Lecture-1

Water treatment is the process of removing all types of impurities from water, making it suitable for domestic and industrial use.

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 various 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) (3) ***Dissolved gases*** **(**includes O_2, CO_2). Dissolved impurities causes corrosion in boilers and imparts hardness to water.

B. **Suspended & Colloidal impurities:** (1) **Suspended Impurities:** *Organic* (includes vegetable & animal matters, industrial & domestic by-products, oil globules, etc.); *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, etc.). Living matters brings health related issues upon consumptions.

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

N.B.: Chemical constituents like $NaHCO_3$, 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 → Produces 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, Mg, Fe, Mn-salts.	It does not contain dissolved Ca, Mg, Fe, Mn-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	It is not a plumbosolvent	**Plumbo-solvency** occurs

***A residual hardness 100-200 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-Plumbum). Soft water is a plumbo-solvent. Permissible limit of Pb in water is 0.01 ppm.

Why shouldn't drinking water be too soft?

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)

Also minerals like Calcium is needed *for strong teeth and healthy bones in children.*

Q.2. Which of the following salts are non-hardness constituents?

Na_2SO_4, $NaNO_3$, $Al_2(SO_4)_3$, $MnSO_4$, $Mn(HCO_3)_2$

Ans. Na_2SO_4 and $NaNO_3$

Q. 3. What is plumbo-solvency?

Ans: **Plumbosolvency** is the ability of a solvent like water to dissolve lead (Pb stands for plumbum in Latin)

$$\mathbf{2Pb + 2H_2O + O_2 \rightarrow 2Pb(OH)_2}$$

Q. 4. Give reason that hard water is not a plumbo-solvent.

Ans. 1. The solubility of Pb (plumbum) in water is diminished in the presence of HCO_3^- , SO_4^{2-} (i.e., in hard water), 2. bicarbonates and sulphates provide a protective layer on the surface of the pipe.

Q. 5. 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. After some time, Soap + water (Free from hardness)→ Produce enough foam

Q. 6. 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) + $CaCl_2 \rightarrow (C_{17}C_{35}COO)_2Ca$ (*Calcium Stearate, White scum*) + 2NaCl
2. Soap + water → Produce enough foam

Disadvantages of Hard Water

A. In domestic use:

1. **Washing:** Causes wastage of lot of soap. The white scum adheres on the fabric giving spots and streaks. If iron and manganese salts are there then may cause staining of cloth.
2. **Bathing:** Cleansing quality of soap is depressed and a lot of it is wasted.
3. **Cooking:** As boiling pint of hard water is high, more fuel and time are required for cooking. Certain foods such as pulses, beans, peas do not cook soft. Tea of coffee prepared has an unpleasant taste and muddy looking extract. Carbonates were found stuck on the inner walls of utensils.
4. **Drinking:** There is a bad effect on our digestion process. Chances of formation of calcium oxalate in the urinary tract are always there.

B. In industrial use

1. Textile industries

- ✓ Uniform dyeing is not possible if hard water is used
- ✓ Hard water decreases the solubility of acidic dyes and basic dyes precipitate out
- ✓ Fe and Mn salts containing water may cause colored spots on fabrics

2. Sugar Industry

- ✓ Hard water results in the formation of deliquescent sugar
- ✓ Cause difficulty in the crystallization of sugar

3. Paper Industry

Fe and Mn salts affect the brightness and color of the paper
Hardness increases the ash content of the paper

4. Laundry:

Mn and Fe salts impart grey/reddish shade to the fabric
Hard water increases soap consumptions

5. *Boilers in steel industries*: Hard water leads to corrosion and chocking of boiler.

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. Not used in industries like sugar, textiles, paper, etc.*
3. Not a plumbo-solvent	*3. Increases B. Pt. of water.*

Q. 7. Mention some advantages of hard water. (Refer the above table)

Q. 8. Mention some disadvantages of hard water. (Refer above)

Q.9. Mention the disadvantages of hard water in sugar industries. [2 marks]

Ans. Hard water results in the formation of deliquescent sugar. It also cause difficulty in the crystallization of sugar

Q.10. **Mention the disadvantages of hard water in paper and textile industries. [3 marks]**

Ans. Paper Industry:

Fe and Mn salts affect the brightness and color of the paper
Hardness increases the ash content of the paper

***Textile industries*:**

- ✓ Uniform dyeing is not possible if hard water is used
- ✓ Hard water decreases the solubility of acidic dyes and basic dyes precipitate out
- ✓ Fe and Mn salts containing water may cause colored spots on fabrics

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 carbonates and bicarbonates (HCO_3^-) of Ca and Mg, heavy metals like Al, Mn and carbonates of Fe. The salts responsible are $CaCO_3$, $MgCO_3$, $Ca(HCO_3)_2$, $Mg(HCO_3)_2$, 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. 11. 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. 12. 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 $Ca(NO_3)_2$

Q.13. Which of the following salts are permanent-hardness constituents?

$Ca(HCO_3)_2$, $Mg(HCO_3)_2$, $CaCl_2$, K_2SO_4 and $FeSO_4$

Ans. $CaCl_2$ and $FeSO_4$

Q.14. Which of the following salts are temporary-hardness constituents?

$Mg(HCO_3)_2$, $Mn(HCO_3)_2$, $NaHCO_3$, $CaCl_2$, K_2SO_4

Ans. $Mg(HCO_3)_2$ and $Mn(HCO_3)_2$

Degree of Hardness (Equivalents of Calcium Carbonate)

How to express hardness of water?

As $CaCO_3$ is almost insoluble in water, it hardly contributes 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. 15. 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. 16. 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.) + $2CO_2$

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 part = 10^6 ppm ----(1)
   1 ^{0}Fr = 1 part per 10^5 parts of water, => 1 part = 10^5 ^{0}Fr -------(2)
   And 1 ^{0}Cl = 1 part per 70, 000 parts of water => 1 part = 70,000 ^{0}Cl –(3)
   From equation (1), (2), and (3), we found that
   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 ---- (4)
   Now Divide Eq. 4 by 10^6, so that **1 ppm = 0.1 ^{0}Fr = 0.07 ^{0}Cl = 1 mg/L**

Q. 17. Show that 1 ppm = 1 mg/L [1 mark]

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 *** (for water, 1 L is nearly 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)

Numerical on Finding Total Hardness

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

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

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

(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	$Ca(HCO_3)_2$	$CaSO_4$	$MgCl_2$	$CaCl_2$	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.

Impurity	Quantity (mg/L)	n-factor	Mol. Wt.	$CaCO_3$ eq. in mg/L
$Ca(HCO_3)_2$	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

Solution:

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

(i) **Temporary Hardness (due to** $Ca(HCO_3)_2$**) = 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 Total 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. Total 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.

(ii) 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) = 100 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

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.

Example-8. A water sample contains 150 mg/L of $NaHCO_3$, 111 mg/L of NaCl, 12 mg/L of K_2SO_4, and 250 mg/L of Na_2SO_4. Find the total hardness of water.

Ans. Total hardness of water = 0 (as all are non-hardness constituents.)

Alkalinity- A water quality parameter

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

Any substances which can increase the hydroxide ion concentration [OH^-] contribute towards alkalinity of water. Alkalinity is due to presence of ions like CO_3^{2-}, OH^-, HCO_3^- in the water.

N.B.: 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): A Water quality parameter

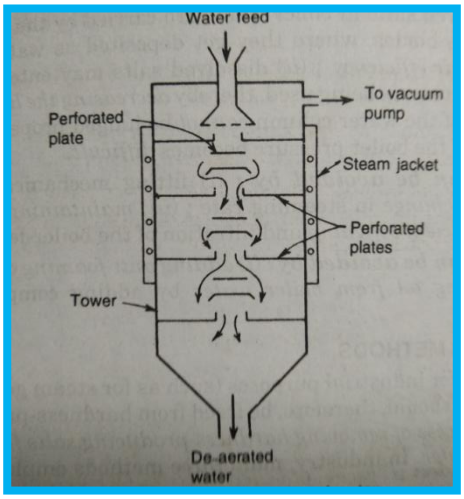
It is the most usual corrosion causing factor in boilers. DO react with the iron (Fe) of boiler in presence of water to form rust (Ferric oxide). Water usually contains 8 mg/L at RT. DO is a temperature dependent parameter.

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 (Thermal deoxygenation): In this process water is heated in a container (**known as degasifier)** to remove DO.



(2) Chemical Deoxygenation: 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. $O_2 + N_2H_4 \rightarrow N_2 + 2H_2O$

Specifications for 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

Common problems found in a 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 ($MgCO_3$, $MgSO_4$) and scales ($MgSiO_3$, $CaSiO_3$, $CaCO_3$)**, respectively
B. Boiler Corrosion

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

Ans. ***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

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.

Causes of boiler corrosion:

1. Presence of dissolved O_2 in water: $Fe + O_2 + H_2O \rightarrow Fe_2O_3.xH_2O$ (Rust)
2. Presence of dissolved CO_2 in water: $Fe + 2H^+$ (from H_2CO_3)$\rightarrow Fe^{2+} + H_2$
3. Presence of alkaline masses in water (e.g. NaOH): $Fe + 2NaOH \rightarrow H_2 + Na_2FeO_2$ (sodium Ferrite)
4. Presence of acidic masses in water (e.g. HCl): $Fe + 2HCl \rightarrow FeCl_2 + H_2$
5. Presence hardness causing substance like $MgCl_2$ in water ($MgCl_2 + H_2O \rightarrow Mg(OH)_2$ (ppt.) + 2 HCl)

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.

Limitations:

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

Q. Mention some causes of boiler corrosion.

Ans. Various causes of boiler corrosion are:
1. Presence of dissolved O_2 in water
2. Presence of dissolved CO_2 in water
3. Presence of alkaline masses in water (e.g. NaOH)
4. Presence of acidic masses in water (e.g. HCl)
5. Presence hardness causing substance like $MgCl_2$ in water ($MgCl_2 + H_2O \rightarrow Mg(OH)_2$ (ppt.) + 2 HCl)

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.*

Water Softening by Lime-Soda Process

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 **$Ca(OH)_2$** 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.

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 → Precipitates + 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.

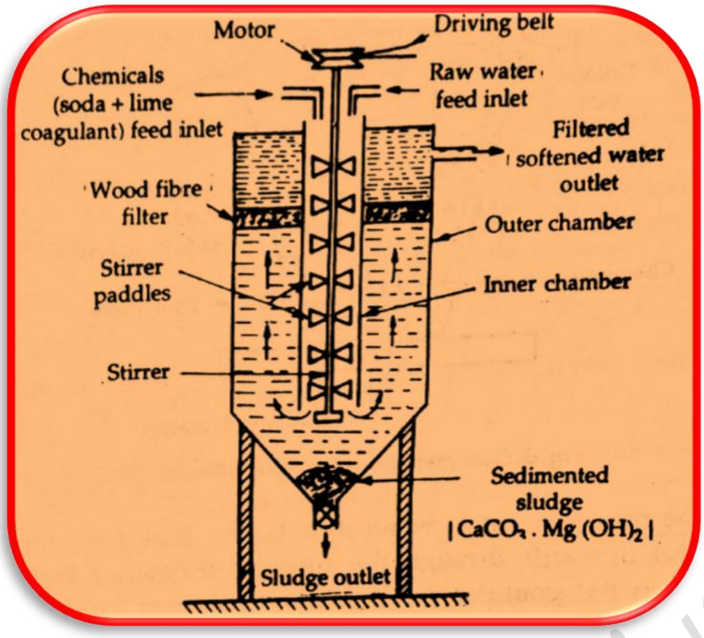


Fig. Cold L-S Softener

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, rate of precipitation is slow; (3) Dissolved gases are not removed; (4) Relatively more chemicals are needed (coagulant is required); (4) Bacteria are not killed; (5) need skilled operator/ supervisor; (5) disposal of huge amount of sludge is a problem

Questions:

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

Q. What is a coagulant? Give an example.

Ans. Coagulant is a substance which helps in settling of fine particles. Example:-Potash Alum

Q. Define coagulation. Mention a reaction between coagulant and hardness causing mass.

Ans. Coagulation is a process by which finer particles are converted into coarser particles by addition of a coagulant.

$Al_2(SO_4)_3$ coagulant + $3Ca(HCO_3)_2 \rightarrow 2\ Al(OH)_3$ 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 particle settling process) and filtration. This softening process proceeds via precipitation reaction.

Q. **What is the basic principle of L-S process? Describe the cold L-S process with a neat softener diagram.**

Ans. Refer above

Q. Mention the limitations of Cold L-S Process

Ans. *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, rate of precipitation is slow; (3) Dissolved gases are not removed; (4) Relatively more chemicals are needed (coagulant is required); (4) Bacteria are not killed; (5) need skilled operator/ supervisor; (5) disposal of huge amount of sludge is a problem

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.

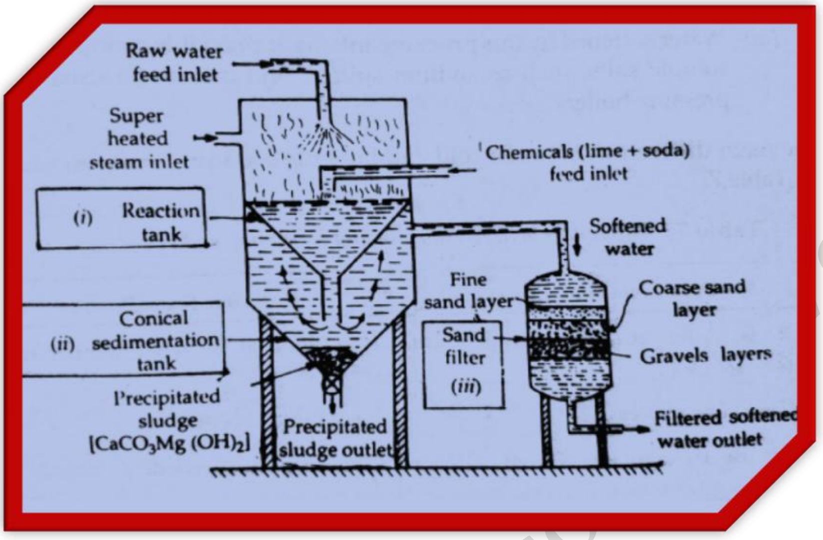


Fig. Hot L-S process

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 removed, 6. Pathogenic bacteria are killed, 7. Residual hardness is relatively low

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. 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

Q. Why is coagulant not required in hot L-S process?

Ans. The hot L-S process is carried out at a temperature of 100-110°C, resulting in the formation of coarse precipitates due to the high reaction rate.

Q. What is the use of sand filter in Hot L-S softener?

Ans. Sand filter is used to remove suspended particles present in the water.