

## WATER TREATMENT

The pure water is composed of two parts of hydrogen and one part of oxygen by volume and dissolves many substances. These dissolved salts are the impurities in water. Water is a very good solvent. So it is called as universal solvent.

### CHARACTERISTICS OF POTABLE(DRINKING) 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.

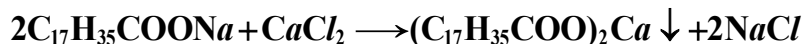
1. It should be clear, colourless and odourless.
2. It should be cool and pleasant to taste.
3. It should be free from harmful bacteria and suspended impurities.
4. It should be free from dissolved gases like CO<sub>2</sub>, H<sub>2</sub>S, NH<sub>3</sub>, etc., and poisonous minerals like lead, arsenic, 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.

### HARDNESS OF WATER

“Hardness of water is defined as **the soap consuming capacity of water or characteristic of preventing lather formation of water with soap**”.

Generally salts like chlorides, carbonates, bicarbonates and sulphates of Ca<sup>2+</sup>, Mg<sup>2+</sup> and Fe<sup>2+</sup> make water hard.

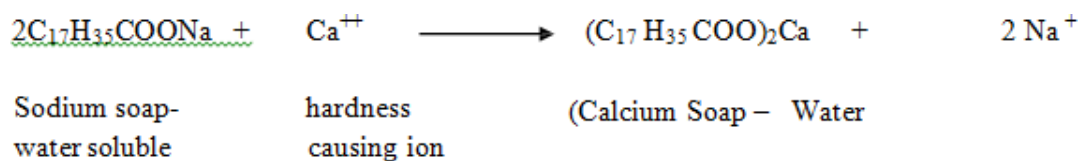
This hard water on treatment with stearic or palmitic acid salts of sodium or potassium (soap) causes white precipitate formation of calcium or magnesium stearate or palmitate.



When the hardness causing ions are removed as insoluble soaps, water becomes soft and forms lather.

### **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 (calcium and magnesium ions) limit the formation of lather with soap. This is due to the presence of dissolved Ca and Mg salts.

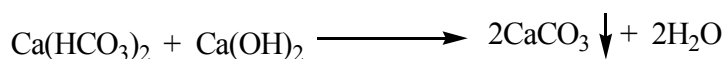
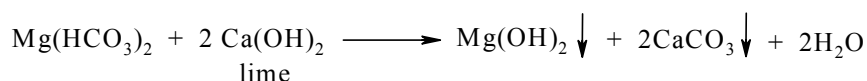
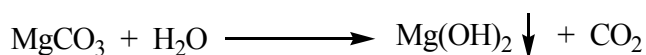


### SOFT WATER

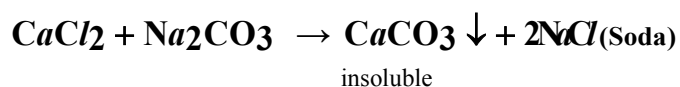
Water, which produces lather, readily with soap solution is called soft water. This is due to the absence of Ca and Mg salts. Water that is not hard (i.e., does not contain mineral salts that interfere with the formation of lather with soap).

### TYPES OF HARDNESS

**(i) Temporary Hardness (or) Carbonate hardness:** due to the presence of bicarbonates and carbonates of Ca and Mg removed by boiling the water; adding lime to the water.



**(ii) Permanent Hardness** is due to the presence of chlorides and sulphates of Ca, Mg, Fe, etc. Permanent Hardness cannot be removed on boiling.



### EXPRESSION OF HARDNESS

Both temporary and permanent hardness are expressed in ppm (parts per million) as  $\text{CaCO}_3$ . The choice of  $\text{CaCO}_3$  is due to the fact that its molecular weight is 100 and equivalent weight is 50 and it is very less soluble salt in water (around 15-20 mg/l).

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Equivalent of  $\text{CaCO}_3$

$$\begin{aligned} & \frac{(\text{Mass of hardness producing substance})}{\text{Chemical equivalent of hardness producing substance}} \\ &= \frac{\times (\text{Chemical equivalent of } \text{CaCO}_3)}{\text{Chemical equivalent of hardness producing substance}} \\ &= \frac{\text{Mass of hardness producing substance} \times 50}{\text{Chemical equivalent of hardness producing substance}} \end{aligned}$$

### UNITS OF HARDNESS

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

It is defined as the number of parts of  $\text{CaCO}_3$  equivalent hardness per  $10^6$  parts of water.

#### 2. Milligrams per litre (mg/l)

It is defined as the number of milligrams of  $\text{CaCO}_3$  equivalent hardness per 1 litre of water.

#### 3. Clarke's degree ( $^{\circ}\text{Cl}$ )

It is defined as the number of parts of  $\text{CaCO}_3$  equivalent hardness per 70,000 parts of water.

#### 4. French degree ( $^{\circ}\text{Fr}$ )

It is defined as the number of parts of  $\text{CaCO}_3$  equivalent hardness per  $10^5$  parts of water.

### Relationship between various units

<i>1 ppm</i>	<i>= 1 mg/l</i>	<i>= 0.1<math>^{\circ}\text{Fr}</math></i>	<i>= 0.07<math>^{\circ}\text{Cl}</math></i>
<i>1 mg/l</i>	<i>= 1 ppm</i>	<i>= 0.1<math>^{\circ}\text{Fr}</math></i>	<i>= 0.07<math>^{\circ}\text{Cl}</math></i>
<i>1<math>^{\circ}\text{Cl}</math></i>	<i>= 1.43<math>^{\circ}\text{Fr}</math></i>	<i>= 14.3 ppm</i>	<i>= 14.3 mg/l</i>
<i>1<math>^{\circ}\text{Fr}</math></i>	<i>= 10 ppm</i>	<i>= 10 mg/l</i>	<i>= 0.7<math>^{\circ}\text{Cl}</math></i>

### Total Hardness

The sum of temporary hardness and permanent hardness.

**Problem 1: If a sample of water contains 50 mgs of  $\text{Ca}^{2+}$  ions per litre, calculate its hardness in terms of  $\text{CaCO}_3$  equivalent?**

**Solution: Given:** The amount of  $\text{Ca}^{2+}$  ions = 50 mgs/lit.

We know that, the molecular weight of calcium = 40

$$\therefore \text{Amount equivalent to } \text{CaCO}_3 = \frac{50 \times 100}{40} = 125 \text{ mgs/lit.}$$

**Problem 2: A water sample contains 204 mgs of  $\text{CaSO}_4$  and 73 mgs of  $\text{Mg}(\text{HCO}_3)_2$  per litre. What is the total hardness in terms of  $\text{CaCO}_3$  equivalent?**

**Solution: Given: Hardness producing salt**

(i)  $\text{CaSO}_4$  (molecular weight = 136)

$$\begin{aligned} \text{Amounts equivalent to } \text{CaCO}_3 &= \frac{204 \times 100}{136} \\ &= 150 \text{ mgs/lit.} \end{aligned}$$

(ii)  $\text{Mg}(\text{HCO}_3)_2$  (Molecular weight = 146)

$$\text{Amounts equivalent to } \text{CaCO}_3 = \frac{73 \times 100}{146}$$

$$\text{Temporary hardness} = \text{Mg}(\text{HCO}_3)_2 = 50 \text{ mgs/lit}$$

$$\text{Permanent hardness} = \text{CaSO}_4 = 150 \text{ mgs/lit}$$

$$\text{Total hardness} = \text{Mg}(\text{HCO}_3)_2 + \text{CaSO}_4$$

$$\Rightarrow 50 + 150 = 200 \text{ mgs/lit.}$$

**Problem 3: Calculate the carbonate and non-carbonate hardness of a sample of water containing the dissolved salts as given below in mgs/lit.  $Mg(HCO_3)_2 = 7.3$ ;  $Ca(HCO_3)_2 = 40.5$ ;  $CaSO_4 = 13.6$ ;  $MgCl_2 = 21.75$  and  $NaCl = 50$ .**

**Solution: Given:**

(i) Hardness producing salt  $Mg(HCO_3)_2$  (Mol. Wt = 146), Amount in mgs/lit = 7.3

$$= \frac{7.3 \times 100}{146} = 5 \text{ mgs/lit.}$$

(ii)  $Ca(HCO_3)_2$  (Mol. Wt = 162), Amount in mgs/lit = 40.5

$$= \frac{40.5 \times 100}{162} = 25 \text{ mgs/lit.}$$

(iii)  $CaSO_4$  (Mol. Wt. = 136), Amount in mgs/lit = 13.6

$$= \frac{13.6 \times 100}{136} = 10 \text{ mgs/lit.}$$

(iv)  $MgCl_2$  (Mol. Wt. = 95), Amount in mgs/lit = 21.75

$$= \frac{21.75 \times 100}{95} = 22.9 \text{ mgs/lit.}$$

(v)  $NaCl$ , Amount in mgs/lit = 50.

But  $NaCl$  does not contribute any hardness to water, hence it is ignored.

Carbonate hardness =  $Mg(HCO_3)_2 + Ca(HCO_3)_2$

$$= 5 + 25 = 30 \text{ mgs/lit}$$

Non-Carbonate hardness =  $CaSO_4 + MgCl_2$

$$= 10 + 22.9 = 32.9 \text{ mgs/lit.}$$

Total hardness = Carbonate Hardness + Non-Carbonate Hardness

$$= 30 + 32.9 = 62.9 \text{ mgs/lit.}$$

**Problem 4:** A sample of water is found to contain the following analytical data in mgs/lit.  
 $\text{Mg}(\text{HCO}_3)_2 = 14.6$ ;  $\text{MgCl}_2 = 9.5$ ;  $\text{MgSO}_4 = 6.0$ ;  $\text{Ca}(\text{HCO}_3)_2 = 16.2$ . Calculate the temporary and Permanent hardness of the sample of water.

**Solution: Given: Hardness producing salt.**

(i)  $\text{Mg}(\text{HCO}_3)_2$  (Mol. Wt. = 146), Amount in mgs/lit. = 14.6

$$= \frac{14.6 \times 100}{146} = 10 \text{ mgs/lit.}$$

(ii)  $\text{MgCl}_2$  (Mol. Wt. = 95), Amount in mgs/lit. = 9.5

$$= \frac{9.5 \times 100}{95} = 10 \text{ mgs/lit.}$$

(iii)  $\text{MgSO}_4$  (Mol. Wt. = 120), Amount in mgs/lit = 6.0

$$= \frac{6.0 \times 100}{120} = 5 \text{ mgs/lit.}$$

(iv)  $\text{Ca}(\text{HCO}_3)_2$  (Mol. Wt. = 162), Amount in mgs/lit = 16.2

$$= \frac{16.2 \times 100}{162} = 10 \text{ mgs/lit.}$$

$$\begin{aligned} \text{Temporary hardness} &= \text{Mg}(\text{HCO}_3)_2 + \text{Ca}(\text{HCO}_3)_2 \\ &= 10 + 10 = 20 \text{ mgs/lit.} \end{aligned}$$

$$\begin{aligned} \text{Permanent hardness} &= \text{MgCl}_2 + \text{MgSO}_4 \\ &= 10 + 5 = 15 \text{ mgs/lit.} \end{aligned}$$

**Effects of hardness: -**

- (1) Hard water is harmful for drinking due to the presence of excess of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions.
- (2) Hard water used in boilers forms scales & sludge and results in corrosion, priming caustic embrittlement of the boilers.
- (3) Hard water used does not give lather with soap, so it sticks to clothes and body.
- (4) Hardness in water causes blockage in holes.
- (5) Hard water is not suitable for laboratory analysis, because hardness producing ions interfere in various reactions.

**Boiler Troubles: -** Boilers are used in Industries for the purpose of steam generation. If the hard water is fed directly to the boilers, there arise many troubles such as:

**1. Priming: -** The carrying out of water droplets with steam is called “priming”. Because of rapid and high velocities of steam, the water droplets move out with steam from the boiler.

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This process of wet steam generation is caused by:

- (i) The presence of large amount of dissolved solids.
- (ii) High stream velocities
- (iii) sudden boiling
- (iv) improper designing of boilers
- (v) sudden increase in steam production rate.
- (vi) The high levels of water in boilers.

**Prevention of priming:** - The priming is avoided by

- (i) Fitting mechanical steam purifiers
- (ii) Avoiding rapid change in steaming rate
- (iii) Maintaining low water levels in boilers and
- (iv) Efficient softening and filtration of boiler feed water.

**2. Foaming:** - Formation of stable bubbles at the surface of water in the boiler is called foaming. More foaming will cause more priming. It results with the formation of wet steam that harms the boiler cylinder and turbine blades. Foaming is due to the presence of oil drops, grease and some suspended solids.

**Prevention of Foaming:-** Foaming can be avoided by:

- (i) Adding antifoaming chemicals like castor oil.
- (ii) Oil can be removed by adding sodium aluminates or alum.
  - (i) Replacing the water concentrated with impurities with fresh water.

**3. Scale & sludge formation:-** The water in boiler is continuously heated causes the increase in the concentration of dissolved and suspended solids. These are precipitated and slowly precipitate on the inner walls of the boiler plate. This precipitation takes place in two ways.

(1) The precipitation in the form of soft loose and slimy deposits (sludge)

(2) The precipitation in the form of hard deposits, which are sticky on the walls of boilers (scale)

**Sludge:** The muddy solid at the bottom of the boiler (or) the loose, slimy and soft deposits in the boiler are called sludge.

**Causes of the sludge:-** The sludge is caused by  $\text{MgCO}_3$ ,  $\text{MgCl}_2$ ,  $\text{CaCl}_2$  which have more solubility in hot water.

**Disadvantages of sludges: -**

1. Sludges are bad conductors of heat and results in wastage of heat and fuel.

2. Excessive sludge formation leads to choking (or) blockage of the pipes.

**Prevention of sludge formation: -**

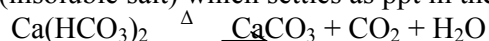
(1) By using soft water which is free from dissolved salts like  $\text{MgCO}_3$ ,  $\text{MgCl}_2$ ,  $\text{CaCl}_2$  &  $\text{MgSO}_4$ .

(2) Blow down operation can prevent sludge formation

**Scale: -** Scales are hard sticky deposits on the inner walls of boiler. The scales are very difficult to remove.

**Causes of Scale:-**

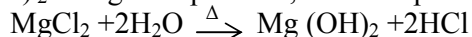
(i) Due to the decomposition of  $\text{Ca}(\text{HCO}_3)_2$  at high temperature & pressure present in boiler, It forms  $\text{CaCO}_3$  (insoluble salt) which settles as ppt in the boiler.



(ii)  $\text{CaSO}_4$  present in water is highly soluble in cold water and less soluble in hot water. So the  $\text{CaSO}_4$  in boiler water is precipitates out as hard scale, whenever the temp of boiler increases.

(iii) Hydrolysis of  $\text{MgCl}_2$ :- The dissolved  $\text{MgCl}_2$  present in water is precipitates as

$\text{Mg}(\text{OH})_2$  at high temperature, which deposits as scale.



(iv)  $\text{SiO}_2$  present in water deposits as calcium silicate or magnesium Silicate. The deposits are very hard.

**Disadvantages of Scale: -** (1) As the scale is hardly sticky on the walls of the boiler and it is very bad conductor of heat. So there is loss of heat and fuel.

2. Due to the scale formation we have to heat the boiler to high temperatures this causes the weakening of boiler material.

3) Due to scale deposits the choking of boiler is observed.

4) Due to uneven heat there may be developing of cracks in Scale. Whenever the water passes through this crack comes to contact with boiler plate and generates sudden steam and high pressure results explosion of boiler.

**Removal of Scales:-**

(1) If the scale is soft. It can be removed by scraper.

(2) By giving thermal shocks done by heating to higher temperature and suddenly cooling.

(3) The  $\text{CaCO}_3$  scale is removed by the washing with 5-10%  $\text{HCl}$  Solution and  $\text{CaSO}_4$  scale is removed washing with EDTA solution.

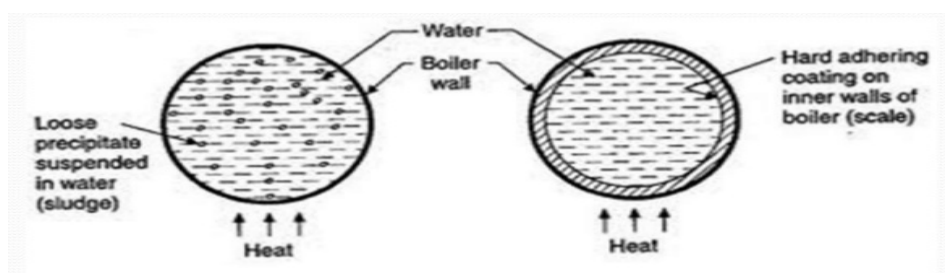
(4) If the scales are loosely adhering, they can be removed by frequent blow down operation.



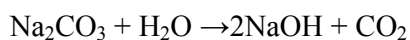
Sludge	Scale
It is soft, loose and slimy precipitate.	It forms hard deposits.
They form non-adherent deposits and can be easily removed.	They stick firmly to the inner surface of the boiler and are very difficult to remove.
They are formed by substances like $\text{CaCl}_2$ , $\text{MgCl}_2$ , $\text{MgSO}_4$ , $\text{MgCO}_3$ , etc.	They are formed by substances like $\text{CaSO}_4$ , $\text{Mg}(\text{OH})_2$ etc.
They are formed at comparatively colder portions of the boiler.	They are formed at heated portions of the boiler.
They decrease efficiency of boiler but are less dangerous.	They decrease efficiency of boiler and chances of explosion are also there.
They can be removed by blow down operation.	They can't be removed by blow down operation.

### SLUDGE

### SCALE



**4. Caustic embrittlement:-** The  $\text{Na}_2\text{CO}_3$  present in water hydrolysed to  $\text{NaOH}$  at high pressures in boilers.



The  $\text{NaOH}$  formed concentrates after long use. It causes inter-granular cracks on the boiler walls, especially at the stress points.

The formation of cracks in boilers due to  $\text{NaOH}$  is called caustic embrittlement.

Prevention of caustic embrittlement:-

- 1) By using sodium phosphate as softening agent instead of  $\text{Na}_2\text{CO}_3$ .
- 2) By adding tannin or lignin to boiler water which block the hair cracks and pits in boiler.
- 3) By adding sodium sulphate to soften the water and this also blocks the hair cracks present on the surface of the boiler plate.

### Treatment of boiler feed water (Softening of water):-

Treatment of Boiler feed water is of two types.

#### External Treatment

(Carried out before the entry of water into the boiler)

- Zeolite Process
- Ion Exchange Process
- Lime Soda Process

#### Internal Treatment

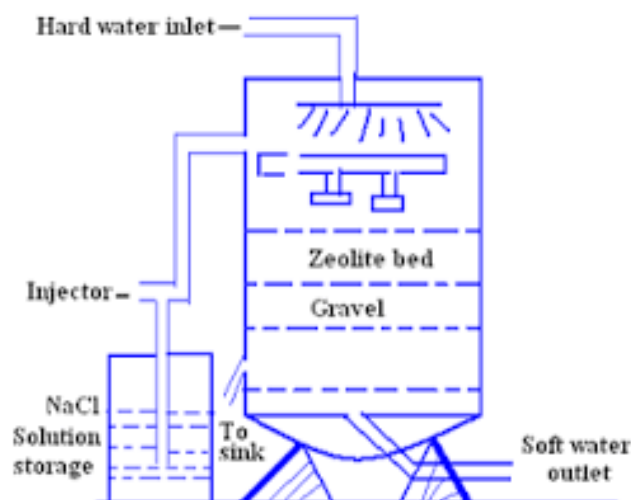
(Carried out inside the boiler)

- Calgon Conditioning
- Phosphate Conditioning
- Carbonate Conditioning

### ZEOLITE METHOD OF WATER TREATMENT

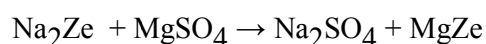
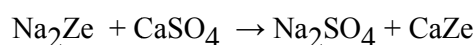
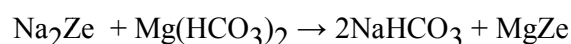
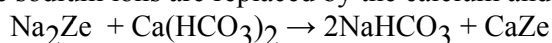
Zeolites are hydrated sodium alumina silicates having porous structure with molecular formula  $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot x\text{SiO}_2 \cdot y\text{H}_2\text{O}$  ( $x = 2$  to  $10$  and  $y = 2$  to  $6$ ). They are represented as  $\text{Na}_2\text{Ze}$  where  $\text{Ze}$  represents the insoluble framework and  $\text{Na}$  are the loosely held sodium ions.

Principle of zeolite process: They are capable of exchanging their loosely held sodium ions reversibly with the hardness producing anions in water ( $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ ).

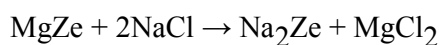
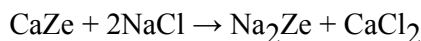


**Working:** It involves two steps:

1. Water softening: When  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions containing hard water is passed through a bed of sodium zeolite, the sodium ions are replaced by the calcium and magnesium ions.



2. **Regeneration:** When all sodium ions are replaced by calcium and magnesium ions, the zeolite becomes inactive. Then the zeolite needs to be regenerated. Brine solution is passed through the bed of inactivated zeolite. The following reactions are taken place and form  $\text{Na}_2\text{Ze}$  is regenerated.



**Advantages :**

1. It produces water with about 10 ppm hardness left behind.
2. There is no danger of sludge formation.
3. Requires less time and operation is clean.
4. Process automatically adjusts itself for variation in hardness of incoming water.
5. Equipment is compact, maintenance and operation is easy.

**Disadvantages:**

1. This method only replaces cationic impurities; anions are left behind in water.
2. Treated water contains more sodium salts, so this water cannot be used in boilers else it will cause caustic embrittlement.

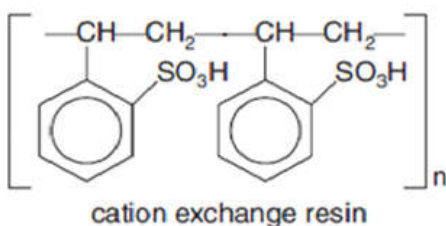
**Limitations:**

1. Turbid water cannot be feeded as it will clog the pores of zeolite
2. Acidic water cannot be feeded as it will destroy the zeolite bed.
3. Hot water cannot be used as zeolite tends to dissolve in it.

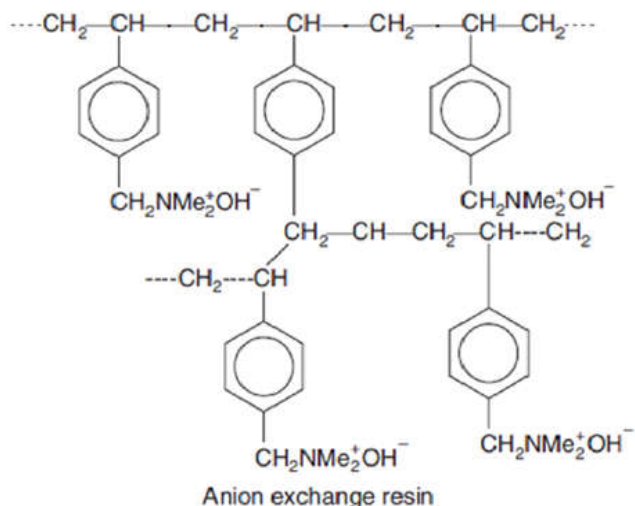
**Ion exchange resins:**

These are high molecular weight, cross linked, organic polymers having porous structure and are capable of exchanging hardness producing ions in water with their  $\text{H}^+$  and  $\text{OH}^-$  ions held on their porous insoluble matrix reversibly.

- (i) **Cation Exchange Resins ( $\text{RH}^+$ )** are phenol-sulphonic acid-formaldehyde resin, styrene- divinyl benzene copolymers which exchange their  $\text{H}^+$  ions with the cations present in the water i.e.,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ .



- (ii) **Anion Exchange Resins (ROH):** The styrene divinyl benzene or amine formaldehyde copolymers contain quaternary ammonium tertiary sulphonium or amino group in the resin. The resin on treatment with hard water is capable of exchanging the  $\text{OH}^-$  with different anions of water i.e.,  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$  etc.



#### **Purification of water by ion exchange process :**

Ion exchange process consists of two columns- Cation exchanger column and anion exchanger column.

- i) First hard water is passed through cation exchanger which exchanges hardness causing cations like  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Fe}^{2+}$  etc in water with  $\text{H}^+$  ions held loosely on the porous cation exchange resin.
  - ii) Then hard water is passed through anion exchanger which exchanges hardness causing anions like  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$  etc in water with  $\text{OH}^-$  ions held loosely on the porous anion exchange resin.
  - iii) The  $\text{H}^+$  and  $\text{OH}^-$  ions thus released in water by the cation and anion exchangers respectively combine to form water molecule.
- Hence water coming out of the columns is free from hardness causing cations as well as anions and thus it is known as deionised or demineralised water.

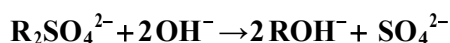
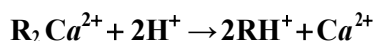
#### **Reactions:**

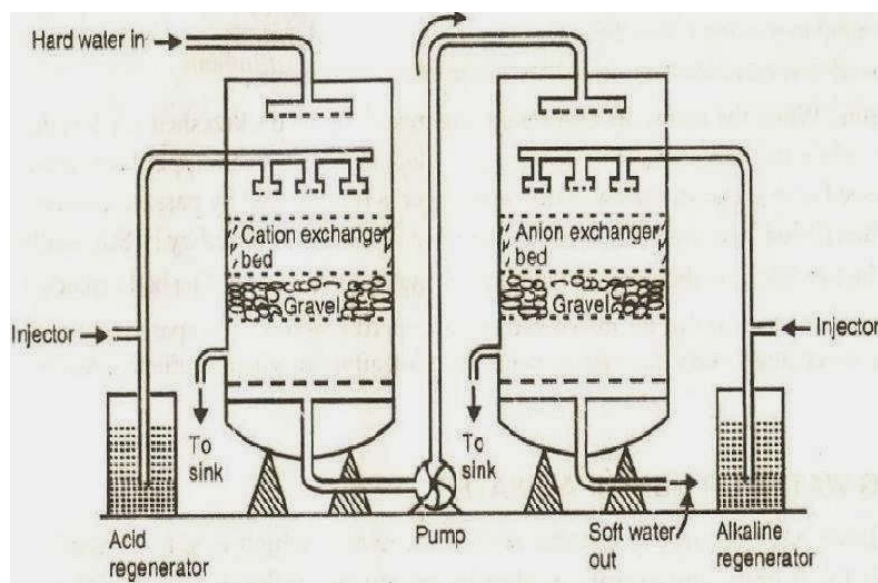
##### **Step 1:**

Cation exchanger -  $2R-H + \text{Ca}^{+2} \rightleftharpoons R_2-Ca + 2H^+$  (R = insoluble matrix)

Anion exchanger -  $R-OH + \text{Cl}^- \rightleftharpoons RCl + \text{OH}^-$  (R = insoluble matrix)

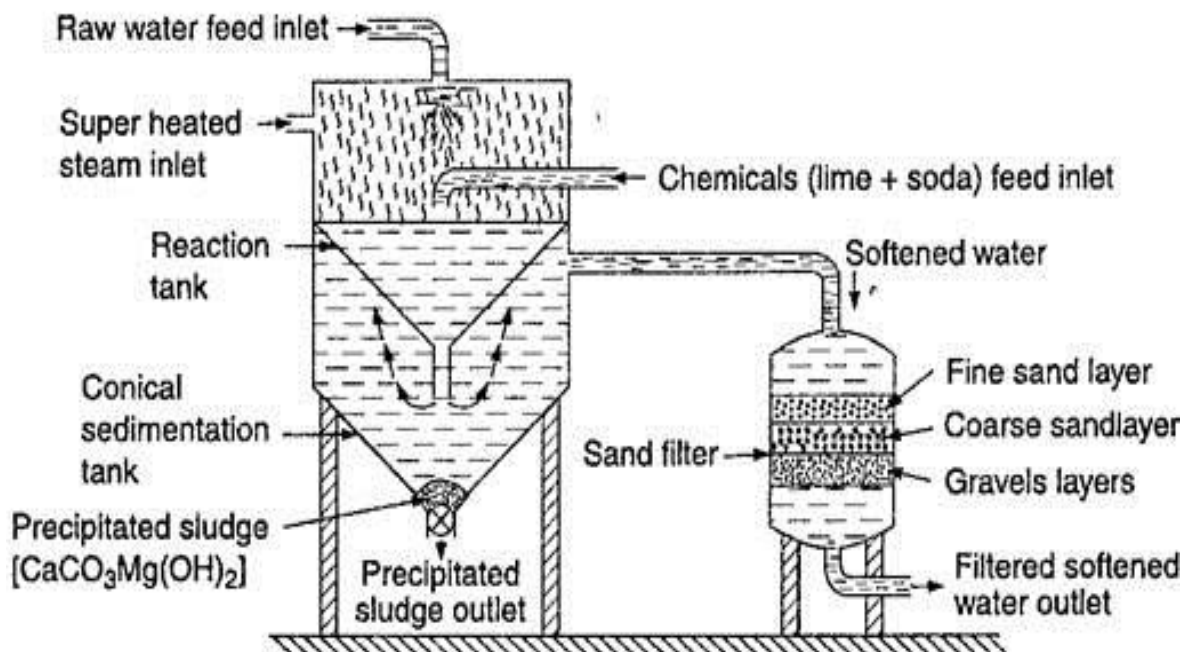
**Step 2:** After some time these two exchangers are exhausted when all their  $\text{H}^+$  and  $\text{OH}^-$  ions are replaced by hardness causing ions. At this stage hard water supply is stopped and cation and anion exchangers are regenerated by treating with acid and base respectively





### Lime soda process of water softening.

Principle: 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  $\text{Na}_2\text{CO}_3$ . All the calcium salts are precipitated out as calcium carbonate  $\text{CaCO}_3$  and magnesium salts as magnesium hydroxide  $\text{Mg}(\text{OH})_2$  which can be easily filtered off.



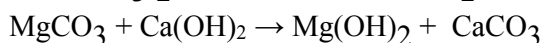
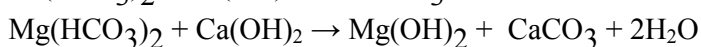
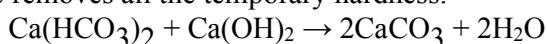
## ENGINEERING CHEMISTRY (KAS-102/202) UNIT- 4

There are two types of lime soda processes:

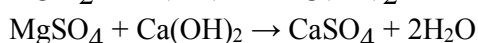
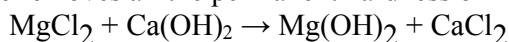
Cold Soda Lime Process	Hot Soda Lime Process
It is carried out at room temperature (25-30°C).	It is carried out at high temperature (95-100°C).
It is a slow process.	It is a rapid process.
Use of coagulant is necessary.	No coagulant is required.
Filtration is not easy.	Filtration is easy as viscosity of water is low.
Residual hardness is 60 ppm.	Residual hardness is 15-30 ppm.
Dissolved gases are not removed.	Dissolved gases are removed.
It has low softening capacity.	It has high softening capacity.

**Working:** Following reactions are involved:

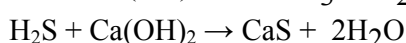
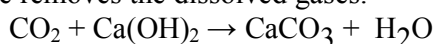
1. Lime removes all the temporary hardness.



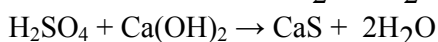
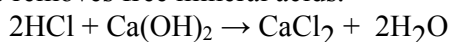
2. Lime removes all the permanent hardness of magnesium salts.



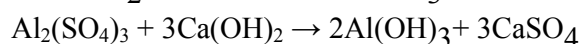
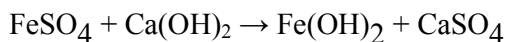
3. Lime removes the dissolved gases.



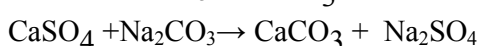
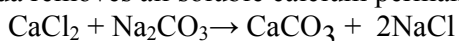
4. Lime removes free mineral acids.



5. Lime removes dissolved iron and aluminium salts.



6. Soda removes all soluble calcium permanent hardness.



**Advantages of L.S. Process:**

1. It is very economical process.
2. The process increases the pH value of the treated water, thereby corrosion of the distribution pipes is reduced
3. Besides the removal of hardness, the quantity of minerals in the water are reduced
4. To certain extent, iron and manganese are also removed from the water.
5. Due to alkaline nature of treated- water, amount of pathogenic bacteria's in water is considerably reduced

### **Disadvantages of L.S. Process:**

1. For efficient and economical softening, careful operation and skilled supervision is required
2. 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
3. This can remove hardness only up to 15ppm, which is not good for boilers.

### **CALCULATIONS OF THE REQUIREMENT OF LIME AND SODA**

Rules for solving numerical problems on lime-soda requirements for softening of hard water:

1. The units in which the impurities are analyzed and expressed are to be noted.
2. Substances which do not contribute towards hardness (KCl, NaCl, SiO<sub>2</sub>, Na<sub>2</sub>SO<sub>4</sub> etc.) should be ignored and explicitly stated.
3. A substances causing "hardness should be converted into their respective CaCO<sub>3</sub> equivalents.

CaCO<sub>3</sub> equivalent of hardness causing impurity =

$$\frac{100 \times \text{wt. of the impurity}}{2 \times \text{chemical equivalent of impurity}} \\ = \text{Multiplication factor} \times \text{wt. of impurity}$$

Salt	Molecular Weight	Chemical equivalent	Multiplication Factor
Ca(HCO <sub>3</sub> ) <sub>2</sub>	162	81	100/162
Mg(HCO <sub>3</sub> ) <sub>2</sub>	146	73	100/146
CaSO <sub>4</sub>	136	68	100/136
CaCl <sub>2</sub>	111	55.5	100/111
MgSO <sub>4</sub>	120	60	100/120
MgCl <sub>2</sub>	95	47.5	100/95
CaCO <sub>3</sub>	100	50	100/100
MgCO <sub>3</sub>	84	42	100/84
CO <sub>2</sub>	44	22	100/44
Mg(NO <sub>3</sub> ) <sub>2</sub>	148	74	100/148
HCO <sub>3</sub>	61	61	100/122
OH	41	17	100/34
CO <sub>3</sub> <sup>2-</sup>	60	30	100/60
NaAlO <sub>2</sub>	82	82	100/164
Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	342	57	100/114
FeSO <sub>4</sub> .7H <sub>2</sub> O	278	139	100/278
H <sup>+</sup>	1	1	100/2
HCl	36.5	36.5	100/73



4. If the impurities are given as  $\text{CaCO}_3$  or  $\text{MgCO}_3$ , these should be considered due to  $\text{Ca}(\text{HCO}_3)_2$  and  $\text{Mg}(\text{HCO}_3)_2$  respectively and they must only be expressed in terms of  $\text{CaCO}_3$  and  $\text{MgCO}_3$

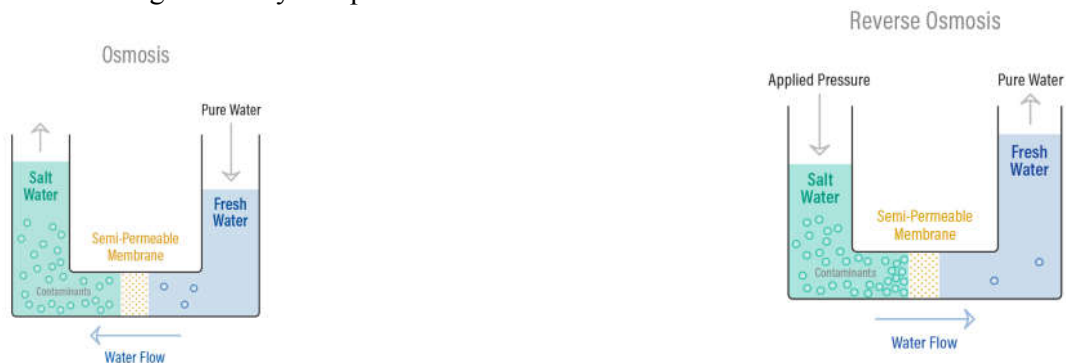
**Lime** =  $(74/100) \{ \text{temporary calcium hardness} + (2 \times \text{temporary magnesium hardness}) + \text{Perm Mg hardness} + \text{CO}_2 + \text{HCl} + \text{H}_2\text{SO}_4 + \text{HCO}_3^- + \text{salts of } 100 \text{ Fe}^{2+}, \text{Al}^{3+} - \text{NaAlO}_2 \} \times 100/\%$   
purity  $\times$  volume of water

**Soda** =  $(106/100) \{ \text{Perm Ca hardness} + \text{Perm Mg hardness} + \text{salts of } \text{Fe}^{2+}, \text{Al}^{3+} + \text{HCl} + \text{H}_2\text{SO}_4 - \text{HCO}_3^- \} \times 100/\%$  purity  $\times$  volume of water.

## Desalination of brackish water

The removal of dissolve solids ( $\text{NaCl}$ ) from water is known as desalination process. It can be carried out by Reverse osmosis.

**Reverse Osmosis or super filtration** commonly referred to as **RO**, is a process to demineralize or deionize water by pushing it under pressure through a semi-permeable membrane separates two solutions, solvent from the lower concentration passes to the higher concentration to equalize the concentration of both. But in the reverse osmosis, pressure higher than osmotic pressure is applied from the higher concentration side so that the path of the solvent is reversed, i.e. from higher concentration to lower concentration. This method is applicable mainly for the desalination of sea water. Sea water and pure water are separated by a semi-permeable membrane. The process is very easy. It is used to make pure water. It removes the ionic and non-ionic substances in the water. It also can remove suspended colloidal particles. The life of a membrane is nearly 2 years and it should be replaced after this period. By this process, sea water is made to fit for drinking. Water obtained after being treated by this process is used in boilers.



### Advantages:

1. Reverse Osmosis is capable of removing up to 99% of the dissolved salts (ions), particles, colloids, organics, bacteria and pathogens from the feed water.
2. Requires extremely low energy.
3. Operating expenses are low.
4. Reverse Osmosis is very effective in treating brackish, surface and ground water for both large and small flows applications.

### Applications or Uses for Demineralised Water:

Department of Applied Sciences, MIET, Meerut



1. Industrial uses for engineering and scientific purposes
2. Lab applications and testing
3. Can be used by computer chip manufacturers and other microelectronics
4. Automotive uses such as lead acid batteries and cooling systems
5. High-pressure boiler feed
6. Laser cutting
7. Pharmaceutical manufacturing
8. Cosmetics
9. Aquariums
10. Fire extinguishers.

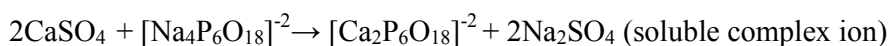
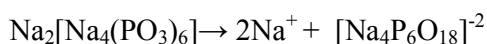
### INTERNAL TREATMENT OF WATER

In this method raw water is treated inside the boiler. This is a process of adding suitable chemical to reduce scale & sludge formation. It is mainly based on solubility. This is a corrective method. This method is also called conditioning method.

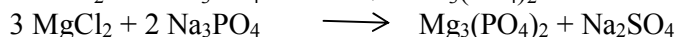
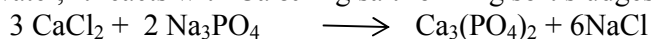
**1. Carbonate conditioning:-** In low pressure boilers, scale formation can be avoided by treating the boiler water with  $\text{Na}_2\text{CO}_3$ . Where,  $\text{CaSO}_4$  is converted into  $\text{CaCO}_3$ .  $\text{CaSO}_4$  is precipitated as loose sludge in the boiler which can be scrapped off.

### **2. Calgon Conditioning:**

Calgon means calcium gone i.e. the removal of  $\text{Ca}^{2+}$  by Sodium hexa-meta phosphate is called calgon. It reacts with calcium ion and forms a water soluble compound. Involves adding Calgon (sodium hexa meta phosphate  $(\text{NaPO}_3)_6$  to boiler water. It prevents the scale and sludge formation by forming soluble complex compound with  $\text{CaSO}_4$ .



**3. Phosphate conditioning:** It is applied to high pressure boilers. When sodium phosphate is added to boiler water, It reacts with Ca & Mg salt forming soft sludges.



### Numericals

Q1. Covert 60 ppm hardness of water in terms of mg/L, degree french and degree Clarke.

$$\begin{aligned}\text{Ans. } 60 \text{ ppm} &= 60 \text{ mg/L} \\ &= 60 \times .1^\circ\text{Fr} \\ &= 6^\circ\text{Fr} \\ 60 \text{ ppm} &= 60 \times .07^\circ\text{Cl} \\ &= 4.2^\circ\text{Cl}\end{aligned}$$

Q2. A water sample contains 408 mg of  $\text{CaSO}_4$  per litre. Calculate the hardness in terms of  $\text{CaCO}_3$  equivalent.

$$\begin{aligned}\text{Ans. Hardness} &= \text{Strength of hardness producing subs.} \times \frac{\text{Chemical equivalents of } \text{CaCO}_3}{\text{Chemical equivalents of hardness producing substance}} \\ &= 400 \text{ mg/L} \times 50/68 \\ &= 300 \text{ mg/L} = 300 \text{ ppm}\end{aligned}$$

Q3. How many grams of  $\text{MgCO}_3$  dissolved per litre gives 84 ppm hardness?

Ans. Hardness = Strength of  $\text{MgCO}_3$  in mg/L  $\times \frac{\text{Chemical equivalents of CaCO}_3}{\text{Chemical equivalents of MgCO}_3}$

$$\begin{aligned} \text{Strength of MgCO}_3 \text{ in mg/L} &= \text{Hardness} \times \frac{\text{Chemical equivalents of CaCO}_3}{\text{Chemical equivalents of MgCO}_3} \\ &= 84 \text{ ppm} \times \frac{42}{50} = 70.56 \text{ ppm} = 70.56 \text{ mg/L} \end{aligned}$$

So, .07056 gms of  $\text{MgCO}_3$  dissolved per litres gives 84 ppm of hardness.

Q4. A sample of water on analysis was found to contain the following impurities:

Impurity	Quantity (mg/L)	Mol. Wt.
$\text{Ca(HCO}_3)_2$	4	162
$\text{Mg(HCO}_3)_2$	6	146
$\text{CaSO}_4$	8	136
$\text{MgSO}_4$	10	120

Calculate the temporary, permanent and total hardness of water in ppm, degree french and degree clarke.

Ans. Conversion into  $\text{CaCO}_3$  equivalent.:

Constituents	Amount (mg/L)	Multiplication factor	$\text{CaCO}_3$ equivalent
$\text{Ca(HCO}_3)_2$	4	100/162	$4 \times 100/162 = 2.47 \text{ mg/L}$
$\text{Mg(HCO}_3)_2$	6	100/146	$6 \times 100/146 = 4.11 \text{ mg/L}$
$\text{CaSO}_4$	8	100/136	$8 \times 100/136 = 5.88 \text{ mg/L}$
$\text{MgSO}_4$	10	100/120	$10 \times 100/120 = 8.33 \text{ mg/L}$

Temporary hardness is due to bicarbonates of calcium and magnesium

So, Temporary hardness =  $2.47 + 4.11 = 6.58 \text{ mg/L}$

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

$$\begin{aligned} \text{Hence temporary hardness} &= 6.58 \text{ mg/L} = 6.58 \text{ ppm} \\ &= 6.58 \times 0.1 = 0.658^\circ\text{Fr} \\ &= 6.58 \times 0.07 = 0.46^\circ\text{Cl} \end{aligned}$$

Permanent hardness in this case is due to  $\text{CaSO}_4$  and  $\text{MgSO}_4$

$$\begin{aligned} \text{So, permanent hardness} &= 5.88 + 8.33 = 14.21 \text{ mg/L} \\ &= 14.21 \text{ ppm} = 14.21 \times 0.1 = 1.421^\circ\text{Fr} \\ &= 14.21 \times 0.07 = 0.995^\circ\text{Cl} \end{aligned}$$

Q5. 100 ml of water sample has a hardness equivalent of 12.5 ml of 0.08 N  $\text{MgSO}_4$ . What is its hardness in ppm?

Ans.  $N_1 V_1$  of water sample =  $N_2 V_2$  of  $\text{MgSO}_4$

**Example** Calculate quantities of lime and soda required for softening of 20,000 litres of water containing following salts in ppm (16.4 ppm  $\text{NaAlO}_2$  used as a coagulant)

$$\text{Ca}^{+2} = 160 \text{ ppm}$$

$$\text{Mg}^{+2} = 72 \text{ ppm}$$

$$\text{HCO}_3^- = 73.2 \text{ ppm}$$

$$\text{CO}_2 = 44 \text{ ppm}$$

$$\text{Al}_2(\text{SO}_4)_3 = 34.2 \text{ ppm}$$

$$\text{HCl} = 36.5 \text{ ppm}$$

**Solution:** Conversion into  $\text{CaCO}_3$  equivalents.

Iron or salt	Amount present (ppm)	Conversion	$\text{CaCO}_3$ equivalent (ppm)
$\text{Ca}^{+2}$	160	$\frac{100}{40}$	$160 \times \frac{100}{40} = 400$
$\text{Mg}^{+2}$	72	$\frac{100}{24}$	$72 \times \frac{100}{24} = 300$
$\text{HCO}_3$	73.2	$\frac{100}{122}$	$73.2 \times \frac{100}{122} = 60$
$\text{CO}_2$	44	$\frac{100}{44}$	$44 \times \frac{100}{44} = 100$
$\text{NaAlO}_2$	16.4	$\frac{100}{164}$	$16.4 \times \frac{100}{164} = 10$
$\text{Al}_2(\text{SO}_4)_3$	34.2	$\frac{100}{342}$	$34.2 \times \frac{100}{342} = 10$
HCl	36.5	$\frac{100}{36.5}$	$36.5 \times \frac{100}{36.5} = 100$

$$\text{Lime required} = \frac{74}{100} [300 + 3(10) + 1/2(100) + 100 + 60 - 10]$$

$$= \frac{74}{100} [300 + 30 + 50 + 100 + 60 - 10]$$

$$\begin{aligned}
 &= \frac{74}{100} [530] \\
 &= 392.2 \text{ mg/lit} \\
 &= 392.2 \times 20000 \times \frac{1}{10^6} \\
 &= \mathbf{7.84 \text{ kg}}
 \end{aligned}$$

$$\begin{aligned}
 \text{Soda required} &= \frac{106}{100} [400 + 300 + 3(10) + 1/2(100) - 60 - 10] \\
 &= \frac{106}{100} [400 + 300 + 30 + 50 - 70] \\
 &= 752.6 \text{ mg/lit} \\
 &= 752.6 \times 20.000 \times \frac{1}{10^6} \\
 &= \mathbf{15.05 \text{ kg}}
 \end{aligned}$$

**Example** A water sample contains the following impurities per litre.

Ca(HCO <sub>3</sub> ) <sub>2</sub>	–	81 mg
Mg(HCO <sub>3</sub> ) <sub>2</sub>	–	73 mg
CaSO <sub>4</sub>	–	68 mg
MgSO <sub>4</sub>	–	60 mg
KCl	–	100 mg

Calculate (a) temporary and permanent hardness in water.

(b) Quantity of lime and soda required in kg for softening 50,000 litres of water if the purity of lime and soda are 80% and 90% respectively.

**Solution:** 1. Conversion of the impurities into CaCO<sub>3</sub> equivalents.

Substance	Quantity mg per/ litre	Conversion factor	CaCO <sub>3</sub> equivalent mg/litre
Ca(HCO <sub>3</sub> ) <sub>2</sub>	81	$\frac{100}{162}$	$\frac{100}{162} \times 81 = 50$
Mg(HCO <sub>3</sub> ) <sub>2</sub>	73	$\frac{100}{146}$	$\frac{100}{146} \times 73 = 50$
CaSO <sub>4</sub>	68	$\frac{100}{136}$	$\frac{100}{136} \times 68 = 50$
MgSO <sub>4</sub>	60	$\frac{100}{120}$	$\frac{100}{120} \times 60 = 50$

KCl does not react with lime or soda and its presence can be ignored.

$$\begin{aligned}
 2. \text{ Lime requirement} &= \frac{74}{100} [\text{Temp. Ca H} + 2 \times \text{Temp. Mg H} + \text{Perm. Mg H}] \\
 &= \frac{74}{100} \left[ \frac{50}{\text{Ca(HCO}_3)_2} + \frac{2 \times 50}{\text{Mg(HCO}_3)_2} + \frac{50}{\text{MgSO}_4} \right]
 \end{aligned}$$

Salt	Amount present ppm	Conversion factor	CaCO <sub>3</sub> equivalents ppm
Ca(HCO <sub>3</sub> ) <sub>2</sub>	162	$\frac{100}{162}$	$162 \times \frac{100}{162} = 100$
MgCl <sub>2</sub>	9.5	$\frac{100}{95}$	$9.5 \times \frac{100}{95} = 10$
Fe <sub>2</sub> O <sub>3</sub>	100 ppm	Does not contribute hardness	—
NaCl	58.5 ppm		—
SiO <sub>2</sub>	25 ppm		—
H <sub>2</sub> SO <sub>4</sub>	98	$\frac{100}{49}$	$98 \times \frac{100}{49} = 200$
MgSO <sub>4</sub>	60	$\frac{100}{120}$	$60 \times \frac{100}{120} = 50$
CaCO <sub>3</sub>	100	$\frac{100}{100}$	$100 \times \frac{100}{100} = 100$

$$\begin{aligned}
 \text{Amount of lime required} &= \frac{74}{100} [200 + 10 + 50 + 100] \\
 &= \frac{74}{100} [360] \times 50,000 \times \frac{1}{10^6} = 266.4 \text{ mg/lit}
 \end{aligned}$$



$$= 13.32 \text{ kg} = \text{Rs. } 70.59$$

$$\text{Amount of soda required} = \frac{106}{100} [10 + 50 + 100]$$

$$= \frac{106}{100} [160] \times 50,000 \times \frac{1}{106}$$

$$= 169.6 \text{ mg/lit}$$

$$= \mathbf{8.48 \text{ kg}}$$

$$\text{Cost } 38.16 \text{ Rs.}$$

$$\text{Total cost} = 70.59 + 38.16 = \mathbf{\text{Rs. } 108.6}$$

**Problem:-**

Calculate the quantity of lime and soda required for softening 1,00,000 litres of water containing the following impurities.

$$\text{Ca(HCO}_3)_2 = 30.2 \text{ ppm}$$

$$\text{Mg(HCO}_3)_2 = 20.8 \text{ ppm}$$

$$\text{CaCl}_2 = 28.1 \text{ ppm}$$

$$\text{MgCl}_2 = 8.7 \text{ ppm}$$

$$\text{CaSO}_4 = 35.00 \text{ ppm}$$

$$\text{MgSO}_4 = 6.7 \text{ ppm}$$

The purity of lime is 70% and the purity of soda 85% [At. wt. for H = 1, C = 12, O = 16, Na = 23, Mg = 24]

<i>Impurity</i>	<i>Amount in ppm</i>	<i>Molecular weight</i>	<i>Multiplication factor</i>	<i>CaCO<sub>3</sub> equivalent in ppm</i>
Ca(HCO <sub>3</sub> ) <sub>2</sub>	30.2	162	100/162	$30.2 \times 100/162 = 18.64$
Mg(HCO <sub>3</sub> ) <sub>2</sub>	20.8	146	100/146	$20.8 \times 100/146 = 14.24$
CaCl <sub>2</sub>	28.1	111	100/111	$28.1 \times 100/111 = 25.31$
MgCl <sub>2</sub>	8.7	95	100/95	$8.7 \times 100/95 = 9.15$
CaSO <sub>4</sub>	35.00	136	100/136	$35 \times 100/136 = 25.73$
MgSO <sub>4</sub>	6.7	120	100/120	$6.7 \times 100/120 = 5.58$

$$\text{Lime required} = \frac{74}{100} [\text{TempCa}^{2+} + 2 \times \text{Temp mg}^{2+} + \text{Perm mg}^{2+}]$$

$$\frac{74}{100} [18.64 + (2 \times 14.24) + 9.15 + 5.58]$$

$$= 45.769 \text{ ppm}$$

$$\begin{aligned}\text{Soda required} &= \frac{106}{100} [(25.31 + 25.73) + (9.15 + 5.58)] \\ &= 69.71 \text{ ppm}\end{aligned}$$

Lime is 70%

∴ for 100,000 lit. of water.

$$\begin{aligned}\text{Lime required} &= \frac{100}{70} \times (100,000 \times 45.769) \text{ mg} \times \frac{1}{106} \\ &= 65.384 \text{ kg}\end{aligned}$$

$$\begin{aligned}\text{Soda required} &= \frac{100}{85} \times (100,000 \times 69.71) \text{ mg} \times \frac{1}{106} \\ &= 82.01 \text{ kg}\end{aligned}$$

**Problem:-**

Calculate the quantity of lime and soda required for softening 10,000 litres of H<sub>2</sub>O containing the following impurities per litre



(Atomic weights for H = 1, C = 12, O = 16, Na = 23, Mg = 24)

**Solution:**

NaCl and SiO<sub>2</sub> are not hardness causing substances. Hence, they do not consume lime and soda.

Molecular weight of the impurities are,

$$(i) \text{ Ca (HCO}_3)_2 = 40 + 2 [1 + 12 + 3 \times 16] = 162$$

$$(ii) \text{ Mg (HCO}_3)_2 = 24 + 2 [1 + 12 + 3 \times 16] = 162$$

$$(iii) \text{ CaSO}_4 = 40 + 32 + (4 \times 16) = 136$$

$$(iv) \text{ MgSO}_4 = 24 + 32 + (4 \times 16) = 120$$

$$(v) \text{ Molecular weight of CaCO}_3 = 100$$

**Solution:**

NaCl and SiO<sub>2</sub> are not hardness causing substances. Hence, they do not consume lime and soda.

Molecular weight of the impurities are,

- (i)  $\text{Ca}(\text{HCO}_3)_2 = 40 + 2 [1 + 12 + 3 \times 16] = 162$
- (ii)  $\text{Mg}(\text{HCO}_3)_2 = 24 + 2 [1 + 12 + 3 \times 16] = 146$
- (iii)  $\text{CaSO}_4 = 40 + 32 + (4 \times 16) = 136$
- (iv)  $\text{MgSO}_4 = 24 + 32 + (4 \times 16) = 120$
- (v) Molecular weight of  $\text{CaCO}_3 = 100$

Impurity	Amount	Molecular weight	Multiplication factor	$\text{CaCO}_3$ equivalent in ppm
$\text{Ca}(\text{HCO}_3)_2$	7.8	162	100/162	$7.8 \times 100/162 = 4.8$
$\text{Mg}(\text{HCO}_3)_2$	8.00	146	100/146	$8 \times 100/146 = 5.4$
$\text{CaSO}_4$	12.2	136	100/136	$12.2 \times 100/136 = 8.9$
$\text{MgSO}_4$	10.6	120	100/120	$10.6 \times 100/120 = 8.8$

$$\begin{aligned}
 \text{Lime required} &= \frac{74}{100} [\text{Temp Ca}^{2+} + 2 \times \text{Temp Mg}^{2+} + \text{Perm Mg}^{2+}] \\
 &= \frac{74}{100} [4.8 + (2 \times 5.4) + 8.8] \text{ mg/lit.} \\
 &= 18.05 \text{ mg/lit}
 \end{aligned}$$

For 10, 000 litres of water lime required

$$\begin{aligned}
 &= (18.5 \times 10,000) \text{ mg} \\
 &= 18050 \text{ mg.}
 \end{aligned}$$

$$\begin{aligned}
 \text{Soda required} &= \frac{106}{100} [\text{perm Ca}^{2+} + \text{Perm mg}^{2+}] \\
 &= \frac{106}{100} [8.9 + 8.8] \\
 &= 18.23 \text{ mg/lit}
 \end{aligned}$$

For 10, 000 litres of water soda required  $(18.23 \times 10, 000) \text{ mg}$

$$= 182340 \text{ mg}$$



**Problem:-**

Hardness of 77500 litres of water was completely removed by zeolite method. The exhausted zeolite softener then required 15 litres of NaCl (2%). For regeneration calculate hardness of water sample.

**Solution:**

1 litre of NaCl contains = 20 gm of NaCl

∴ 15 litres of NaCl contains =  $20 \times 15 = 300$  gm of NaCl

Now 58.5 gm NaCl = 50 gm of  $\text{CaCO}_3$  equivalent

$$\begin{aligned}\therefore 300 \text{ gm NaCl} &= \frac{300 \times 50}{58.5} \\ &= 256.41 \text{ gm}\end{aligned}$$

Total quantity of water = 77,500 litres

77,500 litres of water = 256.41 gm  $\text{CaCO}_3$  emits

1 litre of water = 0.0033 gm = 3.30 ppm

Hardness of water = 3.30 ppm

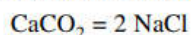
**Problem:-**

By passing 50 litres of NaCl solution containing 250 gm/litre of NaCl, a exhaust zeolite softener bed was regenerated. Calculate the litres of hard  $\text{H}_2\text{O}$  sample (hardness equal to 200 ppm as  $\text{CaCO}_3$ ) which can be softened by regenerated bed of zeolite softener.

**Solution:**

First, we have to calculate total NaCl in terms of  $\text{CaCO}_3$  equivalent, used for the regeneration of zeolite.

50 litres of NaCl solution contain =  $50 \times 250 = 12,500$  gm of NaCl as



$$100 = 2(58.5)$$

$$50 = 58.5$$

$$\therefore \text{CaCO}_3 \text{ equivalent would be} = 12,500 \times \frac{50}{58.5} \text{ gm}$$

As the hardness is 200 ppm, i.e., 200 mg/lit. of  $\text{CaCO}_3$  of 0.2 gm/lit. of  $\text{CaCO}_3$  are present.

$$\therefore 12500 \times \frac{50}{58.5} \text{ gm will be present in}$$

$$\frac{1200 \times 50}{0.2 \times 58.5} = 53,418.80 \text{ lit. of water.}$$

The zeolite bed can soften 53,418.80 lit. of  $\text{H}_2\text{O}$ .