

UNIT-1 WATER

Water Technology: Introduction, sources of water, types of impurities in water, hardness of water - temporary and permanent hardness, units of hardness, disadvantages of hard water. Estimation of hardness by EDTA method, boiler troubles.

Softening methods: Internal treatment, external treatment; zeolite process, ion exchange process, desalination of brackish water - reverse osmosis.

Introduction:

Water is nature's most wonderful, abundant and useful compound. Without food, human can survive for a number of days, but water is such an essential that without it one cannot survive. Water is not only essential for the lives of animals and plants, but also occupies a unique position in industries. Probably, its most important use as an engineering material is in the steam generation. Water is also used as coolant in power and chemical plants.

Water is widely distributed in nature. It has been estimated that about 75% matter on the earth's surface consists of water. Besides visible water on earth, there is large amount of water under earth to an average depth of over three kilometres. The air consists 12 to 15% of volume of water vapour. Water is found in living things. The body of human being consists of about 60% of water. Plants, fruits and vegetables contain 90 to 95% of water.

Sources of water:

(A) Surface water (B) Underground water

Surface water:

1. Rain water:

It is the purest form of natural water, since it is obtained as a result of evaporation from the surface water. However, during the journey downwards, through the atmosphere, it dissolves a considerable amount of gases like CO₂, SO₂, NO₂, etc. and suspended solid particles.

2. River water:

In general, the greater the contact that water has with the soil, or the more soluble the minerals of the soils with which it has come in contact, the greater is the amount of dissolved impurities in river water. River water thus contains dissolved minerals of the soil such as chlorides, sulphates, bicarbonates of calcium, magnesium and iron. River water also contains the organic matter, derived from the decomposition of plants, and small particles of sand and rock in suspension. Thus, river water contains considerable amounts of dissolved as well as suspended impurities.

3. Lake water:

It has a more constant composition. It, usually, contains much lesser amounts of dissolved minerals than even well water, but quality of organic matter present in it is quite high.

4. Sea water:

It is the most impure form of natural water. It contains, on an average, about 3.5% of dissolved salts, out of which about 2.6% is sodium chloride. Other salts present are sulphate of sodium; bicarbonates of potassium, magnesium and calcium etc.

Surface water, generally, contains suspended matter, which often contains the disease producing bacteria. Hence, such water is not considered to be safe for human consumption.

Underground water:

A part of the rain water, which reaches the surface of the earth, percolates into the earth. As this water journeys downwards, it comes in contact with a number of mineral salts present in the soil and dissolves some of them. Water continues its downwards journey, till it meets a hard rock, when it retreats upwards and it may even come out in the form of *spring or well*. In general, it is clear in appearance due to the filtering action of the soil, but contains more of the dissolved salts. Thus, water from these sources contains more hardness. Usually, underground water is of high organic purity.

Types of impurities in water:

Natural water is, usually contaminated three types of impurities.

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

Physical impurities:

- (a) **Colour:** Colour in water is usually caused by *metallic substances* like salts of iron, manganese, peat, industrial effluents. Usually, yellowish tinge indicates the presence of chromium and appreciable amount of organic matter. Yellowish red colour indicates the presence of iron; while red-brown colour indicates the presence of peaty matter.
- (b) **Turbidity:** It is due to the colloidal, extremely fine suspension such as clay, silt, finely divided matter etc. Turbidity expresses the optical properties of water, which scatter light rather than to transmit in straight lines. Turbidity in water can be eliminated by sedimentation, followed by coagulation, filtration, etc.
- (c) **Taste:**
- Bitter taste can be due to the presence of iron, aluminium, manganese sulphate or excess of lime.
 - Soapy taste can be due to the presence of large amount of sodium bicarbonate.
 - Brackish taste is due to the presence of unusual amount of salts.
 - Palatable taste is due to the presence of dissolved gases like CO₂.
- (d) **Odour:**
The causes of odour in polluted rivers are;
- Presence of inorganic and organic compounds of N, S and P and the putrefaction of proteins and other organic materials present in sewage;
 - Industrial effluents containing organic substances such as alcohols, aldehydes, phenols etc. flowing into the water bodies.

Chemical impurities:

(a) **Acidity:**

Surface water and ground water attain acidity from industrial wastes like acid, mine, drainage, pickling liquors, etc. Usually, acidity is caused by the presence of free CO₂, mineral acids (H₂SO₄) and weakly dissociated acids. Mineral acids are released when iron and aluminium salts hydrolyse.

(b) **Gases:**

- All natural waters contain dissolved atmosphere CO₂. Its solubility depends upon temperature, pressure and dissolved mineral content of water.
- Concentration of dissolved atmosphere O₂ in water depends on temperature, pressure and salt content in water. Dissolved O₂ in industrial water is a nuisance, since it induces corrosion reactions. On the other hand, dissolved O₂ in water is essential to the life of aquatic organisms such as fishes.

- Dissolved NH₃ in water arises from the decomposition of nitrogenous organic matter. Polluted water and sewage contains nitrogen in the form of nitrogenous organic compounds and urea, which are partially converted into NH₃.

(c) Mineral matter:

It has origin from rocks and industrial effluents. These include Ca²⁺, Mg²⁺, Na⁺, K⁺, Fe²⁺, CO₃⁻², Mn²⁺, HCO⁻³, Cl⁻, SO⁻², etc. However, from industrial point of view, alkalinity and hardness are important.

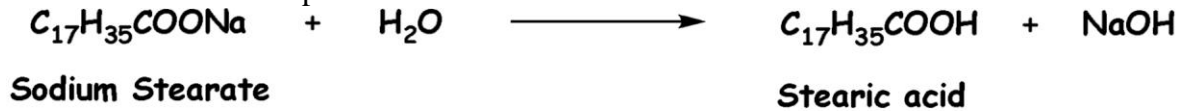
Biological impurities:

These are algae, pathogenic bacteria, fungi, viruses, pathogens, parasite worms etc. The source of these contamination is discharge of domestic and sewage wastes, excreta, etc. Micro-organisms are, usually, abundant in surface water, but their count is often quite low or even nil in deep-well waters. The common type of micro-organisms from the point of treatment are algae, fungi and bacteria, which often form slime, thereby causing fouling as well as corrosion. The slime so-formed clogs the spray nozzles and screens of the circulating pumps in air-conditioning and other industrial plants. The growth of micro-organisms takes place at temperature in between 20 to 35°C. In order to control the micro-organisms, chemical treatment like chlorination is done.

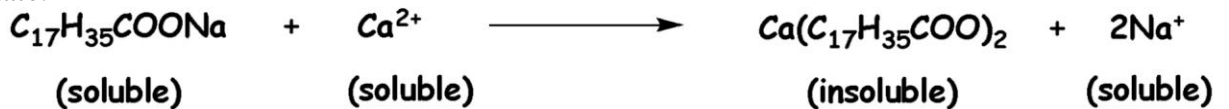
Hardness of water:

The water which does not produce lather with soap is called hard water. Thus, hardness in water is the characteristic, which “prevents the lathering of soap”. On the other hand, the water which produce lather easily on shaking with soap solution, is called soft water.

The hardness of water is caused by the presence of dissolved salts such as bicarbonates, sulphates, chlorides and nitrates of divalent metal ions like calcium and magnesium. Soap is sodium or potassium salt of higher fatty acids like stearic, oleic and palmitic acids. When soap is mixed with soft water lather is produced due to stearic acid and sodium stearate.



When soap comes in contact with hard water, sodium stearate will react with dissolved calcium and magnesium salts and produce calcium stearate or magnesium stearate which is white precipitate.



The different types of water are commercially classified on the basis of degree of hardness as follows;

Hardness	Name of water
0-70 mg/L	Soft water
70-150 mg/L	Moderate hard water
150-300 mg/L	Hard water
>300	Very hard water

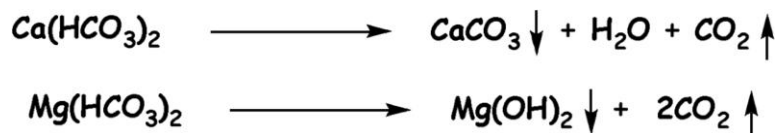
Types of Hardness:

The hardness of water is two types;

1. Temporary hardness.
2. Permanent hardness.

1. **Temporary hardness** or Carbonate hardness:

This hardness is caused by two dissolved bicarbonate salts $\text{Ca}(\text{HCO}_3)_2$ and $\text{Mg}(\text{HCO}_3)_2$. The hardness is called temporary because, it can be removed easily by boiling. During boiling, bicarbonates are decomposed to yield insoluble carbonates or hydroxides, which are deposited as a crust at the bottom of vessel.



2. **Permanent hardness** or non-carbonate hardness:

This hardness is due to the dissolved chlorides, sulphates and nitrates of calcium and magnesium. These salts are CaCl_2 , MgCl_2 , CaSO_4 , MgSO_4 , $\text{Ca}(\text{NO}_3)_2$, $\text{Mg}(\text{NO}_3)_2$. It cannot be removed easily by boiling. Hence, it is called permanent hardness. Only chemical treatment can remove this hardness.

$$\text{Total Hardness} = \text{Temporary hardness} + \text{Permanent hardness}$$

Expression of hardness:

Hardness of water is expressed in terms of calcium carbonate equivalents. The weights of different salts causing hardness are converted to weights equivalent to that of CaCO_3 .

If a sample of water contains two or more than two salts, their quantities are converted in equivalent to CaCO_3 as mentioned above and then the sum will give the total hardness. CaCO_3 was selected for expression of the degree of hardness because;

1. The Molecular Weight of CaCO_3 is 100, which is easy for calculation.
2. It is an insoluble salt, and all the dissolved salts of calcium are precipitated as CaCO_3 .

Hardness causing salt	Molecular weight
$\text{Ca}(\text{HCO}_3)_2$	162
$\text{Mg}(\text{HCO}_3)_2$	146
CaSO_4	136

CaCl ₂	111
MgSO ₄	120
MgCl ₂	95
Ca(NO ₃) ₂	164
Mg(NO ₃) ₂	148

Thus, 120 parts by weight of MgSO₄ would react with the same amount of soap as 100 parts by weight of CaCO₃. Hence, weight in terms of CaCO₃ would be equal to weight of MgSO₄ in water multiplied by 100/120.

The method of calculating hardness will be clear from the following formula.

Hardness of hardness causing salt in terms of CaCO₃

$$= \frac{\text{Amount of the hardness causing salt} \times 100}{\text{Molecular weight of hardness causing salt}}$$

Units of hardness:

There are five units in which the hardness of water is expressed.

1. Parts per million.
2. Milligrams per litre.
3. Degree Clark.
4. Degree French.
5. meq per litre.

1. Parts per million (ppm):

It is the parts of calcium carbonate equivalent hardness per 10⁶ parts of water.

i.e. 1 ppm = 1 part of CaCO₃ eq hardness in 10⁶ parts of water.

2. Milligrams per litre (mg/L):

It is the number of milligrams of calcium carbonate equivalent hardness present per litre of water.

Thus,

1 mg/L = 1 mg of CaCO₃ eq hardness per 1 L of water

But 1 L water = 1 kg = 1000g = 10⁶ mg

1 mg/L = 1 mg of CaCO₃ eq per 10⁶ mg of water

= 1 part of CaCO₃ eq per 10⁶ parts of water = 1 ppm

3. Degree Clark (°Cl):

It is the number of grains of CaCO₃ equivalent hardness per gallon of water. (or) It is the parts CaCO₃ equivalent hardness per 70,000 parts of water.

1°Cl = 1 grain of CaCO₃ eq hardness per gallon of water

1°Cl = 1 part of CaCO₃ eq hardness per 70,000 parts of water

4. Degree French (°Fr):

It is the parts of calcium carbonate equivalent hardness per 10⁵ parts of water.

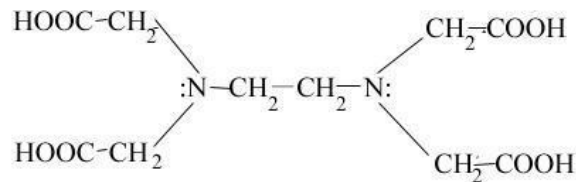
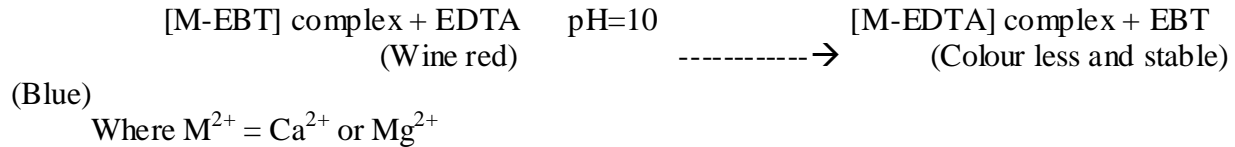
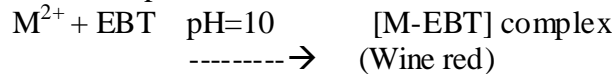
i.e. 1°Fr = 1 part of CaCO₃ eq hardness in 10⁵ parts of water.

Relationship between various units of hardness:

1ppm = 1 mg/L = 0.1 °Fr = 0.07 °Cl = 0.02 meq/L

Estimation of hardness by EDTA method:

EDTA forms a colourless stable complex with Ca^{2+} and Mg^{2+} ions in water at pH 10. Ammonia buffer is used to maintain the pH. In this method EBT (Eriochrome Black-T) is used as an indicator. Initially EBT forms an unstable complex with Ca^{2+} and Mg^{2+} ions, giving wine red colour to the solution. During the titration EDTA reacts with this complex (Ca-EBT or Mg-EBT complex), forms a stable complex (Ca-EDTA or Mg-EDTA) and releases the blue EBT into the solution. Hence the end point is wine red to blue colour.



structure of EDTA

Various steps involved in this method are;

1. Preparation of standard hard water (1 mg of CaCO_3 per 1 mL of water).

2. Standardization of EDTA solutions:

Pipette out 50 mL of standard hard water in a conical flask. Add 10-15 mL of buffer solution and 4 to 5 drops EBT indicator. Titrate with EDTA solution, till wine red colour changes to clear blue. Let volume used be V_1 mL.

3. Titration of unknown hard water:

Titrate 50 mL of water sample just as indicated above. Let the volume used be V_2 mL.

4. Titration for permanent hardness:

Take 250 mL of the water sample in a large beaker. Boil it, till the volume is reduced to about 50 mL. Filter, wash the precipitate with distilled water, and collect the filtrate and washings in a 250 mL measuring flask. Finally, make up the volume to 250 mL with distilled water. Then, titrate 50 mL of boiled water sample just as in step (2). Let the volume of EDTA used be V_3 mL.

Calculations:

50 mL of standard hard water = V_1 mL of EDTA

50 mg of CaCO_3 = V_1 mL of EDTA

1 mL of EDTA = $50/V_1$ mg of CaCO_3

Now 50 mL of given hard water = V_2 mL of EDTA

$= \frac{V_2 \times 50}{V_1}$ X mg of CaCO_3

V_1

$$1 \text{ L (1000mL) of given hard water} \\ = 1000V_2/V_1 \text{ mg of CaCO}_3 \text{ eq}$$

$$\text{Total hardness of water} = 1000V_2/V_1 \text{ mg/L} = 1000V_2/V_1 \text{ ppm}$$

$$\text{Now 50 mL of boiled water} = \frac{V_3 * 50}{V_1} \text{ mg of CaCO}_3$$

$$1 \text{ L of given hard water} = 1000V_3/V_1 \text{ mg of CaCO}_3 \text{ eq}$$

$$\text{Permanent hardness} = 1000V_3/V_1 \text{ mg/L} = 1000V_3/V_1 \text{ ppm}$$

$$\text{And Temporary hardness} = \text{Total hardness} - \text{permanent hardness}$$

$$\text{Temporary hardness} = \frac{1000(V_2 - V_3)}{V_1} \text{ ppm}$$

Disadvantages of hard water:

1. In domestic use. 2. In industrial use. 3. In steam generation.

1. In domestic use:

(a) Washing:

Hard water, when used for washing purpose, does not lather freely with soap. On the other hand, it produces sticky precipitates of calcium and magnesium. This causes a wastage of lot of soap being used. Also presence of iron salts may cause stains on cloth.

(b) Bathing:

Hard water, does not lather freely with soap, but produces sticky scum on the bathtub and body. Thus, the cleaning quality of soap depressed and a lot of it wasted.

(c) Cooking:

Due to the presence of dissolved hardness causing salts, the boiling point of water is elevated. Consequently, more fuel and time are required for cooking. Certain foods do not cook soft in hard water. Also, tea or coffee, prepared in hard water has an unpleasant taste and muddy-looking extract.

(d) Drinking:

Hard water causes bad effect on our digestive system. Moreover, the possibility of forming calcium oxalate crystals in urinary tracks is increased.

2. In Industrial use:

(a) Textile industry: Hard water causes much of the soap to go as waste. Moreover, precipitates of calcium and magnesium soaps adhere to the fabrics. These fabrics, when died later on, do not produce exact shades of colour. Iron and manganese salts-containing water may cause coloured spots on fabrics, thereby spoiling their beauty.

(b) Sugar industry: Water containing sulphates, nitrates, alkali carbonates, etc., if used in sugar refining, it causes difficulties in the crystallization of sugar. Moreover, the sugar so-produced may be deliquescent.

(c) Concrete making: Water containing chlorides and sulphates, if used for concrete making, affects the hydration of cement and the final strength of the hardened concrete.

(d) Pharmaceutical industry: Hard water, if used for preparing pharmaceutical product like drugs, injections and ointments etc. may produce certain undesirable products in them.

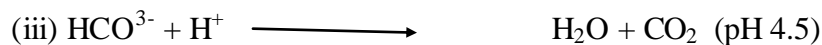
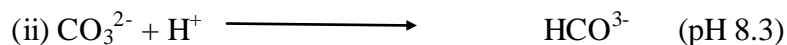
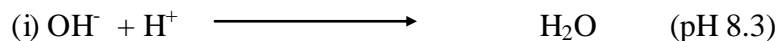
3. In steam generation:

For steam generation, boilers are almost invariably employed. If the hard water is fed directly to the boilers, there arise many troubles such as:

- (i) Scale and sludge formation
- (ii) corrosion
- (iii) priming and foaming
- (iv) caustic embrittlement.

DETERMINATION OF ALKALINITY OF A WATER SAMPLE

Principle: Alkalinity of water means the total content of those substances in it which causes an increased OH^- ion concentration up on dissociation or due to hydrolysis. The alkalinity of water is attributed to the presence of (i) Caustic alkalinity (Due to OH^- and CO_3^{2-}) (ii) Temporary hardness (Due to HCO_3^{2-}) Alkalinity is a measure of ability of water to neutralize the acids Determination of alkalinity OH^- , CO_3^{2-} and HCO_3^{2-} can be estimated separately by titration against standard acid using phenolphthalein and methyl orange as indicators The determination is based on the following reactions



The titration of water sample against a standard acid up to phenolphthalein end point (P) marks the completion of reaction (i) and (ii) only. This amount of acid used thus corresponds to OH^- plus one half of the normal CO_3^{2-} present On the other hand, titration of the water sample against a standard acid to methyl orange end point (M) marks the completion of reaction (i), (ii) and (iii). Hence the total amount of acid used represents the total alkalinity.

$$\text{Thus,} \quad P = \text{OH}^- + \frac{1}{2} \text{CO}_3^{2-}$$

$$M = \text{OH}^- + \text{CO}_3^{2-} + \text{HCO}_3^-$$

Procedure: Part A: phenolphthalein alkalinity

1. Pipette out 20 ml of water sample into a conical flask. Add 1-2 drops of Phenolphthalein indicator.
2. Rinse and fill the burette with N/10 HCl
3. Titrate the water sample in conical flask with N/10 HCl till the pink colour just disappears.
4. Note down the reading and repeat to get concordant readings.
5. Calculate phenolphthalein alkalinity by using formula given below

$$\text{Phenolphthalein alkalinity} = \frac{V_1 \times \text{normality of acid} \times 50 \times 1000}{20}$$

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Part B: Total alkalinity (Methyl orange)

1. Take 20 ml of water sample in conical flask and add methyl orange indicator to it.
2. Titrate the water sample in conical flask with N/10 HCl taken in the burette till the yellow orange colour changes to orange red.
3. Note down the reading and repeat to get concordant readings.
4. Calculate total alkalinity by using formula given below.

$$\text{Total alkalinity} = \frac{V_2 \times \text{normality of acid} \times 50 \times 1000}{V_1}$$

DETERMINATION OF ACIDITY OF A WATER SAMPLE:

Principle: The mineral acids present in the sample which are contributing mineral acidity can be calculated by titrating with strong base NaOH at PH 4.3. The CO₂ and Bi carbonates present and contribute CO₂ Acidity in the sample can be neutralized completely by continuing the titration up to PH 8.2

Interference: Colour turbidity, iron, aluminium or Manganese and residual chlorine are Prime sources of interference, colour and turbidity can be avoided using Potentiometric titrations. Residual chlorine can be removed by adding Sodium thiosulphate iron aluminium and manganese is prevented by the addition of NaOH burette.

Procedure:

1. Take 100 ml of given sample in an Erlenmeyer flask
2. Add one drop of 0.1N Na₂S₂O₃ solution to remove the residual chlorine if present
3. Add 2 drops of methyl orange. The sample turns Orange
4. Proceed the titration until colour changes to yellow
5. Note down the volume of NaOH added (V₁)
6. Take another conical flask containing 100 ml water sample, add 2 drops of Phenolphthalein
7. Proceed the titration until the sample turns Pink.
8. Note down the total volume of NaOH added.

Environmental Significance :

1. Acidity Interferes in the treatment of water
2. It corrodes Pipes (zinc coating of G.I pipes got dissolved)
3. Aquatic life will be affected.
4. PH is critical factor for bi-Chemical reaction. the favourable PH is 6.8 to 7.5.
5. Water contains mineral acidity more than 50 mg/l cannot be used in R.C.C works.

Application of Acidity data in Environmental Engineering Practice:-

1. The amount of CO₂ Present is an Important factor in determining whether removed by aeration or simple neutralization with lime or Sodium hydroxide will be chosen as the treatment method.
2. The size of equipment, chemical requirement storage space and cost of treatment all depend upon amount CO₂ Present.

3. CO₂ is an important consideration in estimating chemical requirements for lime or lime soda ash softening process.

4. Most industrial wastes containing mineral acidity must be eutralized be for they are subjected to biological treatment or direct discharge into water course or sewers quantities of chemicals size of chemical feeders storage space and costs are determined from the laboratory data of acidity.

CALCULATION:

$$\text{Mineral Acidity due to mineral acids} = \frac{V_1 \times \text{normality of acid} \times 50 \times 1000}{100}$$

$$\text{CO}_2 \text{ Acidity due to CO}_2 = \frac{V_2 \times \text{normality of acid} \times 50 \times 1000}{100}$$

Determination of the Chloride content in water

Procedure:

Transfer 100ml of water sample into a clean conical flask. Add about 1 ml of K₂CrO₄ indicator solution & titrate against standard (say 0.02N) AgNO₃ solution until a reddish brown color persists in the white precipitate. Record the volume of AgNO₃ consumed (Let 'a' cm³). Perform a blank titration taking 100 ml of distilled water. The volume of AgNO₃ consumed Let 'b' cm³.

Calculation:

$$\text{Volume of AgNO}_3 \text{ required for chlorine estimation} = (a-b) \text{ cm}^3 = V \text{ 1000ml of } 1 \text{ N AgNO}_3 = 35.45\text{g/Cl}$$

$$\begin{aligned} 1 \text{ ml of } 1\text{N AgNO}_3 &= 0.03545\text{g/Cl} \\ V \text{ ml of } 0.02 \text{ N AgNO}_3 &= 0.03545 \times V \times 0.02 \text{ g/Cl} \\ \text{Cl content in the sample} &= \frac{0.03545 \times V \times 0.02}{100} \text{ grams /Cl} \end{aligned}$$

$$\text{Cl content in the sample} = \frac{0.03545 \times V \times 0.02 \times 1000}{100} \text{ mg/Cl}$$

TREATMENT OF WATER FOR DOMESTIC PURPOSE

The processes & technologies used to remove the contaminants from water & to improve its quality is recognized all over the world. The choice of which treatment to use from a great variety of available processes depends on the characteristics of the water, the type of the water quality problems to be present, & the costs of different treatments. There are different methods of water treatment the selection of which depends upon the type of source & purpose of use of water. Some of the methods are:

- a) Screening
- b) Plain sedimentation
- c) Sedimentation by coagulation

- d) Filtration
- e) Disinfection

The following are different steps in treatment of water.

.REMOVAL OF SUSPENDED IMPURITIES

a) Screening : The process of removing floating matter from water is known as screening . In this process, water is passed through a screen. The floating matter is arrested by the screen and the water is free from floating matter.

b) Plain sedimentation : The process of removing big sized suspended solid particles from water is called as plain sedimentation. In this process, water is stored in big tanks for several hours. 70% of solid particles settle down due to force of gravity.

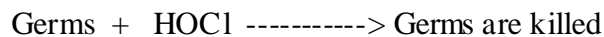
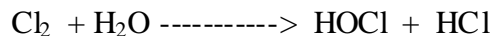
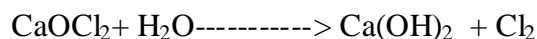
c) Sedimentation by coagulation : This is the process of removing fine suspended and colloidal impurities by adding coagulants like alum($K_2SO_4Al_2(SO_4)_3 \cdot 24 H_2O$), $FeSO_4$, $NaAlO_2$. When coagulant is added to water, floc formation takes place due to hydroxide formation which can gather tiny particles together to form bigger particles and settle down quickly.

d) Filtration: The process of passing a liquid containing suspended impurities through a suitable porous material so as to effectively removed suspended impurities and some microorganisms is called filtration. It is a mechanical process. When water flows through a filter bed, many suspended particles are unable to pass through the gaps and settle in the bed.

e) Disinfection or sterilization

The process of killing pathogenic bacteria and other microorganisms is called disinfection or sterilization. The water which is free from pathogenic bacteria and safe for drinking is called potable water. The chemicals used for killing bacteria are called disinfectants.

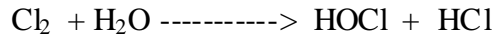
i) By adding bleaching powder: Water is mixed with required amount of bleaching powder, and the mixture is allowed to stand for several hours.



The disinfection action of bleaching powder is due to available chlorine in it. It forms hypochlorous acid which acts as a powerful germicide(disinfectant).

ii) Chlorination:

Chlorine is mixed with water in a chlorinator, which is a high tower having a number of baffle plates. Water and required quantity of concentrated chlorine solution are introduced from its top during their passage through the tower. They get thoroughly mixed and thn sterilized water is taken out from the bottom.



Germ + HOCl -----> Germ are killed

Advantages:

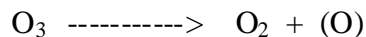
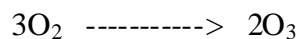
- 1) Storage requires less space
- 2) Effective and economical
- 3) Produce no salts
- 4) Ideal disinfectant

Disadvantages:

- 1) Excess of chlorine causes unpleasant taste and odour.
- 2) More effective at below pH 6.5 and less effective at higher pH values.

iii) Ozonisation:

Ozone is an excellent, disinfectant which can be prepared by passing silent electric discharge through pure and dry oxygen. Ozone is highly unstable and breaks down, liberating nascent oxygen.



Advantages :

Removes colour , odour and taste.

Disadvantages:

The method is costly

Boiler troubles:

There are four important boiler troulbers.

(1) Scale and sludge formation (2) Corrosion (3) Priming and foaming (4) Caustic embrittlement.

1. **Scale and sludge formation:**

In boilers, water evaporates continuously and the concentration of the dissolved salts increase progressively. When their concentration reach saturation point, they are thrown out of water in the form of precipitates on the inner walls of the boiler. If the precipitation takes place in the form of loose and slimy precipitate, it is called sludge

On the other hand, if the precipitated matter forms a hard adhering coating on the inner walls of the boiler, it is called *scale*.

Sludge:

It is a soft, loose and slimy precipitate formed within the boiler. Sludge can easily be scrapped off with a wire brush. It is formed at colder portions of the boiler. Sludge is formed by substances which have greater solubilities in hot water than cold water.

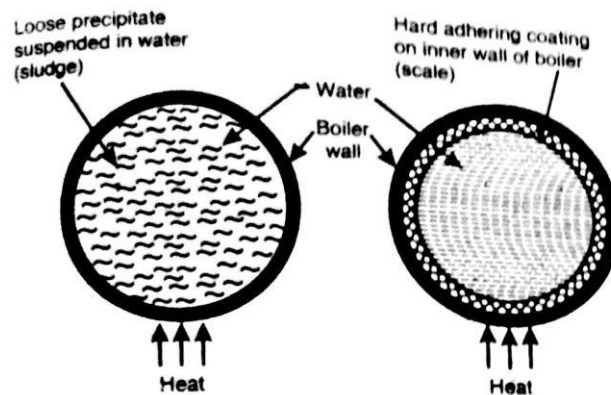
E.g. $MgCO_3$, $MgCl_2$, $CaCl_2$, $MgSO_4$, etc.

Disadvantages of sludge formation:

- Sludges are poor conductors of heat, so they tend to waste a portion of heat generated.
- If sludges are formed along with scales, then former gets entrapped in the latter and both get deposited as scales.
- Excessive sludge formation disturbs the working of the boiler. It settles in the regions of poor water circulation such as pipe connections.

Prevention of sludge formation:

- By using well softened water which is free from $MgCO_3$, $MgCl_2$, $CaCl_2$, $MgSO_4$ salts.
- By frequent "blow-down" operation, i.e. drawing off a portion of the concentrated water.

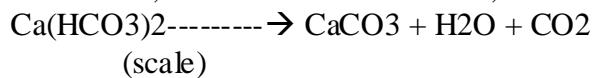


Scale:

These are hard deposits, which stick very firmly to the inner surfaces of the boiler. Scales are difficult to remove, even with the help of hammer. These are main sources of boiler troubles. Formation of scales may be due to;

(a) *Decomposition of calcium bicarbonate:*

Due to high temperature and pressure present in the boilers, the calcium bicarbonate salt decomposes in to $CaCO_3$, which is an insoluble salt, forms scale.

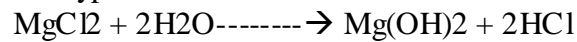


(b) *Deposition of calcium sulphate:*

The solubility of calcium sulphate in water decreases with rise of temperature. Thus, solubility of $CaSO_4$ is 3,200 ppm at 150C and it reduces to 55 ppm at 2300C and 27 ppm at 320⁰C. In other words, $CaSO_4$ is soluble in cold water, but almost completely insoluble in super-heated water. Consequently, $CaSO_4$ gets precipitated as hard scale on the heated portions of the boiler.

(c) *Hydrolysis of magnesium salts:*

Dissolved magnesium salts undergo hydrolysis to form magnesium hydroxide precipitate, which forms a soft type of scale.



(d) *Presence of silica:*

SiO₂, even present in small quantities, deposits as calcium silicate (CaSiO₃) and magnesium silicate (MgSiO₃). These deposits stick very firmly on the inner side of the boiler surface and are very difficult to remove.

Disadvantages of scales:

- (a) **Wastage of fuel:** Scales have a low thermal conductivity, so the rate of heat transfer from boiler to inside water gradually decreased. In order to provide a steady supply of heat to water, excessive or over-heating is done and this causes increase in fuel consumption. The wastage of fuel depends upon the thickness of scale.

Thickness of scale mm)	0.325	0.625	1.25	2.5	12
Wastage of fuel	10%	15%	50%	80%	150%

(b) **Lowering of boiler safety:**

Due to scale formation, over-heating of boiler is to be done in order to maintain a constant supply of steam. This over-heating of the boiler tube makes the boiler material softer and weaker and this causes distortion of boiler tube and makes the boiler unsafe to bear the pressure of the steam.

(c) **Danger of explosion:**

When thick scales crack, due to uneven expansion, the water comes suddenly in contact with overheated iron plates. This causes in formation of a large amount of steam suddenly. So sudden high pressure is developed, which even cause explosion of the boiler.

Removal of scales:

- (i) With the help of scraper or wire brush, we can remove the scales, if they are loosely adhering.
- (ii) By giving thermal shocks, we can remove the scales, if they are brittle.
- (ii) Calcium carbonate scales can be dissolved by using 5-10% HCl. Calcium sulphate scales can be dissolved by adding EDTA, with which they form soluble complexes.
- (iv) By frequent blow-down operation, if the scales are loosely adhering.

2. Boiler corrosion:

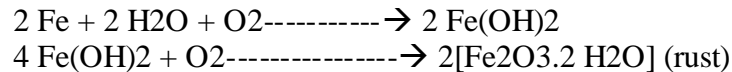
Boiler corrosion is “the decay of boiler material by a chemical or electro-chemical attack by its environment”.

Main reasons for boiler corrosion are:

- (i) Dissolved oxygen. (ii) Dissolved carbon dioxide. (iii) Acids from dissolved salts.

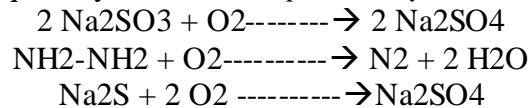
(i) Dissolved oxygen:

Water usually contains about 8 ppm of dissolved oxygen at room temperature. At high temperature this D.O. can attack boiler material.

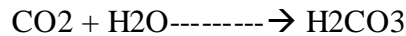


Removal of dissolved oxygen:

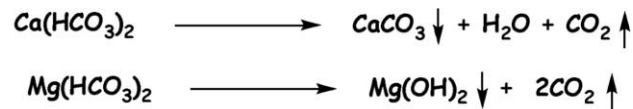
By adding calculated quantity of *sodium sulphite* or *hydrazine* or *sodium sulphide*. Thus;



(ii) Dissolved carbon dioxide:

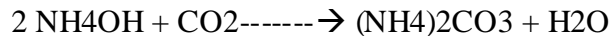


Carbon dioxide is also released inside the boiler, if water used for steam generation contains bicarbonates.



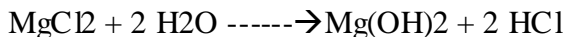
Removal of dissolved carbon dioxide:

By adding calculated quantity of ammonium hydroxide.

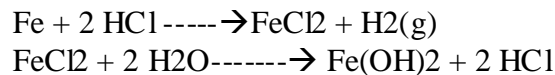


(iii) **Acids from dissolved salts:**

Water, containing dissolved magnesium salts, liberate acids on hydrolysis.



The liberated acid reacts with iron (of the boiler) in chain-like reactions, producing HCl again and again. Thus;



Consequently, presence of even a small amount of MgCl₂ will cause corrosion of iron to a large extent.

3. **Priming and foaming:**

Priming:

When a boiler is producing steam rapidly, some particles of the liquid water are carried along with the steam. This process of 'wet steam' formation, is called *Priming*.

Priming is caused by:

- (i) The presence of large amount of dissolved solids.
- (ii) High steam velocities.
- (iii) Sudden boiling.
- (iv) Improper boiler design.
- (v) Sudden increase in steam-production rate.

Priming can be avoided by:

- (i) Fitting mechanical steam purifiers.
- (ii) Avoiding rapid change in steam rate.

- (iii) Maintaining low water levels in boilers.
- (iv) Efficient softening and filtration of boiler-feed water.

Foaming:

Foaming is “the production of persistent foam or bubbles in boilers, which do not break easily”.Foaming is due to the presence of substances like oils, which greatly reduce the surface tension of water.

Foaming can be avoided by:

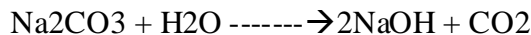
- (i) Adding anti-foaming chemicals like castor oil.
- (ii) Removing oil from boiler water by adding compounds like sodium aluminate.

Dis-advantages of priming and foaming:

- (i) Dissolved salts in boiler water are carried by the wet steam to turbine blades, where they get deposited as water evaporates. This deposit reduces their efficiency.
- (ii) Dissolved salts may enter the parts of other machinery, where steam is being used, thereby decreasing the life of the machinery.
- (iii) Actual height of the water levels cannot be judged properly, thereby making The maintenance of boiler pressure becomes difficult.

4. Caustic embrittlement:

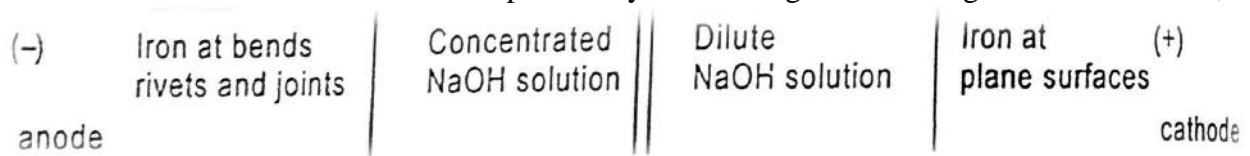
Caustic embrittlement is “a type of boiler corrosion, caused by using highly alkaline water in the boiler”.During softening process of water (in lime-soda process), free Na₂CO₃ is usually present in small proportion in the softened water. In high pressure boilers, Na₂CO₃ decomposes to give sodium hydroxide and carbon dioxide. This makes the boiler water ‘caustic’.



The NaOH containing water flows into the minute hair-cracks, present in the inner side of boiler, bycapillary action. Here water evaporates and the dissolved caustic soda (NaOH) concentration increases progressively. This caustic soda attacks the surrounding area, thereby corroding the iron of boiler as sodium ferrate.

This causes embrittlement (cracking) of boiler parts, particularly stressed parts (like bends, joints), causing even failure of the boiler.

Caustic embrittlement can be explained by considering the following concentration cell;



The iron surrounded by the dilute NaOH becomes the cathodic side; while the iron in contact with concentrated NaOH becomes anodic part, which consequently corroded.

Prevention of caustic embrittlement:

- (i) By using sodium phosphate as softening reagent, instead of sodium carbonate.
- (ii) By adding tannin or lignin to boiler water, which blocks the hair-cracks, thereby

Preventing infiltration of caustic soda solution in cracks.

- (iii) *By adding sodium sulphate to boiler water:*

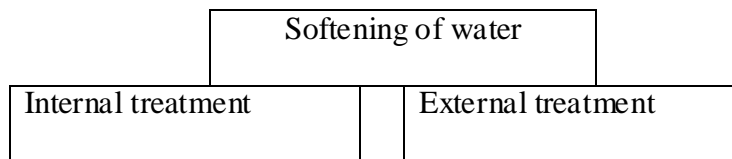
Na₂SO₄ also blocks hair-cracks, thereby preventing infiltration of caustic soda solution in these cracks. It has been observed that caustic embrittlement can be prevented, if Na₂SO₄ is added to boiler water so that the ratio:

NaOH concentration
Na₂SO₄ concentration

is kept as 1 : 1, 2 : 1 and 3 : 1 in boilers working respectively at pressures up to 10, 20 and above 20 atmospheres.

Softening methods:

Water used for industrial purpose (such as for steam generation) should be sufficiently pure. Therefore, it should be freed from hardness producing salts before put to use. *The process of removing hardness producing salts from water, is known as softening of water.* In industry, main methods employed for softening of water are two types.



Internal treatment: (Or) Conditioning of water:

The softening of water carried out inside the boiler is called internal treatment of water. In this process the hardness causing salts are removed

1. By complexing the hardness causing soluble salt by adding appropriate reagents.
2. By precipitating the scale forming impurities in the form of sludge which can be removed by blow down operation.
3. By converting the scale forming salts into other compounds which stay in 'dissolved form' and do not cause any trouble to the boilers.

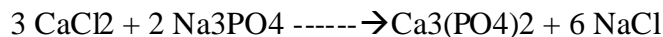
The important internal conditioning methods are;

(a) Colloidal conditioning:

The scale formation in low pressure boilers can be prevented by the addition of kerosene, tannin, agaragar etc. which will be get coated over the scale forming precipitates. These forms loose, non-sticky deposits (sludge) that can be removed by blow down. This type of conditioning is called colloidal conditioning.

(b) Phosphate conditioning:

In this process, the permanent hardness causing salts in high pressure boilers will be removed by reacting with sodium phosphate. The complex formed is soft, non-adherent and easily removable.

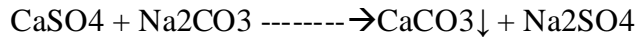


The three phosphates employed in this process are

- Na₃PO₄ – tri-sodium phosphate (alkaline),
- Na₂HPO₄ – disodium hydrogen phosphate (weakly alkaline) and
- NaH₂PO₄ – sodium di-hydrogen phosphate (acidic).

(c) Carbonate conditioning:

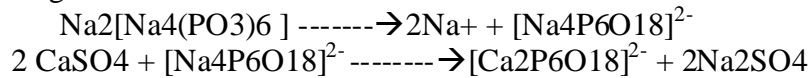
The hard and strong adherent scales formed due to CaSO₄ are avoided by the addition of sodium carbonate to boiler water and this is called carbonate condition.



The CaSO₄ is converted to CaCO₃, which is loose sludge and it can be removed by blow down.

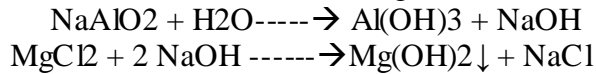
(d) Calgon conditioning:

Sodium hexameta phosphate **Na₂[Na₄(PO₃)₆ or (NaPO₃)₆** is called calgon. This forms soluble complex compounds with CaSO₄. The treatment of boiler water with calgon is called calgon conditioning.



(e) Treatment with sodium aluminate (NaAlO₂):

Sodium aluminate is hydrolysed in boiler to give NaOH. The formed NaOH immediately precipitates by the reaction with some of the magnesium salts as Mg(OH)₂



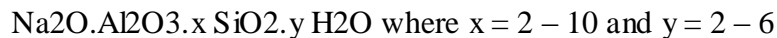
External treatment:

The treatment given to water for the removal of hardness causing salts before it is taken into the boiler is called ‘external treatment’.

External treatment

Zeolite process (Or) Permutit process:

Zeolite is hydrated sodium alumina silicate, which is capable of exchanging reversibly its sodium ions for hardness-producing ions in water. Chemical formula of sodium zeolite may be represented as;



Zeolites are two types;

(i) *Natural zeolites:*

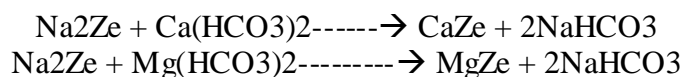
These are non-porous. Eg: Natrolite Na₂O.Al₂O₃.4 SiO₂.2 H₂O

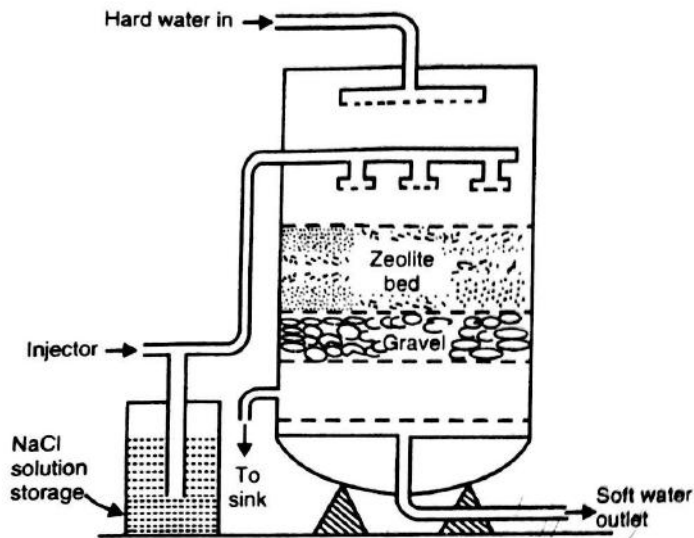
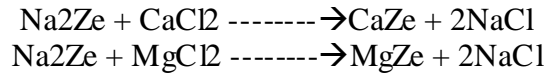
(ii) *Synthetic zeolites:*

These are porous and prepared by heating together china clay, feldspar and soda ash. Such zeolites possess higher exchange capacity per unit weight than natural zeolites.

Process:

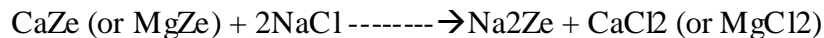
For softening of water by zeolite process, hard water is percolated at a specified rate through a bed of zeolite, kept in a cylinder. The hardness causing ions (Ca²⁺, Mg²⁺) are retained by the zeolite as CaZe and MgZe; while the outgoing water contains sodium salts. Reactions taking place during the softening process are;





Regeneration:

After some time, the zeolite is completely converted into calcium and magnesium zeolites and it ceases to soften water, i.e. it gets exhausted. At this stage, the supply of water is stopped and the exhausted zeolite is reclaimed by treating the bed with brine solution (10% NaCl solution).



The washings (containing CaCl_2 and MgCl_2) are led to drain and the regenerated zeolite bed thus obtained is used again for softening purpose.

Limitations of Zeolite process:

- (1) If the supplied water is turbid, the suspended matter must be removed, before the water is admitted to the zeolite bed; otherwise the turbidity will clog the pores of zeolite bed, thereby making it inactive.
- (2) If water contains large quantities of coloured ions such as Mn^{2+} and Fe^{2+} , they must be removed first, because these ions produce manganese and iron zeolites, which cannot be easily regenerated.
- (3) Mineral acids, if present in water, destroy the zeolite bed and, therefore, they must be neutralised with soda, before admitting the water to the zeolite softening plant.

Advantages of zeolite process:

- (1) It removes the hardness almost completely, and water of about 10 ppm hardness is produced.
- (2) The equipment used is compact, occupying a small space.
- (3) No impurities are precipitated, so there is no danger of sludge formation in the treated water at a large scale.
- (4) The process automatically adjusts itself for variation in hardness of incoming water.
- (5) It requires less time for softening.

Disadvantages of zeolite process:

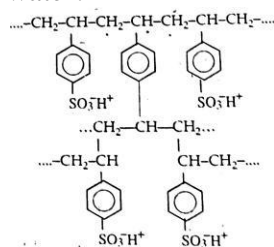
- (1) The treated water contains more sodium salts than in lime-soda process.
- (2) The method only replaces Ca^{2+} and Mg^{2+} ions by Na^{+} ions, but leaves all the acidic ions (HCO_3^- and CO_3^{2-}) as such in the softened water. When such softened water (containing NaHCO_3 and Na_2CO_3) is used in boilers for steam generation, sodium bicarbonate decomposes producing CO_2 , which causes corrosion; and sodium carbonate undergoes hydrolysis to sodium hydroxide, which causes caustic embrittlement.
- (3) High turbidity water cannot be treated efficiently by this method, because fine impurities get deposited on the zeolite bed, thereby creating problem for its working.

Ion exchange process (or) de-ionisation (or) de-mineralization process:

Ion exchange resins are insoluble, cross-linked, long chain organic polymers with a micro porous structure, and the 'functional groups' attached to the chains are responsible for the ion-exchange properties. Resins containing acidic functional groups ($-\text{COOH}$, $-\text{SO}_3\text{H}$) are capable of exchanging their H^+ ions with other cations, which comes in their contact. Resins containing basic functional groups (amino groups) are capable of exchanging their anions with other anions, which comes in their contact. Thus, ion-exchange resins may be classified as follows;

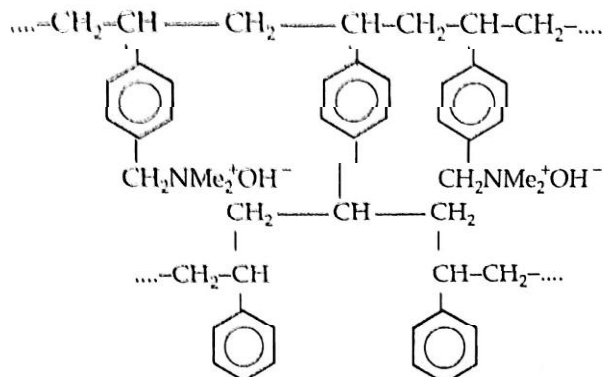
(i) Cation exchange resins (RH^+):

These are mainly styrene-divinyl benzene copolymers, which on sulphonation or carboxylation, become capable to exchange their hydrogen ions with the cations in their water.



(ii) Anion exchange resins ($\text{R}'\text{OH}^-$):

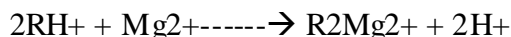
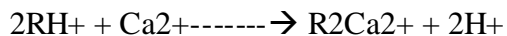
These are styrene-divinyl benzene or amineformaldehyde copolymers, which contain amino or quaternary ammonium or quaternary phosphonium or tertiary sulphonium groups as an integral part of resin matrix. These, after treatment with dil. NaOH solution, become capable to exchange their OH^- anions with anions in water.



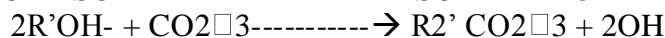
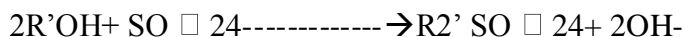
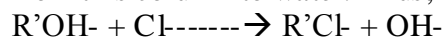


Process:

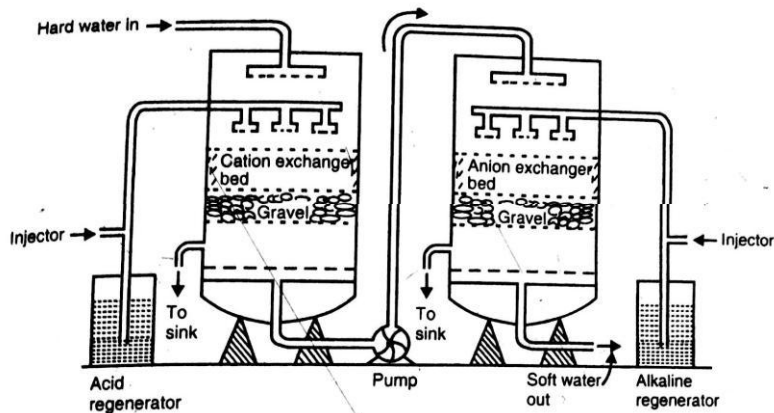
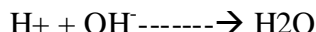
The hard water is passed first through cation exchange column, which removes the cations like Ca^{2+} and Mg^{2+} etc from it, and equivalent amount of H^+ ions are released from the column to water. Thus;



After cation exchange column, the hard water is passed through anion exchange column, which removes all the anions like SO_4^{2-} , Cl^- , CO_3^{2-} etc. present in the water and equivalent amount of OH^- ions are replaced from this column to water. Thus;



H^+ and OH^- ions (released from cation exchange and anion exchange columns respectively) get combined to produce water molecule.

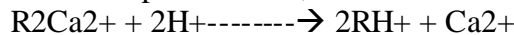


Thus, the water coming out from the exchanger is free from cations as well as anions. Ion-free water is known as deionised or demineralised water.

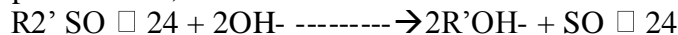
Regeneration:

When capacities of cation and anion exchangers to exchange H^+ and OH^- ions respectively are lost, they are then said to be exhausted.

The exhausted cation exchange column is regenerated by passing a solution of dil. HCl or dil. H_2SO_4 . The regeneration can be represented as;



The exhausted anion exchange column is regenerated by passing a solution of dil. NaOH . The regeneration can be represented as;



The regenerated ion exchange resins are then used again.

Advantages of ion-exchange process:

1. The process can be used to soften highly acidic or alkaline waters.

2. It produces water of very low hardness (about 2 ppm). So it is very good for treating Water used in high – pressure boilers.

Disadvantages:

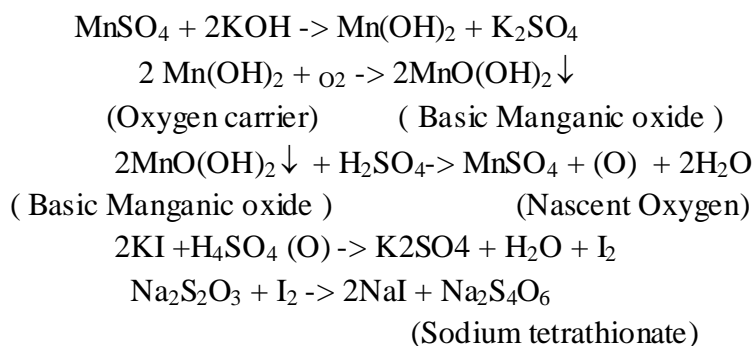
1. The equipment is costly and more expensive chemicals are needed.
2. If water contains turbidity, then the output of the process is reduced. The turbidity must Be below 10 ppm. If it is more, it has to be removed first by coagulation and filtration.

ESTIMATION OF DISSOLVED OXYGEN:

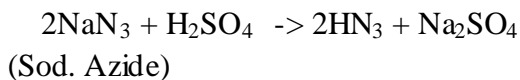
The amount of oxygen present in the water in dissolved state is called dissolved oxygen

PRINCIPLE:

Dissolved oxygen can be determined by iodometric titrations. The dissolved oxygen present in water oxidizes KI liberating an equivalent amount of Iodine, which is titrated against standard hypo solution using starch as an indicator. An oxygen carrier like manganese hydroxide must be used to bring about the reaction between KI and dissolved oxygen because molecular oxygen in water is not capable of reacting with KI.



The nitrates present in water interfere with the estimation of dissolved oxygen of water, since these ions liberate iodine KI . Sodium azide is added to water which reacts with nitrate to decompose it as follows.



PROCEDURE:

STEP:I PREPARATION OF STANDARD POTASSIUM DICHROMATE:

- Weigh out accurately the given pure crystalline sample of potassium dichromate and transfer into 100 ml standard (volumetric) flask provided with a funnel.
- Dissolve the dichromate in a small quantity of distilled water, and make up to the mark.
- The contents in the flask are shaken well for uniform concentration. Calculate the normality of potassium dichromate.

STEP:II STANDARDIZATION OF SODIUM THIOSULPHATE:

- Rinse the burette and fill it up with hypo solution without any air bubbles. Note the burette reading.
- Take about 20 ml of 10% KI solution in a clean conical flask and add 2 grams of sodium bicarbonate followed by 5 ml of concentrate HCl gently rotate the flask for mixing the liquids.
- Rinse the pipette with a little of potassium dichromate solution and then transfer 20 ml of the same to the conical flask. Shake it well, stopper it, and keep it in dark place for 5 minutes.
- Titrate the liberated iodine by running down hypo from the burette with constant stirring. When the solution attains a pale yellow colour add 2 ml of freshly prepared starch solution.
- The colour changes to blue. Continue the titration drop-wise till the colour changes from blue to light green indicating the end point. Repeat the titration for concurrent values.

STEP: III ESTIMATION OF DISSOLVED OXYGEN:

- Collect water sample in 300 ml capacity of BOD bottle and add 2 ml of manganese sulphate solution.
 - To this add 2 ml of alkali-iodine–azide solution.
 - Stopper the BOD bottle immediately.
 - Appearance of brown precipitate indicates the presence of dissolved oxygen.
 - Mixed well by inverting the bottle 2-3 times and allow the brown precipitate settle down.
 - Add 2 ml of Conc H₂SO₄ to dissolve the precipitate
 - Take 20 ml of the above solution in to a clean conical flask.
 - Titrate the liberated iodine with standard hypo solution present in burette.
 - Add 1 ml of starch solution when the color of the solution becomes blue color.
 - Note the volume of the Hypo solution(v ml) repeat the titration till concurrent readings are obtained.
 - Calculate the amount of dissolved oxygen present in water sample by using the formulae given below
 -
- Dissolved oxygen in the given sample = $V \times \text{Conc. of Hypo} \times 8 \times 1000 / 20$ PPM

Desalination of brackish water:

The process of removing common salt (sodium chloride) from water, is known as *desalination*. The water containing dissolved salts with a peculiar salty (or brackish) taste, is called *brackish water*. Sea water, containing on an average about 3.5% salts, comes under this category. Brackish water is totally unfit for drinking purpose.

Commonly used methods for the desalination of brackish water are;

1. Electro dialysis (out of syllabus).
2. Reverse osmosis.

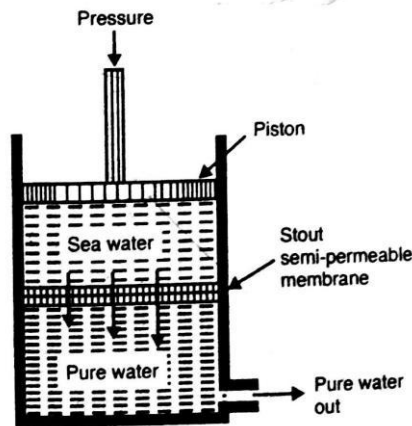
Reverse osmosis:

When two solutions of unequal concentrations are separated by a semipermeable membrane, flow of solvent takes place from dilute to concentrated sides, due to osmosis. If, however, a hydrostatic pressure in excess of osmotic pressure is applied on the concentrated side, the solvent flow reverses, i.e. solvent is forced to move from concentrated side to diluted side across the membrane. This is the principle of *reverse osmosis*. Thus, in reverse osmosis

method, pure solvent is separated from its contaminants, rather than removing contaminants from water. This membrane filtration is sometimes also called **superfiltration** or **hyper-filtration**.

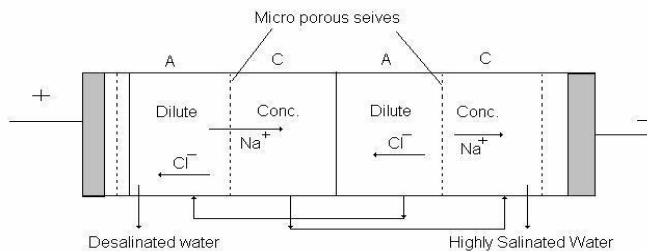
Advantages:

1. This process removes, ionic as well as non-ionic, colloidal and high molecular weight organic matter.
2. It removes colloidal silica, which is not removed by demineralization process.
3. The life time of membrane is quite high, about 2 years.
4. The membrane can be replaced within a few minutes, thereby providing nearly uninterrupted water supply.
5. Due to low cost, simplicity and high reliability, the reverse osmosis is gaining ground at present for converting sea water into drinking water.



Electrodialysis.

Principle: Passage of an electric current through a solution of salt results in migration of cations towards the cathode & anions towards the anode. The use of semi permeable cation or anion exchange membrane in an electrolytic vessel permits the passage of only cations or anions respectively in the solution. An electro dialyzer consists of a chamber carrying a series of compartments fitted with closely spaced alternate cation (C) & anion (A) exchange semi permeable membranes between the electrodes. An electro dialyzer unit will have 200 to 1000 compartments. The feed water is taken in the dialyzer & the electrodes are connected to a source of an electric current.



The anions pass through the anion permeable membrane towards the anode. However, these ions do not pass through the next membrane which is permeable only to cations. Similarly the cations moving in the other direction will pass through the cation exchange membrane but not the next. These anions & cations collect in the alternate chambers; the water in these is enriched with salt while that in the other compartments is desalinated. Micro porous sieves provided near the electrodes prevent the reentry of any deposit, which might have been formed on the electrodes, into the feed water. The enriched & desalinated waters are withdrawn separately. The former is rejected & the desalinated water is recycled to further reduce the salt content.

