and engineering industries
- v) Construction and demolishing wastes

## **Effect**

- i)Alter the chemical and biological activities of soil
- ii)Hazardous chemicals enter into the human and animal food chain.
- iii)Disturb the biological process of living organisms.

#### 2. Urban wastes

- ➤ Both commercial and domestic wastes
- Form dry sludge of sewage
- Domestic and commercial refuse often termed as Municipal solid waste

## **Constituents**

Garbage and rubbish material Remains of food, vegetables, Garden wastes Plastics, glasses, fibers, rubbers, fuel residues, abandoned vehicles,

## 3. Agricultural practices

Modern agricultural process pollute the soil Fertilizers, pesticides, herbicides, livestock yards Feedlots, Crop residues, Soil erosion Farm wastes

# Control measures of soil pollution

- > Agriculture activities are increased for two reasons
- Population growth
- Urbanization (Decrease of farms)

## Control of soil erosion

- It is controlled by forestry and farm practicesExample
- Tree plantation on slopes
- Terracing and building diversion channel may be undertaken
- Reducing deforestation

## Proper dumping of unwanted materials

- Waste of human and animal form chronic problem
- Open dumping method should be changed
- Controlled tipping method should be followed

## **Production of natural fertilizers**

- Fertilizers and pesticides should not exceed the limit
- Bio fertilizers should be preferred over chemical fertilizers

Example : Animal's dung are used for composting

manure

## **Public awareness**

- Public awareness programs should be conducted
- Problems of health hazards should be educated to the people.

## Recycling and reuse of wastes

The waste paper, plastics, glasses, petroleum products and industrial effluents should be reused and re-cycled.

## Ban on toxic chemicals

DDT, BHC pesticides should be banned

Improper disposal of radioactive wastes should be banned

Nuclear explosion should be banned.

## Thermal pollution

### **Definition**

- Thermal pollution is due to the entry of excess heat generated by human activity
- It is a common and addition of water pollution. Addition of excess heat to water that makes it harmful to living things.
- This is the heat released to the environment during the generation of electricity in stream power plants. The heated water casus a lowering of DO level in the body of water. This creates anaerobic conditions and disrupt the ecological balance.
- The other reason for thermal pollution is deforestation due to developmental activities.

## Sources of thermal pollution

- 1. Thermal power plants
- 2. Coal-fired power plants
- 3. Industrial effluents
- 4. Domestic sewage
- 5. Hydro electric power plant



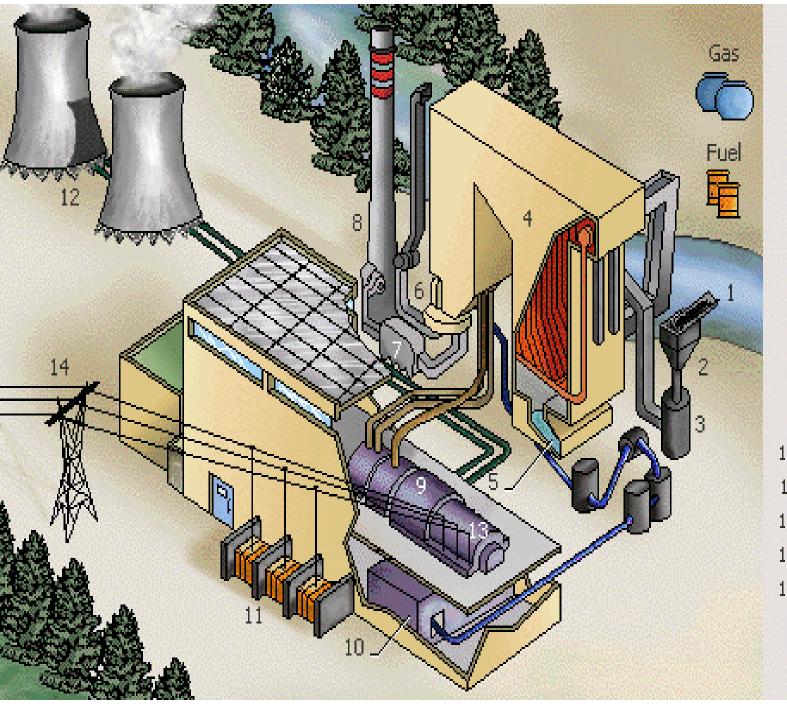


## 1. Thermal power plants

- ➤ Nuclear explosions and experiments
- Emissions from power plant and nuclear reactor
- > Heated effluents from power plants.

Increases the temperature of the water bodies.





## Thermal power plant

- 1 Coal conveyer
- 2 Stoker
- 3 Pulverizer
- 4 Boiler
- 5 Coal Ash
- 6 Air preheater
- 7 Electrostatic precipitator
- 8 Smokestack
- 9 Turbine
- 10 Condenser
- 11 Transformers
- 12 Cooling towers
- 13 Generator
- 14 High-voltage power lines

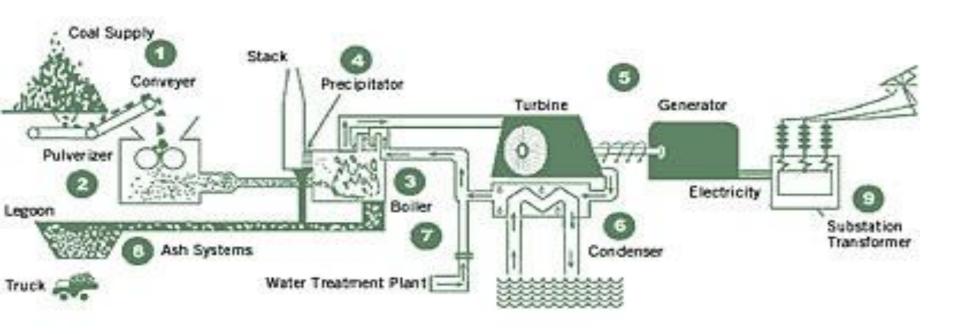
## 2. Coal-fired power plants

- Condensers in the thermal power plants are cooled with water from river and lakes; discharge the hot water back to them increasing the temperature of the water bodies.
- The heated effluents decrease the dissolved oxygen content in water.

It kills the fishes and other micro organisms



#### Components of a coal-fired thermal plant



Source: Canadian Clean Power Coalition

#### 3.Industrial effluents

Electricity generating industries like

- Coal power plants
- Nuclear power plants
- Textile, paper and pulp industries Directly mix the

hot

effluents into water bodies

It increases 10°C of temperature of water and the





# 4.Domestic sewage

These are discharged into river, lakes, and channels without treatment.

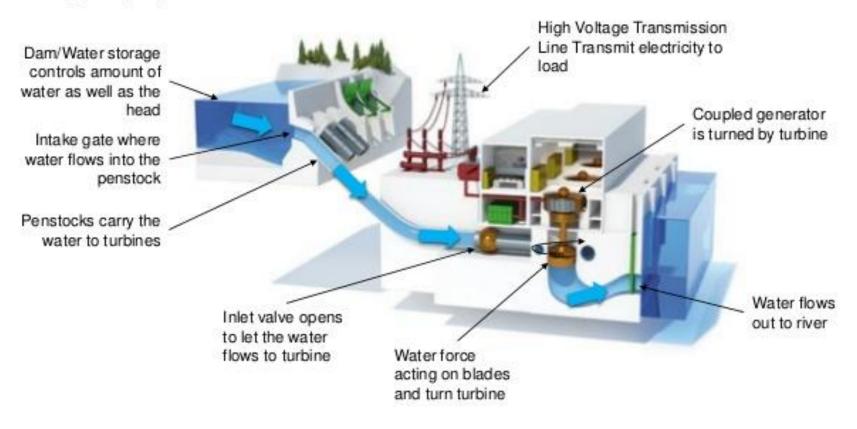
- The municipal sewage has high temperature
- The demand of dissolved oxygen increases.
- Water organisms will die.
- The offensive gases evolved

# 5. Hydroelectric power

- > Negative thermal loading takes place in water.
- ➤ 8% more heat is given to the water bodies by nuclear power plants

# Hydro Power Plant: How It Works

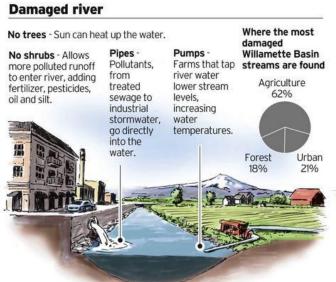
Hydropower utilizing the water mass that flows due to gravity to turn the turbine and thus turns the coupled generator. The generated electricity from generator passes through step-up transformer and transmitted to the load in the distance.



#### **Human activities**

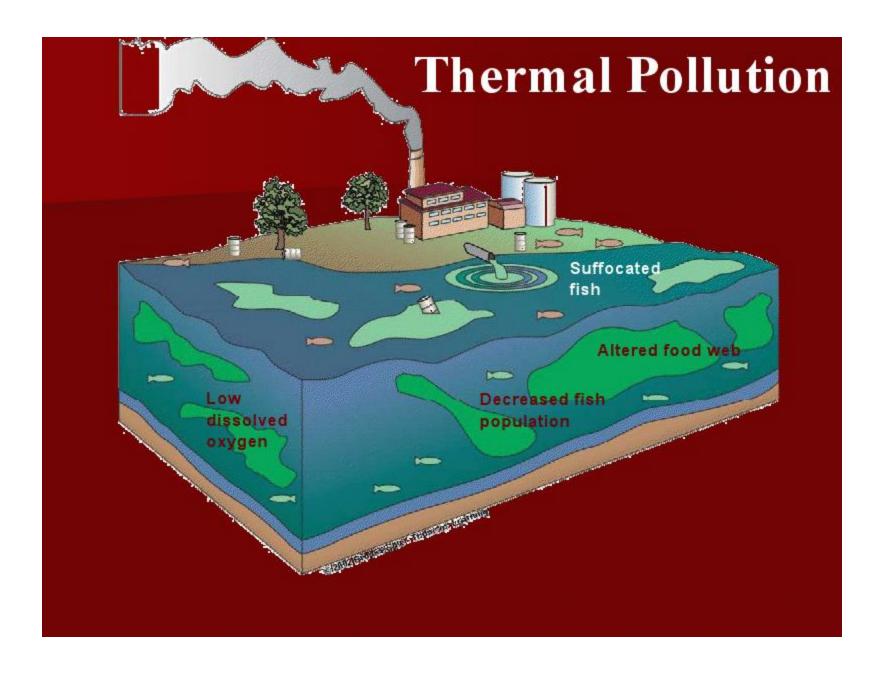
- ➤ Industries and power plants use water to cool are mixed with water bodies
- > Cutting the trees and plants
- ➤ Soil erosion by construction
- ➤ Removal of streamside vegetation (vital part of good water quality)
- ➤ Poor farming practices





#### Effects of thermal pollution

- a) Reduction in dissolved oxygen
- >When temperature increases DO level decreases
- b) Increase in toxicity
- ➤ When temperature increases toxic effect of Potassium cyanide and O-xylene increases
- C) Interference with biological activities
- ➤It controls the respiratory, digestive, excretion systems.
- d) Interference with reproduction
- ➤ Breeding and reproduction are affected by high temperature
- e) Direct mortality
- ➤ Death occurs to fishes in high temperature
- f) Food storage for fish
- ➤ Change in temperature alters the seasonal variation which affect the food storage system of fishes.



# Control measures of thermal pollution

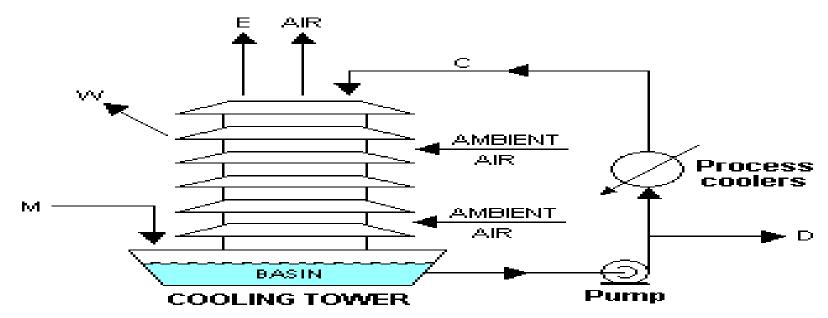
# 1. Cooling towers

- Cooling towers are designed to reduce the temperature of water
- ➤ Cooling tower spread the heat from hot water to the surrounding by evaporation
- ➤ There are two types
  - a) Wet cooling tower
  - b) Dry cooling tower

### 1. Wet cooling tower

- ➤ Water coming out from the condenser is allowed to spray.
- ➤ Cool air with high velocity is passed from

#### COOLING TOWER SYSTEM



C = CIRCULATING COOLING WATER

E = EVAPORATED WATER

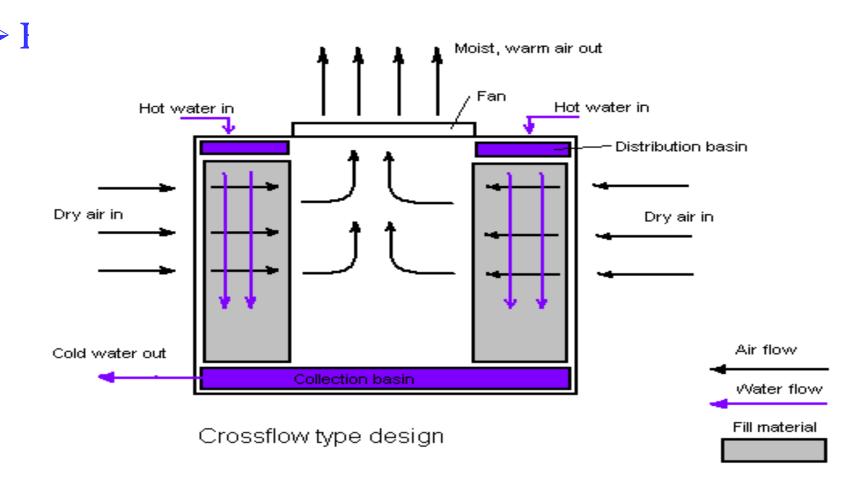
W = WINDAGE or DRIFT LOSS

M = MAKEUP WATER

D = DRAWOFF or BLOWDOWN WATER

# Dry cooling tower

- ➤ Hot water is allowed to travel in a spiral path.
- ➤ Cool air with help of fans is passed over this hot water

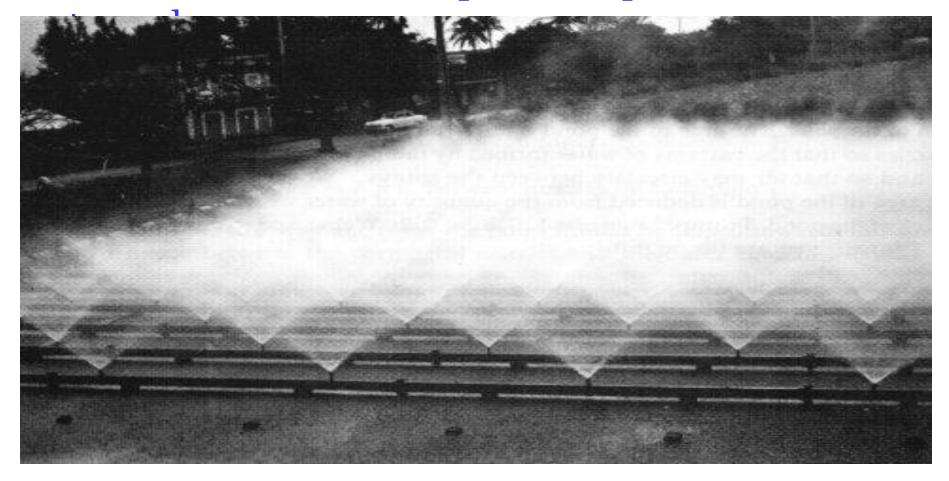


### **Cooling ponds**

- ➤ It is a simplest method of cooling the thermal discharges
- > Heated effluents transferred to cooling pond
- ➤ Water surface dissipate the heat to atmosphere
- > Water area minimized and volume reduced
- ➤ Water wedge acts like a cooling pond.

# **Spray ponds**

- > 1. The hot water is allowed to enter in sprayer
- ➤ 2. Water is sprayed as fine droplets through nozzles
- > 3. Heat from the fine droplets dissipated to



#### **Artificial lakes**

- > These are man made bodies of water
- ➤ The heated effluents can be discharged into lake at one end and cooling water withdrawn from other end.



#### 4. Radio active pollutants

Radium, thorium, uranium and carbon -14 isotopes, Explosion of hydrogen weapons, Cosmic radiations, Nitrogen-15, Strontium-90, Iodine-129, Cesium-137, and isotopes of iron

#### **Sources**

- i) Unused Spent fuels
- ii) Wastes from nuclear plant industry,
- iii) Scrapped Electronic goods
- iv) Medical equipment's releasing radioactivity

#### 5. Biological Wastes:

Biomedical, Pathological wastes, potentially infectious wastes from hospitals, clinic laboratories etc.

#### 6. Particulate pollutants in air settle in the soil

#### **RADIO ACTIVE POLLUTION**

Radiation or radioactive polllution is emission of radiation from the radioactive substances such as U, Pu etc. also from of nuclear waste, contaminates air, water and soil and directly affects the human being

#### **Sources of Radiations**

- Nuclear power stations, Nuclear bomb, Nuclear accident
- Waste from nuclear power plants
- The leakages from stored radioactive wastes
- X ray testing laboratories
- Radio, TV units, electronic devices
- High energy photons and electrons released from sun as cosmic rays.
- Radioactive isotopes

### **Effects of Radioactive pollution**

- ➤ Brain and central nervous system affected by delirium, Convulsions and death
- ➤ Loss of sight in eyes
- > Vomiting, bleeding and mouth ulcers
- ➤ Blood vessel damage and red spot on skin
- > Infection of intestinal wall
- ➤ Brain damage, Brain tumor, mental retardation, affecting pregnancy
- ➤ EMR from cell phones have been linked to development of brain tumors, genetic damage
- ➤ Occupational health hazard, developing various type of cancer.

The Chernobyl disaster, also referred to as the Chernobyl accident, was a catastrophic nuclear accident. It occurred on 26 April 1986 in the No.4 light water graphite moderated reactor at the Chernobyl Nuclear Power Plant near Pripyat, in what was then part of the Ukrainian Soviet Socialist Republic of the Soviet Union (USSR).





Fukushima nuclear disaster" redirects here. For the incidents at Fukushima Daini (Fukushima II), see Fukushima Daini Nuclear Power Plant.

"2011 Japanese nuclear accidents" redirects here. For other 2011 Japanese nuclear accidents/incidents, see Fukushima Daini Nuclear Power Plant, Onagawa Nuclear Power Plant, Tōkai Nuclear Power Plant, and Rokkasho Reprocessing Plant.

#### Control measures of nuclear hazards

- 1. Nuclear tests should not be in air
- 2. Nuclear tests should be in under ground
- 3. Nuclear reactor should be covered by closed cycle coolant
- 4. Production of radio isotopes should be minimized
- 5. Nuclear installation should be controlled
- 6. Fission reaction should be minimized.
- 7. Radio isotopes may be used in the liquid or gas form instead of powder form

- 8. Nuclear mines formed with underground drainage
- 9.Method have to develop for the safe handling and disposal of radio active wastes should be very careful.
- 10. Usage of nuclear medicines should be minimized.
- 11. Steps should be taken to prevent the leakage of the radioactive elements from nuclear reactor
- 12. Radioactive wastes should be stored in such places where they gradually decay to stable products.