Water Treatment

Types of hardness-Units, Alkalinity of water and its significance, Softening methods and Numerical problems based on these methods; Membrane-based processes; Dissolved Oxygen, Problems with Boiler feed water and its treatments.

Course Outcome (CO):

Course Outcomes: *At the end of this course, the students will be able to:*

CO1	Exploit the concept of hardness in softening hard water and determining the hardness of water.
CO2	Utilize the knowledge of electrochemistry and corrosion science in preventing engineering equipments from corrosion.
CO3	Apply the concept of molecular spectroscopy to analyze organic compounds using spectrophotometer.
CO4	Classify various fuels based on combustion parameters and understand the working principle of various batteries.
CO5	Acquire knowledge on synthesis & characterization of oxide based & noble metal nanoparticles through green synthetic route.

Lecture-1

1.0 Introduction

Water is nature's most wonderful, abundant and useful compound. Without food, human can survive for a number of days, but without water one cannot survive. And with good reason – without water, we'd be nothing. Just dust. It's a tremendously valuable resource, yet one we waste and pollute abnormally. It's a finite resource; we only have what we have. And although there is about 332,500,000 cubic miles of it on earth – only one-hundredth of one percent of the world's water is readily available for human use. We really need to learn how to show it some respect. Which is where World Water Day comes in? March 22 is celebrated as World Water Day.

Even though water deserves celebration every day, we'll take this occasion to give a shout-out to this incredible compound that gives us life and sustains the planet around us. So with that in mind, consider the following facts – some wondrous, some disturbing, all eye-opening.

Some facts about water are 1. The average human body is made of 50 to 65 percent water.

2. Newborn babies have even more, ringing in at 78 percent water.

3. Water covers 70.9 percent of the planet's surface.

4. Ninety-seven percent of the water on Earth is salt water; the water found in the Earth's lakes, rivers, streams, ponds, swamps, etcetera accounts for only 0.3 percent of the world's fresh water. The rest is trapped in glaciers or is in the ground.

5. There is more water in the atmosphere than in all of our rivers combined.

6. a lot can live in one drop of water. There can be a lot going on in a single drop of ocean water. It will most likely have millions (yes, millions!) of bacteria and viruses. And it could also have fish eggs, baby crabs, plankton, or even small worms.

Water is not only essential for the lives of animals and planets, but also occupies a unique position in industries. In industries, water is used for steam generation, as coolants in power & chemical plants, in steel, paper, textiles, etc. Have a look on some facts about volume of water use in some of the industries: 1. it takes 924 gallons of water to produce 2.2 pounds of rice. 2. It takes 2.6 gallons of water to make a sheet of paper. 3. It takes 2,641 gallons of water to make a pair of jeans. 4. It takes 6.3 gallons of water to make 17 ounces of plastic. 5. It takes 39,090 gallons of water to manufacture a new car.

2.0 Impurities in water

Once water has fallen on the earth as rain, it will either start to penetrate the soil, remain on the surface in puddles, or run off into rivers or lakes - depending largely on the type of rock strata found immediately below the earth's surface. Therefore, the main source of impurities is the mineral and organic constituents which make up the upper layers of the earth's crust, and which are dissolved or held in suspension by the water. Surface waters are especially prone to seasonal changes in quality caused mainly by varying levels of organic contaminants. For instance, during the autumn and winter months, dead leaves and decaying plants release large quantities of organic matter into streams, lakes and reservoirs.

Water has been called both 'the matrix of life' and 'the universal solvent'. So in addition to providing a life-support system for a broad range of living organisms, it can dissolve virtually every chemical compound, though not necessarily to a detectable degree. It normally contains < 500 mg/l total dissolved solids TDS - equivalent to a purity of 99.95%. Even so, minute quantities of impurities can have a profound effect on industrial and laboratory processes - hence the need for purification.

The impurities present in raw waters can be classified as follows:

A. **Dissolved impurities:** It is of three types: (**1**). *Inorganic salts* (due to presence of dissolved salts like carbonates, bicarbonates, nitrates, chlorides and sulphates of calcium (Ca), magnesium (Mg), iron (Fe),sodium (Na), etc. (**2**). *Organic matters* (due to presence of humic and fulvic Acids, pesticides, detergents, etc.) (3) *Dissolved gases* (includes O_2, CO_2). Dissolved impurities causes corrosion in boilers and imparts hardness to water.

B. **Suspended impurities:** It is of three types: (1) *Organic* (includes vegetable & animal matters, industrial & domestic by-products, oil globules, etc.); (2) *Inorganic* (includes clay/silica/sand particles); (3) *Colloidal (*organic and inorganic)- includes finely divided silica, clay, sand, products from organic wastes, etc. Such impurities impart turbidity, colour and odour to water.

C. **Living Matters:** It is of two types: (1) *Micro-organisms* (include bacteria, fungi, protozoa, and algae); (2) *Macro-organisms* (includes fish, worm, larvae, shrimps, etc.). Living matters brings health related issues upon consumptions.

3.0 Sources of impurities:

Following are the sources of impurities in water:

A. Gases like O_2, CO_2, etc. are picked up from the atmosphere by rain water.
B. Decomposition of plant and animal remains introduce organic impurities in water.
C. Water takes inorganic impurities when it comes in contact with ground, soil or rocks.
D. Suspended/living matters impurities are also introduced in water when it comes in contact with sewage or industrial waste.

4.0 Specification of water for different uses

It is not true that water with same condition will be use in all kinds of industries or purposes. Specifications of water for various industries are different. Few examples are discussed below:

A. ***Boilers in steel industries*** require water of no hardness, dissolved gases, alkaline and acidic masses.
B. ***Paper industries*** need water free from silica, turbidity, alkalinity, hardness, etc.
C. ***Textile industries*** require water of nearly zero hardness and no organic matter content.
D. ***Beverage industries*** need water free from alkaline constituents.
E. ***Sugar industries*** demand water free from salts like sulphates, nitrates, etc.
F. ***Pharmaceutical industries*** need ultra pure water free from pathogenic bacteria.

N.B.: As per the BIS 2012 (Bureau of Indian Standard), we require drinking water of following specifications:

1. pH value-6.5-8.5; 2. Total dissolved solid-500 mg/l; 3. Ca- 75 mg/l; 4. Chloride- 250 mg/l; 5. Fluoride- 1.0 mg/l; 6. Iron-0.3 mg/L; 7. Total hardness- 200 mg/l; 8. Arsenic-0.01 mg/l; 9. Lead-0.01 mg/l; Mercury-0.001 mg/l; cyanide- 0.05 mg/l; 10. Colour-colourless; 11. Pathogenic micro-organisms- nil per 100 ml water.

From the specifications of water for various industries, it can be concluded that water needs to be treated to remove all the undesirable impurities.

Water Treatment is the process by which all types of impurities are removed from water and making fit for domestic & industrial purposes.

5.0 Hardness of water

Hardness in water is a characteristic by virtue of which it prevents lathering/foaming of soap solution. It is also defined as the soap consuming capacity of water. Higher is the hardness of water larger is the consumption of soap. Hardness is due to presence of dissolved salts of calcium (Ca), magnesium (Mg) and other heavy metals like iron (Fe), manganese (Mn), aluminum (Al). In other words hardness in water is due to bicarbonate (HCO_3^-), chloride (Cl^-), sulphate (SO_4^{3-}), and nitrate (NO_3^-) of Ca, Mg, Fe, Mn, Al, etc.

Salts like $Ca(HCO_3)_2$, $Mg(HCO_3)_2$, $CaCl_2$, $MgCl_2$, $CaSO_4$, $MgSO_4$, $Ca(NO_3)_2$, $Mg(NO_3)_2$, $FeSO_4$, $Al_2(SO_4)_3$, $MnSO_4$, etc. are responsible of hardness of water. **The major contributor towards hardness is Ca and Mg-salts.

N.B.: Chemical constituents like $NaHCO_3$, $CaCO_3$, NaCl, KCl, K_2SO_4, Na_2SO_4, $NaNO_3$, KNO_3, Fe_2O_3, etc. are treated as ***non-hardness constituents***.

Soap consuming tendency of hard water *(Why is hard water consumes more soap?)*

Soaps are sodium (Na) or potassium (K) salt of higher fatty acids (e.g.; Stearic acid $C_{17}C_{35}COOH$, oleic acid $C_{17}C_{33}COOH$, palmitic acid $C_{15}C_{31}COOH$). For example, $C_{17}C_{35}COONa$ (Sodium stearate).

A sample of hard water (let say contains hardness constituent as $CaCl_2$) when treated with soap does not produce enough lather, but on the other hand forms a white scum or precipitate. The precipitation process continues till all the hardness constituents are removed as white scum. After this, soap generates enough foam with water. The chemical reactions involved during this process are as follows:

1. $2C_{17}C_{35}COONa$ (soap) + $CaCl_2$ → $(C_{17}C_{35}COO)_2Ca$ (*Calcium Stearate, White scum*) + 2NaCl
2. Soap + water → Produce enough foam

Hard Water and Soft Water

The water which does not produce lather with soap solution readily, but forms a white curd is called hard water. In fact any cations which produce soft precipitate with soap solution will contribute to hardness. Examples include Ca^{+2}, Mg^{+2}, etc. On the other hand, water which lathers easily on shaking with soap solution is called soft water. Soft water is free from dissolved Ca and Mg-salts. The difference between the two is summarized in the following table.

Sl. No.	**Hard Water**	**Soft Water**
1	Water which does not readily produce lather with soap solution, but forms a white curd, is called "Hard Water".	Water which readily form foam on shaking with soap solution, is called "Soft Water".

2	It contains dissolved Ca and Mg-salts.	It does not contain dissolved Ca and Mg-salts.
3	Cleansing quality of soap is depressed and a lot of soap is wasted during washing and bathing.	Cleansing quality of soap is not depressed and a little amount of soap is wasted during washing and bathing.
4	B. Pt. of water is elevated.	Water boils at 104 ^{0}C.
5	Hair and skin becomes hard and dull.	Hair and skin becomes soft.
6	No **Plumbo-solvency** occurs	**Plumbo-solvency** occurs
7	Hardness > 50 ppm	**Hardness** < 50 ppm

***A residual hardness of about 85 ppm as $CaCO_3$ equivalent is needed for drinking purposes.

Plumbosolvency: **Plumbosolvency** is the ability of a solvent like water to dissolve lead (Pb latin name-Plumbus). Soft water is a plumbo-solvent. Permissible limit of Pb in water is 0.05 ppm.

- ✓ Why water should not be soft for drinking purposes?
  The reason is that soft water is plumo-solvent and helps in dissolution of Pb as per the following reaction: $\mathbf{2Pb + 2H_2O + O_2 \rightarrow 2Pb(OH)_2}$
  N.B: The solubility of Pb in water is diminished in the presence of HCO_3^- (i.e., in hard water)

Q. 1. What is plumbo-solvency?

Ans: **Plumbosolvency** is the ability of a solvent like water to dissolve lead (Pb: latin name-Plumbus).

Q. 2. Give reason that hard water is not a plumbo-solvent.

Ans. As the solubility of Pb (plumbus) in water is diminished in the presence of HCO_3^- (i.e., in hard water), it provides a protective layer on the surface of the pipe.

Q. 3. Give reason that hard water consumes a lot of soap.

Ans. A sample of hard water (let say contains hardness constituent as $CaCl_2$) when treated with soap does not produce enough lather, but on the other hand forms a *white scum or precipitate*. The precipitation process continues till all the hardness constituents are removed as white scum. After this, soap generates enough foam with water. The chemical reactions involved during this process are as follows:

3. $2C_{17}C_{35}COONa$ (soap) + $CaCl_2 \rightarrow (C_{17}C_{35}COO)_2Ca$ (*Calcium Stearate, White scum*) + 2NaCl
4. Soap + water → Produce enough foam

Q. 4. Write the chemical reactions involved when hard water reacts with soap.

Ans. The chemical reactions involved during this process are as follows:

1. $2C_{17}C_{35}COONa$ (soap) + $CaCl_2$ → $(C_{17}C_{35}COO)_2Ca$ (*Calcium Stearate, White scum*) + 2NaCl
2. Soap + water → Produce enough foam

Advantages and disadvantages of hard water

Advantages	***Disadvantages***
1. Taste of water is better than soft water	*1. It produces white precipitate with soap solution. Thus, the washed clothes look dull.*
2. Dissolved Ca-salts helps in producing strong teeth and healthy bones in children	*2. Causes boiler corrosion.*
3. Not a plumbo-solvent	*3. Increases B. Pt. of water.*

Q. 5. Mention some advantages of hard water. (Refer the above table)

Q. 6. Mention some disadvantages of hard water. (Refer the above table)

Lecture-2 of Water Treatment

Types of Hardness

It is of two types: (1) Temporary Hardness and (2) Permanent Hardness

1. *Temporary Hardness:* It is caused by the presence of dissolved bicarbonates (HCO_3^-) of Ca and Mg, heavy metals like Al, Mn and carbonates of Fe. The salts responsible are $Ca(HCO_3)_2$, $Mg(HCO_3)_2$, etc. These salts are thermally unstable and undergo thermal decomposition to form insoluble substance as follows;
   a. $Ca(HCO_3)_2 \rightarrow CaCO_3$ (ppt.) + $H_2O + CO_2$
   b. $Mg(HCO_3)_2 \rightarrow Mg(OH)_2$ (ppt.) + $2CO_2$

So, temporary hardness can be removed by boiling. It is otherwise known as *carbonate or alkaline hardness*.

2. *Permanent Hardness:* It is caused by the presence of chloride (Cl^-), nitrates (NO_3^-), sulphates (SO_4^{2-}) of Ca, Mg, Fe, Al, Mn, etc. The salts responsible are $CaCl_2$, $Ca(NO_3)_2$, $CaSO_4$, $MgCl_2$, $Mg(NO_3)_2$, $MgSO_4$, $Al_2(SO_4)_3$, $FeSO_4$, etc. These salts are thermally stable as present in ionic form in water. So, they can't be remove by heating but removed by softening methods. It is also known as *non-carbonate or non-alkaline hardness*.

Total Hardness

All the hardness causing salts contribute towards total hardness. So, total hardness is the sum of temporary and permanent hardness.

Q. 7. Which of the following salt is a non-hardness constituent?

$MgCl_2$, $Mg(NO_3)_2$, $MgSO_4$, $Al_2(SO_4)_3$, $NaHCO_3$

Ans. $NaHCO_3$

Q. 8. Which of the following salts are hardness constituents?

$CaCl_2$, $Ca(NO_3)_2$, K_2SO_4, Na_2SO_4, $NaNO_3$, KNO_3, Fe_2O_3

Ans. $CaCl_2$ and $Ca(NO_3)_2$

5.2 Degree of Hardness

As $CaCO_3$ is insoluble in water, it does not contribute towards hardness of water. But, hardness of water is expressed in terms of equivalent amount of $CaCO_3$ due to following reasons:

A. Ease in calculation as its molecular weight is 100.

B. It is the most insoluble salt that can be precipitated during water treatment.

Equivalent of $CaCO_3$ = (S, strength of hardness substance in mg/L) x [100/ (2 x M/n-factor)]

Where, M = Molar mass of hardness substance.

N.B.: n-factor of all Ca and Mg-salts are 2. For aluminum sulphate, it is 6.

- ✓ All hardness and non-hardness constituents can be expressed as **Equivalent of $CaCO_3$**

Q. 9. Give reason that $CaCO_3$ is used to express hardness of water.

Ans. The hardness of water is expressed in terms of equivalent amount of $CaCO_3$ due to following reasons:

A. Ease in calculation as its molecular weight is 100.
B. It is the most insoluble salt that can be precipitated during water treatment.

Q. 10. What happens when hard water containing temporary hardness constituents are boiled for some time?

Ans. Temporary hardness constituents like $Ca(HCO_3)_2$ $Mg(HCO_3)_2$ are thermally unstable and undergo thermal decomposition to form insoluble substances like $CaCO_3$ & $Mg(OH)_2$ as follows;

c. $Ca(HCO_3)_2 \rightarrow CaCO_3$ (ppt.) + $H_2O + CO_2$
d. $Mg(HCO_3)_2 \rightarrow Mg(OH)_2$ (ppt.) + $2CO_2$

Example-1 Express the following constituents as $CaCO_3$ eq.: (1) 162 mg/L of $Ca(HCO_3)_2$, (2) 111 mg/L of $CaCl_2$, and (3) 117 mg/L NaCl, Given: At mass: Ca = 40, C = 12, O = 16, H = 1, Na = 23, Cl = 35.5

Solution: (1) $Ca(HCO_3)_2$ as $CaCO_3$ eq. = 162 x 100/162 = 100 mg/l, here n-factor = 2

(2) $CaCl_2$ as $CaCO_3$ eq. = 111 x 100/111= 100 mg/l, here n-factor = 2

(3) NaCl as $CaCO_3$ eq. = 117 x 100/2 x 58.5 = 100 mg/l, **here n-factor = 1**

Example-2

A water sample contains 136 mg/L of $CaSO_4$. Calculate the hardness as equivalent amount of $CaCO_3$. (At mass of Ca = 40, S = 32, O = 16)

Solution: Equivalent of $CaCO_3$ = 136 x [100/(2 x 136/2) = 100 ppm

Example-3 How many gram of $MgSO_4$ dissolved per litre gives 200 ppm of hardness as equivalent amount of $CaCO_3$. (At mass: Mg = 24, S = 32, O = 16)

Solution: Equivalent of $CaCO_3$ = (S, strength of hardness substance in mg/L) x [100/ (2 x M/n-factor)]

So, (S, strength of hardness substance in mg/L) = Equivalent of $CaCO_3$/ [100/ (2 x M/n-factor)]

Or S = 200/[100/(120)] = 240 mg/L = 0.24 g/L

5.3 Units of hardness and their inter-relations

Hardness can be expressed by the four units.

1. Parts per million (ppm): It is the 1 part of $CaCO_3$ equivalent hardness per 10^6 parts of water.
2. Millligrams per litre (mg/L): It is the no of mg of $CaCO_3$ equivalent hardness present per litre of water.
3. Degree French (^{0}Fr): It is the 1 part of $CaCO_3$ equivalent hardness per 10^5 parts of water.
4. Clarke's degree (^{0}Cl): It is the part of $CaCO_3$ equivalent hardness per 70,000 parts of water.

Relationships between various units of Hardness

5. We know that, 1 ppm = 1 part per 10^6 parts of water
   1 ^{0}Fr = 1 part per 10^5 parts of water,
   And 1 ^{0}Cl = 1 part per 70, 000 parts of water
   So, 1 part = 10^6 ppm = 10^5 ^{0}Fr = 70,000 ^{0}Cl
   Or, 10^6 ppm = 10^5 ^{0}Fr = 70,000 ^{0}Cl
   Divide all by 10^6, so that **1 ppm = 0.1 ^{0}Fr = 0.07 ^{0}Cl = 1 mg/L**

Q. 11. Show that 1 ppm = 1 mg/L

Answer: 1 mg/L means 1 mg of $CaCO_3$ eq. hardness in 1L of water

= 1 mg of $CaCO_3$ eq. hardness in 10^6 mg of water ***(as for water, 1 L = 1 Kg = 1000 g = 1000,000 mg = 10^6 mg)

= 1 part of $CaCO_3$ equivalent hardness per 10^6 parts of water = 1 ppm (Proved)

Example-4 A sample of water on analysis was found to contain the following impurities:

Impurity	$Ca(HCO_3)_2$	$Mg(HCO_3)_2$	$MgSO_4$	$CaSO_4$	K_2SO_4
Quantity (mg/L)	4	6	8	10	10
Mol Wt.	162	146	120	136	134

Calculate the temporary, permanent, and total hardness of water in ppm, ^{0}Fr and ^{0}Cl.

Solution:

Impurity	**Quantity (mg/L)**	**n-factor**	**Mol. Wt.**	**$CaCO_3$ eq. in mg/L**
$Ca(HCO_3)_2$	4	2	162	4 x (100/162)= 2.47
$Mg(HCO_3)_2$	6	2	146	6 x (100/146)= 4.11
$MgSO_4$	8	2	120	8 x (100/120)= 8.33
$CaSO_4$	10	2	136	10 x (100/136)= 5.88

N.B.: K_2SO_4 is a non-hardness constituent.

(i) **Temporary Hardness (due to bicarbonates of Ca and Mg)** = 2.47 + 4.11 = 6.58 ppm = 6.58 x 0.1 ^{0}Fr = 0.658 ^{0}Fr = 6. 58 x 0.07 ^{0}Cl = 0.46 ^{0}Cl

(ii) **Permanent hardness (due to sulphates of Ca and Mg)** = 5.88 + 8.33 = 14.21 ppm = 1.421 **^{0}Cl** = 0.995 ^{0}Cl

(iii) **Total hardness** = 6.58 + 14.21 = 20.79 ppm = 2.079 ^{0}Fr = 0.9947 ^{0}Cl

Example-5

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

Impurity	$Mg(HCO_3)_2$	$CaSO_4$	$MgCl_2$	$CaCl_2$	NaCl
Quantity (mg/L)	16.2	27.2	9.5	22.2	10
Mol Wt.	162	136	95	111	58.5

Calculate the temporary, permanent, and total hardness of water in ppm, ^{0}Fr and ^{0}Cl.

Solution:

Impurity	**Quantity (mg/L)**	**n-factor**	**Mol. Wt.**	**$CaCO_3$ eq. in mg/L**
$Mg(HCO_3)_2$	16.2	2	162	16.2 x (100/162)= 10
$CaSO_4$	27.2	2	136	27.2 x (100/136)= 20
$MgCl_2$	9.5	2	95	9.5 x (100/95)= 10
$CaCl_2$	22.2	2	111	22.2 x (100/111)= 20

N.B.: NaCl is a non-hardness constituent.

- **(i)** **Temporary Hardness (due to** $Mg(HCO_3)_2$**) = 10 mg/L = 10** ppm = 10 x 0.1 ^{0}Fr = 1.0 ^{0}Fr = 10 x 0.07 ^{0}Cl = 0.7 ^{0}Cl
- **(ii)** **Permanent hardness (due to** $CaSO_4$, $MgCl_2$, $CaCl_2$ **) =** 20 + 10 + 20 = 50 mg/L = 50 ppm = 5.0 ^{0}**F** = 3.5 ^{0}Cl
- **(iii)** **Total hardness =** 10 + 50 = 60 ppm = 6 ^{0}Fr = 4.2 ^{0}Cl

Example-6 Find the hardness of water if water containing 100 mg/L of $Ca(HCO_3)_2$, 200 mg/L of $Mg(HCO_3)_2$ and 250 mg/L NaCl is boiled for 15 minute.

Ans. Hardness = 0, as Temporary hardness is removed by boiling. NaCl is non-hardness mass.

Example-7 A water sample contains 150 mg/L of **$Ca(HCO_3)_2$**, 111 mg/L of $CaCl_2$, 12 mg/L of $MgSO_4$, and 250 mg/L of Na_2SO_4. Find the temporary, permanent and total hardness of water after boiling for 10 minute.

Ans. (i) **$Ca(HCO_3)_2$ can be removed by boiling. So, temp. Hardness = 0**

Na_2SO_4 is a non-hardness mass.

Here, Permanent hardness is due to presence of dissolved $CaCl_2$ and $MgSO_4$ in water.

So, at first we have to express these hardness constituents as $CaCO_3$ eq.

$CaCl_2$ as $CaCO_3$ eq. = (111 x 100/111) = 111 mg/L; Molar mass of $CaCl_2$ = 111, n-factor = 2

$MgSO_4$ as $CaCO_3$ eq. = (12 x 100/120) = 10 mg/L; Molar mass of $MgSO_4$ = 120, n-factor = 2

(ii) So, **Perm. Hardness** = 100 + 10 = 110 mg/l = 110 ppm = 11 ^{0}Fr = 7.7 ^{0}Cl.

(iii) **Total hardness** = temp + perm. = 0 + 110 = 110 mg/l = 110 ppm = 11 ^{0}Fr = 7.7 ^{0}Cl.

Lecture-3

6.0 Water Quality Parameters

Water quality parameters include chemical, physical, and biological properties. Parameters that are frequently monitored for water quality include hardness, acidity, alkalinity, temperature, dissolved oxygen, pH, conductivity, turbidity, colour, odour, etc.

1. **Hardness:** (already discussed)
2. **Alkalinity: It is a measure of the ability of water to neutralize the acids.**
3. **Dissolved oxygen: It is the mass of the oxygen gas present, in milligrams per liter of water. Oxygen is more easily dissolved in cold water.**
4. **Acidity:** Acidity of water is its quantitative capacity to react with a strong base.
5. **Temperature:** Water Temperature is a controlling factor for aquatic life: it controls the rate of metabolic activities, reproductive activities and therefore, life cycles.
6. **pH:** pH is an important limiting chemical factor for aquatic life. If the water in a stream is too acidic or basic, the H+ or OH- ion activity may disrupt aquatic organisms biochemical reactions by either harming or killing the stream organisms.
7. **Conductivity:** It is a measure of how well water can pass an electrical current. It is an indirect measure of the presence of inorganic dissolved solids such as chloride, nitrate, sulfate, phosphate, sodium, magnesium, calcium, iron and aluminum.
8. **Turbidity:** Turbidity is a measure of the cloudiness of water. Cloudiness is caused by suspended solids (mainly soil particles) and plankton (microscopic plants and animals) that are suspended in the water column.
9. **Colour:** It is due to the presence of natural organic matter (humic substance giving the yellow color. The color may also be caused by certain industrial waste and by some metallic complexes.
10. **Odour:** It is often due to dissolved organic impurities, such as phenols, chlorophenols, sewage component.

Alkalinity

It is a measure of the ability of water to neutralize the acids.

Any substances which can cause an increase in the hydroxide ion concentration [OH^-] upon dissociation or due to hydrolysis or due to decomposition contribute towards alkalinity of water. Alkalinity is due to presence of ions like CO_3^{2-}, OH^-, HCO_3^- in the water. So, presence of constituents like NaOH, Na_2CO_3 and $NaHCO_3$ in water makes the water alkaline as per the following reactions:

1. $NaOH \rightarrow Na^+ + OH^-$ (Dissociation)
2. $Na_2CO_3 + H_2O \rightarrow 2NaOH + CO_2$ (Hydrolysis)
3. $NaHCO_3 \rightarrow NaOH + CO_2$ (Thermal decomposition)

N.B.: Alkalinity in water is due to only CO_3^{2-}/OH^-/HCO_3^- or due to OH^- and CO_3^{2-} together or due to CO_3^{2-} and HCO_3^- together. But, the possibility of OH^- and HCO_3^- together in water is ruled out. (Why?)

*** Because they combine to form CO_3^{2-} in water as per the following reaction:

$OH^- + HCO_3^- \rightarrow CO_3^{2-} + H_2O$ (or $NaOH + NaHCO_3 \rightarrow Na_2CO_3 + H_2O$)

Drawbacks of highly alkaline water

Some of the drawbacks are: 1. It causes alkaline corrosion in boiler known as caustic embrittlement.
2. It may leads to deposition of precipitates in boiler tubes and pipes.
3. Not fit for human consumption for a longer period of time.

Q. Which of the following combination is ruled out and why?

A. OH^- and CO_3^{2-}
B. CO_3^{2-} and HCO_3^-
C. OH^- and HCO_3^-

Ans. **C.** Because they combine to form CO_3^{2-} in water as per the following reaction:

$OH^- + HCO_3^- \rightarrow CO_3^{2-} + H_2O$ (or $NaOH + NaHCO_3 \rightarrow Na_2CO_3 + H_2O$)

Dissolved Oxygen (DO)

It is the most usual corrosion causing factor in boilers. DO react with the iron (Fe) of boiler in presence of water to form rust (Ferric oxide).

Chemical reaction:

$2Fe + 2H_2O + O_2 \rightarrow 2Fe(OH)_2$ (ferrous form is unstable)

$Fe(OH)_2$ oxidizes in presence of oxygen to form Ferric oxide ($Fe_2O_3 . xH_2O$).

Removal of DO: (1) By heating

(2) By addition of dilute solution of Hydrazine (NH_2-NH_2 or N_2H_4), Sodium sulphite Na_2SO_3 and sodium sulphide Na_2S

1. $O_2 + N_2H_4 \rightarrow N_2 + 2H_2O$
2. $O_2 + 2Na_2SO_3 \rightarrow 2Na_2SO_4$
3. $2O_2 + Na_2S \rightarrow Na_2SO_4$

Q. How to remove DO by adding hydrazine to water?

Ans. $O_2 + N_2H_4 \rightarrow N_2 + 2H_2O$

6.1 Boiler feed water

Lot of water is used in boilers of steel industries for generation of steam. But, water with specific characteristics is fit for feeding into it.

A boiler feed water should have the following characteristics:

a. Total hardness should be either 0 or less than 2 ppm.
b. Alkalinity should be less than 1 ppm.
c. Should be free from acidic masses
d. Should be free from dissolved gases like oxygen and carbon dioxide

6.2 Common problems in boiler

The common problems which were arising in boiler due to feeding of hard/alkaline/acidic water are as follows:

A. Formation of soft and hard precipitates known as **sludges and scales**, respectively
B. Boiler Corrosion

Q. What should be the characteristics of boiler feed water?

Ans. *A boiler feed water should have the following characteristics:*

e. Total hardness should be either 0 or less than 2 ppm.
f. Alkalinity should be less than 1 ppm.
g. Should be free from acidic masses
h. Should be free from dissolved gases like oxygen and carbon dioxide

Boiler Corrosion

It is the decay or loss of boiler body material (usually made of iron) either due to chemical or electrochemical reactions with its environment.

Disadvantages:

1. Reduces the life of boiler
2. Causes leakages at joints
3. Increases the cost of repair & maintenance

Q. What is boiler corrosion? Mention some of its limitations.

Ans. Boiler corrosion is the decay or loss of boiler body material (usually made of iron) either due to chemical or electrochemical reactions with its environment.

Disadvantages:

1. Reduces the life of boiler
2. Causes leakages at joints
3. Increases the cost of repair & maintenance

Lecture-4

7.0 Softening of hard water

Since hard water is unsuitable for domestic as well as industrial use, it is advisable to remove or reduce the amount of hardness causing salts from the water. *The process by which we remove or reduce the hardness of water is termed as "**softening**" of water.* The hardness causing salts can be removed or its amount can be reduced from the water by the two ways:

A. External Treatment, and
B. Internal treatment

External Treatment: It is carried out before its entry into the boiler. This treatment prevents boiler problems. Hence, it's a preventive method. The various external treatment or water softening methods are: *(A) Lime-Soda Process; (B) Zeolite process; an (C) Ion-exchange resin process.*

Internal treatment: It is carried inside the boiler after the external treatment by addition of chemicals. It is a corrective method to remove those salts which were not completely removed by external treatment. The various internal treatments are: *(A) Colloidal conditioning; (B) Phosphate conditioning; (C) Carbonate conditioning; (D) Calgon conditioning; (E) EDTA conditioning, etc.*

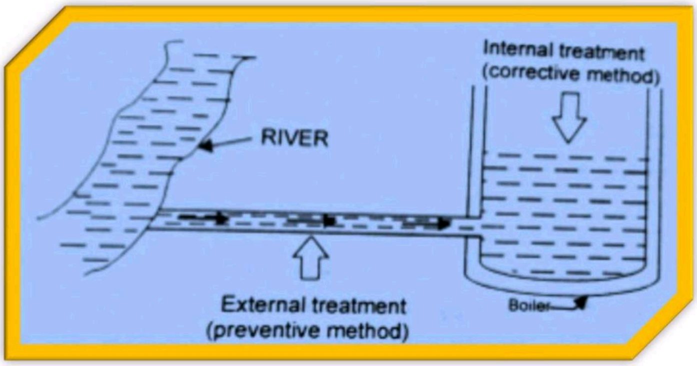

Fig.1. Types of water treatment

Q. ***Differentiate between External and Internal Treatment of water.***

Sl. No.	*Internal Treatment*	*External Treatment*
1	It is carried out in the boiler itself.	It is carried out outside the boiler, before water enters the boiler.
2	It is a corrective method	It is a preventive method
3	It includes: (A) Colloidal conditioning; (B) Phosphate conditioning; (C) Carbonate	It includes: (A) Lime-Soda Process; (B) Zeolite process; an (C) Ion-

	conditioning; (D) Calgon conditioning, etc.	exchange resin process.

Q. Define softening with a suitable example.

Ans. The process by which we remove or reduce the hardness of water is termed as "softening" of water. Example:- Lime-Soda process

7.1 External Treatment of Water Softening

(A) Lime (L)-Soda (S) Softening Process

Basic Principle: The basic principle of this process is to convert all the soluble hardness causing constituents into insoluble masses (known as precipitates) by addition of calculated amount of lime $\mathbf{Ca(OH)_2}$ and soda $\mathbf{Na_2CO_3}$ to the hard water. The precipitates [$CaCO_3$ and $Mg(OH)_2$] are then removed by sedimentation (a settling process) and filtration.

Types of L-S process: Based on the working temperature of the softener, it is of two types.

(1) Cold L-S Process, and (2) Hot L-S Process

Cold L-S Process: In this process calculated amount of chemicals (L & S) are added to the water at room temperature (RT).

But, at RT, the precipitates formed are very fine and do not settle down easily under the force of gravity and can easily pass through the filter too. So, in order to avoid such situation a small amount of **coagulants** like potash alum [$K_2SO_4.Al_2(SO_4)_3.24H_2O$], Aluminium sulfate $Al_2(SO_4)_3$, or sodium aluminate $NaAlO_2$ are added to the water along with L & S. Thus coagulant helps in converting fine particles to coarse particles. This process provides water with a residual hardness of 50-60 ppm.

Hard water + L + S + Coagulant → precipitate + soften water

1. $CaCl_2$ (hard water) + Na_2CO_3 (soda) → $CaCO_3$ (ppt) + 2 NaCl
2. $MgCl_2$ + $Ca(OH)_2$ (lime)+ Na_2CO_3 (soda) → $Mg(OH)_2$ (ppt) + $CaCO_3$ (ppt) + 2 NaCl

Working process: Hard water and calculated amount of lime, soda and coagulant are fed from the top of the softener fitted with a paddle stirrer at RT (see Figure). Vigorous stirring ensures continuous mixing and softening takes place. The soften water rising up passes through a wood-fibre filter whereby traces of sludge are removed. The precipitates settle down at the bottom by the time the softened water reaches the outlet. Coarse precipitates are settled down and relatively finer one is retained by the wood filter. The precipitates are periodically removed through the sludge outlet.

Limitations of cold L-S process: Some of the limitations are: (1) Residual hardness is high (50-60 ppm), so not fit for boiler operation; (2) As it operates at RT, softening capacity is low; (3) Dissolved gases are not removed; (4) Relatively more chemicals are needed (coagulant is required)

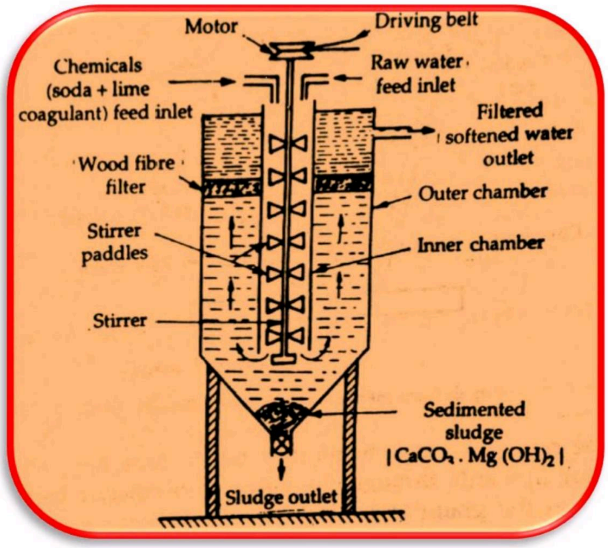

Fig. 2. Cold L-S softening method

Hot L-S Process: In this process water is treated with calculated amount of lime and soda at a temperature of 90-100 ^{0}C.

Working process: Raw water, chemicals and steam are thoroughly mixed in a reaction tank maintained at ~100 ^{0}C using steam. The sludge formed after reaction is settled down in a conical *sedimentation vessel*. Then water passed through a ***sand filter*** to obtain clear and soften water with a residual hardness 15-30 ppm.

Advantages of Hot L-S process over cold process:

1. Process is faster, 2. Good softening capacity, 3. No coagulant is required, 4. Relatively less amount of chemicals are needed, 5. Dissolved gases are also removed, 6. Pathogenic bacteria are also killed, 7. Residual hardness is relatively low

Limitations of L-S process: Some limitations are: (1) It requires careful operation and skilled supervision for economical and efficient softening. (2) Sludge disposal is a problem, (3) Softened water has high concentration of soluble salts like sodium sulfate, NaCl, etc. and has high residual hardness. So, not fit for boiler operation.

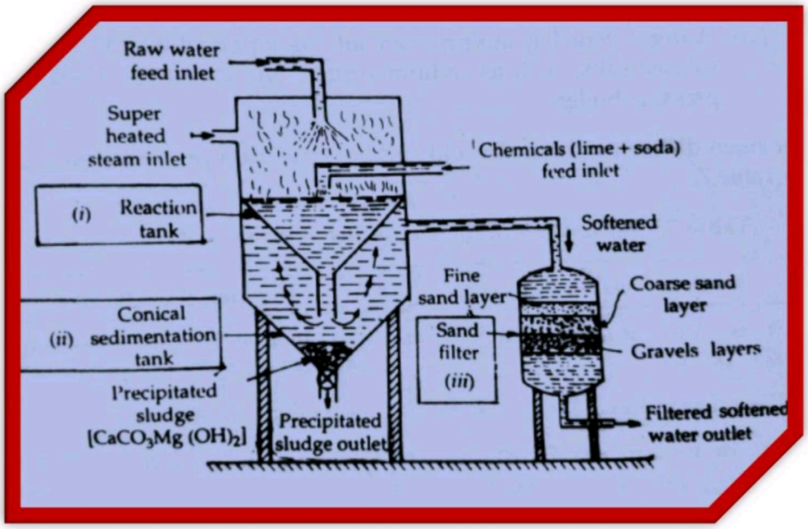

Fig. 3. Hot L-S process

Q. Differentiate between Cold and Hot L-S process.

Sl. No.	*Cold L-S process*	*Hot L-S process*
1	*Performed at RT*	*Performed at ~100 ^{0}C*
2	*Slow process*	*Fast process*
3	*Coagulant is needed*	*Coagulant is not needed*
4	*Filtration is not easy*	*Filtration is easy as viscosity decreases at high temperature*
5	*Residual hardness is 60 ppm*	*Residual hardness is 15-30 ppm*
6	*Dissolved gases are not removed*	*Dissolved gases are removed*
7	*Low softening capacity*	*High softening capacity*
8	*Bacteria are not killed*	*Bacteria are killed*

Q. What is a coagulant? Give an example.

Ans. Coagulant is a substance which converts the finer ppt. into coarser one. Example:-Potash Alum

Q. What is coagulation? Give an example of a coagulation reaction

Ans. Coagulation is a process of converting finer ppt. into coarse ppt. by adding a coagulant.

$Al_2(SO_4)_3 + 3Ca(HCO_3)_2 \rightarrow Al(OH)_3$ (gelatinous ppt.) $+ 3CaSO_4 + 6CO_2$

Q. What is the basic principle of L-S process?

Ans. The basic principle of this process is to convert all the soluble hardness causing constituents into insoluble masses (known as precipitates) by addition of calculated amount of lime **$Ca(OH)_2$** and soda **Na_2CO_3** to the hard water. The precipitates [$CaCO_3$ and $Mg(OH)_2$] are then removed by sedimentation (a settling process) and filtration. This softening process proceeds via precipitation reaction.

Q. Mention some advantages of Hot L-S process over cold process.

Ans: Some of the advantages of hot L-S process are:

1. Process is faster
2. Good softening capacity
3. No coagulant is required
4. Relatively less amount of chemicals are needed
5. Dissolved gases are also removed
6. Pathogenic bacteria are also killed
7. Residual hardness is relatively low

Lecture-5 & 6

7.2 Calculation of Lime-Soda requirement

Points to be remembered:

1. Substances like NaCl, Na_2SO_4, $NaNO_3$, KCl, K_2SO_4, KNO_3, SiO_2, Fe_2O_3, etc. do not consume any L & S. So, these should not be taken into consideration for calculating the L & S requirements.
2. All the substances should be converted into their respective $CaCO_3$ equivalent.
3. Ca-hardness precipitated as $CaCO_3$ and Mg-hardness as $Mg(OH)_2$

Chemicals requirement for Temporary hardness constituents:

A. $Ca(HCO_3)_2 + Ca(OH)_2 \rightarrow 2CaCO_3 + 2H_2O$ -------- needs 1 mole of L (1L)

B. (i) $Mg(HCO_3)_2 + Ca(OH)_2 \rightarrow \mathbf{Ca(HCO_3)_2} + Mg(OH)_2$ ----- 1L

(ii) $\mathbf{Ca(HCO_3)_2} + Ca(OH)_2 \rightarrow 2CaCO_3 + 2H_2O$ ----- 1L

$\left.\right\}$ **1L + 1L = 2 L**

Or by combining eq. (i) and (ii) we get

$Mg(HCO_3)_2 + 2Ca(OH)_2 \rightarrow 2CaCO_3 + Mg(OH)_2 + 2\,H_2O$ --- 2L

- ✓ *1 mole of $Ca(HCO_3)_2$ needs 1 mole of Lime whereas 1 mole of $Mg(HCO_3)_2$ needs 2 moles of Lime.*

Chemicals requirement for Permanent hardness constituents:

A. ***Calcium permanent hardness*** ($CaCl_2$, $Ca(NO_3)_2$, $CaSO_4$)

(i) $CaCl_2 + Na_2CO_3 \rightarrow CaCO_3 + 2\,NaCl$ ------- needs 1 mole of Soda (1S)

(ii) $Ca(NO_3)_2 + Na_2CO_3 \rightarrow CaCO_3 + 2\,NaNO_3$ ----- needs 1 mole of Soda (1S)

(iii) $CaSO_4 + Na_2CO_3 \rightarrow CaCO_3 + Na_2SO_4$ ----- needs 1 mole of Soda (1S)

- ✓ *** *All Calcium permanent hardness constituents* [$CaCl_2$, $CaSO_4$, $Ca(NO_3)_2$] *need only 1-mole of Soda (1S)*

B. ***Magnesium permanent hardness*** ($MgCl_2$, $Mg(NO_3)_2$, $MgSO_4$)

(i) $MgCl_2 + Ca(OH)_2 + \rightarrow Mg(OH)_2 + CaCl_2$ ------- needs 1 mole of Lime (1L) *but releasing 1 mole of CaCl2. For its removal we need 1 mole of Soda*

$CaCl_2 + Na_2CO_3 \rightarrow CaCO_3 + 2\,NaCl$ ------- needs 1 mole of Soda (1S)

- ✓ **So, 1 mole of *Magnesium permanent hardness needs 1 mole of lime and 1 mole of Soda* (1L + 1S).**

Chemicals requirement for coagulants* ($\mathbf{FeSO_4}$, $\mathbf{Al_2(SO_4)_3}$)*:

(i) $FeSO_4 + Ca(OH)_2 + \rightarrow Fe(OH)_2 + CaSO_4$ ------- needs 1 mole of Lime (1L) *but releasing 1 mole of* $CaSO_4$. *Its removal needed 1 mole of Soda*

$CaSO_4 + Na_2CO_3 \rightarrow CaCO_3 + Na_2SO_4$ ------- needs 1 mole of Soda (1S)

- ✓ ***So,*** $FeSO_4$ ***needs 1 mole of lime and 1 mole of Soda* (1L + 1S).**

(ii) $2Al_2(SO_4)_3 + 3Ca(OH)_2 + \rightarrow 2Al(OH)_3 + 3CaSO_4$ – 3 moles of Lime (3L)

$3CaSO_4 + 3Na_2CO_3 \rightarrow 3CaCO_3 + 3Na_2SO_4$ ------- needs 3 mole of Soda (3S)

- ✓ ***So,*** $Al_2(SO_4)_3$ ***needs 3 mole of lime and 3 mole of Soda* (3L + 3S).**

Q.1 Give reason that 1 mole of *$Ca(HCO_3)_2$ needs 1 mole of Lime whereas 1 mole of $Mg(HCO_3)_2$ needs 2 moles of Lime. (write chemical reactions)*

Ans.

A. $Ca(HCO_3)_2 + Ca(OH)_2 \rightarrow 2CaCO_3 + 2H_2O$ -------- needs 1 mole of L (1L)

B. (i) $Mg(HCO_3)_2 + Ca(OH)_2 \rightarrow \mathbf{Ca(HCO_3)_2} + Mg(OH)_2$ ----- 1L

(ii) $\mathbf{Ca(HCO_3)_2} + Ca(OH)_2 \rightarrow 2CaCO_3 + 2H_2O$ ----- 1L

$\Big\}$ 1L + 1L = 2 L

Q. 2. Give reason that *Calcium permanent hardness constituents need only 1- mole of Soda (1S).*

Ans.

(i) $CaCl_2 + Na_2CO_3 \rightarrow CaCO_3 + 2\,NaCl$ ------- needs 1 mole of Soda (1S)

(ii) $Ca(NO_3)_2 + Na_2CO_3 \rightarrow CaCO_3 + 2\,NaNO_3$ ----- needs 1 mole of Soda (1S)

(iii) $CaSO_4 + Na_2CO_3 \rightarrow CaCO_3 + Na_2SO_4$ ----- needs 1 mole of Soda (1S)

Q.3. Give reason that 1 mole of *Magnesium permanent hardness needs 1 mole of lime and 1 mole of Soda* (1L + 1S).

Ans.

(i) $MgCl_2 + Ca(OH)_2 + \rightarrow Mg(OH)_2 + CaCl_2$ ------- needs 1 mole of Lime (1L) *but releasing 1 mole of CaCl2. For its removal we need 1 mole of Soda*

$CaCl_2 + Na_2CO_3 \rightarrow CaCO_3 + 2\,NaCl$ ------- needs 1 mole of Soda (1S)

Q.4. Give reason that lime is not consumed by $CaCl_2$ or any calcium-permanent hadness constituents.

Ans. $CaCl_2 + Ca(OH)_2 \rightarrow CaCl_2 + Ca(OH)_2$

See the above reaction, there is no change in reactant and product side. It means there is no reaction between these two constituents.

7.3 Solved numerical on Lime-soda requirements

Example-1 A sample of water on analysis has been found to contain 100 mg/L of $Ca(HCO_3)_2$ and 200 mg/L of Na_2SO_4. Calculate the amount of lime and soda required for softening of 10,000 litres of hard water. (At. mass: Na = 23, Ca = 40, H =1, C = 12, O =16, S = 32 g/mol)

Solution: Na_2SO_4 does not consume chemicals like lime and soda.

N.B: if purity of lime and soda is not mention then take % purity = 100

$Ca(HCO_3)_2$ as $CaCO_3$ eq. = 100 x (100/162) = 61.72 mg/L

$Ca(HCO_3)_2$ require only 1L (**no soda requirement**, that is soda amount = 0)

So, lime required for softening of 10,000 L of hard water = 74/100($Ca(HCO_3)_2$ $CaCO_3$ eq.) x V x (100/% purity of lime)

= (74/100) x 61.72 mg/L x 10,000 L x 100/100 (here purity of lime 100%)

= 456728 mg = 456.728 g (Ans.)

Example-2 A sample of water on analysis has been found to contain 150 mg/L of $Ca(HCO_3)_2$ and 100 mg/L of Na_2SO_4. Calculate the amount of lime and soda required for softening of 15,000 litres of hard water after boiling the water for 20 min. (At. mass: Na = 23, Ca = 40, H =1, C = 12, O =16, S = 32 g/mol)

Solution: As boiling removes $Ca(HCO_3)_2$, lime and soda required will be zero.

Example-3 A sample of water on analysis has been found to contain 150 mg/L of $Ca(HCO_3)_2$ and 100 mg/L of $CaSO_4$. Calculate the amount of lime and soda required for softening of 15,000 litres of hard water after boiling the water for 20 min. (At. mass: Ca = 40, H =1, C = 12, O =16, S = 32 g/mol)

Solution: Boiling will remove the $Ca(HCO_3)_2$. So only $CaSO_4$ will be remain in the hard water after boiling.

$CaSO_4$ consumes only soda (Mol .mass = 136 g)

$CaSO_4$ as $CaCO_3$ eq. = 100 x (100/136) = 73.52 mg/L

Soda required = 106/100 ($CaSO_4$ as $CaCO_3$ eq.) x V x (100/%purity of soda)

= 106/100 x 73.52 x 15,000 x 100/100 (purity of soda is 100%)

= 1168968 mg = 1.168968 Kg (take 1 mg = 10^{-6} Kg)

Lime reqd. = 0

Example-4 Calculate the amount of Lime and soda needed for the softening of 10,000 litres of hard water having 10 mg/l of $MgSO_4$. (Given: % purity of lime = 90 and % purity of soda = 95; At. mass of Mg =24, S = 32 and O = 16))

Solution: We know that all magnesium permanent hardness consumes both lime and soda

$MgSO_4$ as $CaCO_3$ eq. = 10 x 100/120 = 8.33 mg/L or ppm

(i) **Lime reqd.** = 74/100 ($MgSO_4$ as $CaCO_3$ eq.) x Vol. of hard water x (100/% purity)
= (74/100) x 8.33 mg/L x 10,000 L x (100/90) = 6851.85 mg = 6.851 g
(ii) **Soda Reqd.** = 106/100 ($MgSO_4$ as $CaCO_3$ eq.) x Vol. of hard water x (100/% purity)
= (106/100) x 8.33 mg/L x 10,000 L x (100/95) = 9298.24 mg = 9.298 g

Example-5 Calculate the amount of Lime and soda needed for the softening of 50,000 litres of hard water having $Mg(HCO_3)_2$ = 144 ppm, $Ca(HCO_3)_2$ = 25 ppm, $MgCl_2$ = 95 ppm, $CaCl_2$ = 111 ppm, Fe_2O_3 = 25 ppm, and Na_2SO_4 = 15 ppm.

Solution:

As Fe_2O_3 and Na_2SO_4 are non-hardness constituents, they do not consume Lime (L) and Soda (S)

Constituents	Strength (ppm or mg/L)	Mol. Mass	Chemical Need	$CaCO_3$ eq. (mg/L)
$Mg(HCO_3)_2$	144	146	2L	144 x (100/146) =98.6
$Ca(HCO_3)_2$	25	162	1L	25 x (100/162) =15.4
$MgCl_2$	95	95	L + S	95 x (100/95) =100
$CaCl_2$	111	111	S	111 x (100/111) =100

**n-factor = 2 for all the salts

Remember that Lime is reqd. by $Mg(HCO_3)_2$, $Ca(HCO_3)_2$, and $MgCl_2$

(i) **Lime reqd.** = 74/100 [(2 x $Mg(HCO_3)_2$ + $Ca(HCO_3)_2$ + $MgCl_2$); all as $CaCO_3$ eq.] x Vol. of hard water x (100/% purity)
= (74/100) x [2 x 98.6 + 15.4 + 100] mg/L x 50,000 L x (100/100)
= 11566200 mg = 11566200 x 10^{-6} Kg = 11.5666 Kg

Soda is reqd. by only $CaCl_2$ and $MgCl_2$

(ii) **Soda reqd.** = 106/100 [($CaCl_2$ + $MgCl_2$); all as $CaCO_3$ eq.] x Vol. of hard water x (100/% purity)
= (106/100) x [100 + 100] mg/L x 50,000 L x (100/100)
= 10600000 mg = 10600000 x 10^{-6} Kg = 10.6 Kg

Example-6 A water sample contains $Mg(HCO_3)_2$ = 73 ppm, $Ca(HCO_3)_2$ = 81 ppm, $MgCl_2$ = 95 ppm, $CaSO_4$ = 68 ppm, and Na_2SO_4 = 30 ppm. Calculate the cost of chemicals for softening of 20,000 litres of hard water, if purity of lime is 95% and that of soda is 90%. The costs per 1 Kg of lime and soda are Rs. 75 and Rs. 1200, respectively.

Solution: As Na_2SO_4 is a non-hardness constituent, it does not consume Lime (L) and Soda (S)

Constituents	Strength (ppm or mg/L)	Mol. Mass	Chemical Need	$CaCO_3$ eq. (mg/L)
$Mg(HCO_3)_2$	73	146	2L	73 x (100/146) =50
$Ca(HCO_3)_2$	81	162	1L	81 x (100/162) =50
$MgCl_2$	95	95	L + S	95 x (100/95) =100
$CaSO_4$	68	136	S	68 x (100/136) =50

Lime is reqd. by $Mg(HCO_3)_2$, $Ca(HCO_3)_2$, and $MgCl_2$

(i) **Lime reqd.** = 74/100 [(2 x $Mg(HCO_3)_2$ + $Ca(HCO_3)_2$ + $MgCl_2$); all as $CaCO_3$ eq.] x Vol. of hard water x (100/% purity)
= (74/100) x [(2 x 50) + 50 + 100] mg/L x 20,000 L x (100/95)
= 3894736.842 mg = 3894736.842 x 10^{-6} Kg = 3.894 Kg
Cost of lime = 3.894 x 75 = Rs. 292.05

Soda is reqd. by only $MgCl_2$ and $CaSO_4$

(i) **Soda reqd.** = 106/100 [($CaSO_4$ + $MgCl_2$); all as $CaCO_3$ eq.] x Vol. of hard water x (100/% purity)
= (106/100) x [50 + 100] mg/L x 20,000 L x (100/90)
= 3533333.333 mg = 3533333.333 x 10^{-6} Kg = 3.533 Kg
Cost of soda = 3.533 x 1200 = Rs. 4239.6

Now, total cost of chemicals (cost of lime + cost of soda) = Rs. 292.05 + Rs. 4239.6 = **Rs. 4,531.65**

Lecture-7 & 8

Zeolite as a softner

What are zeolites?

Zeolites are naturally occurring hydrated sodium alumino silicate minerals. They are capable of exchanging reversibly its sodium ions (Na^{+}) for hardness causing ions (e.g., Ca^{2+}, Mg^{2+}, etc.) in water. This ion-exchange property makes them a suitable candidate for softening process.

The chemical representation of zeolites are $Na_2O.Al_2O_3.xSiO_2.yH_2O$, where x = 2-10 & y = 2-6. It is mentioned as Na_2Ze.

Zeolite is derived from the *Greek* word *Zein* + *Lithos*, meaning "*boiling Stone"*. If heated strongly, zeolite melts with bubbling moisture, which look like as if a stone is boiling. The term zeolite was coined by Swedish Geologist Axel Cronsted in 1756. Zeolite has open structure with many cavities or pores. This porous structure permits free movement of water molecules and ions.

Zeolites are of two types: (1) *Natural zeolites:* They are relatively less porous, more durable and amorphous in nature. Example: $Na_2O.Al_2O_3.4SiO_2.2H_2O$; (2) *Synthetic/artificial* zeolites: They are made in the laboratories of industries. Such zeolites are relatively more porous and less durable, but *having large ion exchange capability per unit weight*. They are prepared by heating together sodium carbonate Na_2CO_3, alumina Al_2O_3 and silica SiO_2 in a muffle furnace maintained at about 1000 ^{0}C. Artificial zeolites are also called as **Permutit**.

Q. Give reason that artificial zeolites are preferred over natural one for the softening of hard water.

Answer: As the artificial is more porous *it has large ion exchange capability per unit weight* than natural one.

Zeolite Softening Process

Softening of Hard water is done in a **Zeolite softener**. The hard water is passed/percolated at a specified rate through a bed of zeolites fixed in a cylindrical stainless steel softener so that hardness causing ions (Ca^{+2}, Mg^{+2}, etc.) are retained by the zeolite bed and outgoing water contains sodium ions (Na^{+}). The reaction taking place during the softening process is mentioned as below:

$$Na_2Ze + CaCl_2 \rightarrow CaZe + 2NaCl$$

$$Na_2Ze + Ca(HCO_3)_2 \rightarrow CaZe + 2\ NaHCO_3$$

$$Na_2Ze + Mg(HCO_3)_2 \rightarrow MgZe + 2\ NaHCO_3$$

From the above reaction we learnt that with the progress of softening process more and more Na_2Ze are converting into CaZe/MgZe and the sodium salt concentration is increasing in the outgoing water. In other words, the Na^+ ion content responsible for ion exchange is decreasing with time. So, after some time the zeolite (Na_2Ze) is completely converted into calcium and magnesium zeolite of no ion exchange capability. It means after some time it ceases to soften water and zeolite is said to be gets exhausted. At this stage, the feeding of hard water to the softener is temporarily stopped and regeneration is done for the exhausted zeolite.

Regeneration of exhausted zeolite: It is done by treating with a concentrated (10%) NaCl solution (known as *Brine solution*). The reaction taking places during the regeneration process are:

$$CaZe + 2NaCl \rightarrow Na_2Ze \text{ (reclaimed zeolite)} + CaCl_2 \quad \text{(washings)}$$

$$MgZe + 2\ NaCl \rightarrow Na_2Ze + MgCl_2$$

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

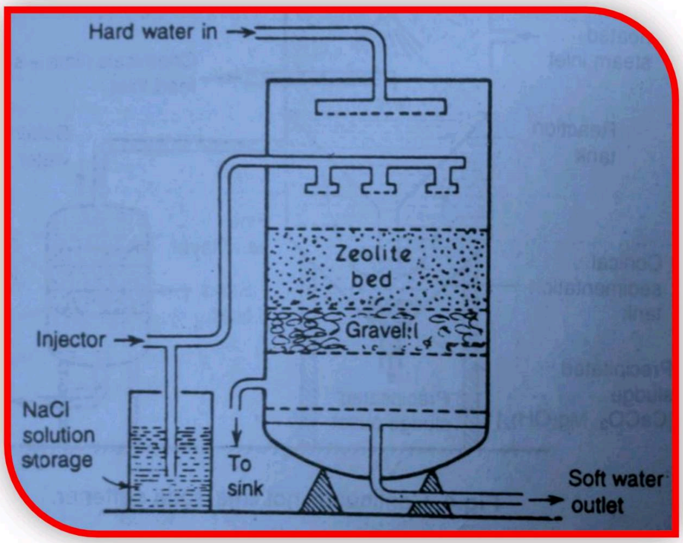

Fig. Zeolite softener

Q. Give reason that sodium chloride is preferred for regeneration exhausted zeolite.

Answer: It is of low cost and the products of regeneration (washings) are highly soluble so that can be easily rinsed out from the zeolite bed.

Limitations of zeolite process:

1. Turbid water clogs the pores of the zeolite and thereby making it inactive.
2. Water containing ions like Mn^{2+} and Fe^{2+} are firmly stick to the zeolite bed so very difficult to be regenerated.
3. Acidic water destroys the zeolite bed.
4. Hot water tends to dissolve the zeolite bed.
5. Water softened by this process contains salts like $NaHCO_3$ causes boiler corrosion.
6. Higher cost of the plant is also a limiting factor.

Q. Turbid water should not be softened by zeolite process. Give reason

Ans. Turbid water clogs the pores of the zeolite and thereby making it inactive

Q. How to soften turbid hard water using a zeolite softener?

Ans. At first suspended matter must be removed by coagulation before it is fed into the softener.

Q. **Acidic water should not be softened by zeolite process. Give reason**

Ans. Acidic water destroys the zeolite bed.

Q. How to soften acidic hard water using a zeolite softener?

Ans. Acidic water must be neutralized with soda in advance before feeding into zeolite bed.

Q. How to regenerate an exhausted zeolite bed?

Ans. It is done by treating with a concentrated (10%) NaCl solution (known as *Brine solution*). The reaction taking places during the regeneration process are:

$$CaZe + 2NaCl \rightarrow Na_2Ze \text{ (reclaimed zeolite)} + CaCl_2 \quad \text{(washings)}$$

$$MgZe + 2\,NaCl \rightarrow Na_2Ze + MgCl_2$$

Q. Water softened by zeolite softener is not fit for boiler. Give reason.

Ans. It contains salt like $NaHCO_3$ which undergoes decomposition under boiler condition to form NaOH, a caustic mass.

$$NaHCO_3 \rightarrow NaOH + CO_2$$

The caustic mass makes the water alkaline and leads to alkaline boiler corrosion called as ***Caustic Embrittlement*****.**

Q. Water should be free from ions like Mn^{2+} and Fe^{2+} before fed into the boiler. Give reason.

Ans. Water containing ions like Mn^{2+} and Fe^{2+} are firmly stick to the zeolite bed so very difficult to be regenerated.

Advantages of Zeolite process

1. The residual hardness is about 10 ppm whereas in L-S process it lays between 15-60 ppm.
2. Equipment used is compact and occupies less space.
3. It is clean in use. No sludge formation occurs during the process.
4. Less skilled people can operate as well as maintain easily.
5. Less time is needed for softening as compared to L-S process.

Comparison between Zeolite and L-S process

Sl. No.	**Zeolite process**	**L-S process**
1.	Produces water of residual hardness of 10-15 ppm	Produces water of residual hardness lays between 15-60 ppm
2.	Based on ion exchange principle	Based on precipitation principle
3.	Softened water contain large amount of sodium salts	Treated water contains lesser % of Na-salts
4	Capital cost is higher	Capital cost is lower
5	Not suitable for treating acidic and turbid water	No such limitation
6	Equipment occupies less space	Occupies more space
7	No sludge formation	Sludge formation occurs
8	Dissolved gases are not removed	They are removed in hot L-S process
9	No bacteria are killed	They are killed in hot L-S process
10	Treated water contains large amount of $NaHCO_3$	Free from $NaHCO_3$
11	Less skill is required to operate it	Skilled operate can operate it successfully

Solved Numerical

Example-1 The hardness of 10,000 liters of a sample of water was removed by passing it through a zeolite softener. The Exhausted zeolite needed 200 liters of NaCl solution containing 150 g/L of NaCl for regeneration. Find the harness of water.

Solution:

Method-1

Strength of NaCl = 150 g/L

It means, 1L solution contains 150 g of NaCl

So, 200 L will contains = 150 x 200 = 30, 000 g = 30,000 x 1000 mg of NaCl

NaCl as $CaCO_3$ eq = 30,000,000 x (100/2x58.5) [**eq wt of NaCl = 58.5]**

= 25641000 mg

Now, 10,000 L of water = 25641,000 mg eq of $CaCO_3$

⇨ 1 L of water = (25641,000/10,000) = 2564.1 mg/l or ppm.

Method-2

We know that $S_1V_1 = S_2V_2$

That is S_{NaCl} x V_{NaCl} = S_{water} x V_{water} , Here S = strength and V = Volume

So, 150 x 200 = S_{water} x 10,000

⇨ S_{water} = (150 g/Lx 200 L)/10,000 L= 3 g/L = 3000 mg/L

In terms $CaCO_3$ eq, hardness = 3000 x 100/(2 x 58.5) = 2564 ppm. [**eq wt of NaCl = 58.5]**

Example-2 An exhausted zeolite softener was regenerated by passing 150 L of NaCl solution having a strength of 150 g/L of NaCl. Find the total volume of water that can be softened by this zeolite softener, if the hardness of water is 500 ppm.

Solution:

Method 1

Strength of NaCl = 150 g/L

It means, 1L solution contains 150 g of NaCl

So, 150 L will contains = 150 x 150 = 22500 g = 22500 x 1000 mg of NaCl

NaCl as $CaCO_3$ eq. = 22500,000 x (100/2x58.5), eq wt of NaCl = 58.5

= 1.932 x 10^7 mg $CaCO_3$ eq.

Hardness is given as 500 ppm = 500 mg/l

So, it means 500 mg in 1L

Then, 1 mg in 1/500 L

Now, 1.932×10^7 mg in = $(1/500) \times 1.932 \times 10^7$ = 38461 L (Ans.)

Method 2

$S_{NaCl} \times V_{NaCl} = S_{water} \times V_{water}$, Here S = strength and V = Volume

- ⇨ **(150,000 mg/L x 100/117) as $CaCO_3$ eq. x 150 L = 500 mg/L as $CaCO_3$ eq. x** V_{water}
- ⇨ V_{water} = 38641 L

Polymeric Material (Resin) as a Softner

What is a Resin?

Resin is a macromolecule i.e., organic polymer. It may be thermoplastic or thermosetting. For example, Epoxy resin, Bakelite, Urea-formaldehyde resin, etc.

Ion-exchange Resins: They are insoluble, cross-linked organic polymers with a porous structure attached with some functional groups (FG) like –OH, -SO_3H, -COOH, -NH_2, etc. responsible for reversibly exchange with ions (e.g., Ca^{2+}, Mg^{2+}, Cl^-, NO_3^-, SO_4^{2-}, etc.) present in hard water.

Types of Ion-exchange resins: Depending on the nature of FG attached to the polymer, they are of two types: (1) Cation exchange resin, and (2) Anion exchange resin

Cation exchange resins: They are mainly styrene-divinyl benzene copolymers containing sulphonic acid (-SO_3H) or carboxylic acid (-COOH) FG. The acidic FG having hydrogen ions (-H^+) are *exchange with cations* like Ca^{2+}, Mg^{2+} etc. present in the hard water. It means these hardness causing cations are retained by the resin.

Some commercial cation exchange resins are **Amberlite IR-120 and Dowex-50**.

Anion exchange resins: They are mainly styrene-divinyl benzene or amine-formaldehyde copolymers containing basic FG like amino or quaternary ammonium or quaternary phosphonium. As such they are of no use. To act as an *anion exchange resin,* it is treated with dil. NaOH solution to introduce –OH group into it. This basic group –OH is capable of *exchange with anions* of water. It means these anions are retained by it after passing through it.

Some commercial anion exchangers are **Amberlite IR-400 and Dowex-3**.

Softening of hard water using polymeric ion-exchangers

An ion-exchanger consists of two vertical columns: (1) cation exchange and (2) anion exchange.

The hard water is first passed through the cation exchange column so that all cations are removed from it and equivalent amount of H^+-ions are released from the column to water. Let us represent the cation exchange resin as **Res-H^+.** Here the loosly bound H+ ions are capable of exchanging with cations like Ca^{2+} and $Mg^{2+.}$

$$\mathbf{2Res\text{-}H^+ + Ca^{2+} \rightarrow (Res)_2Ca + 2H^+}$$

$$\mathbf{2Res\text{-}^{-}H^+ + Mg^{2+} \rightarrow (Res)_2Mg + 2H^+}$$

After passing through the first column, the water is passed through anion exchange column to remove all the anions like Cl^-, NO_3^-, SO_4^{2-}, etc. present in the water and an equivalent amount of –OH- ions are released from the column to the water. Let us represent this resin as **Res-OH$^+$.**

$$2Res\text{-}OH^- + Ca^{2+} \rightarrow (Res)_2Ca + 2OH^-$$

$$2Res\text{-}OH^- + Mg^{2+} \rightarrow (Res)_2Mg + 2OH^-$$

Now the outgoing water is free from all ions so it is ion-free or *deioinized* water. This water also called as *de-mineralized* water. This water is free from any acidic or alkaline masses. Finally the ion-free water is passed through a *de-gasifier* maintained at about 100 ^{0}C to remove dissolved gases like O_2, CO_2, etc.

Regeneration of ion exchange resins

After working for some time , the ion-exchange resins lost their ion-exchange capacity and are said to be exhausted.

The exhausted cation exchange resin column can be regenerated by passing a solution of dil HCl or H_2SO_4.

$(Res)_2Ca + 2H^+$ (from HCl) $\rightarrow$ $2Res\text{-}H^+ + Ca^{2+}$

The exhausted anion exchange resin column can be regenerated by passing a solution of dil NaOH or KOH.

$(Res)_2Ca + 2OH^-$ (from NaOH) $\rightarrow$ $2Res\text{-}OH^- + Ca^{2+}$

The regenerated resins are then used again for softening.

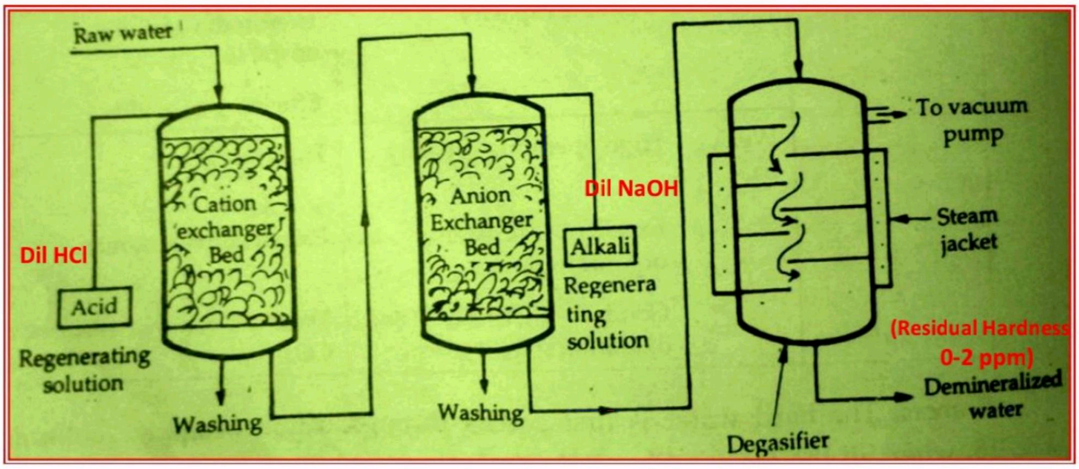

Fig. Polymeric ion-exchanger

Advantages:

1. This process can be used for softening highly acidic and alkaline waters.
2. Residual hardness lies between 0-2 ppm.
3. De-gasifier removes dissolved gases
4. Water is germ free

Limitations:

1. It is an expensive process
2. Turbid water causes problem
3. Water is not fit for human consumption. (we need minerals like Ca)

Q. 1 What is the use of a de-gasifier in ion-exchange resin softener?

Ans. It is a device used to remove unwanted dissolved gases like O_2, CO_2, etc from the soften water.

Q. 2 Differentiate between soft water and de-mineralized/de-ionised water

Sl. No.	Soft Water	De-mineralized Water
1	We called water as soft when its hardness <= **50 ppm**	Hardness lays between 0-2 ppm
2	Used for domestic use	Not recommended as such for drinking purpose
3	Obtain using L-S or zeolite process	Made by distillation or resin process
4	Not suitable for boiler	Fit for boiler operation

Q 3. Mention some advantages of resin process.

1. **Ans.** This process can be used for softening highly acidic and alkaline waters.
2. Residual hardness lies between 0-2 ppm.
3. De-gasifier removes dissolved gases
4. Water is germ free

Q. 4. Mention some limitations of resin process.

Ans.

1. It is an expensive process
2. Turbid water causes problem
3. Water is not fit for human consumption. (we need minerals like Ca)

Q.5 How to regenerate an exhausted cation-exchange resin?

1. **Ans.** The exhausted cation exchange resin column can be regenerated by passing a solution of dil HCl or H_2SO_4.
2. **$(Res)_2Ca + 2H^+$ (from HCl) → $2Res\text{-}H^+ + Ca^{2+}$**

Q.6 How to regenerate an exhausted anion-exchange resin?

Ans. The exhausted anion exchange resin column can be regenerated by passing a solution of dil NaOH or KOH.

$(Res)_2Ca + 2OH^-$ (from NaOH) → $2Res\text{-}OH^- + Ca^{2+}$