

Unit – I:

Water Treatment

Introduction:

Water is the most useful, wonderful and abundant compound on earth. It is a vital component of the life forms. It is a proven theory that one can live without food for many number of days but one cannot live without water. Water is the important constituent of all the body fluids, without which all the cells or organisms are in crystalline or dead state. (For example, the human body contains 70%, land plants 50 – 75% and aquatic plants 95 – 99%).

Water is not only essential for the lives of animals and plants, but also occupies a unique position in industry.

- Water is used in power generation. As steam in steam turbines and as coolants.
- Blasting and water jet cutters. Very high pressure water guns are used for precise cutting. It is also used in the cooling of machinery to prevent over-heating, or prevent saw blades from over-heating.
- Industry requires pure water for many applications and utilizes a variety of purification techniques both in water supply and discharge.
- Water plays many critical roles within the field of food science.
- Water is widely used in the production of steel, rayon, paper, atomic energy, textiles, chemicals, ice and for air conditioning, drinking, bathing, sanitary, washing, irrigation and fire-fighting etc.

Sources of water:

The chief sources of water supply for industrial use are:

- Rain water. The purest form of water, collected on the roofs. Yet this method is seldom adopted in industry.
- Surface waters.
 - Flowing waters, such as rivers, streams etc.
 - Still waters, such as lakes, ponds etc.
- Ground water.
 - Water from springs.
 - Water from shallow wells. In the case of shallow wells, the boring is done only through one geological stratum.
 - Water from deep wells. Here the boring is done through many geological strata.
- Sea water. Its use is very limited as its uses entails very great problems of chemical engineering.

Source and nature of impurities of water:

Water in the form of vapour in clouds is said to be pure. Yet when it condenses as rain and flows on the ground it takes many impurities from atmosphere and ground. The major situations in which water gets impure are as followed:

- Dissolved gases: during raining water absorbs much of the gases like oxygen, carbon dioxide, hydrogen sulphide etc. from atmosphere. The resultant water will be slightly acidic and on high concentrations of impurities it may result into acid rain.
- Soluble crystalloids: water when flow over the surface of the land (like rivers, streams),

dissolves soluble minerals. The most of the soluble minerals include chlorides, sulphates, bicarbonates of sodium, calcium, magnesium and iron.

- Where as in seawater 3.5% of dissolved salts are seen in which 2.5% include sodium chloride.
- Organic matter: This is derived from the decomposition of plants and small particles of sand and rock in suspension.

Characteristics imparted by impurities of water:

As such pure water is odourless, colourless, tasteless, etc., but the presence of impurities imparts various physical and chemical changes to water nature which are as followed.

- Colour: The metallic substances like humus, tannins, peat, algae, weeds, protozoa, industrial effluents and salts of iron, manganese in the colloidal form imparts color to water. For example yellowish tinge is due to the presence of chromium or appreciable amount of organic matter, yellowish – red colour due to the presence of iron, while reddish brown is due to the presence of peat. (The intensity of the colour indicates the severity of toxic nature of water).
- Turbidity: The colloidal, extremely fine suspension particles such as clay, silt, finely divided matter, micro-organisms etc. increases the turbidity of the water. The turbid water is not fit for either consumption or industrial purpose.
- Taste: Usually this property is linked to odour. Yet under certain conditions taste is not accompanied by odour. For example,
 - Bitter taste can be due to the presence of iron, aluminum, 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 (CO₂) and minerals like nitrates.
- Odour: The odour may be due to the presence of living organisms, decaying vegetation. The common disagreeable odour is due to the presence of sulphides. The odour of sewage water is due to the presence of organic compounds of N, S and P along with the putrefaction of proteins and the industrial effluents like alcohols, aldehydes, phenols, esters, ketones etc. Besides these,
 - The presence of algae in water impart strong grassy odour.
 - Growth of iron and sulphur bacteria produces offensive odour.
 - Sand in finely divided state imparts faint earthy odour.
 - When water passes through iron pipes, it gives tarry odour.
 - The faint odour when the water passes through galvanized iron pipes is due to the impure hydrogen.

Hardness of water:

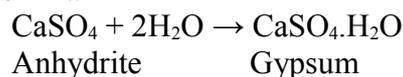
Hardness in water is the character, which “prevents the lathering of soap”. This is due to the presence of bicarbonates, chlorides and sulphates of calcium, magnesium and other heavy metals like strontium and iron.

For example:

Insoluble carbonates of Ca, Mg and Fe readily transform into soluble bicarbonates in the presence of carbon dioxide.

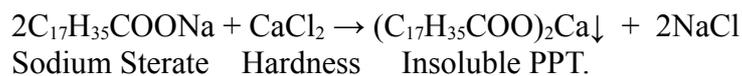


Many of the mineral constituents of rocks like NaCl, CaSO₄.H₂O readily dissolve in water and collect in it.

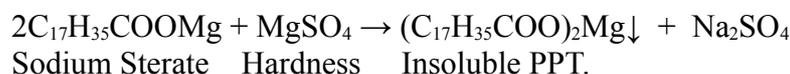
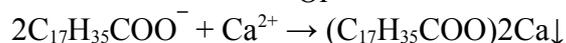


If a sample of water is treated with soap (Na/K salt of higher fatty acids like oleic, palmitic/stearic) like sodium stearate and if the water does not produce lather, then the water is said to be hard water, else soft water.

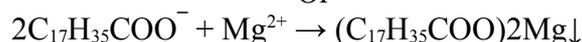
In hard water the soap produces precipitate or white scum, which is due to the formation of insoluble soap of calcium & magnesium. For example a typical soap (Sodium Stearate) reactions with salts like calcium chloride & magnesium sulphate are depicted as follows.



Or



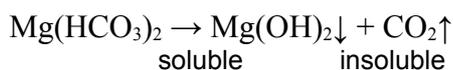
Or



Hardness of water can be classified as

- Temporary or Carbonate Hardness:

Temporary hardness of water is due to the presence of dissolved bicarbonates of calcium, magnesium and other heavy metals or carbonate of iron. It is easily destroyed by mere boiling of water. When the water is boiled, the bicarbonates are decomposed yielding insoluble carbonates or hydroxides which are deposited as a crust or scales at the bottom of the vessel, while carbon dioxide escapes out.



- Permanent or Non – Carbonate Hardness:

Permanent hardness is due to the presence of chlorides, sulphates of calcium, magnesium, iron and other heavy metals. It cannot be removed by boiling, it is removed by using softeners or chemical treatment.

Disadvantages of Hard water:

- Domestic:
 - Washing & Bathing: Hard water does not form lather easily with soap. As a result, a large amount of soap is wasted.
 - Drinking: Hard water causes bad effects on our digestive system. Sometimes, stone formation takes place in kidneys.
 - Cooking: The boiling point of water is increased due to the presence of salts. Hence, more fuel and time are required for cooking.
- Industrial:
 - Textile industry: Hard water causes wastage of soap. Precipitates of calcium and magnesium soaps adhere to the fabrics and cause problem.
 - Paper industry: Calcium and magnesium salts in water may affect the quality of paper.
 - Sugar industry: Water containing sulphates, carbonates, nitrates affects the crystallisation of sugar.
 - Dyeing industry: The salts of calcium and magnesium in hard water react with dyes and spoil the desired shade.
 - Pharmaceutical industry: Hard water may form some undesirable products while preparation of pharmaceutical products.
 - Concrete making: Chloride and sulphates present in hard water will affect the hydration of cement and the final strength of the hardened concrete.
 - Finally in industries where steam is employed, if hard water is used in steam production, the troubles like corrosion, scale & sludge formation, priming & foaming & caustic embrittlement are seen.

Expression of Concentration of Hardness:

The concentration of hardness as well as non – hardness constituting ions is expressed in terms of an equivalent amount of CaCO_3 . The equivalence of CaCO_3 is used because it permits the addition & subtraction of concentration, when required. The choice of CaCO_3 in particular is due to its molecular weight is 100 (equivalent wt. is 50). Not only that, it is the most insoluble salt that can be precipitated in the water treatment easily.

The equivalents of CaCO_3 can be defined as:

$$= \frac{\text{Mass of Hardness producing substance} \times \text{Chemical equivalent of CaCO}_3}{\text{Chemical equivalent of hardness producing substance}}$$

$$= \frac{\text{Mass of Hardness producing substance} \times 50}{\text{Chemical equivalent of hardness producing substance}}$$

or commonly

$$= \frac{\text{Weight of the salt} \times 50}{\text{Equivalent weight of the salt}} \quad \text{or} \quad = \frac{\text{Weight of the salt} \times 100}{\text{Molecular weight of the salt}}$$

in mg/L

For example, 162 parts by mass of $\text{Ca}(\text{HCO}_3)_2$ (or 2 equivalents) would react with the same amount of soap as 100 parts of mass of CaCO_3 (or 2 equivalents). i.e. The mass of $\text{Ca}(\text{HCO}_3)_2$ is multiplied by the factor 100/162 will give the weight in terms of CaCO_3 .

i.e. If a sample of water contains 40.5 mg/L then the CaCO₃ equivalent will be equal to

$$\frac{40.5}{162} \times 100 = 25 \text{ mg/L}$$

Hard salt	Molecular Weight	Equivalent Weight
Mg(HCO ₃) ₂	146	73
Ca(HCO ₃) ₂	162	81
MgCl ₂	95	47.5
MgSO ₄	120	60
CaCl ₂	111	55.5
CaSO ₄	136	68
Mg(NO ₃) ₂	148	74

Units of Expression of Hardness of Water:

Normally the hardness of water is represented in ppm. i.e. Parts per million. Or mg/L

$$1 \text{ mg/L} = 1 \text{ ppm.}$$

ppm: It is the number of parts by weight of CaCO₃ equivalent hardness present per million (10⁶) parts by water.

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

mg/L: It is the number of milligrams of calcium carbonate equivalent present per liter of water.

i.e. 1mg/L = 1 mg of CaCO₃ equivalent hardness per liter of water.

But, it is known that 1lit = 1kg = 1000 g = 1000 x 1000 mg = 10⁶mg.

==> 1 mg/L = 1 mg of CaCO₃ equivalent hardness per 10⁶ mg of water.

= 1 part of CaCO₃ equivalent hardness per 10⁶ mg of water.

= 1 ppm.

Hardness is also expressed in the following ways.

- Degree clark (°Cl): 1 °Cl = 1 part of CaCO₃ equivalent hardness per 70,000 parts of water.
i.e. 1ppm = 0.07°Cl.
- Degree French (°Fr): 1 oFr = 1 part of CaCO₃ equivalent hardness per 10⁵ parts of water.
i.e. 1Ppm =0.1 °Fr.

Analysis of Water:

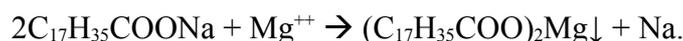
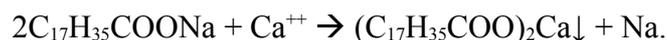
- Estimation of Hardness.
- Estimation of Dissolved oxygen.

Determination of Hardness of water:

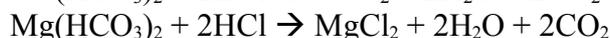
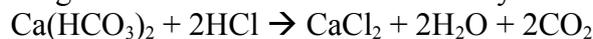
The degree of hardness of water is estimated by the following ways:

- Soap titration method.
- O.Hener's alkalimetric method.
- EDTA method.

Soap titration method: It is a simple technique. Soft water gives lather with soap where as hard water does not. The dissolved salts in the hard water react with soap and are precipitated. Thus the amount of soap initially consumed before the formation of lather is a measure of the total hardness and indirectly the dissolved magnesium and calcium salts. The hardness is easily estimated by adding a soap solution of a definite strength to a known volume of the sample of water until a permanent lather is formed on shaking. The standard solution of soap can be obtained from the market or otherwise it is prepared and then standardized in the laboratory with standard CaCl_2 solution.



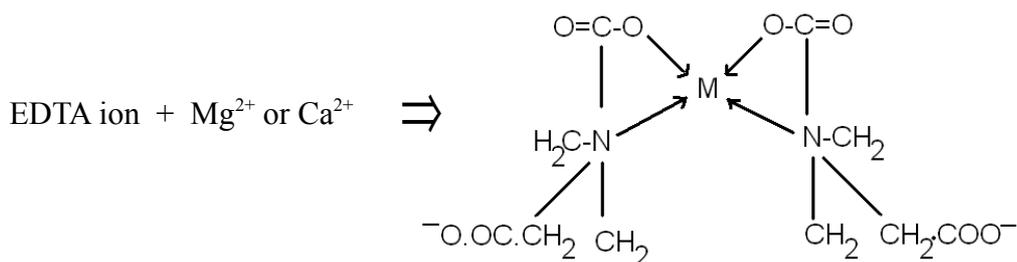
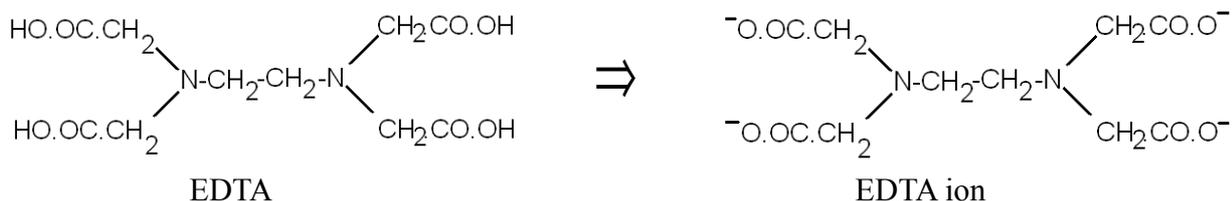
O.Hehner's alkalimetric method: Temporary hardness of water can be determined by using HCl or H_2SO_4 , as the calcium or magnesium bicarbonates react directly with dilute acids.



The water sample is titrated with dilute hydrochloric acid solution taking in a burette after adding methyl orange indicator. The change of colour from yellow to pale pink indicates the end point. From the titre value the amount of temporary hardness in terms of CaCO_3 equivalents is calculated.

Estimation of Hardness in water by EDTA :

Principle: Ethylene diamine acetic acid (EDTA) in the form of sodium salt yield the anion which forms stable complex ions with Ca^{2+} or Mg^{2+} .



filter the water into a conical flask. Wash the beaker and the filter paper twice and add the filtrate to conical flask. Make up the filtrate up to 250ml. pipette 50ml of the sample add 5ml of buffer solution. Add 2 – 3 drops of EBT indicator, the solution turns to wine red. The contents of conical flask are titrated against EDTA. The end point is achieved with the turning of wine red solution to deep blue coloured solution. The volume of EDTA rundown is noted as V_3 ml.

With the volumes of the solutions utilized are known, the hardness can be estimated by the following procedure:

Volume of standard hard water used = 50 ml.

Volume of EDTA used for Standardisation of Standard hard water = V_1 ml.

Volume of EDTA used for Standardisation of water sample = V_2 ml.

Volume of EDTA used for Standardisation of water sample subjected to boiling = V_3 ml.

Calculations:

50ml of standard hard water $\equiv V_1$ ml of EDTA consumed.

i.e. 50 x 1mg of $\text{CaCO}_3 = V_1$ ml of the EDTA consumed.

$$\Rightarrow 1\text{ml of EDTA} \equiv \frac{50}{V_1} \text{mg of CaCO}_3 \text{ eqt. hardness}$$

Now for 50ml of sample hard water given:

50ml of sample hard water $\equiv V_2$ ml of EDTA consumed.

50ml of standard hard water : V_1 ml of EDTA :: 50ml of sample water : V_2 ml of EDTA

$$\Rightarrow 1\text{ml of sample water contain } \frac{V_2 \times 50}{V_1 \times 50} \text{mg of CaCO}_3 \text{ eqt. hardness}$$

Since the hardness is estimated per 1 litre (1000 ml) the equivalent hardness will be

$$\frac{V_2 \times 50}{V_1 \times 50} \times 1000 \text{mg of CaCO}_3 \text{ equivalent} \Rightarrow \frac{1000 \times V_2}{V_1} \text{mg of CaCO}_3 \text{ equivalent}$$

$$\therefore \text{Total Hardness of water} = \frac{1000 \times V_2}{V_1} \text{mg / L or ppm}$$

Similarly 1000ml of the boiled water = 1000ml of sample water

$$\therefore \text{Permanent Hardness of water} = \frac{1000 \times V_3}{V_1} \text{mg / L or ppm}$$

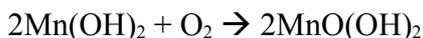
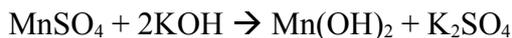
Temporary hardness = Total Hardness – Permanent Hardness

$$\Rightarrow 1000 \left[\frac{V_2}{V_1} - \frac{V_3}{V_1} \right] \Rightarrow 1000 \left[\frac{V_2 - V_3}{V_1} \right]$$

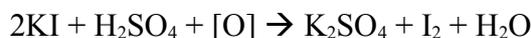
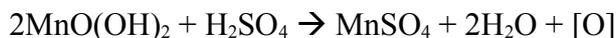
Estimation of Dissolved oxygen:

A good amount of oxygen is dissolved in water at room temperature and pressure i.e. 8 mg/L. It is essential for sustaining of aquatic life and also serves as an indicator for the extent of water pollution. Hence, determination of dissolved oxygen content is of significance both in environmental and industrial point of view. Dissolved oxygen in water is determined by Winkler's method.

Principle: The determination of dissolved oxygen is based on the "oxidation of potassium iodide by dissolved oxygen". The liberated iodine is titrated against a standard solution of sodium thiosulphate (hypo) using starch indicator. As the dissolved oxygen is non reactive with KI, the oxygen carrier Manganese hydroxide is used to bring the reaction between KI and Oxygen.



Oxygen carrier Basic manganic oxide



Sodium tetrathionate

Note: Some times, water (like rain water) contains nitrites, sulphites etc. The nitrates present in water interfere with the estimation of dissolved oxygen of water, since these ions liberate iodine from KI. Sodium azide is added to water in alkaline solution to decompose nitrates.

Preparation of standard solutions:

Standard $\text{K}_2\text{Cr}_2\text{O}_7$ solution: 0.49 g. of Pottasium di chromate is weighed accurately into clean 100ml standard flask. The content of standard flask is dissolved in little distilled water and the solution is made up to the mark by adding distilled water. The solution is shaken well for uniform concentration.

Sodium thiosulphate solution: 2.48g. of sodium thiosulphate(hypo) is weighed accurately into 1000ml standard flask. Dissolve the hypo with little water and add the distilled water up to the mark. Shake the solution well to get uniform concentration.

MnSO_4 solution: Dissolve 40 g. of MnSO_4 in 100ml of distilled water and stir the solution well.

Alkaline Iodie-Azide solution: 15g. of KI, 50 g. of NaOH and 2 g. of NaN_3 is dissolved in 100ml of distilled water in a standard flask. Stopper the flask and shake well for uniform concentration.

Starch indicator: 1g. of starch is added to little water and 100ml of boiling water is added to the contents. The contents are stirred to get colourless, colloidal solution of starch.

Experimental procedure:

Standardisation of sodium thiosulphate solution:

A burette is rinsed first and then filled with hypo solution. A 250ml conical flask / Iodine flask is taken; in to it 20ml of KI, spatula of NaHCO_3 and 5ml of Conc. HCl is added. 20ml of $\text{K}_2\text{Cr}_2\text{O}_7$ solution is pipetted out into conical flask. Stopper the flask, shake it well and keep it in the dark for 5 minutes. We will get dark red coloured solution. The contents of conical flask are titrated against hypo. The endpoint is attained with the appearance of greenish yellow colour in the conical flask. Now 1ml of starch indication is added. The solution turns into blue. Again the solution is titrated against hypo till the light green colour endpoint is obtained. The titrations are repeated to get the concurrent values. Let the titre value be x ml.

Standardisation of water sample:

The burette is rinsed and filled with hypo solution. 100 ml of water sample is taken in a 250ml iodine flask (care should be taken to avoid air bubbles) and stoppered immediately. Then add 0.2 ml of manganese sulphate with the help of pipette, dipping the end well below the water surface. Add

2m of alkaline iodide azide solution to the flask, stopper the flask and shaken thoroughly. Allow the precipitate to settle half way and mix again. Repeat the process of shaking and settling at least three times. Then add 10ml of concentrated H_2SO_4 . Stopper the flask and shake the bottle again. Keep the flask in dark for 5 minutes, and titrate the yellow coloured solution and continue the titration with hypo till the blue colour of the solution disappears. Repeat the titration to get concurrent values. Let the titer value be y ml.

Calculations:

Normality of $K_2Cr_2O_7$ (N_1) =

$$\frac{\text{wt. of } K_2Cr_2O_7 \times 1000}{M.Wt. \text{ of } K_2Cr_2O_7 \times \text{vol. of Solvent taken (ml)}} \Rightarrow \frac{\text{wt. of } K_2Cr_2O_7 \times 1000}{49 \times 100} \Rightarrow \frac{\text{wt. of } K_2Cr_2O_7 \times 10}{49}$$

Normality of Sodium thiosulphate (hypo) (N_2) = $N_1V_1 = N_2V_2$

$$\Rightarrow N_2 = \frac{N_1V_1}{V_2} = \frac{20 \times N_1}{\text{titre value with hypo (xml)}}$$

where N_1 = normality of $K_2Cr_2O_7$

V_1 = Volume of $K_2Cr_2O_7$

V_2 = Volume of hypo.

N_2 = Normality of hypo.

Normality of O_2 in water (N_3) = $N_2V_2 = N_3V_3$

$$\Rightarrow N_3 = \frac{N_2V_2}{V_3} = \frac{\text{titer value of water sample (y ml)} \times N_2}{100}$$

where N_2 = normality of hypo

V_2 = Volume of hypo (titer value with water sample (y ml)).

V_3 = Volume of the water sample.

Then the amount of dissolved oxygen in the water sample is given by: $N_3 \times 8 \times 100$ ppm

Methods of water treatment:

Water treatment for domestic purpose: The water obtained from natural sources like rivers, lakes and ponds will have impurities. Water for drinking and other domestic uses should be free from disease producing bacteria, chemicals or other substances. Hence water is treated before using for drinking or other domestic purpose.

There are mainly two stages involved in water treatment for domestic purpose:

- Removal of suspended impurities.
- Disinfection or Sterilisation.

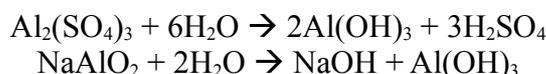
Various impurities of water are removed in the following stages:

- Screening: The process of removing floating matter from the water is known as screening. In this process, water is passed through a screen, which arrests all the floating matter.
- Aeration: The water is subjected to aeration, which helps in
 - Exchange of gases,
 - Increased oxygen content and
 - By removing the impurities like Fe & Mn by precipitating as their hydroxides.
- Plain sedimentation: This is the process of removing big sized suspended solid particles

form water. The principle involved is to slow down the flow of water so that substances held up by the turbulence of fast moving water can fall gravitationally to the bottom of the tank when water flow is stilled. In this process, the water is stored in huge tanks for several hours. 70% of solid particles settle down due to the force of gravity. Periodically the accumulation of the debris is scraped away and the floating impurities are continuously cleaned using screens (Bar screen, Band and drum screens and micro strainers etc.)

- Sedimentation by coagulation: This is the process of removal of suspended colloidal impurities by using coagulants like
 - Alum ($K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$)
 - Ferrous Sulphate ($FeSO_4$)
 - Sodium Aluminate ($NaAlO_2$)

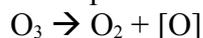
When a coagulant is added to water, floc formation takes place due to hydroxide [$Al(OH)_3$] formation which can gather tiny particles together to form bigger particles and settle down quickly.



- Filtration: This process helps in removal of the colloidal and suspended impurities not removed by sedimentation. Usually the water is passed through filters or suitable porous material so as to remove the suspended impurities and some microorganisms. Normally filters made of three layers like sand, gravel and charcoal is employed. Yet the Indian Cotton sariee four fold will work as ultra filter. (Proved by the NASA testing, reported in News papers).

Sterilisation or Disinfection: The process of killing pathogens or other microorganisms in the water is known as Sterilisation or Disinfection. The water which is free from microorganisms or other pathogens is known as potable water. Sterilisation is done in the following ways:

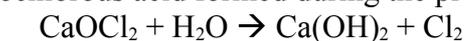
- Boiling: Boiling water for 15 – 20 minutes, will kill the bacteria in water. Yet this method is not suitable for municipal supply of water. This is adopted for domestic purpose.
- Aeration or UV treatment: Exposing water to UV rays or pumping water through nozzles in to air in broad day light will kill the germs and microorganisms in water.
- Ozonisation: Ozone passed into water acts as disinfectant. Ozone is an unstable isotope of oxygen, produces nascent oxygen which is a powerful disinfectant.



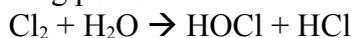
Nascent oxygen

This treatment is expensive and ozone cannot be stored for longtime due to its instability.

- Chemicals: Chemicals like chlorine tablets and bleaching powder are more commonly
- Chlorination: Chlorine is also a powerful disinfectant. The use of chlorine for disinfecting water is known as chlorination. The chlorination is done in the following ways:
 - By adding Bleaching power: Bleaching power contains 80% chlorine. When it is used as disinfectant, it is called hypo – chlorination because the disinfection is due to the formation of Hypochlorous acid formed during the process.



Bleaching powder

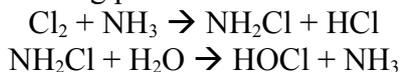


Disinfectant

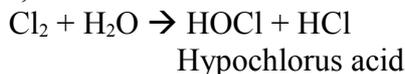


- By passing Chloramines: Chlorine mixed with ammonia in the ratio of 2:1 by

volume will produce a stable chloramine. This is a very powerful disinfectant. This is normally employed in swimming pools.



- Passing chlorine: Directly administering the chlorine gas along with water in a chlorinator will be an effective process. The passed chlorine react with water and generates hypochlorous acid, which acts as disinfectant.



Chlorine is a powerful disinfectant than chloramines and bleaching powder.

Calculated amount must be added to water because in excess will be toxic and tastes bad. The amount of chlorine required to kill bacteria and to remove organic matter is called break point of chlorination.

Water for Industrial use:

Water plays a key role in industry. Without it no industry runs. The major use is in production of steam and as a coolant. The water used for making steam should be free from dissolved salts, gases, oil, silica and suspended impurities. The steam is used in the production of electricity, as a heat source where temperature is an important criteria (like food processing plants) etc.

Boiler troubles:

If the concentration of salts is more in water that is used for boilers, the following troubles may arise:

- Carry over: Priming and foaming
- Scale and Sludge formation
- Caustic embrittlement
- Corrosion

Carry over:

The phenomenon of carrying of water by steam along with the impurities is called carry over. This is mainly due to priming and foaming. As the steam rises from the surface of the boiling water in the boiler, it may be associated with small droplets of water. Such steam, containing liquid water, is called wet steam. These droplets of water naturally carry with them some suspended and dissolved impurities present in the boiler water.

Priming:

Priming is the phenomenon of carrying out droplets of water with steam in boilers. Because of very rapid and violent boiling of water inside the boiler, the water particles mix up with steam and pass out of the boiler. This process of wet steam generation is due to the following reasons.

- Presence of large quantity of suspended organic matter, oily matter and alkalies.
- Very high steam velocity.
- Sudden boiling.
- Defective boiler design.
- High water level in boiler.
- Sudden increase in steam – production rate.

Priming can be avoided in the following ways:

- Using mechanical purifiers or purifying the water by effecting softening and filtration

process.

- Avoiding rapid change in steam rate.
- Maintaining the low water level.
- Using well designed boiler providing for proper evaporation of water with uniform heat distribution and adequate heating surfaces.
- Minimizing foaming.
- Blow down of the boiler (replacing the water concentrated with impurities with fresh water).

Foaming is the phenomenon of formation small but persistent bubbles on the surface of water inside the boiler. Foams are generally formed when there is a difference in concentration of solute or suspended matter between the surface film and the bulk of the liquid.

Causes:

- Presence of oily or soapy substances.
- Presence of dissolved impurities and suspended matter in high concentrations.

Preventive measures:

- Adding anti foaming agents like castor oil. (It should be noted that excess castor oil also produces foam and the amount of castor oil required differs from boiler to boiler)
- Use of coagulants like sodium aluminate for sedimenting the suspended oily impurities before feeding the water to boiler.
- Blow down of the boiler.

Disadvantages of Priming & Foaming: Priming and foaming causes the following boiler troubles:

- The actual height of water in the boiler can not be judged.
- Wastage of heat results in decrease of steam pressure and efficiency of boiler.
- Water concentrated with dissolved salts may deposit on the parts of the machinery, which cause corrosion.

Scale & sludge formation:

In the boiler the continuous steam production results in the concentration of the dissolved impurities. Then the salts start separating out from the solution in order of their solubility, the least soluble one separating out first. The concentrations of the solids that separate in the liquid and form soft and muddy deposits or form suspension are known as sludges. Where as some of the solids deposit on the surface form sticky and coherent deposits called scales.

The most commonest solids that separate from boiler water are the sparingly soluble calcium salts e.g. CaSO_4 , $\text{Ca}(\text{OH})_2$, CaCO_3 , $\text{Ca}_3(\text{PO}_4)_2$ and magnesium compounds.

Disadvantages of Scale formation:

1. Scale effect like an insulator coating on the metal, which results in the reduced rate of heat transfer hindering the boiler efficiency.
2. Scale formation on boiler acts as insulator for water and over heats the metal, making it soft and weak. This is unsafe for boiler at high pressures.
3. The overheating of boiler metal and rapid reaction between water and iron at high temperatures, cause additional thinning of the walls.
4. Under high pressure of steam, the metal expands and causes the cracks in the scales. Sudden entry of water through these cracks to the very hot metal causes sudden cooling of the boiler in the metal with the simultaneous conversion of water into steam. The sudden increase in

the pressure of steam may lead to explosion.

Prevention of scale formation:

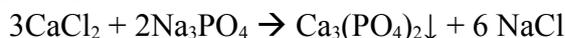
External treatment:

This involves removal of hardness causing impurities and silica before the water fed into boiler.

Internal treatment:

The internal treatment consists of adding chemicals directly to the water in the boilers for removing scales and sludges.

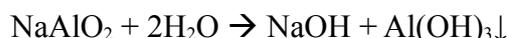
1. Colloidal conditioning: organic substances like kerosene and agar-agar are added to water which prevent the scales.
2. Phosphate conditioning: Phosphates react with water and a loose sludge is formed which can be easily removed by blow-down operation.
3. Carbonate conditioning: In low pressure boilers, scale formation can be avoided by adding sodium carbonate to the boiler water.



4. Calgon conditioning: Sodium hexa meta phosphate(calgon) is added to boiler water to prevent scale formation by formation of soluble complex.

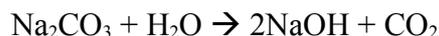


5. Sodium aluminate conditioning: Sodium aluminate gets hydrolysed yielding NaOH and aluminium hydroxide precipitate. The sodium hydroxide reacts with magnesium salts to magnesium hydroxide. These hydroxides entrap finely divided particles and neutralize the charge on colloidal particles, and the loose precipitate can be removed by the blow-down operation.



Caustic Embrittlement:

Caustic embrittlement is a form of corrosion caused by high concentration of sodium hydroxide in the boiler water. It is characterized by the formation of irregular cracks on the boiler metal, particularly at places of high local stress, such as riveted seams, bends and joints. The caustic embrittlement occurs in boilers at high pressures, where NaOH is produced in the boiler by the hydrolysis of Na_2CO_3 .



The extent of the hydrolysis increases with temperature and may reach even 90% of the carbonate present. The rate and extent of corrosion by caustic embrittlement increases with the concentration of NaOH and the temperature and hence with increasing operating pressure:

Preventing of caustic embrittlement:

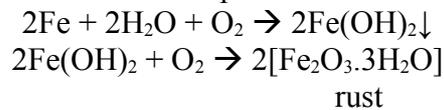
1. By using sodium phosphate as softening reagent instead of sodium carbonate. Disodium hydrogen phosphate is the best softening reagent because it not only forms complex with Ca^{2+} and Mg^{2+} resulting the softening of water but also maintains pH of water at 9-10. The other phosphates used are trisodium phosphate and sodium dihydrogen phosphate etc.
2. By adding tannin or lignin to the boiler water which block the hair cracks and pits that are present on the surface of the boiler plate thus preventing the infiltration of caustic soda solution.
3. By adding sodium sulphate to boiler water, which also blocks the hair cracks and pits present on the surface of the boiler plate, preventing the infiltration of the caustic soda solution. The amount of sodium sulphate added to boiler water should be in the ratio

$\frac{[Na_2SO_4 \text{ concentration}]}{[NaOH \text{ concentration}]}$ kept as 1:1, 2:1 and 3:1 in boilers working as pressures upto 10, 20 and above 30 atmospheres respectively.

Boiler Corrosion: The decay of boiler material by chemical or electrochemical attack of its environment is called boiler corrosion. The prime reasons of boiler corrosion are

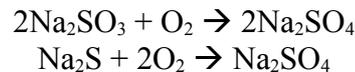
- Dissolved oxygen
- Dissolved carbon dioxide
- Acids from dissolved salts

Dissolved oxygen: Among the dissolved gases oxygen is the most corroding impurity. At room temperature water contains 8cc of oxygen per liter. The dissolved oxygen at high temperatures attacks the boiler plate creating serious corrosion problem.

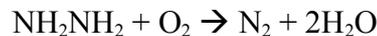


Removal of dissolved oxygen:

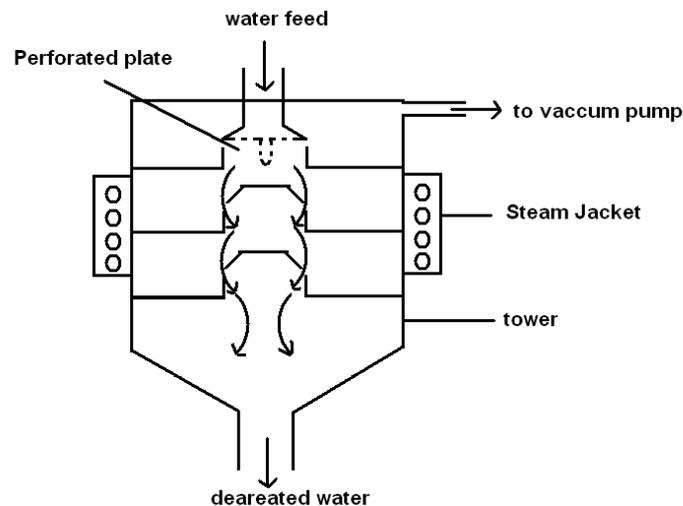
1. Addition of sodium sulphite or sodium sulphide removes O_2 by converting O_2 to sodium sulphate. (Na_2SO_3 or Na_2S should be added in very little quantity [5-10ppm] as the residual sodium sulphite may decompose to SO_2 under high pressure, which finally appear as sulphurous acid)



2. Addition of hydrazine (NH_2NH_2) is an ideal reagent added to boiler to remove dissolved oxygen as H_2O .

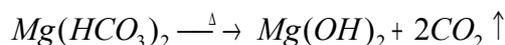


3. A polyvalent organic compound under the trade name A2 aming 8001-RD is employed to degasify water nowadays.
4. Mechanical deaeration is another method of degasification. Water is sprayed through a perforated plate, fitted in the degasification tower, heated from sides and connected to vacuum pump as shown in the figure. High temperature, low pressure and large exposed surface reduce dissolved oxygen and other gases in water.

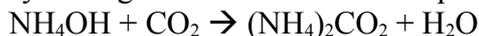


Dissolved CO₂:

Dissolved Carbon dioxide has a slow corrosive effect on the materials of boiler plate. Source of carbon dioxide into water is the boiler feed water which contains bicarbonates. Under high temperature and pressure, maintained in the boiler the bicarbonates decompose to produce CO₂.



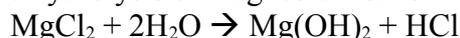
The carbon dioxide is removed by adding addition of calculated quantity of ammonia.



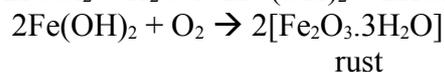
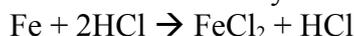
Carbon dioxide is also removed by the using mechanical deareator.

Action of Acids in boiler:

The acids are produced due to the hydrolysis of magnesium salts in the boiler.



The acids produced react with iron of the boiler and decay the metal.



Consequently even a small amount of MgCl₂ can cause corrosion to a large extent.

Preventive measures:

- Water softened before fed into boiler.
- Frequent blow – down of the boiler.
- Addition of inhibitors like Sodium silicate, sodium phosphate and sodium chromate to slow down corrosion. The inhibitors form a thin film on the surface of the boiler and protect the metal from the attack of acid.

External Water Treatment:**Softening of water:**

The process of removing hardness causing salts from water is known as softening of water.

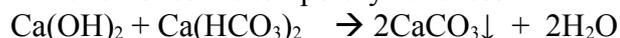
Generally water is softened by the following methods.

- Temporary hardness is removed by prolonged heating of water. The dissolved gases like O₂ and CO₂ are also removed simultaneously.
- Lime-soda treatment.
- Ion-exchange process.

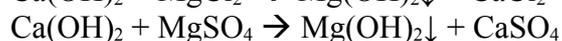
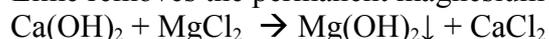
Lime-Soda Process:

This is the most important and economical treatment of water softening. The principle involved is, to chemically convert all the soluble hardness-causing substances into insoluble precipitates and latter removed by settling and filtering. A calculated amount of lime and soda along with coagulants are added to the water for softening. The reactions can be summarised as follows.

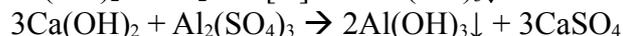
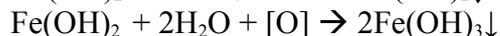
1. Lime removes the temporary hardness.



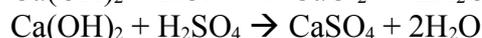
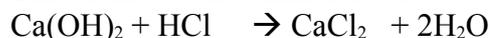
2. Lime removes the permanent magnesium hardness.



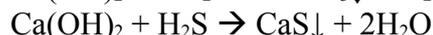
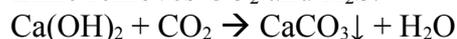
3. Lime removes dissolved iron and aluminium salts.



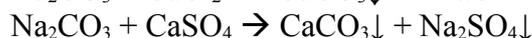
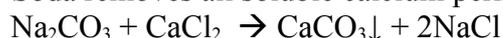
4. Lime removes free mineral acids.



5. Lime removes CO_2 and H_2S .



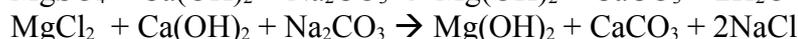
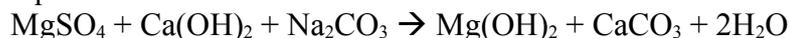
6. Soda removes all soluble calcium permanent hardness.



Calculation of Lime-Soda required for softening:

From the above said reactions it is evident that

- One equivalent of calcium temporary hardness requires one equivalent of lime. [From 1]
- One equivalent of magnesium temporary hardness requires two equivalents of lime. [From 1]
- One equivalent of calcium permanent hardness requires one equivalent of soda. [From 6]
- One equivalent of magnesium permanent hardness requires one equivalent of lime and one equivalent of soda.



- Similarly the lime required for the reactions of acids and dissolved gases should be considered with their respective equivalents. [From 4,5]
- Lime while reacting with HCl , H_2SO_4 , MgSO_4 , MgCl_2 , $\text{Mg(NO}_3)_2$, salts of Fe, Al etc. generates the corresponding quantities of calcium permanent hardness. Accordingly these constituents also should be considered while calculating soda requirements.

Impurity	Multiplicative factor
$\text{Al}_2(\text{SO}_4)_3$	3
HCl	0.5
$\text{Mg(HCO}_3)_2$	2
NaHCO_3 , KHCO_3 , NaAlO_2	0.5
NaCl , KCl , Silica, K_2SO_4 , Fe_2O_3	Not considered

- Two equivalents of HCO_3^- reacts with two equivalents of lime.



It is evident that in the above reaction, 2 equivalents of CO_3^{2-} are generated. Thus for every one equivalent of HCO_3^- present, the corresponding reduction in the dose of soda has to be made in the calculations for soda requirement.

Steps to be followed for calculating the Lime-Soda requirement:

1. The units in which the impurities are analysed should be one (ppm or mg/L or °C etc.).
2. The substances which do not contribute to hardness like KCl , NaCl , SiO_2 , Na_2SO_4 , Fe_2SO_3 , K_2SO_4 , etc. can be ignored from the calculations. This fact should be explicitly stated.
3. All the substances causing hardness should be converted into their respective CaCO_3

equivalents.

4. Lime Soda requirement is calculated as followed.

$$\left. \begin{array}{l} \text{Lime required} \\ \text{for softening} \end{array} \right\} = \frac{74}{100} \times \left\{ \begin{array}{l} \text{Temporary Calcium Hardness} + (2 \times \text{Temporary magnesium} \\ \text{hardness}) + \text{Perm.Mg.hardness} + \text{calcium carbonate equivalents of} \\ \text{CO}_2 + \text{HCl} + \text{H}_2\text{SO}_4 + \text{HCO}_3^- + \text{Salts of Fe}^{2+}, \text{Al}^{3+} \text{ etc.} \end{array} \right.$$

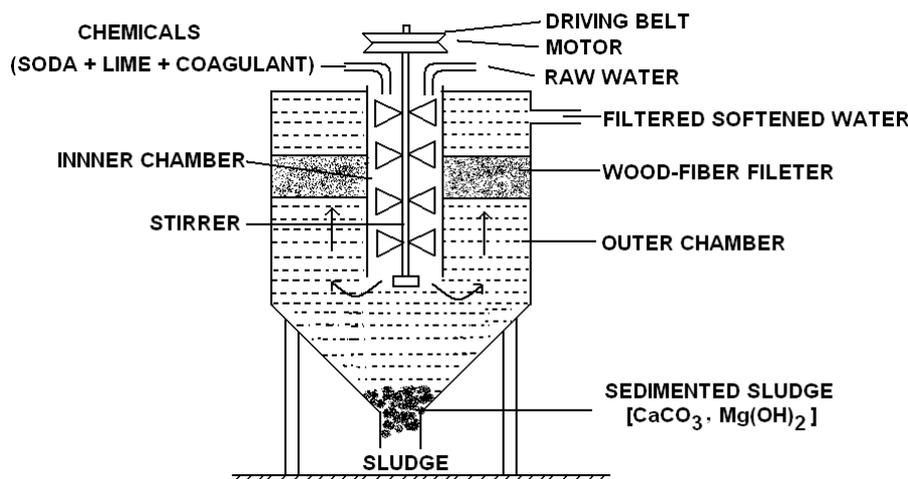
$$\left. \begin{array}{l} \text{Soda required} \\ \text{for softening} \end{array} \right\} = \frac{106}{100} \times \left\{ \begin{array}{l} \text{Permanent Ca.hardness} + \text{Perm.Mg.hardness} + \\ \text{calcium carbonate equivalents of} \\ \text{CO}_2 + \text{HCl} + \text{H}_2\text{SO}_4 + \text{HCO}_3^- + \text{Salts of Fe}^{2+}, \text{Al}^{3+} \text{ etc.} \end{array} \right.$$

Note:

1. The multiplicative factors 74/100 and 106/100 is taken since 100 parts by weight of $\text{CaCO}_3 = 74$ parts of Lime and 106 parts of soda
2. If the impurities are given as CaCO_3 and MgCO_3 , they should be considered as $\text{Ca}(\text{HCO}_3)_2$ and $\text{Mg}(\text{HCO}_3)_2$ respectively.
3. If the lime and soda are impure and if the % of purity is given, then the actual requirements of chemicals should be calculated accordingly by having multiplicative factor $\frac{100}{\% \text{ of impurity}}$. eg. If impurity is 85%, the multiplicative factor is $\frac{100}{85}$

Softening with cold lime soda: (conventional type)

Cold lime soda method consists of using calculated quantities of lime at room temperatures. When soda and lime are mixed with water at room temperature, finely divided precipitates are formed which can be removed through filtration after sedimentation. To facilitate sedimentation and filtration small amounts of alum is added. Addition of sodium aluminate (NaAlO_2) can help in coagulation and also helps in the removal of silica and oil. In this process a softener plant as shown below is used.



Raw water along with calculated amounts of chemicals (lime+soda+coagulant) are fed from the top into the inner chamber, fitted with a vertical rotating shaft carrying a number of paddles. As the water and chemicals flow down the chamber vigorous mixing will soften the water. As the water comes out into the outer chamber and rises up, the settling of the sludge takes place. The water passes through the wood-fiber filter and flows out continuously from the outlet at the top. The

sludge settling at the bottom of the outer chamber is drawn off occasionally. The water sample contains residual hardness 50 – 60 ppm.

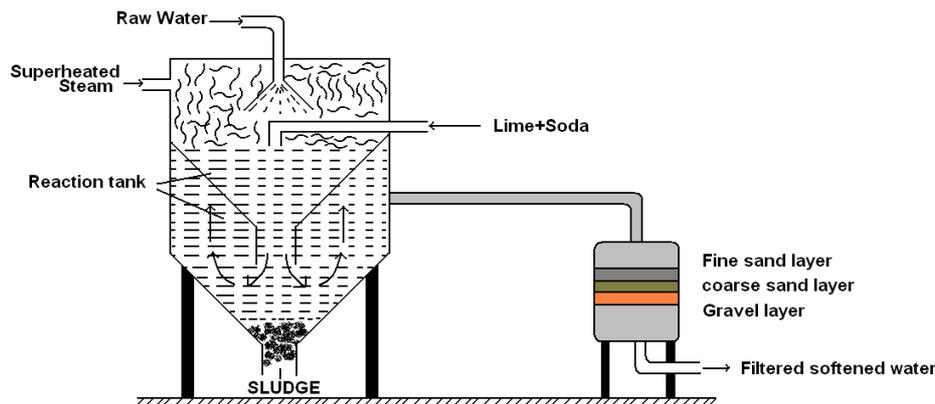
Hot lime – soda process:

In this process the raw water is treated with softening chemicals at 80 – 150°C. This method is better than cold lime – soda process as

- The reaction proceeds faster.
- The precipitates formed settle down rapidly.
- No coagulant is required.
- Filtration is fast and
- Dissolved gasses like CO₂ are driven out.
- This process increases the pH value of the treated water, thereby reducing the corrosion of the distribution pipes.
- Due to the alkaline nature of water, the pathogens in the water are also reduced.
- Besides removal of hardness causing salts, minerals, iron and manganese present in water is also removed.

Disadvantages:

- Skilled supervision is required.
- Disposal of sludge will be a problem.
- The water softened contains 15 to 30 ppm of residual hardness which is not good for boilers.



The hot lime-soda process contains essentially 3 parts (shown above).

1. A reaction tank in which water + chemical + steam are thoroughly mixed.
2. A conical sedimentation vessel in which sludge settles down.
3. A sand filter, which ensures complete removal of sludge from the softened water.

Ion-exchange process of water softening:

This is a reversible exchange of ions between a liquid phase and a solid phase. Materials capable of exchange of cations are called cation exchangers and those which are capable of exchanging anions are called anion exchangers.

In the Ion Exchange process the cations are exchanged with H⁺ and anions are exchanged with OH⁻ ions. For this two types of ion-exchangers are commonly employed, which are insoluble, cross-linked long chain organic polymers with microscopic structure.

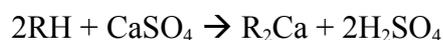
The cation exchangers are represented with general formula RH. These are mainly styrene-divinyl

benzene copolymers containing the functional groups $-\text{COOH}$ or SO_3H . In RH , R is the general structure of the resin and H is exchangeable with cation.

Anion exchangers are phenol-formaldehyde or amine formaldehyde copolymer resins which exchange their OH^- ion with any anion present in the dissolved salts. The anion exchangers are represented by the formula $\text{R}'\text{OH}$. R' is the general structure of the resin and OH is the exchangeable anion.

Principle:

When raw water is first passed through cation exchanger, the exchange of cations takes place as shown below.



The Ca^{2+} and Mg^{2+} are retained by the cation exchangers as CaR and MgR releasing H^+ into water. Thus the water coming out of the resin is highly acidic because the H^+ released by the exchange combine with anion of the dissolved salt to produce the corresponding acids.

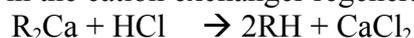
Then the water is passed through anion exchanger where the anions of the acids present in the water are removed by the exchanger releasing OH^- into water. The H^+ and OH^- released from exchangers get combined and produce H_2O .

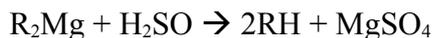


Thus the water coming out from exchanger is free from all ions known as deionised or dematerialised water.

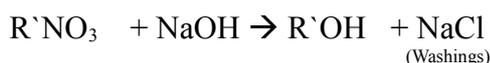
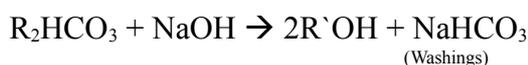
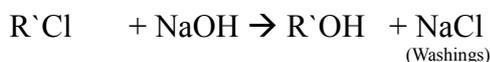
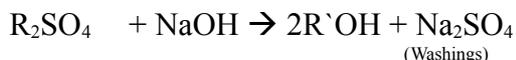
When water sample is completely deionised, it has the tendency to absorb gases like CO_2 , O_2 etc, from atmosphere which cause boiler corrosion. Hence deionization must be followed by degasification.

Regeneration: After the deionization of certain amount of raw water the cation and anion exchangers will be exhausted. Regeneration of cation exchanger is carried out by passing dil. HCl or H_2SO_4 solution into the bed. The H^+ ions of the acid are exchanged with the cations (Ca^{2+} and Mg^{2+}) present in the cation exchanger regenerating it the following way.

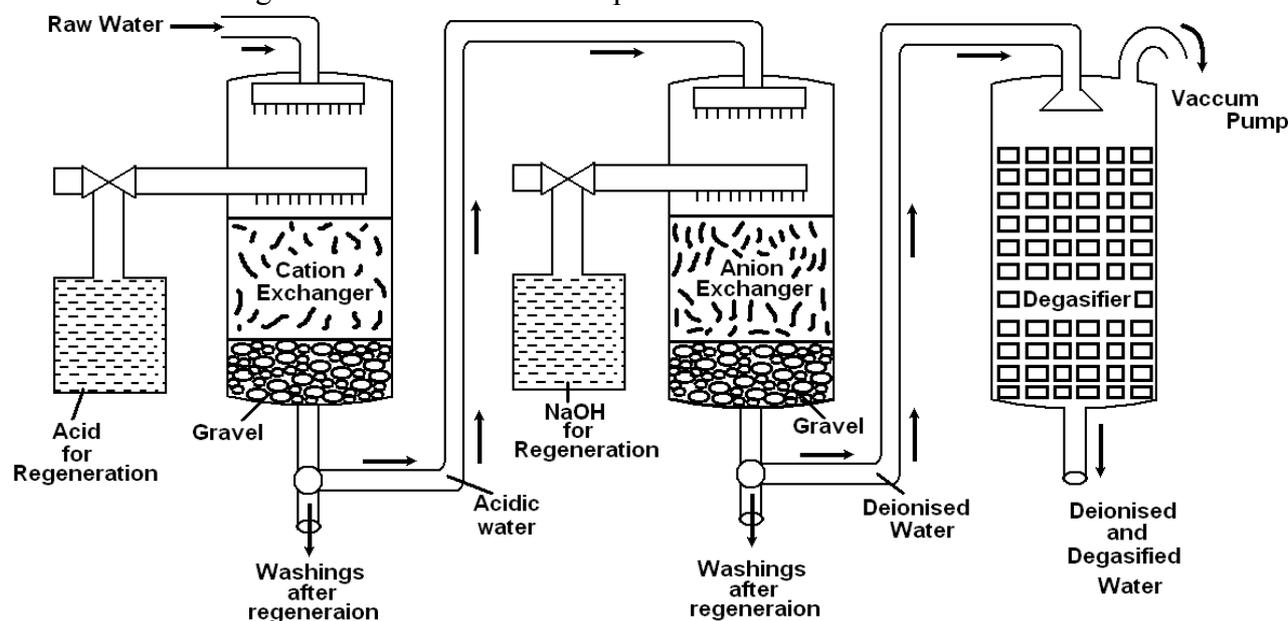




The washings containing $CaCl_2$ and $MgSO_4$ etc, were passed to sink or drain. Similarly the exhausted anion exchanger is treated with dil. $NaOH$ solution. The regeneration can be represented as



The washings are discarded into sink. The regenerated ion-exchangers are used for softening. Thus deionization and regeneration are the alternate process.



Advantages:

1. Highly acidic or alkaline water samples can be purified by this process.
2. The hardness possessed by the deionised water is 2 ppm.
3. The deionised water is most suitable for high pressure boilers.

Disadvantages:

- The ion exchanging resins are expensive; hence the cost of purification is high.
- Raw water should contain turbidity below 10 ppm. Otherwise pores in the resin will be blocked and output of the process is reduced.

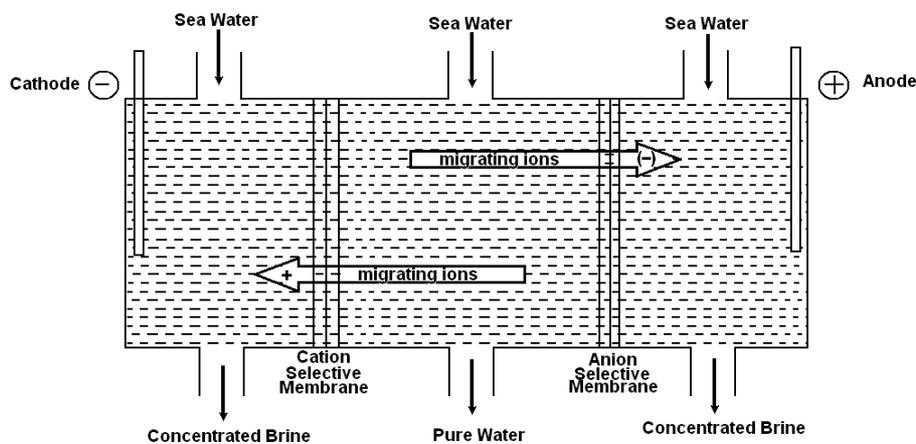
Desalination of Brackish water:

Water containing high concentrations of dissolved solids with a peculiar salty or brackish taste is called brackish water containing about 3.5% of dissolved salts. This water cannot be used for domestic and industrial applications unless the dissolved salts are removed by desalination.

The common desalination of Brackish water are

- Electrodialysis
- Distillation
- Reverse osmosis

Electrodialysis is based on the principle that the ions present in saline water migrate towards their respective electrodes through ion selective membrane, under the influence of applied e.m.f. The electro dialysis unit consists of a chamber, two electrodes a cathode and an anode. The chamber is divided into three compartments with the help of thin, rigid, ion-selective membranes which are permeable to either cation or anion. The anode is placed near anion selective membrane. While the cathode placed near cation selective membrane. The anion selective membrane is containing positively charged functional groups such as R_4N^+ and is permeable to anions only. The cation selective membrane consists of negatively charged functional groups. Such as RSO_3^- and is permeable to cations only. Under the influence of applied e.m.f. across the electrodes the cations move towards anode through the membrane. The net result is depletion of ions in the central compartment while it increases in the cathodic and anodic compartments. Desalinated water is periodically drawn from the central compartment while concentrated brackish water is replaced with fresh sample.

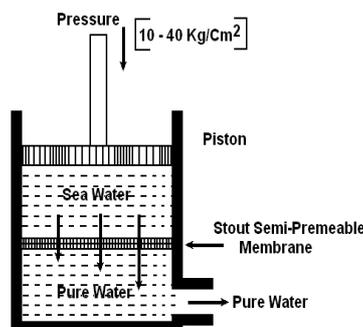


Advantages:

- The unit is compact.
- The process is economical as far as capital cost and operational expenses are concerned.

Reverse Osmosis:

When two solutions of unequal concentration are separated by a semi-permeable membrane which does not permit the passage of dissolved solute particles, (i.e, molecules and ions) flow of solvent takes place from the dilute solution to concentrated solution. This is called Osmosis. If a hydrostatic pressure in excess of osmotic pressure is applied on the concentrated side the solvent, the solvent is forced to move from higher concentration to lower concentrated side across. Thus the solvent flow is reversed hence this method is called reverse osmosis. Thus in reverse osmosis, pure water is separated from contaminated water. This membrane filtration is also called super filtration or hyper-filtration. The reverse osmosis cell is as shown as below.



The reverse osmosis cell consists of a chamber fitted with a semi-permeable membrane, above which sea water. Impure water is taken and a pressure of 15 to 10 kg/cm² is applied on the seawater/ impure water. The pure water is forced through the semi-permeable membrane. Which is made of very thin films of cellulose acetate. However superior membrane made of polymethacrylate and polyamide polymers have come to use.

Advantages:

- Both ionic and non-ionic, colloidal and high molecule weight organic matter is removed from water sample.
- Cost of purification of water is less and maintenance cost is less.
- This water can be used for high pressure boilers.