

## Chemistry of Water Analysis

### Introduction:

Water is the most useful, wonderful and abundant compound on earth. It's a vital component of the life forms. It's 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

**WATER PURIFICATION:**

Impurities are removed from water by seaming, sedimentation, filtration, chlorination or irradiation. Aeration removes odours and tastes caused by decomposing organic matter, industrial wastes and some gases. Various salts and metals cause hardness in water. Hardness may be removed by boiling, by adding sodium carbonate and lime or by filtering through natural or artificial zeolites. Water is also purified by processes such as desalination, reverse osmosis, electrolysis etc.

**CHARACTERISTICS OF WATER**

As per the suggestion given by World Health Organisation (WHO) and by Indian Council of Medical Research (ICMR), the following are the important characteristics of potable water.

1. It should be clear, colourless and odourless.
2. It should be cool and pleasant to taste.
3. It should be free from harmful bacteria and suspended impurities.
4. It should be free from dissolved gases like CO<sub>2</sub>, H<sub>2</sub>S, NH<sub>3</sub>, etc., and poisonous minerals like lead, arsenic, manganese, etc.,
5. Hardness should be less than 500 ppm.
6. Chloride ion content should be less than 250 ppm.
7. Fluoride ion content should be less than 1.5 ppm.
8. Total Dissolved Solids (TDS) content should be less than 500 ppm.
9. pH of the potable water should be 6.5 – 8.5.

**CHEMICAL CHARACTERISTICS OF WATER**

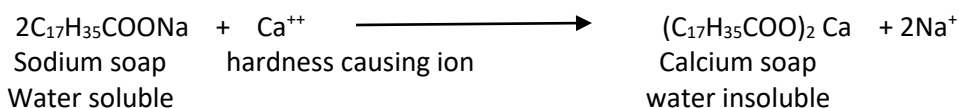
The most important chemical characteristics of water are its acidity, alkalinity, hardness and corrosiveness. Chemical impurities can be either natural, man made (Industrial) or be deployed in raw water sources by enemy forces. Some chemical impurities cause water to behave as either an acid or a base. Since either condition has an important bearing on the water treatment process, the pH value must be determined. Generally the pH influences the corrosiveness of the water, chemical dosages necessary for proper disinfection and the ability to detect contaminants.

## HARDNESS

Hardness is caused by the soluble salts of calcium, magnesium, iron, manganese, sodium, sulphates, chlorides and nitrates. The degree of hardness depends on the type and amount of impurities present in the water. Hardness also depends on the amount of carbon-di-oxide in solution. Carbon-di-oxide influences the solubility of the impurities that cause hardness. The hardness caused by carbonates and bicarbonates is called carbonate hardness. The hardness caused by all others (chlorides, sulphates, nitrates) is called non-carbonated hardness.

### HARD WATER

Water which does not produce lather with soap solution, but produces white precipitate (scum) is called hard water. In other words, water that contains mineral salts (an calcium and magnesium ions) that limit the formation of lather with soap. This is due to the presence of dissolved Ca and Mg salts.



### SOFT WATER

Which produces lather, readily with soap solution is called soft water. This is due to the absence of Ca and Mg salts. Water that is not hard (ie. does not contain mineral salts that interfere with the formation of lather with soap)

#### HARDNESS OF WATER

How to detect hardness?

Hardness of water can be detected in two ways.

- When the water is treated with soap solution, if it prevents lathering and forms white scum, the water contains hardness.
- Water containing hardness, gives wine red colour with Eriochrome Black –T indicator. The total water hardness (including both  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions) is read as parts per million (ppm) or weight / volume (mg/L) of Calcium Carbonate ( $\text{CaCO}_3$ ) in the water. Although water hardness usually measures only the total concentrations of calcium and magnesium (the two most prevalent, divalent metal ions), iron, aluminum and manganese may also be present at elevated levels in some geographical locations. The predominant source of magnesium is dolomite ( $\text{CaMg}(\text{CO}_3)_2$ ).

### TYPES OF HARDNESS

Depending upon the types of dissolved salts present in water, hardness of water can be classified into two types:

- Temporary Hardness
- Permanent Hardness

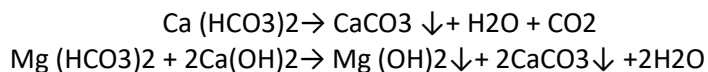
#### Temporary Hardness (or) Carbonate Hardness (CH) (or) Alkaline Hardness

Temporary hardness is caused by a combination of calcium and magnesium bicarbonate ions in the water. It can be removed by

- boiling water

· by the addition of lime (Ca(OH)<sub>2</sub>)

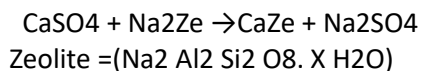
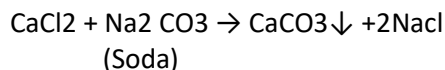
Boiling promotes the formation of carbonate from the bicarbonate and precipitates calcium carbonate out of solution, leaving water that is softer upon cooling.



### **Permanent Hardness (or) Non – Carbonate Hardness (NCH) (or) Non – alkaline Hardness**

Permanent hardness is hardness (mineral content) that cannot be removed by boiling. It is usually caused by the presence of calcium and magnesium sulphates and /or chlorides which become more soluble as the temperature rises. Despite the name, permanent hardness can be removed using water – softener or ion-exchange column, where the calcium and magnesium ions are exchanged with the sodium ions in the column. It can be removed by

- Lime – Soda process
- Zeolite process



Hard water causes scaling, which is the left- over mineral deposits that are formed after the hard water had evaporated. This is also known as lime scale.

### **UNITS OF HARDNESS**

#### **1. Parts per million (ppm)**

It is defined as the number of parts of CaCO<sub>3</sub> equivalent hardness per 10<sup>6</sup> parts of water.

#### **2. Milligrams per litre (mg/lit)**

It is defined as the number of milligrams of CaCO<sub>3</sub> equivalent hardness per 1 litre of water.

#### **3. Degree Clarke's (°Cl)**

It is defined as the number of parts of CaCO<sub>3</sub> equivalent hardness per 70,000 parts of water.

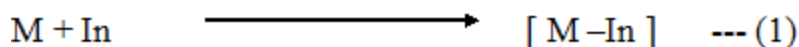
#### **4. Degree French (°Fr)** It is defined as the number of parts of CaCO<sub>3</sub> equivalent hardness per 10<sup>5</sup> parts of water.

### **Relationship between various units**

$$1\text{ppm} = 1\text{ mg/lit} = 0.1^\circ\text{Fr} = 0.07^\circ\text{Cl}$$

### **ESTIMATION OF TOTAL HARDNESS OF WATER BY EDTA METHOD**

The hardness of water is estimated by EDTA method using Eriochrome Black –T [EBT]. Principle: The calcium ion in the water is capable of forming complex with Indicator EBT and also with the EDTA in the pH range 8- 10. To keep the solution at this pH range , a buffer [ mixture of ammonium chloride and ammonium hydroxide ] is used . The complex between EDTA and indicator is more stable than that of between the metal ion and indicator



(2) is more stable than (1)

#### Experiment :

##### 1. Preparation of Standard hard water :

Hard water is prepared in such a way that 100 ml of hard water containing 100 mg of Calcium carbonate; So, 1 ml of Std. hard water = 1mg of  $CaCO_3$

##### 2. Standardisation of EDTA :

EDTA is taken in the burette; 20 ml of Std. hard water is pipette out in beaker; 5ml of buffer solution and 2 a few drops of indicator are added ; now the solution becomes wine –red colour because the colour of the complex between calcium and indicator [ M- In ] is wine –red. Then it is titrated against EDTA; at the end point the colour changes to Pale blue, which is colour of the free indicator. Since the complex between metal ion -EDTA is more stable that of between the metal ion and indicator , the Metal moves from [M-In] towards EDTA and forms complex with that , which is colourless; now the indicator is freed and the solutions attains steel blue colour , which is the colour of the free indicator. Let the titre value be  $V_1$ .

$$1\text{ml of Std. hard water} = 1\text{mg of } CaCO_3$$

$$20\text{ ml of Std. hard water} = 20\text{ mg of } CaCO_3$$

$$V_1\text{ ml of EDTA} = 20\text{ of Std. hard water}$$

$$= 20\text{ mg of } CaCO_3$$

$$1\text{ ml of EDTA} = 20 / V_1 \times 20\text{ mg of } CaCO_3$$

$$= \frac{1\text{mg of } CaCO_3}{V_1}$$

### 3. Determination of Total hardness of water :

20 ml of the given sample of water is taken and titration is conducted as before; let the titre value be  $V_2$  ;

$$20\text{ml of Sample of water} = V_2\text{ ml of EDTA}$$

$$= V_2 \times \frac{1 \text{ mg of CaCO}_3}{V_1}$$

$$= \frac{V_2}{V_1} \text{ mg of CaCO}_3$$

$$1000 \text{ ml of sample} = V_2 / V_1 \times 1000 \text{ mg of CaCO}_3$$

The weight in milligrams of calcium carbonate in 1000 ml of the sample of water

$$= V_2 / V_1 \times 1000 \text{ mg of CaCO}_3$$

$$\text{Total hardness of the given water} = V_2 / V_1 \times 1000 \text{ ppm}$$

#### PREPARATION OF SOLUTIONS;

1. **Standard hard water:** 1 gm of dry  $\text{CaCO}_3$  is dissolved in minimum quantity of HCl and evaporate the solution to dryness on a water bath, and then diluted to 1 lit with water. Each ml of this solution then contains 1 mg of  $\text{CaCO}_3$  hardness.
2. **EDTA solution:** 4 gm of EDTA crystals + 0.1 gm  $\text{MgCl}_2$  in 1lit
3. **Indicator:** 0.5 gm of EBT in 100 ml of alcohol.
4. **Buffer solution:** 67.5 gm  $\text{NH}_4\text{Cl}$  + 570 ml of Con. Ammonia solution diluted with distilled water to 1 lit.

#### Procedure:

##### Step-1: Standardization of EDTA:

Pipette out 10 ml of standard hard water into a conical flask. To this add 2ml of buffer solution followed by addition of 1 to 2 drops of EBT indicator. Then titrate against EDTA which is taken in the burette. Continue the titration till wine red colour changes to blue colour. Repeat this process until two concurrent values are obtained.

##### Step-2 : Estimation of total hardness of sample water:

Take 50 ml of sample water into a conical flask. To this add 5ml of buffer solution followed by addition of 1 to 2 drops EBT indicator. Then titrate against with EDTA which is taken in burette. Continue the titration till wine red colour to blue colour. Repeat this titration until two concurrent values are obtained.

##### Step-3 : Estimation of permanent hardness of sample water

Take 100 ml of sample water in the beaker. Boil the water until its volume reduces to 75 ml. Take 50 of this boiled and cool water in conical flask. To this add 1 to 2 drops of EDTA indicator.

Then titrate it against EDTA which is taken in burette. Continue the titration till wine red colour changes to blue colour. Repeat this process until two concurrent values are obtained.

**Observation table:**

S.no.	Volume of water sample( ml)	Burette Reading (ml)	Volume of EDTA used (ml)
Boiled water			

Calculations: Let the volume used by standard hard water is V1 ml

50 ml of standard hard water = V1 ml of EDTA ∴

50 x1 mg of CaCO<sub>3</sub> = V1 ml of EDTA ∴

1 ml of EDTA = 50/V1 mg of CaCO<sub>3</sub> eq.

**Total hardness of water**

50 ml. of given hard water = V2 ml EDTA = V2 x 50/V1 mg of CaCO<sub>3</sub>eq.

∴ 1 L (1,000 mL) of given hard water = 1000 V2/V1 mg of CaCO<sub>3</sub> eq. ∴

**Permenent hardness of water** = 1000 V2/V1 mg/L = 1000 V2/V1 ppm

Now 50 ml of boiled water =V3 ml of EDTA . . . V3 x 50 /V1 mg of CaCO<sub>3</sub> eq.

1000 ml (= 1 L) of boiled water = 1000 V3 /V1 mg of CaCO<sub>3</sub> eq.

**Temporary hardness of water =**

Temporary hardness = Total hardness – Permanent hardness = . . . ppm

**Advantages of EDTA method:**

This method is definitely preferable to the other methods, because of the

(i) Larger accuracy; (ii) Convenience; (iii) Rapid procedure

## ALKALINITY

**Alkalinity** is a chemical measurement of water's ability to neutralize acids.

**Alkalinity is classified as**

Depending up on the anions that are responsible for the alkalinity of water, there are three types of alkalinity:

1. Hydroxide alkalinity – due to hydroxide ions
2. Carbonate alkalinity - due to carbonate ions
3. Bicarbonate alkalinity - due to bicarbonate ions

The alkalinity due hydroxide and carbonate can be detected by Phenolphthalein indicator and so they are collectively called as Phenolphthalein Alkalinity , represented by P.

The alkalinity due hydroxide, carbonate and bicarbonate can be detected by Methyl orange indicator and so it is called as in Methyl orange Alkalinity, represented by M.

**1.Determination of Phenolphthalein Alkalinity ,P :**

100 ml of given water sample is taken in the conical flask , a few drops of Phenolphthalein indicated are added and titrated against N/50  $\text{H}_2\text{SO}_4$  ; let the titre value when the solution becomes colourless, be  $V_1$ .

**2.Determination of Methyl orange Alkalinity ,M :**

The in the same solution a few drops of Methyl orange indicator are added and titrated against the same acid until the colour changes from yellow to red ; let the titre value be  $V_2$  .

**(a)Calculation of P:**

Volume of the acid =  $V_1$  cc

Normality of the acid ,  $N_1 = 1/50$

Volume of water ,  $V_2 = 100$  cc

Normality of water

$$N_1V_1=N_2V_2$$

$$N_2 = V_1 \times 1/50 \times 1/ 100$$

P in terms of  $\text{CaCO}_3 = N_2 \times \text{equivalent of } \text{CaCO}_3 \times 1000 \text{ mg of } \text{CaCO}_3$

$$= V_1 \times 1/50 \times 1/ 100 \times 50 \times 1000 \text{ mg of } \text{CaCO}_3$$

$$= 10 V_1$$

$$\mathbf{P = 10 V_1 \text{ ppm}}$$

**(b)Calculation of M:**

Volume of the acid =  $V_2$  cc

Normality of the acid,  $N_2 = 1/50$

Volume of water,  $V_3 = 100$  cc

Normality of water  $N_3 = V_2 \times 1/50 \times 1/ 100$

M in terms of  $\text{CaCO}_3 = N_1 \times \text{equivalent of } \text{CaCO}_3 \times 1000 \text{ mg of } \text{CaCO}_3$

$$= V_2 \times 1/50 \times 1/ 100 \times 50 \times 1000 \text{ mg of } \text{CaCO}_3$$

$$= 10 V_2$$

$$\mathbf{M = 10 V_2 \text{ ppm}}$$

Now calculate the carbonate and bicarbonate alkalinity as per table given



Relation between P & M	Phenomenal Condition	Hydroxide Alkalinity (ppm)	Carbonate alkalinity (ppm)	Bicarbonat alkalinity (ppm)
<b>P = 0</b>	If phenolphthalein end point is zero, then alkalinity is due to only bicarbonate.	-----	-----	<b>M</b>
<b>P = M</b>	If methyl orange end point is zero & only there is phenolphthalein end point, then the alkalinity is due to hydroxide alone.	<b>P</b>	-----	-----
<b>P = ½M</b>	If phenolphthalein end point is exactly half the total titration, then only carbonate alkalinity is present.	-----	<b>2P</b>	-----
<b>P &gt; ½M</b>	If phenolphthalein end point is greater than half the total titration, then alkalinity is due to both carbonate & hydroxide.	<b>2P – M</b>	<b>2( M – P )</b>	-----
<b>P &lt; ½ M</b>	If phenolphthalein end point is less than half the total titration, then alkalinity is due to both carbonate & bicarbonate.	-----	<b>2P</b>	<b>M – 2P</b>

### METHODS OF REMOVING HARDNESS

Water used for industrial purposes (such as for steam generation) should be sufficiently pure. It should, therefore, be freed from hardness-producing salts before it is being put to use. The process of removing hardness-producing salts from water is known as softening of water. In industry three methods are mainly employed for softening of water.

#### Lime soda process:

In this method, the soluble calcium and magnesium salts in water are chemically converted into insoluble compounds, by adding calculated amounts of lime  $[\text{Ca}(\text{OH})_2]$  and soda  $[\text{Na}_2\text{CO}_3]$ . Calcium carbonate  $[\text{CaCO}_3]$  and magnesium hydroxide  $[\text{Mg}(\text{OH})_2]$  are precipitated and removed.

#### Lime-Soda Softening Soda Softening

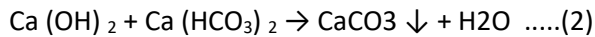
In this process Calcium and Magnesium ions are precipitated by the addition of lime  $(\text{Ca}(\text{OH})_2)$  and soda ash  $(\text{Na}_2\text{CO}_3)$ . Following are the reactions that take place in this process:

- As slacked lime is added to a water, it will react with any carbon dioxide present as follows:



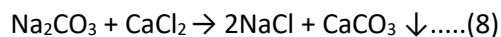
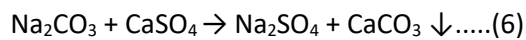
- The lime will react with bicarbonate hardness as follows:

- Removal of temporary hardness



The product magnesium carbonate in equation 3 is soluble. To remove it, more lime is added:

- Removal of permanent magnesium hardness



- Also, magnesium non-carbonate hardness, such as magnesium sulfate, is removed:

• Lime addition removes only magnesium hardness and calcium carbonate hardness. In equation 5 and 7 magnesium hydroxide is precipitated, however, an equivalent amount of calcium is added. The water now contains the original calcium non-carbonate hardness and the calcium non-carbonate hardness produced in equation 5 and 7. Soda ash is added to remove calcium non-carbonate hardness. To precipitate  $\text{CaCO}_3$  requires a pH of about 9.5; and to precipitate  $\text{Mg(OH)}_2$  requires a pH of about 10.8, therefore, an excess lime of about 1.25 meq/l is required to raise the pH.

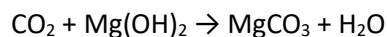
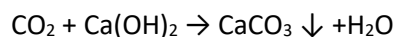
- **The amount of lime required:**

$$\text{lime (meq/l)} = \text{carbon dioxide (meq/l)} + \text{carbonate hardness (meq/l)} + \text{magnesium ion (meq/l)} + 1.25 \text{ (meq/l)}$$

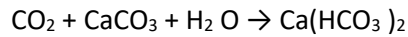
- **The amount of soda required:**

$$\text{soda ash (meq/l)} = \text{non-carbonate hardness (meq/l)}$$

After softening, the water will have high pH and contain the excess lime and the magnesium hydroxide and the calcium carbonate that did not precipitate. Recarbonation (adding carbon dioxide) is used to stabilize the water. The excess lime and magnesium hydroxide are stabilized by adding carbon dioxide, which also reduces pH from 10.8 to 9.5 as the following:



Further recarbonation, will bring the pH to about 8.5 and stabilize the calcium carbonate as the following:



It is not possible to remove all of the hardness from water. In actual practice, about 50 to 80 mg/l will remain as a residual hardness.

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- **Lime**

Lime is commercially available in the forms of:

- quicklime
- hydrated lime

- **Quicklime**

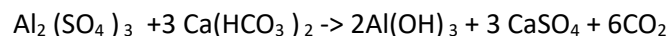
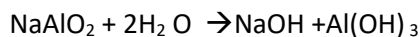
- available in granular form
- contains minimum of 90% CaO
- magnesium oxide is the primary impurity

- **Hydrated Lime**

- contains about 68% CaO
- Slurry lime is written as  $\text{Ca}(\text{OH})_2$ .

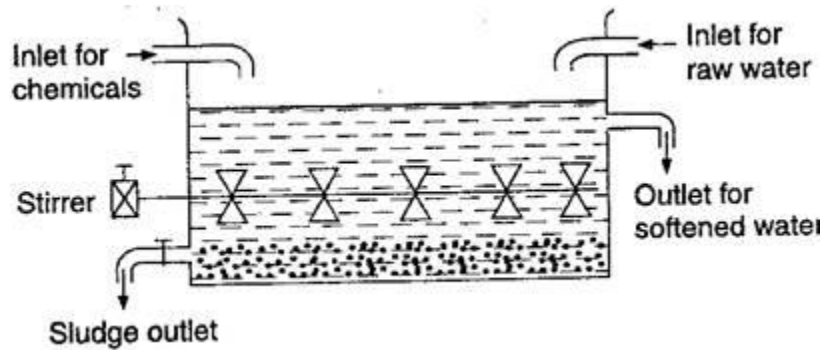
#### A) COLD LIME-SODA PROCESS:

In this Method, Calculated quantity of chemical (lime and soda) is mixed with water at room temperature. At room temperature, the precipitates formed are finely divided, so they do not settle down easily and cannot be filtered easily. Consequently, it is essential to add small amounts of coagulants (Like Alum, aluminum sulphate, sodium aluminate, Etc.) Which hydrolyse to flocculent, gelatinous precipitate of aluminium hydroxide, and entraps the fine precipitates. Use of sodium aluminate as coagulant, also helps the removal of silica as well as oil, if present in water. Cold L-S process provides water, containing a residual hardness of 50 to 60 ppm.



#### Method:

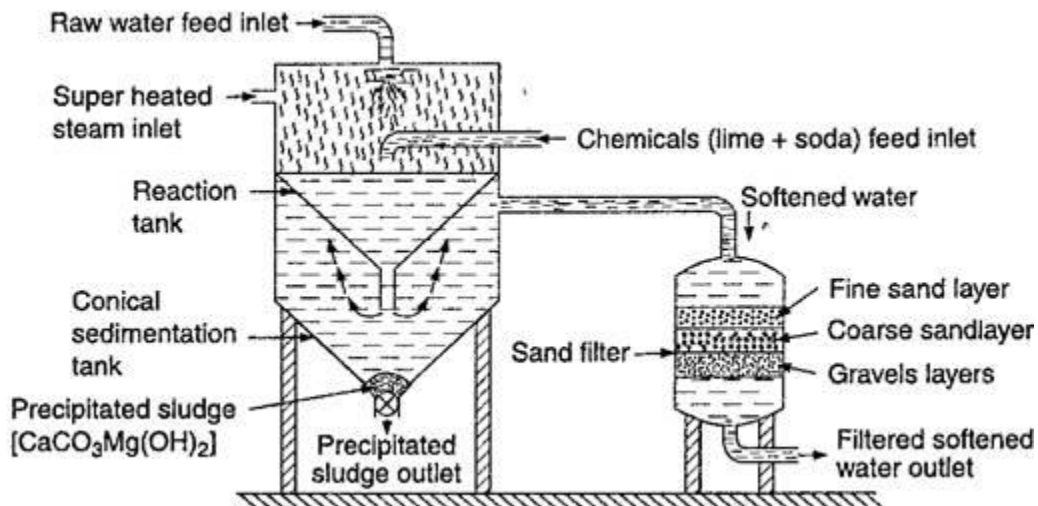
Raw water and calculated quantities of chemicals ( Lime+soda+coagulant) are fed from the top into the inner vertical circular chambers, fitted with a vertical rotating shaft carrying a number of paddles , As the raw water and chemicals flow down there is a vigorous stirring and continuous mixing, whereby softening of water takes place. As the softened water comes into the outer chamber of the lime the softened water reaches up. The softened water then passes through a filtering media (usually made of wood fibers) to ensure complete removal of sludge. Filtered soft water finally flows out continuously through the outlet at the top sludge settling at the bottom of the outer chamber is drawn off occasionally.



### HOT LIME-SODA PROCESS:

Involves in treating water with softening chemicals at a temperature of 80 to 150 C. Since hot process is operated at a temperature close to the boiling point of the solution, so (a) the reaction proceeds faster; (b) the softening capacity of hot process is increased to may fold; (c) the precipitate and sludge formed settle down rapidly and hence, no coagulants are needed; (d) much of the gases (Such as CO<sub>2</sub> and air) Driven out of the water; (e) Viscosity of softened water is lower, so filtration of water becomes much easier. This in-turn increases the filtering capacity of filters, and (f) Hot Lime-Soda Produces water of comparatively lower residual hardness of 15 to 30ppm.

Hot lime-soda plant consists essentially of three parts (a) a 'reaction tank' in which raw water, chemicals and steam are thoroughly mixed; (b) a 'conical sedimentation vessel' in which sludge settles down, and (c) a 'Sand filter' which ensures complete removal of sludge from the softened water.



### Advantages of Lime Soda Process:

- (i) It is a very economical
- (ii) If this process is combined with sedimentation with coagulation, lesser amounts of coagulants shall be needed
- (iii) The process increased the pH value of the treated water, thereby corrosion of the distribution pipes is reduced
- (iv) Besides the removal of hardness, the quantity of minerals in the water are reduced
- (v) To certain extent, iron and manganese are also removed from the water.

- (vi) Due to alkaline nature of treated- water, amount of pathogenic bacteria's in water is considerably reduced

#### **Disadvantages of Lime Soda Process:**

For efficient and economical softening, careful operation and skilled supervision is required

- (i) Disposal of large amounts of sludge (insoluble precipitate) poses a problem. However, the sludge may be disposed off in raising low-lying areas of the city
- (ii) This can remove hardness only up to 15ppm, which is not good for boilers.

#### **Limitation of Soda Lime Process:**

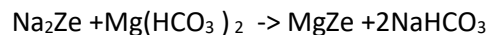
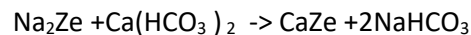
Lime soda softening cannot produce a water at completely free of hardness because of the solubility (little) of  $\text{CaCO}_3$  and  $\text{Mg(OH)}_2$ . Thus the minimum calcium hardness can be achieved is about 30 mg/L as  $\text{CaCO}_3$ , and the magnesium hardness is about 10 mg/L as  $\text{CaCO}_3$ . We normally tolerate a final total hardness on the order of 75 to 120 mg/L as  $\text{CaCO}_3$ , but the magnesium content should not exceed 40 mg/L as  $\text{CaCO}_3$  (because a greater hardness of magnesium forms scales on heat exchange elements).

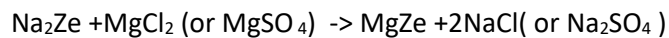
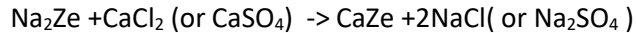
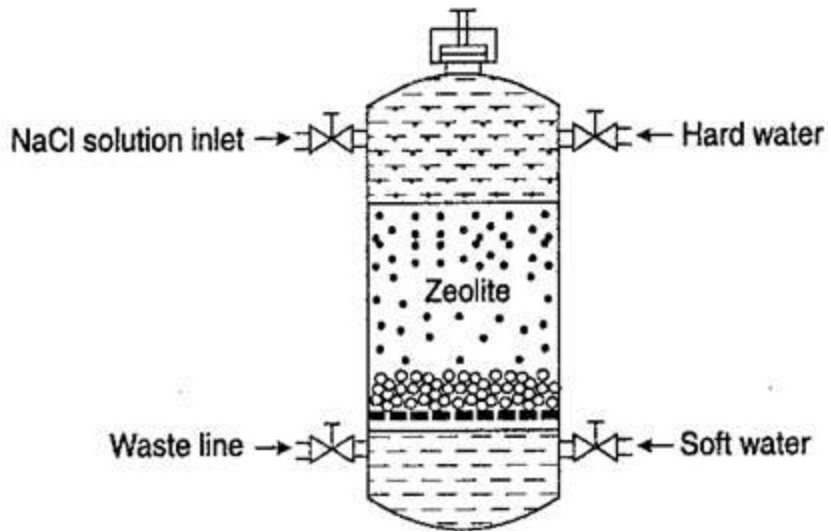
## **2) ZEOLITE PROCESS:**

Chemical structure of sodium zeolite may be represented as  $\text{Na}_2\text{O}_3 \cdot \text{SiO}_2 \cdot \text{YH}_2\text{O}$  where  $x=2-10$  and  $y=2-6$ . Zeolite is hydrated sodium aluminosilicate, capable of exchanging reversibly its sodium ions for hardness, producing ions in water. Zeolite are two types,

- (i) Natural zeolites are non porous for Ex; Natrolite  $\text{Na}_2\text{Al}_3\text{O}_3 \cdot 4\text{SiO}_2 \cdot 22\text{H}_2\text{O}$
- (ii) Synthetic zeolites possess gel structure. Synthetic Zeolites possess higher exchange capacity than natural Zeolites

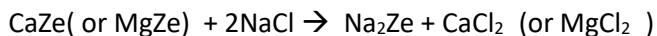
**Process:** - For Softening of water by Zeolite process, hard water is percolated at a specified rate through a bed of zeolite; kept in a cylinder. The Hardness causing ions ( $\text{Ca}^{+2}$ ,  $\text{Mg}^{+2}$  etc.) are retained by the zeolite as  $\text{CaZe}$  and  $\text{MgZe}$ ; while the outgoing water contains sodium salts. Reactions taking place during the softening process are





#### REGENERATION:

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



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

#### Limitations:

- (i) If the supply of water is turbid in will clog the pores of zeolite bed
- (ii) Water contains large quantities of colored ions such as  $\text{Mn}^{+2}$  and  $\text{Fe}^{+2}$  they may be removed first because these ions produce Mn and Fe Zeolites ,which can't be easily regenerated
- (iii) Mineral acids destroy the zeolite bed

#### ADVANTAGES:

- (i) It removes the hardness almost completely
- (ii) Equipment occupying a small space
- (iii) Requires less time
- (iv) It is quite clean

#### DISADVANTAGES:

- (i) Treated water contains more sodium salts than in time soda process
- (ii) The method only replaces  $\text{Ca}^{+2}$  and  $\text{Mg}^{+2}$  ions by  $\text{Na}^{+}$  ions leaves all the acidic ions

### Ion exchange or de-ionization or de-mineralization process:

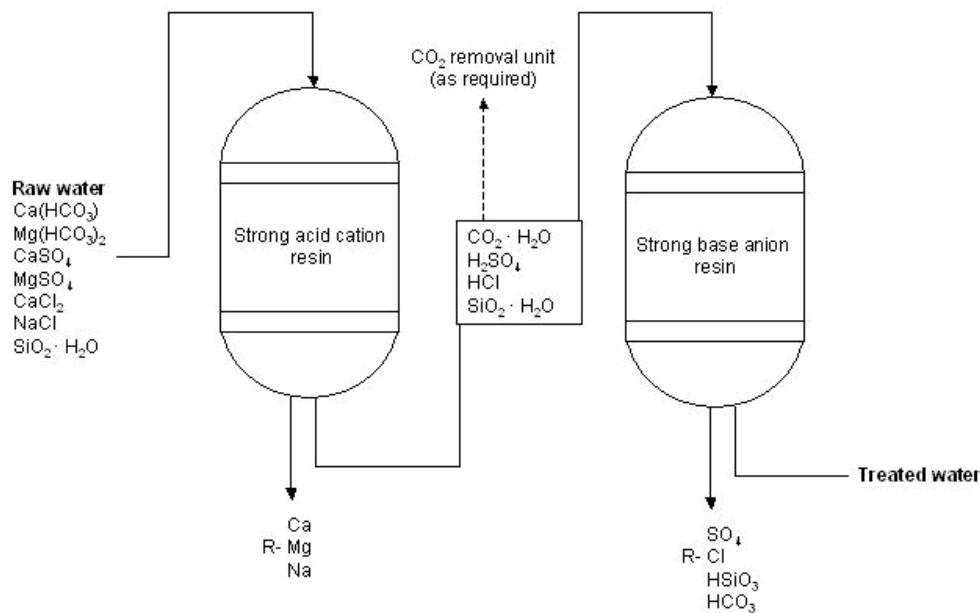
Ion-exchange resins are insoluble, cross-linked, long chain organic polymers with a microporous structure, and the “functional groups’ attached to the chains are responsible for the ionexchanging

properties. Resins containing acidic functional groups ( $-\text{COOH}$ ,  $-\text{SO}_3\text{H}$  etc.) are capable of exchanging their  $\text{H}^{+}$  ions with other cations, which come into their contact; whereas those containing basic functional groups ( $-\text{NH}_2$  as hydrochloric acid) are capable of exchanging their anions with other anions, which come into their contact.

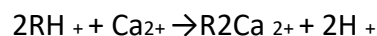
The ion-exchange resins may be classified as: (i) Cation exchange resins ( $\text{RH}^{+}$ ) are mainly styrene-divinyl benzene copolymers, which on sulphonation or carboxylation become capable to

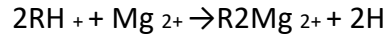
exchange their hydrogen ions with the cations present in the raw water

(ii) Anion exchange resins ( $\text{R}^{+}\text{OH}^{-}$ ) are styrene-divinyl benzene amineformaldehyde copolymers, which contains amino or quaternary ammonium or quaternary phosphonium or tertiary sulphonium groups as an integral part of the resin matrix. These, after treatment with dil.  $\text{NaOH}$  solution, become capable to exchange their  $\text{OH}^{-}$  anions with anions present in the raw water.

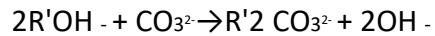
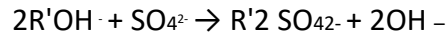
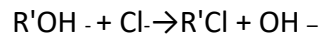


Process: The hard water is passed first through cation exchange column, which removes all the cations like  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , etc., from it and an equivalent amount of  $\text{H}^{+}$  ions are released from this column to water. Thus: 2

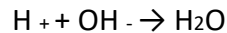




The water which is now free from cations, is passed through anion exchange column, which removes all the anions like  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$ , etc., present in the water and equivalent amount  $\text{OH}^-$  ions are released from this column to water. Thus:



$\text{H}^+$  and  $\text{OH}^-$  ions (released from cation exchange and anion exchange columns respectively) combine to produce water.



Thus the water coming out from the exchanger is free from all cations as well as anions. Ion-free

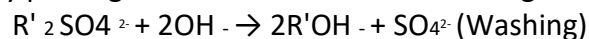
water is known as deionised or demineralised water.

**Regeneration:** When capacities of cation and anion exchangers to exchange  $\text{H}^+$  and  $\text{OH}^-$  ions respectively are lost, they are then said to be exhausted

The exhausted cation exchange column is regenerated by passing a solution of dil. HCl or  $\text{H}_2\text{SO}_4$ . The regeneration can be represented as:



The column is washed with deionized water and such washing (which containing  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , etc. and anion  $\text{SO}_4^{2-}$ ) is passed into sink or drain. The exhausted anion exchange column is regenerated by passing a solution of dil. NaOH. The regeneration can be represented as:



The column is washed with deionized water and such washing (which contains  $\text{Na}^+$  and  $\text{SO}_4^{2-}$  or  $\text{Cl}^-$  ions) is passed into sink or drain.

### Advantages

(1) The process can be used to soften highly acidic or alkaline waters. (2) It produces water of very low hardness (2 ppm) .

### Disadvantages

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

### INTERNAL TREATMENT:

In this process; an ion is prohibited to exhibit its original character by converting it into other more soluble salt by adding appropriate reagent. An internal treatment is accomplished by adding a proper chemical to the boiler water either to precipitate the scale forming impurities in the form of sludge, which can be removed by blow down operations, or to convert them into compounds, which will stay in dissolved form in water and they do not cause any harm .

Important Internal treatment methods are:

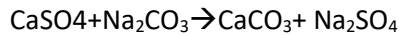


- (i) **Colloidal conditioning:** In low pressure boilers, scale formation can be avoided by adding organic substances like Kerosene, tannin, agar-Agar etc; which get coated over the scale forming precipitates, thereby yielding coated non-sticky and loose deposits
- (ii) **Phosphate conditioning:** In High pressure boilers, scale formation can be avoided by adding sodium phosphate which reacts with hardness of water forming non-adherent and easily removable soft sludge

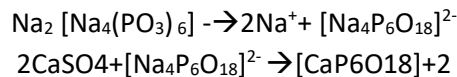


The main phosphates employed are (a)  $\text{NaH}_2\text{PO}_4$  (b)  $\text{Na}_2\text{HPO}_4$  (c)  $\text{Na}_3\text{PO}_4$

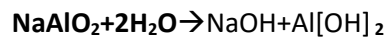
- (iii) **Carbonate Conditioning:** In low pressure boilers, scale formation can be avoided by adding sodium carbonate to boiler water, then  $\text{CaSO}_4$  converted into  $\text{CaCO}_3$  in equipment  $\text{CaCO}_3$  forms loose sludge



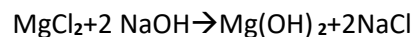
- (iv) **Calgon Conditioning:** Involves in adding calgon  $[(\text{NaPO}_3)_6]$  to boiler water then it forms soluble complex compound with  $\text{CaSO}_4$



- (v) **Treatment with sodium aluminate ( $\text{NaAlO}_2$ ).** Sodium aluminate gets hydrolyzed yielding  $\text{NaOH}$  and a gelatinous precipitate of aluminium hydroxide



The  $\text{NaOH}$ , so formed precipitates some of the magnesium as  $\text{Mg}(\text{OH})_2$  i.e.;



The precipitate of  $\text{Mg}(\text{OH})_2$  and  $\text{Al}(\text{OH})_3$  produced inside the boiler entraps finely suspended and colloidal impurities including oil drops and silica.