UNIT- I

WATER QUALITY AND TREATMENT

Water is one of most abundant, widely, distributed substance but is also most misused one. It covers 3/4 of earth's surface and essential for all organisms like animals, plants, human beings. It is not only essential for organisms but also used in engineering side for steam generation. In addition to it, It is used in domestic purposes like drinking, washing, bathing, cooking used in industries like production of paper, rayon, textiles, tires, irrigation, atomic energy, steel etc...

Sources of water:

Based on their sources water is broadly divided into 2 types

1) Surface water
2) Underground water

I. Surface water: It is the purest form of water. It is obtained from evaporation of surface water. During the downward movement through the atmosphere it dissolves considerable amount of industrial gases (CO_2, SO_2) and suspended particles (organic & inorganic).

River water: Rivers are fed by rain water and spring water. Water from these sources floe over the surface of earth and dissolves soluble minerals present in the soil. River water also contain organic matter derived from decomposition of plants and small particles of sand and rock in suspension i.e. it contain both dissolved and suspended impurities.

Lake water: It belongs to still water type. It contains constant chemical composition. It consists of much lesser amounts of dissolved impurities than well water. It has high concentration of organic matter.

Sea water: It is the most impure form of natural water. All rivers join sea along with their impurities. It contain 3.5% dissolved salts of which 2.6% is NaCl and other salts are sulphates of Na^+, bicarbonates of K^+, Mg^{+2},Ca^{+2} and bromides of K^+ and number of other compounds.

II. Underground water: The rain water passed down to the lower layers of earth continuously until it comes in contact with rocks. It comes out of the earth in the form of spring water.

Well and spring water: it has high organic purity and consists of more amounts of dissolved salts. It has more hardness.

IMPURITIES OF WATER

Water has following impurities. They are

1. Physical impurities
2. Chemical impurities
3. Biological impurities

Physical impurities:

1. **Colour:** Pure water is colourless. Colour to water is caused by the presence of metallic substances like Fe, Al, Humus materials, peat, tannins, algae, fungi, weeds etc...the change in colour is not harmful unless it comes in contact with toxic substances.

   Eg: Yellow colour- presence of Cr and Organic matter

   Yellowish red colour- presence of Fe

   Reddish brown colour- presence of peaty matter

2. **Turbidity:** pure water has no turbidity. It is caused by the presence of clay, slit. finely divided matter, micro organisms etc...it depends on the quantity of insoluble substances and also their size, shape, refractive index. Turbidity is eliminated by filtration, sedimentation and coagulation.

3. **Taste:** in pure water it is interlinked with odour but in waste water it is accomplished by odour.

   Eg: Bitter taste- presence of minerals (Fe, Al, Sulphates, Mg and excess amount of lime)

   Soapy taste- presence of large amounts of $NaHCO_3$

   Brackish taste- presence of unusual amounts of salts

   Palatable taste- presence of dissolved CO_2 and minerals (nitrides)

4. **Odour:** pure water has no odour. It is not necessary for domestic purposes and Industrial purposes. Odour is caused by the presence of living organisms, decaying of algae, fungi, and bacteria etc....the most disagreeable odour is caused by sulphites.

Chemical impurities:

Chemical impurities are released from industries, dyes, paints, varnishes etc.. Surface and ground water attains acidity from industrial wastes like acids, mines, drainage etc... Acidity is caused by the presence of free CO_2, mineral salts etc... Chemical impurities are of three types.

1. **Gases:**

A) Dissolved CO_2: All natural water contains dissolved CO_2. Its concentration depends on temperature, pressure and dissolved mineral content of water. It is acquired from the biological oxidation of the organic matter.

B) Dissolved O_2: Its concentration also depends on temperature, pressure and content of salts. If it is present in the industrial water it induces the corrosion. Its presence is necessary to aquatic organism such as fishes, frogs etc... (for respiration)

C) Dissolved NH_3: It comes from decomposition of nitrogenous organic matter, sewage containing nitrogenous matter.

2. **Organic materials:** These are formed by decaying of micro organism or decaying of vegetable matter.

3. **Inorganic materials:** They arise from industrial effluents and rocks. Na^+, K^+, Mg^{+2}, Ca^{+2}, Mn^{+2}, HCO_3^-, CO_3^{-2}, Cl^- etc...

Biological impurities:

Algae, pathogenic bacteria, fungi, virus, parasites, worms etc... The source of these contaminations is t5he discharge of domestic sewage wastes, excreta etc...

Microorganisms: Abundant in surface water, bur their count is quite low or even nil in deep well water. (Microscope). Commonly microorganisms form slime there by causing fouling as well as corrosion. They can grow at 25-350C which can be prevented by sterilization (chlorination)

Water bodies: Bacteria, organisms inhabit ting the bottom sludge and planktons developed at the water surface. These are inhabitated by different group of worms like flat worms, hair worms, tiny round worms etc…Most of the worms are parasitic in nature and harmful to human health and fishes.

Hardness of water:- Hardness is characteristic property of water, which prevents formation of lather with soap. This is due to presence of certain salts of Ca, Mg, Fe & heavy metals dissolved in water. When a sample of hard water is treated with soap it forms a white scum or precipitate instead of lather. Soaps are Na/K salts of higher fatly acid like palmitic acid, stearic acid, oleic acids.

Reactions of soap with hard water [$CaCl_2$, $MgSo_4$]are as follows:-

$$2C_{17}H_{35}CooNa+CaCl_2 \longrightarrow (C_{17}H_{35}Coo)_2Ca + 2NaCl$$

$$2C_{17}H_{35}CooNa+MgSo_4 \longrightarrow (C_{17}H_{35}Coo)_2Mg + Na_2So_4$$

Soft water:- A sample of water which produce lather easily with soap is called as soft water. This doesn't have salts of Ca, Mg, Fe& heavy metals.

Types of Hardness:- Hardness of water is of two types

1) Temporary hardness

2) Permanent hardness

1. Temporary or carbonate hardness: It is caused by the presence of bicarbonates of calcium, magnesium, heavy metals and carbonates if Fe. It is destroyed by boiling. On boiling the bicarbonates are converted to carbonates and hydroxides which are deposited as a crust at the bottom of the vessel.

$$Ca(HCO_3)_2 \longrightarrow CaCO_3+H_2O+O_2$$

$$Mg(HCO_3)_2 \longrightarrow Mg(OH)_2+2CO_2$$

2. Permanent or non-carbonate hardness: It is due to the presence of chlorides, sulphates of calcium, magnesium and heavy metals. Unlike temporary hardness it is not destroyed by boiling.

Disadvantage of hard water: - There are several disadvantages with hard water when used in domestic &industrial purposes and also in boilers.

1. Domestic use

2. **Industrial use**
3. **Boilers**

These are briefly described here as follows.

Drinking: - If hard is used for drinking, it destroys the digestive system it also forms Calcium Oxalates (Stones) in urinary tracks

Washing: - When hard water is used for washing does not produce lather freely with soap and produces sticky precipitates of it forms Calcium/Mg soaps. After that the soap gives lather with water.

$$C_{17}H_{35}COONa + H_2O \longrightarrow C_{17}H_{35}COOH + NaOH$$

$$\text{Stearic acid} + \text{Soap} \longrightarrow \text{Lather}$$

A lot of soap gets wasted and a sticky precipitate gets adhere on to the fabrics of cloth giving spots and presence of Fe salts may cause staining of cloth.

Bathing:- Wastage of soap takes place and forms sticky scum on the bath tub and body.

Cooking: - Due to the formation of calcium and magnesium soaps water boiling point is elevated hence more time and fuel are required for cooking. Certain foods such as pulses, peas are not cooked soft with hard water if it is used to making of tea and coffee it exhibits unpleasant odour and muddy looking extract.

In industrial use:

Textile industry: - The precipitates of Ca and Mg soaps adheres on the fabric and do not produce correct shapes to fabric and iron stain the cloth and produces spots on fabric. Hard water destroys the beauty of fabrics.

Sugar industry: - SO_4^{-2}, NO_3^{-2}, Alkali, carbonates of hard water arise the problem in crystallsation of sugar. The resulting sugar may be deliquescent.

Dying industry: - Hard water gives impure shapes to the cloth in dying industry due to the presence of precipitates of Ca and Mg.

Paper industry: - Chlorides and sulfates of ca and Mg affects the quality of paper.

Laundry: - A lot of soap was wasted in laundry due to the formation of precipitates of Ca and Mg

Concrete making: - Chlorides and sulfates of hard water affect the hydration of cement and final strength of the hardened concrete.

Pharmaceuticals: - Hard water may form some undesirable products while preparation of the pharmaceuticals (drugs, ointments, injections)

Boilers: - Boilers are used for steam generation. If hard water is used in boilers it may lead to the following troubles

1. Formation of scales & sludges
2. Boiler corrosion
3. Caustic embrittlement.
4. Priming & foaming

Boiler troubles

DEGREE OF HARDNESS

Hardness of water is expressed in terms of $CaCO_3$ equivalents. The molecular weight of $CaCO_3$ is 100 and its equivalent weight is 50 which is easy for calculation and $CaCO_3$ is insoluble salt. All the dissolved salts of Ca are precipitated as $CaCO_3$

$$CaCO_3 \text{ equivalent} = \text{wt of salt} \times \frac{\text{Equivalent of } CaCO_3 \ (50)}{\text{Eq. wt of that salt}}$$

OR

$$= \frac{\text{wt of salt} \times \text{Molecular weight of } CaCO_3 \ (100)}{\text{Mol wt of that salt}}$$

Salt	Mol.Wt	Eq.Wt	$CaCO_3$ Equivalent
$Mg(HCo_3)_2$	146	73	100/146
$Ca(HCo_3)_2$	162	81	100/162
$MgCl_2$	95	47.5	100/95
$MgSo_4$	120	60	100/120
$CaCl_2$	111	55.5	100/111
$CaSo_4$	136	68	100/136

$Mg (No_3)_2$	148	74	100/148

Units of hardness: -

The following units are used to measure hardness. They are

1. Parts per million (PPM)
2. Milligrams per liter (Mg/L)
3. Degree clark (°Cl)
4. Degree French (°Fr)
5. Milli equivalents per liter (Meq/L)

1. PPM: - PPM is parts of $CaCO_3$ equivalent hardness per one million parts of water i.e. 10^6 parts of water

1PPM = 1 part of $CaCo_3$ equivalent hardness in 10^6 parts of water

2. Milligrams per liter: - It is defined as no of milligrams of $CaCO_3$ equivalent hardness present per liter of water.

1mg/L = 1mg of $CaCo_3$ equivalent hardness per liter of water

1 liter water weighs 1 kg = 1000gm

= 1000 x 1000 = 10^6 mg

Therefore 1 mg/L = 1mg of $CaCO_3$ Equivalent hardness per 10^6 mg of water

1PPm = 1mg/L

3. Degree Clark (°Cl):- It is defined as no. of parts of $Caco_3$ equivalent hardness per 70,000 parts of water or one gallon of water.

1 °Cl = 1 part of $CaCo_3$ eq: hardness per 70,000 of water.

1PPM =0.07 °Cl

4. Degree French (°Fr):- it is defined as no: of parts of $CaCO_3$ equivalent hardness per 10^5 parts of water.

1^0 Fr= one part of $CaCO_3$ equivalent hardness in 10^5 parts of water

1PPM=0.1^0 Fr

5. Milli equivalents per liter:- it is no of milli equivalent of $CaCO_3$ hardness of present per liter.

1Meq/L=1 milli equivalent of $CaCO_3$ equivalent hardness in One liter of water

$=10^{-3}$x50 gm of $CaCO_3$ equivalent per liter

= 50mg of $CaCO_3$ equivalent hardness

= 50PPM

1PPM = 0.02 Meq/L

Relationship between various units of hardness;

1PPM = 1mg/L 0.07 ^{0}Cl = 0.10Fr = 0.02 meq/L.

Problems

1. Find temporary , permanent &total hardness of sample of water containing $Ca(HCO_3)_2$=40.5 mg/L , $Mg(HCO_3)_2$= 46.5 mg/L , Mg SO_4 = 27.6 mg/L , $CaCl_2$ =22.4 mg/L , $CaSO_4$=32.4 mg/L.

Hard salt	Weight(mg/l)	Molecular weight	$CaCO_3$ Eq=weight/mwt X100
$Ca(HCO_3)_2$	40.5	162	25
$Mg(HCO_3)_2$	46.5	146	31.8
Mg SO_4	27.6	120	23
$CaCl_2$	22.4	111	20.18
$CaSO_4$	32.4	136	23.8

Ans: Temporary hardness =hardness due to Ca $(HCO_3)_2$+ $Mg(HCO_3)_2$

=25+31.8=56.8 mg/L

Permanent hardness=hardness due to $MgSO_4$+$CaCl_2$+$CaSO_4$

= 23+20.18+23.8=66.7mg/l

Total hardness=56.8+66.7=123.5 mg/L

Hard salt	Weight(mg/l)	Molecular weight	$CaCO_3$ Eq=weight/mwt X100
$Ca(HCO_3)_2$	10.5	162	6.48
$Mg(HCO_3)_2$	12.5	146	8.56
Mg SO_4	2.6	120	2.16
$CaCl_2$	8.2	111	7.3

$CaSO_4$	7.5	136	5.5

2. A sample of water to contain following. Ca $(HCO_3)_2$ =10.5PPm, Mg $(HCO_3)_2$=12.5PPM, $MgSO_4$ =2.6PPM, $CaCl_2$ =8.2PPM, $CaSO_4$ =7.5PPM. Find Temp & permanent hardness in ^{0}Cl

Ans: Temporary hardness =hardness due to Ca $(HCO_3)_2$+$Mg(HCO_3)_2$

= 6.48+8.56

= 15.04 PPM

=15.04X0.07=1.05 ^{0}Cl

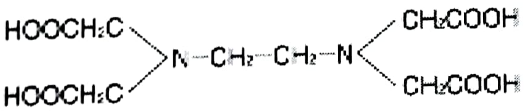
Permanent hardness= hardness due to $MgSO_4$+$CaCl_2$+$CaSO_4$

= 2.16+7.3+5.5=14.96PPM

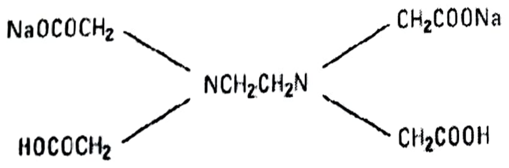
=14.96X0.07=1.05 ^{0}Cl

Estimation of hardness by EDTA method

The hardness of water is quantitatively measured by EDTA method. Ethylene diamine tetra acetic acid (EDTA) is used to estimate hardness. Disodium salt of EDTA can form stable complex (M-EDTA) with Ca& Mg ions at pH9 -10



Structure of EDTA



Disodium salt of EDTA

Principle: - An indicator Eriochrome black-T is used, which forms an unstable wine red complex with Ca& Mg ions (in hard water) at pH-10. When this solution is titrated against EDTA solution , the color of complex changes from wine red to blue which indicates end point i.e., M-EDTA Complex release blue colored indicator EBT into water.

$$M^{+2} + EBT \longrightarrow [M\text{-}EBT] \text{ (Wine red)}$$

$$\underset{\text{(Colorless)}}{[M\text{-}EBT] + EDTA} \longrightarrow [M\text{-}EDTA] + EBT \text{ (Blue)}$$

Preparation of solutions:-

Standard hard water: - Dissolve 1 gm of pure $CaCO_3$ in small quantity of dil. HCl & then evaporate the solution to dryness on a water bath .Dissolve the residue in distilled water to make 1 liter. Therefore 1 ml of solution contains 1mg of $CaCO_3$ equivalent hardness

EDTA solution: - Dissolve 4 gm of pure EDTA crystals along with 0.1gm of $MgCl_2$ in 1 liter of distilled water.

Indicator: - Dissolve 0.5 gm of EBT in 100ml of alcohol.

Buffer: - Add 67.5 gm of NH_4Cl to 570 ml of conc. NH_3 solution and make up with distilled H_2O to 1 liter.

Procedure:-

Standardization of EDTA: -

1. Rinse and fill the burette with EDTA solution.
2. Pipette out 50ml of standard hard water + 10-15 ml of Ammoniac buffer +few drops of EBT indicator in conical flask.
3. Titrate with EDTA solution till wine red color changes to clear blue.

Let the volume of EDTA used be V_1 ml

B. Estimation of total hardness : - Take 50ml of given hard water. To this add buffer and few drops of EBT indicator and then titrate with EDTA solution.

Let the volume of EDTA used be V_2 ml

C. Estimation of permanent hardness: - Take 250ml of hard water sample in a beaker and evaporate it to nearly 50 ml (all bicarbonates are converted to carbonates and hydroxides). Filter, wash and make up the filtrate to 250ml with distilled water. From this pipette out 50ml boiled water. To this add buffer and few drops of indicator. Titrate with EDTA until wine red color changes to deep blue.

Let the volume of EDTA used be V_3 ml

CALCULATIONS

Standardization of EDTA: - 1ml of standard hard water = 1mg of $CaCO_3$ equivalent

50 ml of standard hard water = V_1ml of EDTA

50 mg of $CaCO_3$ =V_1 ml of EDTA

1 ml of EDTA =50/V_1 mg of $CaCO_3$ eq.

Estimation of total hardness:-

50 ml of given hard water = V_2 ml of EDTA

50 ml of given hard water = V_2 X50/ V_1 mg of CaCO3 eq

1 ml of given hard water = V2/50X50/V_1 mg of $CaCo_3$

1 liter of given hard water =V_2/V_1 X1000 mg/L

Total hardness = V_2/V_1 X1000 mg/L

Estimation of permanent hardness:-

50 ml of given boiled H_2O = V_3 ml of EDTA

= V_3 x 50/V_1 mg of $CaCO_3$ eq

1 ml of given boiled H_2O = V_3/50 X50/V_1 mg of $CaCO_3$ eq

1 liter of given boiled H_2oO= V_3/V_1 X1000 mg/L

Permanent hardness= V_3/V_1 X1000mg/L

Estimation of temporary hardness:-

Temporary hardness = Total hardness – Permanent hardness

= (V_2/V_1 X1000 – V_3/V_1 X1000)

= (V2 – V_3/ V_1) X 1000PPM

Temporary hardness = (V2 . V_3 / V_1) X1000PPM

Problems

1.1gm of $CaCO_3$ was dissolved in diluted HCl & made up to 1000 ml of distilled H_2O. 50 ml of this solution required 48 ml of EDTA solution for titration .50 ml of hard water sample required 15ml of EDTA solution for titration .50 ml of same water sample on boiling , filtering etc. required 10 ml of EDTA solution. Find different types of hardness in PPM?

Ans:- 1 gm of $CaCO_3 \longrightarrow$ 1000 ml of H_2O

1 ml of standard H_2O = 1mg of $CaCO_3$ eq.

50 ml of standard hard water consumes 48 ml of EDTA: V_1 = 48 ml

50 ml of hard water consumes 15 ml of EDTA: V_2=15ml

50 ml of same hard water on boiling consumes 10 ml of EDTA: V_3= 10 ml

Total hardness =V_2/V_1 X 1000PPPM

= 15/48 X1000PPPM=312.5 mg/l or 312.5PPM

Permanent hardness =V_3/V_1 X 1000PPM

= 10/48 X1000=208.3 mg/l or 208.3PPM

Temporary hardness = Total hardness- Permanent hardened

=312.5-208.3

= 104.2 PPM

2. 0.28 gm of $CaCo_3$ was dissolved in dill HCl & solution made up to 280 ml with distilled H_2o. 100 ml of above sol. Required 28 ml of EDTA for titration .100ml of water sample required 33 ml of EDTA for titration after boiling 100 ml of this water consumes 10 ml of EDTA. Find temporary , permanent hardness of water in mg/L.

Ans . 1 gm of $CaCO_3 \longrightarrow$ 1000ml of H_2O

0.28 gm of $CaCO_3$ =280 ml of H_2O

1ml of standard hard water = 1 mg of $CaCO_3$ eq

100ml of standard hard water consumes 28 ml of EDTA: V_1 =28 ml

100 ml of given water sample consumes 33 ml of EDTA: V_2 =33 ml

100ml of boiled water consumes 10 ml of EDTA: V_3 = 10ml

Temporary hardness =$V_2 - V_3 / V_1$ X1000

= 33 - 10/28X1000= 821.42 mg/l

Permanent hardness =V_3/V_1X1000=10/28 X1000= 357.14 mg/l.

Analysis of water –Estimation of dissolved O_2

At room temperature and pressure the amount of dissolved oxygen in water is about 8mg/l. dissolved oxygen is essential for aquatic organisms and it also serve as an indicator of the extent of water pollution by impurities. Hence the determination of dissolved oxygen content is important both for environmental and industrial point of view. The amount of dissolved oxygen in water is determined by 'WINKLER'S METHOD.

Principle: - The determination of dissolved O_2 is based on the oxidation of KI by dissolved O_2 . The liberated iodine is titrated against standard sodium trio sulfate (Hypo) solution using starch as indicator blue color disappears. The dissolved molecular oxygen is unable to react with KI in water. Hence the carrier Mn (OH) $_2$ carries oxygen and brings about the reaction between KI and O_2. Mn (OH) $_2$ is produced by KOH and $MnSO_4$.

oxidizes Mn^{+2} $\xrightarrow[to]{made}$ liberate Iodide from KI.
↓
liberate Iodide is estimating hyposo
↓
by using Starch Soln. color

EQUATIONS:-

$$MnSo_4 + 2KOH \longrightarrow Mn(OH)_2 + K_2So_4$$

$$2Mn(OH)_2 + O_2 \longrightarrow 2\,MnO(OH)_2$$

Oxygen carrier magnetic oxide

$$MnO(OH)_2 + H_2So_4 \longrightarrow MnSo_4 + 2H_2o + [O]$$

$$2KI + H_2So_4 + [O] \longrightarrow K_2So_4 + H_2O + I_2$$

$$2Na_2S_2O_3 + I_2 \longrightarrow 2NaI + Na_2S_4O_6\ (Hypo)$$

$$Starch + I_2 \longrightarrow starch - iodine\ (blue)$$

Sodium Tetra thi [illegible]

Preparation of solutions:-

1. $MnSO_4$ solution:- 400 gm of $MnSO_4$ dissolved in 1 liter of water .

2. alkaline KI solution:- 150 gm of KI , 500gm of NaOH , 20 gm of sodium azide (NaN_3) which destroys impurities in water, all are dissolved in 1 liter of water.

Standard Hypo (N/100): - 2.48 gm of Hypo dissolved in 1 liter water.

Method / procedure: - 250 ml of water is collected in bottle avoiding as far as possible contact with air, immediately add 2 ml $MnSo_4$ &2 ml of alkaline KI solution. Stopper the bottle &shake it thoroughly for 10 – 15 minutes and allow to stand for few minutes to settle precipitate .Repeat this process of shaking and settling at least 3 times. Add 20 ml of conc. H_2SO_4 , stopper and shake to dissolve precipitate. Pipette out 100ml of solution in conical flask & titrate against standard Hypo using freshly prepared starch as indicator. End point is disappearance of blue color.

Calculation: - $N_1V_1 = N_2V_2$

N_1 = Normality of Hypo, N_2 = Normality of dissolved O_2

V_1 = volume of Hypo, V_2 = volume of dissolved O_2

Weight of dissolved $O_2 = N_1V_1 X 8 X 10^6 / 100 X 1000$ PPM.

Treatment of water for domestic purpose

For domestic purposes, the required water is collected from natural sources like rivers. lakes, ponds etc. However this water contains organic, inorganic & suspended impurities. Hence it must be purified before using. The domestic used water should have the following features:

1. It should be clear &odor less.
2. It should be pleasant in taste.
3. It should be perfectly cool.
4. Its turbidity should not exceed 10PPM.
5. It should be free from dissolved gases like hydrogen sulfide, minerals like lead. arsenic, chromium &manganese salts
6. It should be free from disease causing micro organisms.
7. Its alkalinity shouldn't be high and its pH should be about 8.
8. It should reasonably soft.
9. Its total dissolved solids content should be less than 500ppm.

PURIFICATION OF WATER FOR DOMESTIC USE:

Various types of methods are used for purification of domestic water. They are: -

1. Screening
2. Sedimentation
3. Filtration.

1. Screening: - This method is used for removing of suspended impurities. The process of removing floating matter from water is known as screening. In this process water is passed through a screen. The movement of floating matter is stopped by the screen and the water is free from floating matter.

2. Sedimentation: - Sedimentation is a process of allowing water to stand in big tanks. Then most of the suspended particles settle down at the bottom due to force of gravity. It is of two types

I) Plain sedimentation

II) Sedimentation by coagulation.

I. Plain sedimentation: - This process is mainly used for sedimentation of big size suspended particles. In this process water is stored in big tanks for several hours. 70% of solid particles settle down due to force of gravity.

II. Sedimentation by coagulation: - It is the process of removing of fine suspended and colloidal impurities by addition of requisite amount of chemicals called coagulants to water before sedimentation. When coagulant is added to water, it forms an insoluble gelatinous, flocculent precipitate which gathers tiny particles to form bigger flocks which settle down easily. (Usually coagulation neutralizes negative charge on colloidal clay and forms hydroxides which are involved in formation of bigger flock.)

Eg:

Name	Formula
Alum	K_2So_4 $Al_2(So_4)_3$ $24H_2o$
Sodium aluminates	$NaAlO_2$
Ferrous sulfate	$Fe\ So_4.7H_2o$

3. Filtration: - Even though water is subjected to screening & sedimentation, it contains fine clay, colloidal matter and also micro organisms. At that time filtration is used for purification of water. Usually filtration is carried by using sand filters. Sand filters consist of tank which has beds of fine sand which occupy top layer, Coarse sand, fine gravel forms the bottom layer. The tank has inlet for sedimented water and under drain at the bottom of tank for exit of filtered water. Sediment water enters in to sand filter and is uniformly distributed over the entire sand bed and it flows through the various beds slowly due to gravity. Retention of impurities takes place. Hence the sand pores get clogged and the rate of filtration slowly decreases.

Sterilization: - When water is subjected to sedimentation, coagulation & filtration still it contains a small percentage of micro organisms. It is a process by which killing of micro organisms using chemical substances, called as chemical disinfectants. Chlorination & ozonization are sterilization methods used for purification of water for domestic purposes.

Chlorination: - Treatment of water with chlorine is called chlorination, which is one of best methods for sterilization of water .Chlorine is a powerful germicide by means of HOCl.

$Cl_2+H_2O \longrightarrow$ HOCl + HCl (Hypo chorus acid)

Micro organisms+ HOCl $\longrightarrow$ micro organisms are killed.

Mechanism: - Earlier believed that the disinfecting action of chlorine was due to liberation of (O) which oxidizes harmful bacteria etc... However the scientist Glean & Stumpf identified that the death of micro organism is caused by chemical reaction of HOCl . It destroys the enzymes of micro organisms such enzymes are necessary for metabolic process of microorganisms so death of microorganism is due to in activation of its metabolic enzymes by HOCl.

$$HOCL \longrightarrow H^{+}+OCl^{-}$$

When compared to HOCl ion, liquid chlorine is more powerful at low pH i.e. HOCl is 80 times more destructive on bacteria than HOCl ions. Hence liquid chlorine is more effective when applied to filtered water.

Chlorination is done in apparatus called chlorinator which is large tower containing a number of baffel plates &two inlets for chlorine and water & one outlet for sterilized water. Water and proper quantity of conc. Chlorine solution are introduced to its related inlets. During their passage through the tower they get thoroughly mixed. The treated water is taken out from the bottom.

Factors affecting efficiency of chlorine:

1. Time of contact: - The no: of microorganism destroyed by chlorine per unit time is inversely proportional to the no of microorganisms remaining alive. So the rate is maximum to start with & it goes on decreasing with time.

2. Temp of water: - The rate of reaction with enzymes increases with temp. So death rate of microorganisms by chlorine increases with raising water temp.

pH of water: - Lower pH values (5 -6.5) are required for killing of some percentage of microorganisms.

Advantages	Disadvantages
1. It is most effective &economical.	1. Excess of chlorine used for purification produces unpleasant odor and taste.
2. It requires very little place for storage.	2. Excess produces irritation on mucous membrane.
3. It is stable & doesn't deteriorate on keeping.	3. The quantity of free chlorine in treated water shouldn't exceed 0.1 to 0.2 PPM
4. It can be used at low and also high temp.	4. It is less effective at higher pH values.
5. It doesn't introduce salt impurities in treated water.	
6. It is most ideal des infect ant	

Chloramines ($ClNH_2$):- when chlorine and NH_3 are mixed in ratio 2:1 by volume chloramines will be formed.

$$Cl_2 + NH_3 \rightarrow ClNH_2 + HCl$$

It is better bactericidal than chlorine alone. Now- a- days chloramines are used to disinfection of water because its excess doesn't produce any irritating odor. More over it gives good taste to treated water.

OZONIZATION:-

Treatment of water by ozone is called ozonization. Ozone is an excellent disinfectant, which is produced by passing silent electric discharge through cold& dry oxygen.

$$3O_2 \xrightarrow{S.E.D} 2O_3 \text{ (ozone)}$$

Ozone is highly unstable and break down liberates nascent oxygen which is powerful oxidizing agent & kills all the bacteria as well as oxidizes the organic matter present in water.

$$O_3 \longrightarrow O_2 + (O)$$

Ionization is carried out by ozone in ozoniser. For des infection of H_2O, ozone is injected into water & the two are allowed to come in contact in a sterilized tank .the disinfected water is removed from the top. The contact period is about 10 – 15 min &usual dose strength is 2 -3 PPM.

Advantages	Disadvantages
1. It simultaneously removes color, odor and taste without giving any residue. 2. Its excess is not harmful since it is unstable and decomposes in to oxygen.	1. This method is quite expensive hence not employed for disinfection of municipal water supply.

WATER FOR INDUSTRIAL USES

Water for steam generation:-

Water is used for making steam. Such water should be free from dissolved salts, gases, suspended impurities, oils & silica etc…Usually boilers are used for of steam generation. The boilers are heated with fuels such as coal. The steam generated rotates the blades of turbines fast to produce electricity. This electricity produced by making use of water in boiler. The turbine is a magnet wounded by coil wire.

BOILER TROUBLES:-

If hard water is used in boilers the following problems arise

1. Priming and foaming
2. Boiler corrosion
3. Formation of scales and sludges
4. Caustic embrittlement

(I)Priming & foaming or Carry over: - The process of formation of wet steam is called as priming or carries over. The steam carrying water droplets is called as wet steam.

(A) PRIMING: The phenomenon of steam production along with water droplets by rapid boiling of water is nothing but priming.

Reasons:-

1. Very high steam velocity.
2. Sudden boiling.
3. Improper boiler design.
4. High water levels.
5. Presence of large amounts of dissolved salts.

Prevention:-

1. Maintaining low water levels
2. Using softened water
3. Fitting mechanical steam purifiers.
4. Using well designed boiler

(B) Foaming: - The production of persistent bubbles or foam in boiler water surface is called foaming.

Reasons: -

1. The presence of oily or soapy substances.
2. Certain dissolved salts.

Prevention:-

1. It can be avoided by adding anti-foaming agents like cotton seed oil & castor oil
2. By adding $NaAlO_2$ which coagulates oily or soapy substances.

(II) Boiler corrosion: - The decay of boiler material by chemical or electro chemical attack by its environment is called boiler corrosion.

Reasons: -

1. Due to presence of dissolved O_2
2. Dissolved CO_2
3. Acids from f dissolved salts.

Dissolved O_2:- At room temperature one liter water consists eight mg of dissolved O_2. It attacks boiler material causing rust formation.

$$2Fe + 2H_2O + O_2 \longrightarrow 2Fe(OH)_2$$

$$4Fe(OH)_2 + O_2 \longrightarrow 2(Fe_2O_3.2H_2O)$$

Removal: - Dissolved oxygen is eliminated by adding calculated quantity of sodium sulphate and sodium sulphide or hydrazene.

$$Na_2S + 2O_2 \longrightarrow Na_2SO_4$$

$$2Na_2SO_3 + O_2 \longrightarrow Na_2SO_4$$

$$NH_2\text{-}NH_2 + O_2 \longrightarrow N_2 + 2H_2O$$

Among these the hydrazene method is ideal method for removal of dissolved oxygen. The liberated in not harmful to boilers.

2. Dissolved CO_2:- It gives carbonic acid with water. This carbonic acid has corrosive effect on boiler material.

$$H_2O + CO_2 \longrightarrow H_2CO_3$$

Carbon dioxide is also produced from decomposition of bi carbonate salts usually present in water.

$$Mg(HCO_3)_2 \longrightarrow MgCO_3 + H_2O + CO_2$$

Removal: - It is removed from water by adding calculated quantity of NH_3 in the form of NH_4OH to produce ammonium carbonate.

$$2NH_4OH + CO_2 \longrightarrow (NH_4)_2CO_3 + H_2O$$

3. Acids from dissolved Salts: Acids that are produced from dissolved salts are also mainly responsible forcorrosion. Certain salts like magnesium chloride, calcium chloride etc...produce acids by their hydrolysis.

$$Mg\,Cl_2 + 2H_2O \longrightarrow Mg\,(OH)_2 + 2HCl$$

The liberated HCl reacts with Fe produces HCL again and finally leads to formation of rust. $2HCl + Fe \longrightarrow FeCl_2 + H_2\uparrow$

Removal: - It can be removed by neutralizing acids with alkali.

$$HCl + NaOH \longrightarrow NaCl + H_2O$$

(iii) Scales & Sludge's: - In boilers, water evaporates continuously and the concentration of dissolved salts increase progressively. When their concentration reach saturation point they are thrown out of water in the form of precipitates on the surface or inner walls of boilers. The precipitation takes place in two ways.

1. Scales
2. Sludge's

1. Sludge's: - 1. Sludge's are soft, loose, slimy non – stick precipitates produced due to higher conc. of dissolved salts.

2. It can eerily be scrapped off by wire brush.

Reason: - Sludge's are formed by substances which have greater solubility in hot water than in cold water.

Eg; $MgCl_2$, $Mg\,(CO_3)_2$, $Mg\,SO_4$, $CaCl_2$ etc.

Disadvantages: -

1. Sludge's are bad conductors of heat, hence it wastes portion of heat generated.

2. Excessive sludge formation reduces the efficiency of boiler.

3. It settles in the region of poor circulation areas such as pipe connection, plug opening, gauze glass connection leading to checking of the pipes.

Prevention: -

1. By using well softened water.

2. Frequently carried out blow down operations (removal of conc. water from the bottom of boiler).

2. Scales: -

1. Scales are hard, sticky deposits formed on inner walls of boiler.

2. The main source of boiler troubles are scales and are very difficult to remove once they are deposited on the inner walls of boiler.

Reason: - A. Decomposition of $Ca(HCO_3)_2$:- Due to high temperature & pressure present in boilers, the $Ca(HCO_3)_2$ salt decomposes to $CaCO_3$, an insoluble salt forms scale in low pressure boilers but $CaCO_3$ is soluble in high pressure boilers.

$$Ca(HCO_3)_2 \longrightarrow CaCO_3 + H_2O + CO_2$$

B. Decomposition of $CaSO_4$:- The solubility of $CaSO_4$ decreases with raise of temperature. The solubility of $CaSO_4$ is 3200PPM at 15^{0}C. It reduces to 27 PPM at 320^{0} C. $CaSO_4$ is soluble in cold water, but it is insoluble in super heated water. $CaSO_4$ precipitates as hard scale on the heated portion of boiler & difficult to remove.

C. Hydrolysis of Mg salts: - Dissolved Mg salts under go hydrolysis at high temperature forming $Mg(OH)_2$ppts which forms soft scale.

$$MgCl_2 + 2H_2O \longrightarrow Mg(OH)_2 + 2\,HCl$$

D. Presence of silica: - SiO_2 present even in small quantities deposits as Ca/Mg silicate. The deposits forms hard scale and it is very difficult to remove.

DISADVANTAGES:-

1. Wastage of fuel.
2. Decrease in efficiency.
3. Low boiler safety & danger of explosion (at high temp. cracks may be formed on boilers scale leading to explosion).
4. Scales are bad conductor of heat.

Removal of scales:-

1. Scales are not easily removed by wire brush, scrappers or wiped piece.
2. Scale can be removed by thermal shocks (sudden heating and cooling).
3. Using certain chemicals to removal of scales
    a. 5-10% of HCl - used to removal of $CaCO_3$ scales.
    b. EDTA- removal of $CaSO_4$ scales.
    c. i) MgO - removal of silica
4. By adding of anti –coagulants (removal of silica scales)

IV. CAUSTIC EMBRITTLEMENT: - It is at type of corrosion produced by caustic alkalinity (NaOH). Usually water consists of Na_2CO_3 which is hydrolyzed to alkali at high temp.

$$Na_2CO_3 + H_2O \longrightarrow 2NaOH + CO_2$$

The $NaHCO_3$ present in water produce Na_2CO_3 which in turn give NaOH. This NaOH passes in to the small cracks or stress areas on the boiler by capillary action and attacks the surrounding area and dissolves the Fe of boilers as sodium ferroate.

$$Fe + 2NaOH \longrightarrow Na_2(FeO_2) + H_2$$

This causes embrittlement of boiler parts particularly at joints, bends, pipes etc.

DISSADVANTAGE:- Failure of boiler.

PREVENTION:-

1. Neutralizing the alkali with very small quantity of acid.
2. By adding sodium phosphate as softening agent to water.
3. By adding sodium sulphate, lignin to boiler water which blocks hair cracks.

WATER TREATMENT

Water treatment is used for prevention of scales & softening of water. They are two types.

1. Internal treatment used to remove scales
2. External treatment for softening water.

I. Internal treatment: - The following internal conditioning methods are used prevention ofscales.

1. Colloidal conditioning: - When certain chemicals like tannin , agar - agar , kerosene are added to water, these substances coat the outer surfaces of crystalline ppts, and thus

, $CaCl_2$, $MgSO_4$.

forms colloidal non – sticky, sludge like ppt which can be easily removed by mechanical methods like blow – down operation.

2. Carbonate conditioning: - In low pressure boilers scale formation can be avoided by treating boiler water with Na_2CO_3 . The scale forming salts like $CaSO_4$ are partially converted to $CaCO_3$ (loose sludge) , which can be removed by blow down operation .

$$CaSO_4 + Na_2CO_3 \longrightarrow CaCO_3 + Na_2SO_4$$

3. Phosphate conditioning:- In high pressure boilers Na_2Po_4 reacts with water forms loose ppt .when can be easily removed by blow down operation .

$$3CaCl_2 + 2\,Na_3\,PO_4 \longrightarrow Ca_3\,(PO_4)_2 + 6NaCl$$

4. Calgon conditioning: - Na $[Na_4\ (PO_3)]_6$ [calgon] is added to boiler scales forms soluble complex with $CaSO_4$.

$$2CaSO_4 + Na_2\,[Na_4\,(PO_3)_6] \longrightarrow Na_2\,[Ca_2\,(PO_3)_6] + 2Na_2\,SO_4.$$

5.$NaAlO_2$ conditioning: - In water sodium aluminate gives aluminum hydroxide & NaOH . This NaOH reacts with magnesium salts to form $Mg(OH)_2$ ppt. This hydroxide interacts with finely divided particles and neutralizes the charge on colloidal particles and forms loose, soft ppt. removed by blow down operation.

$$NaAlO_2 + 2\,H_2O \longrightarrow NaOH + Al\,(OH)_3$$

$$2NaOH + MgCl_2 \longrightarrow Mg\,(OH)_2 + 2NaCl$$

II. External treatment: - This is used for softening of water. The removal of hardness causing salts from water is nothing but softening of water. The most important method for softening is ion exchange process.

Ion – exchange process / demineralization / deionization:-

Ion exchange resins are used for softening of water. Resins are insoluble, cross linked, long chain, organic polymers with a micro- porous structure, and their functional groups are attached to the chains responsible for the ion –exchanging properties. These Resins are two types.

1. Cation exchanger 2. Anion exchanger

1. Cation exchanger (RH^+):

These resins contain acidic functional groups ($COOH/SO_3H$). These are capable of exchanging their H+ ions with cations of the dissolved salts which comes in their contact. They are represented by the general formula RH^+.

R—Structure of the resin,

H^+-- exchangeable with cation.

Usually they are styrene divinyl benzene copolymers.

2. Anion exchanger (ROH^-):

Styrene divinyl benzene (or) amino formaldehyde (or) phenol formaldehyde copolymers which contain amino or quaternary ammonium or quaternary phosphate or ternary sulphonium groups as an internal part of the resin matrix. These resins exchange their OH^- ions with any anion present in the dissolved salts. These are represented by the formula ROH^-.

R— general structure of resin,

OH^--- exchangeable with anion.

Process: - In demineralization_plant the first chamber is filled with cation exchange resin and second one is with anion exchange resin.

Step 1:- When hard water is passed through bed of caution exchange resin, it exchanges H^+ ions with Ca^{+2}, Mg^{2+}, Na^+ of hard water

$$2RH^+ + Mg^{2+} \longrightarrow R_2Mg^{2+} + 2H^+$$

$$2RH^+ + Ca^{2+} \longrightarrow R_2Ca^{2+} + 2H^+$$

Thus hardness producing cations are removed.

Step2:- Then the water is passed through anion exchange resin, it exchanges anions like Cl^-, HCO_3^-;So_4^{2-} which enter from 1st chamber to 2nd.

$$R^1OH^- + Cl^- \longrightarrow R^1\,Cl^- + OH^-$$

$$R^1\,OH^- + HCO_3 \longrightarrow R^1\,HCO_3^- + OH^-$$

$$2R^1OH^- + SO_4^{-2} \longrightarrow R^1_2SO_4^{-2} + 2OH^-$$

Thus hardness causing anions are removed.

Step 3 :- The H^+ ions that are produced from 1st chamber combine with OH^- ions produced from 2nd chamber to form water.

$$H^+ + OH^- \longrightarrow H_2o$$

Hence the water produced from ion exchange process is completely free from all cations & anions of hard water.

Regeneration of resins: - After deionization of certain amounts of water, the cationic and anionic exchangers will be exhausted. Hence they are employed to regeneration for further uses.

1. The exhausted cationic exchange resin can be regenerated by passing dil.HCl.

$$R_2Mg^{2+} + 2HCl \longrightarrow 2RH^+ + MgCl_2$$

$$R_2Ca^{2+} + 2HCl \longrightarrow 2RH^+ + Ca2Cl$$

2. The exhausted anionic exchange resin can be regenerated bypassing dil. NaOH.

$$R^1Cl^- + NaOH \longrightarrow R^1\,OH^- + NaCl$$

$$R^1HCO_3^- + NaOH \longrightarrow R^1OH^- + NaHCO_3$$

$$R^1\,SO_4^{2-} + 2\,NaOH \longrightarrow 2R^1OH^- + Na_2SO_4$$

Advantages	Disadvantages
1. Highly acidic or alkaline water can be treated by this method. 2. It produces very low hardness nearly 2ppm. 3. the softened water is completely free from salts and fit for use in boilers.	1. This equipment is costly. 2. More expensive chemicals are required for regeneration. 3. Turbid water cannot be treated by this method.

Zeolite or Permutit Process:

Zeolite is hydrated sodium alumino silicate. Its general formula is

$$Na_2O.Al_2O_3.xSiO_2.yH_2O.$$

Here x= 2-10 y=2-6

Eg: Natrolite: $Na_2O.Al_2O_3.3SiO_2.2H_2O$.

Natural zeolite are generally non porous. The artificial zeolite is called Permutit. They are prepared by heating together with china clay; feldspar and soda ash .These are porous and have greater softening capacity than natural zeolite. They exchange Na^+ ions with the hardness producing ions (Ca^{+2}, Mg^{+2} etc.,) in water. Sodium zeolite is denoted as Na_2Ze.

Process:

In this process hard water is passed through a bed of zeolite at ordinary temperature.

The hard water percolates Ca^{+2} and Mg^{+2} present in hard water are exchanged with Na^+ ions.

$$Ca\,(HCO_3)_2 + Na_2Ze \text{ ------> } CaZe + 2NaHCO_3$$

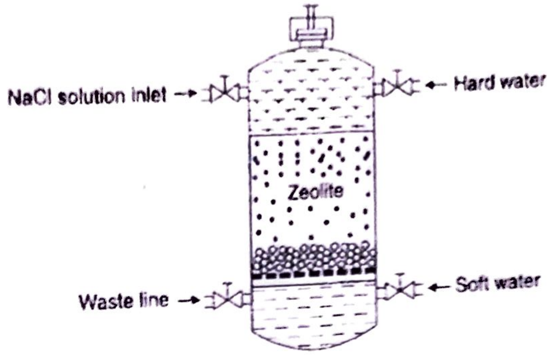
$$Mg\,(HCO_3)_2 + Na_2Ze \text{ ------> } MgZe + 2NaHCO_3$$

$$CaSO_4 + Na_2Ze \text{ ----- > } CaZe + Na_2SO_4$$

$$CaCl_2 + Na_2Ze \text{ ------> } CaZe + CaCl_2$$

$$MgSO_4 + Na_2Ze \text{ ------> } MgZe + Na_2SO_4$$

$MgCl_2 + Na_2Ze$ ------> $MgZe + 2NaCl$



Regeneration:

After Some time the zeolite is completely converted into calcium and magnesium Zeolite and it ceases to soften water i.e.: it gets exhausted. At this stage the supply of hard water is stopped and the exhausted zeolite is reclaimed by treating the bed with a 10% NaCl solution.

$$CaZe + 2NaCl \rightarrow Na_2Ze + CaCl_2$$

$$MgZe + 2NaCl \rightarrow Na_2Ze + MgCl_2$$

The washings are led to drain and the regenerated zeolite bed thus obtained is used again for softening process.

Advantages:

i. The equipment is small and easy to handle.
ii. It requires less time for softening.
iii. Water obtained from this process contains a residual hardness up to 10ppm.
iv. Easy to regenerate.
v. No sludge is formed in this process.

DEMINERATISATION /DESALINATION OF BRACKISH WATER: - (BY REVERSE OSMOSIS)

Reverse osmosis is used for desalination of sea water .The process of removal of salts from sea water is nothing but desalination. Sea water contains an average of about 3.5% of salts. This water is totally unfit for drinking and other domestic uses.

A semi permeable membrane is used for desalination which is made of cellulose acetate, polymethacrylate , polyamide polymers which don't allow dissolved solute particles, molecules, salts, ions etc., By osmosis solvent flow from low concentration to high concentration at constant pressure. However an excess of osmotic pressure is applied to sea water, so that the solvent flow in reverse direction i.e solvent is forced to move from

and + energy

high conc. to low conc. across the membrane. This means semi permeable membrane doesn't allow dissolved salts of sea water through it. This process is called reverse osmosis &this membrane filtration is called super/hyper filtration.

Advantages: -

1. It is used for removal of ionic, non-ionic, colloidal, high molecular weight organic matter.
2. Removes colloidal silica which is not removed by ion exchange process.
3. The life span of semi permeable membrane is about 2 years.
4. The membrane can be replaced with in few minutes.
5. This method is a simple, economical, & highly reliable.

Electro dialysis:

- This is one of the efficient methods used for the Desalination of water.
- The Process of decreasing the concentration of salts in saline water using ion selective membranes under the influence if a direct current is called "Electro-Dialysis"
- It is based on ion migration towards oppositely charged electrodes by passing direct current using ion selective permeable membrane.
- The cation membranes are permeable to only cations and anion membranes are permeable to only anions.
- This process gives pure water by decreasing salt concentration.

Working:

- Electro dialysis cell consists of a series of alternative cation permeable membrane(C) and anion permeable membrane (A).
- Cation and anion permeable membranes are forms as compartments i.e., CA and AC.
- Two electrodes are immersed in saline water to apply electric field.
- Saline water is passed under pressure of about 5-6Kg m^{-2} between membrane pairs and electric field is applied across the two electrodes.
- The Positive ions moves through 'C' while anions moves through 'A' from each compartment of 'CA'.

This is expressed in terms of **specific ratio.**

- The salt content in Compartment 'CA' is decreases and increase salt concentration in 'AC' compartments.
- The fresh water is collected from Compartment 'CA' and concentrated brine from 'AC' is discharged.

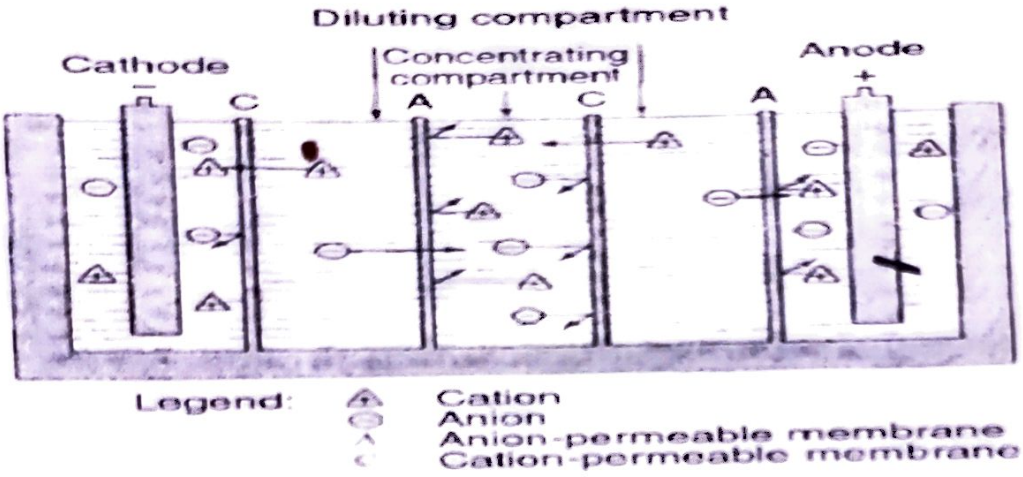


Fig: Electro-dialysis Cell