

MODULE-2

WATER AND ITS TREATMENT

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Introduction, sources of water, impurities in water, standards of water for industrial supply. Hardness of water, determination of total hardness by EDTA method. Boiler feed water and boiler problems, Boiler scales and sludge's, External treatment of boiler feed water- Hot Lime -Soda process and Ion exchange method. Internal treatment of water – phosphate conditioning & Calgon treatment.

Desalination – Meaning, purification of water by reverse osmosis and electrodialysis.

Potable water – Meaning, Standards of potable water, treatment of water for town supply. Sewage treatment- primary, secondary and tertiary treatment. BOD, COD- definition, experimental determination of COD value with problems.

10 hours

WATER TREATMENTS

Water occurs abundantly in nature. It is essential for human beings, animals and plants. It is also essential for industries. In industries, water is mainly used to generate steam. It is also used in the production of steel, paper, textiles, sugar, chemicals, etc. In industries, water is mainly used as a coolant, a reactant, raw material and as a solvent. Before it is used for industrial and domestic purpose, it is essential to know the sources of water and impurities present in water.

Sources of water

The important sources of water are

- Rain water.
- Surface water.
- Ground water and
- Sea water.

Rain water

The important source of water is the rain water. It is the purest form of all natural waters. When it passes through the atmosphere, it dissolves many gases present in the atmosphere like carbon dioxide, sulphur dioxide, oxides of nitrogen, H_2S , etc. It also carries along with it suspended and solid particles. Impurities present in rain water depend on the region in which it is collected.

Surface water

Water present above the earth surface is called surface water. It includes river water, lake water, pond water, etc. It generally contains suspended impurities, dissolved salts such as calcium and magnesium salts, microorganisms, and organic matter from domestic and industrial sewage. Thus, Surface water is not suitable for drinking purpose.

Ground water

Water present below the surface of earth is called ground water. It can be obtained from deep wells, bore wells and in spring forms. Ground water generally free from suspended impurities and microorganisms. It is

clear in appearance due to the filtering action of the soil. Therefore, it is safe for drinking purpose. But it contains many dissolved salts. So, ground water is always hard water due to dissolved salts.

Sea water

It is rich in dissolved salts. Rivers join sea and through the impurities carried by them. Moreover, continuous evaporation of water from the surface of sea makes sea water richer in dissolved impurities. Therefore, Sea water is the most impure form of all natural waters. It contains 3.5% of dissolved salts. Out of which about 2.5% is NaCl.

Impurities in water

We know that water is a good solvent that is why it dissolves many substances and therefore it becomes impure. The common impurities present in water are

- Dissolved impurities (Chemical)
- Suspended impurities (Physical)
- Microscopic impurities (Biological)

Dissolved impurities (Chemical)

Dissolved impurities are mainly due to

- Dissolved salts
- Dissolved gases

Dissolved salts

Natural water contains some dissolved salts like carbonates, bicarbonates, chlorides & sulphates of Ca, Mg, Na, K, Fe, etc. It also contains small amounts of nitrates, nitrites, ammonium and ferrous salts. Due to the presence of these dissolved salts, water becomes “**HARD**”.

Dissolved gases

It contains some dissolved gases like CO₂, NO_x, SO_x, O₂, H₂S, NH₃, etc. Due to the presence of these dissolved gases in water, water becomes “**ACIDIC OR ALKALINE**”.

Suspended impurities(Physical)

These are usually present in surface water but ground water is free from these suspended impurities. These are mainly due to the presence of inorganic and organic impurities in water.

Inorganic impurities

Sand, clay, silica & hydroxides of Fe & Al are some of the inorganic impurities present in water. Size of these particles is not uniform. Some of the particles are large in size. These heavier particles settle down readily due to force of gravity. Some of the other particles are very small in size and colloidal in nature. They don't

settle down easily & they suspension in nature. Due to the presence of these inorganic impurities, water becomes “**TURBID OR MUDDY**”.

Organic impurities

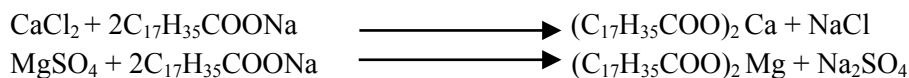
These are mainly due to decaying vegetable matter, animal waste and also due to microorganisms. These organic impurities in water impart “**COLOUR AND BAD TASTE**” to water.

Microscopic impurities (Biological)

These microscopic impurities present only in minute amounts. These are not visible to naked eyes. They are due to microorganisms or pathogens or bacteria's (Substances that produce diseases). These are added to the source of water by domestic and industrial sewage. The presence of these impurities in water, such water is extremely dangerous to health.

Hardness of water

Hardness is the property of water due to which the water does not produce lather easily with soaps. Hardness is mainly due to soluble calcium and magnesium salts like bicarbonates, chlorides and sulphates present in water. Hard water reacts with soap solution forming a **white scum** or **precipitate** without producing lather. This is due to the formation of insoluble soaps of calcium and magnesium salts. Soap is a sodium or potassium salt of higher fatty acids.



Thus, **water which does not produce lather easily with soaps is called hard water**. On the other hand, water which produces lather easily with soaps is called soft water. Soft water does not contain any dissolved salts of calcium and magnesium.

Types of hardness

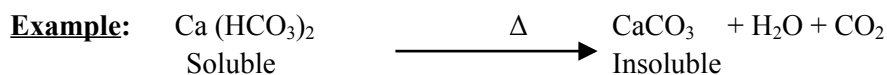
Depending upon the nature of dissolved salts present in water, there are two types of hardness.

1. Temporary hardness
2. Permanent hardness.

Temporary hardness

It is due to the presence of soluble or dissolved bicarbonates of calcium and magnesium. It can be removed just by boiling the water. On boiling, soluble calcium and magnesium bicarbonates are converted into insoluble carbonates, which can be easily removed from the water.





Permanent hardness

It is due to the presence of soluble chlorides and sulphates of calcium and magnesium. It cannot be removed just by boiling the water. It can be removed only by chemical treatments.

Standards of water for industrial purposes

Water used for industrial purpose must have the following Requirements or standards.

1. It should be free from dissolved salts or hardness producing salts
2. It should be free from suspended impurities.
3. It should be free from dissolved gases like CO_2 , O_2 , etc.,.
4. It should be free from microorganisms.
5. It should not be alkaline. (pH water should be around 7-8)

Boiler feed water and boiler problems

Water used for generating steam in boilers, should be as soft as possible. It should be free from, suspended impurities, dissolved salts and dissolved gases like CO_2 , O_2 , etc.,. It should not be alkaline. The use of impure water in boilers, causes many problems like

- Scale and sludge formation
- Priming and foaming
- Corrosion
- Caustic embrittlement.

Therefore, it is necessary to treat the water suitably with chemicals in chemical treatment plants. The water supplied to boiler units for generating steam is called **boiler feed water**. The water present in boiler is called **boiler water**.

Boiler Scales and sludges

In boilers, water is boiled to generate steam. During the generation of steam, water evaporates continuously. As the water evaporates, concentration of dissolved salts increases in boiler water. These dissolved salts get deposited on the inner surfaces of boilers as a sludge or scale.

Boiler sludge

Sludge is a soft, loosely held mud like precipitate formed with in the boiler. Sludge does not cause major trouble to boiler. It can be easily removed with a wire brush or wood piece. It collects in the areas of the system where the water circulation is slow like at bends and plug openings.

Disadvantages

- Sludges are bad conductors of heat. Hence there is wastage of fuel.
- Excessive sludge formation decreases the efficiency of the boiler.
- Excessive sludge formation disturbs the working of boiler since it settles at the regions of poor water circulation and plug openings.

Prevention of sludges

- Sludge formation can be prevented by using **well-softened water**.
- The formed sludge can be removed by **blow down operation** (the removal of portion of water containing sludge and replacing it by fresh boiler feed water).

Boiler Scales

Scale is a very hard & tough deposit, which stick very firmly to the inner surface of boilers. It is very difficult to remove even with the help of hammer & Chisel. Scales are the major source of boiler troubles or problems.

Scale formation

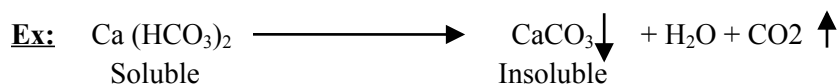
Scale formation is mainly due to the following factors:

- a) Decomposition of bicarbonates
- b) Deposition of calcium sulphate
- c) Hydrolysis of 'Mg' salts

d) Presence of silica or silicon dioxide

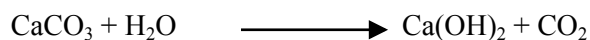
Decomposition of bicarbonates

The use of temporary hard water for generating steam in boilers leads to the formation of boiler scales due to the presence of soluble bicarbonates of Ca & Mg. These soluble bicarbonates are converted into insoluble carbonates (precipitates).



The calcium carbonate is deposited on the inner walls of boilers as boiler scale. This is the main reason for the scale formation in low-pressure boilers.

However, calcium carbonate becomes soluble in high pressure boilers. It reacts with water to form soluble calcium hydroxide.



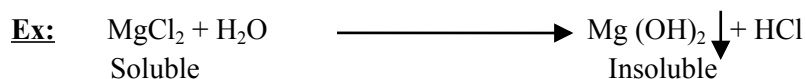
Thus, the temporary hardness causing salts does not form any scales in high-pressure boilers.

Deposition of Calcium sulphate

The use of hard water containing calcium sulphate in high pressure boilers leads to the formation of very hard scale. At high, temp. Calcium sulphate gets separated from water and forms insoluble precipitate. This precipitate gets deposited on the inner walls of boilers as boiler scale. This is because calcium sulphate is soluble in cold but completely insoluble in hot water i.e. the solubility of calcium sulphate decrease with increase in temperature.

Hydrolysis of magnesium salts

The Mg Salts present in water undergo hydrolysis at high temperature, precipitate as Mg (OH)₂ and deposit on the inner walls of the boiler as boiler scale.



Presence of silica

Silica or silicon dioxide even present in very small amount reacts with Ca & Mg salts present in hard water and forms calcium silicate and magnesium silicate. These calcium silicate and magnesium silicates are completely insoluble in water and get deposited on the inner walls of boiler as boiler scales. These calcium

silicate and magnesium silicate forms very hard scales in boilers. It is very difficult to remove these scales from boilers.

Disadvantages or ill effects of boiler scales

- The scales formed in the boilers acts as heat insulating materials, which stick very firmly to the boiler metal surface. The heat applied to boiler is not effectively transfer from boiler surface to water. So the boiler has to be heated to high temperature (over heating has to be done) in order to provide steady supply of heat to generate steam and more fuel is required. **Hence, there is wastage of fuel due to the formation of scales in boilers.**
- **Due to overheating, boiler metal (plate) becomes weak & can't with stand high pressure developed inside the boiler.**
- Due to overheating, some minute cracks are developed in the scales. Some times on further heating, these cracks expand. Suppose if the water seepages through these cracks, water comes directly in contact with overheated boiler metal surface or boiler metal. Water immediately converted into steam. So sudden high pressure developed inside the boiler. **It may cause explosion of boiler or boiler may explode.**

Prevention of boiler scales

The formation of boiler scales can be prevented by

1. Using well soften water and
2. Softening of water

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

Softening of water

Hardness producing salts can be removed by external treatment and by internal treatment.

Treating water chemically before supplying it to boiler is called **external treatment**.

External treatment can be carried out by

- a) Lime –Soda Process
- 
- ```
graph LR; A[Lime –Soda Process] --> B[Cold Lime – Soda]; A --> C[Hot Lime – Soda]
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- b) Ion Exchange process

Treating water chemically inside the boiler is called **internal treatment**.

Internal treatment can be carried out by

- a) Phosphate conditioning and
- b) Calgon treatment

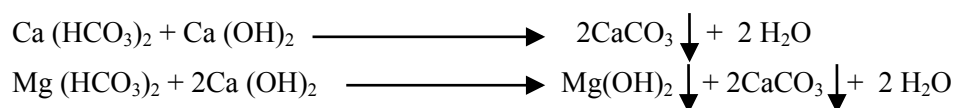
## **EXTERNAL TREATMENT**

### **Lime – Soda process**

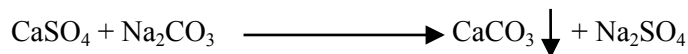
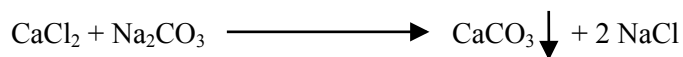
Both temporary and permanent hardness producing salts can be removed by this lime -soda process. In this process, the hard water is treated with lime  $[\text{Ca}(\text{OH})_2]$  and soda  $[\text{Na}_2\text{CO}_3]$ .

**Basic principle :** Convert all soluble salts into insoluble salts.

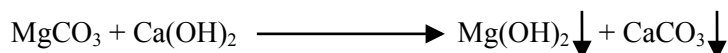
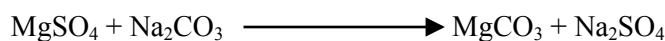
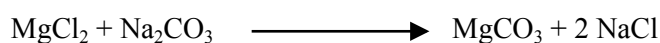
Temporary hardness producing salts like calcium and magnesium bicarbonates can be removed by adding lime only.



Permanent hardness producing salts like chlorides and sulphates of calcium can be removed by adding soda only.



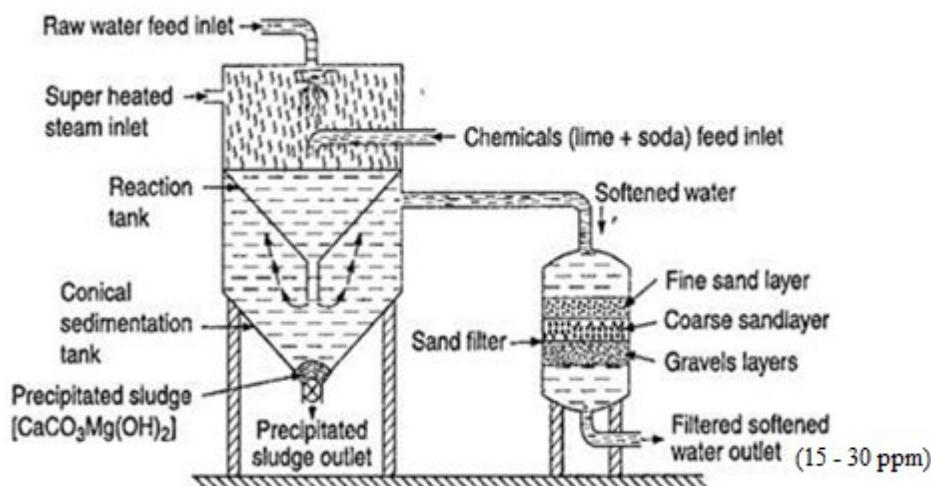
Chlorides and sulphates of magnesium can be removed by adding both soda and lime. First they react with soda forming  $\text{MgCO}_3$ . But  $\text{MgCO}_3$  is sparingly soluble in water, it reacts with lime forming insoluble  $\text{Mg(OH)}_2$ .



Likewise, all soluble calcium and magnesium salts can be converted into insoluble calcium carbonate and magnesium hydroxide. These insoluble salts get precipitated as sludges. This sludge settles down to the bottom of the reaction chamber. The formed sludge can be removed periodically from the reaction tank. Then the water is filtered and used as a boiler feed water.

**The Lime- soda process can be carried out either in cold or hot conditions.**

### HOT LIME SODA PROCESS



Hot lime soda plant consists of a cylindrical vessel with two compartments. Upper portion is called the reaction tank and the lower portion is called the sedimentation tank. The reaction tank is in the form of a funnel. It consists of 3 inlets and has an open lower end.

In this process, raw water is treated with chemicals at a temperature of about 80-150°C.

Hard water and chemicals are introduced into the reaction tank through respective inlets. Steam is passed through the steam inlet. Steam increases the temperature of water. Due to high temperature, water and chemicals mix thoroughly in the reaction tank. As a result of mixing water becomes soft. Soft water comes out of this chamber and it enters into sedimentation tank. In the sedimentation tank, soft water rises upwards. The soft water is then passed through a sand filter to remove sludge completely. The filtered soft water comes out of sand filter through an outlet. It is collected and used as a boiler feed water. The soft water obtained by this method contains a residual hardness of 15-30 ppm. In this process, at high temperature precipitates and suspended particles coagulate and settle down easily to the bottom in the form of sludge. The formed sludge can be removed from the bottom of sedimentation tank by sludge outlet.

### **Reactions**

During the softening of water, the following reactions take place in the reaction chamber.(Refer reactions mentioned in Lime Soda process).

### **Ion- exchange process**

This is the process of softening of water by removing all the ions or salts present in water. In this process, ion exchange resins are used to remove all the ions or salts present in water. These resins capable of exchanging their ions with the ions present in water.

Ion exchange resins are insoluble cross linked organic polymers with a micro porous structure and functional groups. The functional groups attached to the chains are responsible for ion exchanging property.

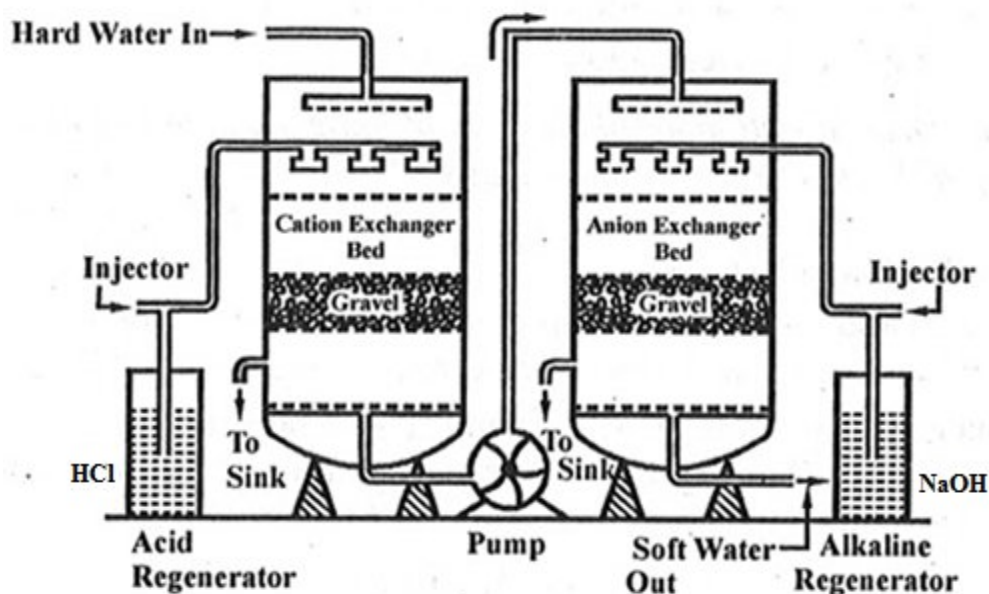
Ion exchange resins are of two types:

**1. Cation exchange resins:**

The ion exchange resins which exchange their  $H^+$  ions with the cations ( $Ca^{2+}$ ,  $Mg^{2+}$ ,  $Na^+$ ,  $K^+$ , etc.) present in water are called cation exchange resins. These resins generally contain acidic functional groups. A cation exchange resin is generally represented as  $R-H$

**2. Anion exchange resins:**

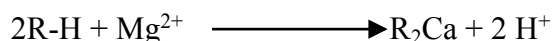
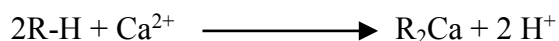
The ion exchange resins which exchange their  $OH^-$  ions with the cations ( $Cl^-$ ,  $SO_4^{2-}$ ,  $CO_3^{2-}$ ,  $NO_3^{2-}$ , etc.) present in water are called anion exchange resins. These resins generally contain basic functional groups. Anion exchange resin is generally represented as  $R^1-OH$

**Process**

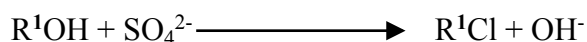
The ion exchange process can be carried out in two cylindrical columns connected in series. The first column consists of cation exchange resin bed & the second column consists of anion exchange resin bed. They are supported on a porous bed of gravel. The cation exchange resin column is

connected to a acid regeneration tank. The anion exchange resin column is connected to an alkaline regeneration tank.

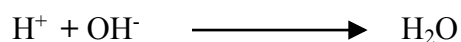
In order to remove hardness producing salts or all types of ions or salts, the hard water is first passed through cation exchange resin column. In this cation exchange column, cations of water like  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ ,  $\text{K}^+$ , etc. are replaced by  $\text{H}^+$  ions of resin & equivalent amount of  $\text{H}^+$  ions are released from this column to water.



The water coming out of cation exchange resin column is free from cations but it contains anions like  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ , etc.,. These are removed by passing water through anion exchange resin column. In the anion exchange column, anions present in water are replaced by  $\text{OH}^-$  ions of resins & equivalent amount of  $\text{OH}^-$  ions are released from this column to water.



The  $\text{H}^+$  &  $\text{OH}^-$  ions are released from cation and anion exchange columns respectively combined to produce water molecule.

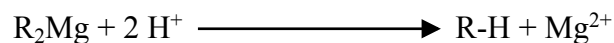
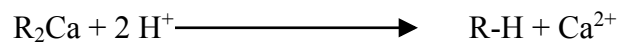


Thus, water comes out of anion exchange column, is free from all types of ions. (anions and cations). The ion free water is called **deionised water** and water free from salts is called **demineralized water**.

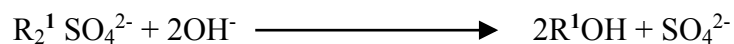
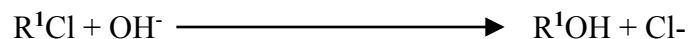
### **Regeneration of ion exchange resins**

Ion exchange resins after exchanging their hydrogen and hydroxyl ions with the ions in water, they lose their ion exchanging property or capacity. Then, they are said to be exhausted. Therefore, softening of water will not take place. However, the ions in the resins are regenerated by passing acid or alkaline solutions through these resins.

The cation exchange resins can be regenerated by passing acid solution through these cation exchange resins (reverse exchange reaction takes place).



The anion exchange resins can be regenerated by passing alkaline solution (NaOH) through these resins (reverse exchange reaction takes place).



After the regeneration, the resins are washed with deionised water and used again for ion exchange process. The soft water obtained by this method contains a very low hardness of about 2 ppm. Therefore, it is useful for high pressure boilers.

### **Internal treatment of boiler water**

Treating water chemically inside the boiler during the generation of steam to remove scale forming (hardness producing) salts from water is called **Internal treatment of boiler water**. After treating the water with external treatment, the water still contains traces of scale forming salts. In order to remove these scale forming salts, water is subjected to internal treatment.

In this internal treatment, chemicals are added to the water in the boiler itself. The added chemicals react with scale forming salts like Ca & Mg salts to form insoluble salts or soluble complexes. The insoluble salts can be removed easily by blow down operation. But it is not necessary to remove these soluble complexes from the boiler because they do not harm the boiler or do not form any scales in boiler. Therefore, it is not necessary to remove these soluble complexes from the boiler.

The internal treatment of water can be carried out by **phosphate conditioning** and by **calogn treatment**.

### **Phosphate conditioning**

In this method, scale formation can be prevented by adding some phosphates to the boiler water.

The important phosphates used during phosphate conditioning are

1. Tri sodium phosphate-  $\text{Na}_3\text{PO}_4$ - alkaline
2. Di-sodium mono hydrogen phosphate-  $\text{Na}_2\text{HPO}_4$ - weakly alkaline
3. Mono sodium di-hydrogen phosphate -  $\text{NaH}_2\text{PO}_4$ - acidic in nature

Based on the nature of water, any one of these phosphates is used to treat the water.

Thus,  $\text{Na}_3\text{PO}_4$  (alkaline) &  $\text{Na}_2\text{HPO}_4$  (weakly alkaline) used to treat the acidic sample of water and  $\text{NaH}_2\text{PO}_4$  (acidic in nature) is used to treat the alkaline sample of water.

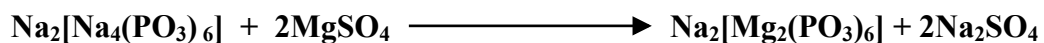
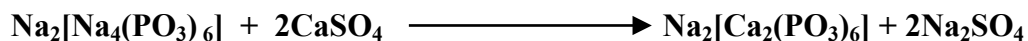
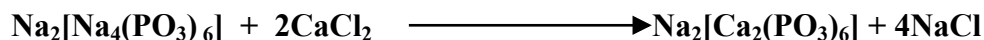
The calcium and magnesium salts present in boiler water react with  $\text{Na}_3\text{PO}_4$  and forms non sticky, easily removable, soft sludge of calcium and magnesium phosphates. The formed sludge can be removed by blow down operation.

#### **Reactions**



**Calogn treatment of boiler water**

In this treatment, scale formation inside the boiler can be prevented by adding calgon (sodium hexameta phosphate-  $(\text{NaPO}_3)_6$  or  $\text{Na}_2 [\text{Na}_4 (\text{PO}_3)_6]$ ) to the water in the boiler. The added calgon reacts with calcium and magnesium salts present in water forming stable and soluble complexes of calcium and magnesium. The formed complexes don't harm the boiler. Therefore, it is not necessary to remove these soluble complexes from the boiler water.

**Reactions**

### **Water for municipal supply**

Water for drinking and domestic purpose is supplied by municipalities. Water supplied by the municipalities should be potable water. Water which is safe for drinking is called potable water. Most of the deadly diseases like cholera, typhoid, jaundice, etc. are caused by drinking unsafe water.

### **Standards of water for municipal supply / Potable water**

Drinking water or potable water, fit for human consumption should satisfy the following requirements or standards,

1. Drinking water should be clear, colourless and odourless.
2. It should have pleasant taste (sweet taste).
3. It should not contain excess of dissolved salts

Turbidity should not exceed 10 ppm and

Dissolved salts should not exceed 500 ppm.

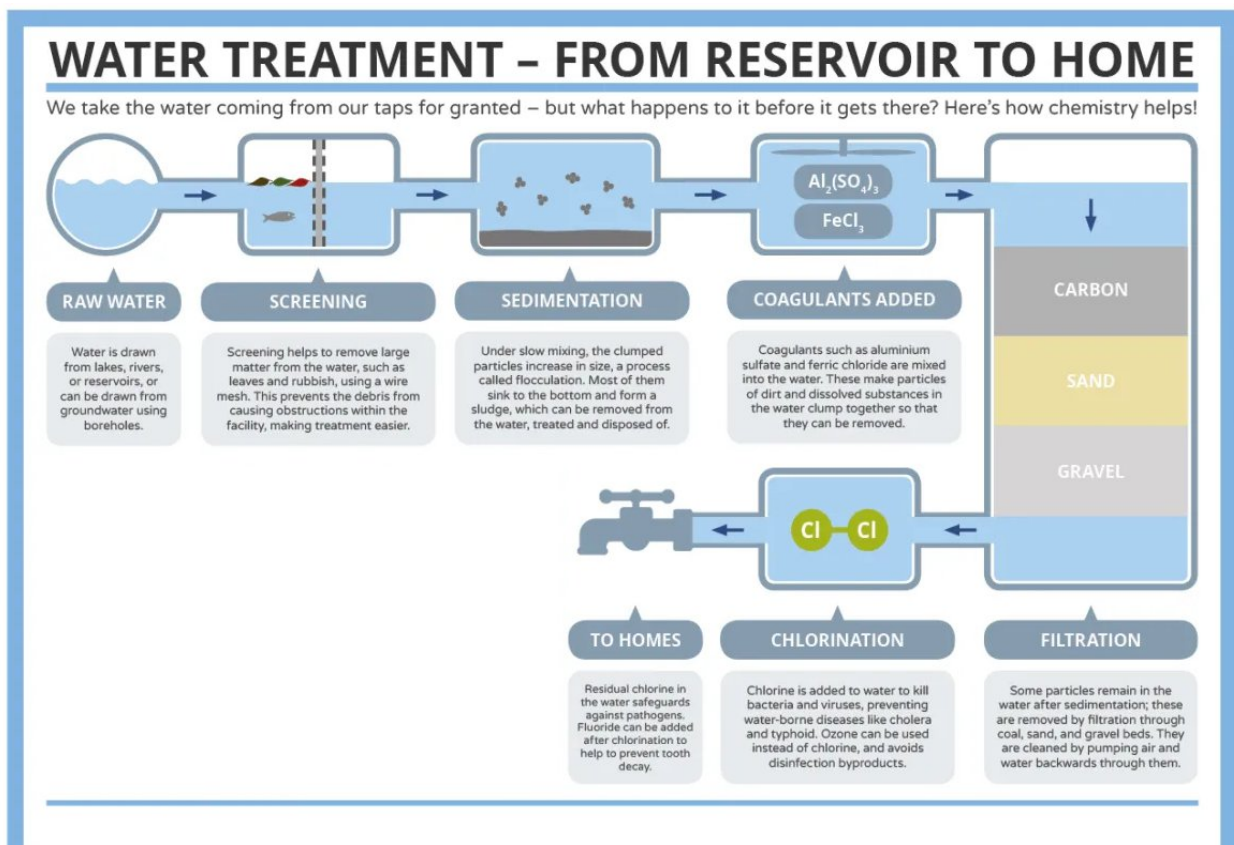
4. It should be free from harmful and poisonous chemicals like lead, arsenic, chromium and manganese salts.
5. It should be free from harmful gases like  $\text{H}_2\text{S}$ ,  $\text{NH}_3$ , etc.
6. It should be free from disease causing microorganisms.
7. Its alkalinity should not be high. Its pH should be around 7.0.

## Treatment of water for municipal supply

The sources of water for municipal supply are rivers, lakes, wells, canals, etc. Natural water from these sources doesn't meet the standards for human consumption. These are treated to make it potable and fit for consumption.

The treatment of water for municipal supply involves

- a) Screening
- b) Sedimentation with coagulation
- c) Filtration and
- d) Sterilization



### **Screening**

The natural water obtained from rivers, lakes, etc is passed through steel screens having large number of holes. The screening removes solid floating materials such as dead fish, animals, wood pieces, leaves, etc. present in water. All these floating materials are simply retained by the screens.

### **Sedimentation with coagulation**

In this method, the screened water is allowed to stand in large tanks for 4-12 hours. The suspended particles heavier than water settle down to the bottom due to force of gravity. The very fine suspended particles are not easily removed by sedimentation. But these fine suspended particles are removed by coagulation.

Coagulation is the process of adding certain coagulants, which helps in removing the very fine and colloidal suspended particles from the water under sedimentation process. The important coagulants used are alum, sodium aluminate etc. They form an insoluble gelatinous precipitate, which absorbs and entangles very fine particles forming bigger particles and settle down easily.

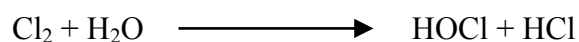
### **Filtration**

It is the process of removal of suspended impurities from water by passing it through the filter tanks. The filter tanks are packed with several layers of gravel, coarse sand and fine sand. On passing the water through filter tank, all the suspended particles and some of the bacteria are retained by the fine sand bed. Filtration removes the suspended matter completely and to some extent bacteria.

### **Disinfection**

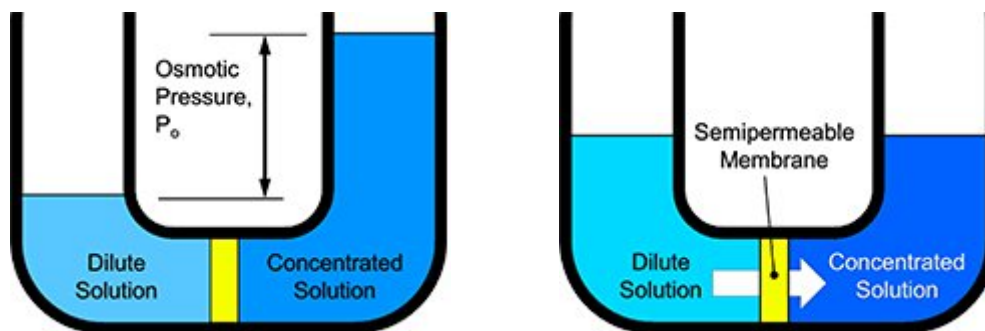
Water purified by sedimentation, coagulation and filtration removes suspended impurities and reduces the amount of bacteria in water. The water still contains many microorganisms like pathogenic bacteria. Such water is not fit for drinking purpose. Bacteria present in water are completely eliminated by disinfection. A chemical that effectively kills bacteria in water is called disinfectant like Chlorination, Chloramine, Bleaching powder, etc.

Disinfection of drinking water is usually achieved by chlorination (adding chlorine to water). Chlorine is one of the best and most widely used disinfectants. Chlorine dissolves in water forming hypochlorous acid.



HOCl is a powerful germicide and kills all the bacteria's in water. The quantity of  $\text{Cl}_2$  should not exceed 0.1 to 0.2 ppm and excess of  $\text{Cl}_2$  gives unpleasant taste and may leads to irritating smell.

## DESALINATION OF WATER



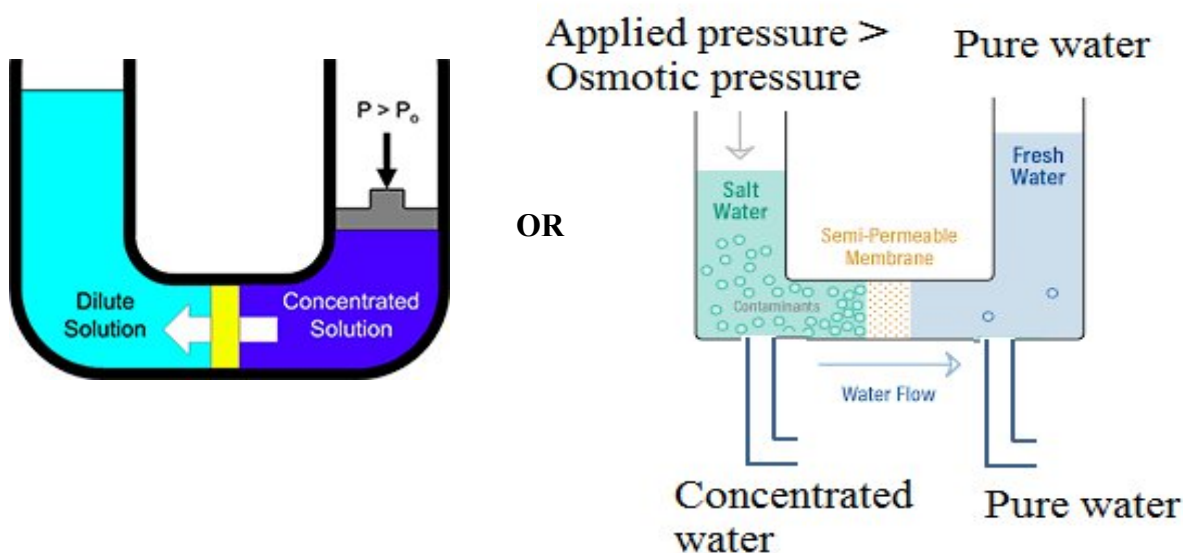
**Desalination is the process of removing excess of sodium chloride (common salt) from sea water or brackish water.** Brackish water is one which contains more of dissolved salts (3.5%) and has a salty or brackish taste. Brackish water is unfit for drinking purposes. Therefore, sea water or brackish water is subjected to desalination process to make it suitable for drinking purpose.

Desalination is usually carried out by **reverse osmosis**. Consider a tank of water with a semipermeable membrane dividing it into two compartments. This membrane allows water to pass through it, but is impermeable to most of the dissolved solids. Semipermeable membranes are made

up of cellulose acetate or poly amide or poly methyl methacrylate. The one compartment has a solution with high concentration of dissolved solids while the other compartment has a solution with low concentration of dissolved solids. If natural osmosis takes place, fresh water flows through a semipermeable membrane from a solution with low concentration of dissolved solids to a solution with high concentration of dissolved solids. Water will continue to flow through the membrane until the concentration is equalized on both sides of the membrane.

This osmosis can be slowdown or stopped, or even reversed if sufficient pressure is applied from the 'concentrated' side of the membrane.

## REVERSE OSMOSIS



Reverse Osmosis works on the same principle as osmosis, but in the reverse direction. In reverse osmosis, external pressure which is greater than the osmotic pressure is applied to the compartment containing salty solution or sea water, and then the water moves from the solution with high-concentration dissolved solids to a solution with low concentration of dissolved solids. In this manner, relatively pure water passes through membrane into the one compartment while dissolved solids are retained in the other compartment. Hence, the water in the one compartment is purified or “demineralized,” and the solids in the other compartment are concentrated.

Reverse osmosis (RO) is defined as **“Reverse osmosis is a process in which water flows through a semipermeable membrane from a solution with high concentration of dissolved solids to a solution with low concentration of dissolved solids on applying external pressure greater than osmotic pressure”**.

### TEXT BOOKS

1. Engineering Chemistry by M.M.Uppal, Khanna Publishers ( 2001 edition).
2. A text Book of Engineering Chemistry- by P C Jain and Monica Jain, Dhanapatrai Publications, New Delhi.(2015 edition)