

CHAPTER

13

Water

Chapter Outline

- Sources of Water
- Impurities in Water
- Hardness of Water
- Softening Methods
- Boiler Feed Water
- Desalination of Brackish Water
- Water for Domestic Use
- Analysis of Water
- Cooling Water
- Waster Water Treatment

Water is considered to be the most common and abundant (in the solid form as ice; in the liquid form, it covers about 70% of the Earth's surface) liquid on our planet, which is vital to all life forms. In atmosphere, it remains in varying amounts. Most of the living tissues are made up of water. It acts as the dispersion medium for all biochemical reactions occurring in living organisms and at the same time also takes part in many of these reactions. Water is not only vital to different life forms but is also an important requirement for industries. The most important use of water as an engineering material is in *steam generation*, an essential component for power generation from fossil fuel. It is also used as a coolant in power plants. Other wide uses of water are irrigation, drinking, sanitary, washings, air-conditioning, firefighting, etc.

Chemically, water is a compound of hydrogen and oxygen, having the formula H_2O . It reacts with metals and metal oxides to form bases, while with non-metallic oxides it forms acids. It is a polar compound and acts as a good solvent. In fact, it is considered to be the universal solvent. Pure water feebly conducts current because of its self-ionization. Both its polarity and ionization are attributed to the high dielectric constant. Water has interesting thermal properties. When heated from $0^{\circ}C$ (the melting point) to $4^{\circ}C$, it contracts and becomes denser. However, most of the other substances expand and become less dense when heated. The molecular association is through hydrogen bonding, which is stronger than the other van der Walls' forces. Because of this hydrogen bonding, the latent heats of fusion and of evaporation and the heat capacity of water are unusually high.

Sources of Water

The main sources of water are as follows:

1. **Surface water:** It includes both flowing (streams and rivers) and still (lakes, ponds, and reservoirs) water.
2. **Underground water:** It includes water from wells and springs.
3. **Rainwater**
4. **Seawater**

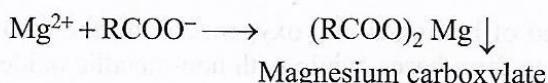
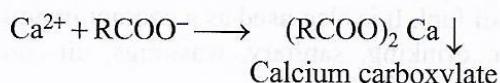
Impurities in Water

Impurities in water can be broadly classified into the following types:

1. **Dissolved impurities:** These include dissolved salts such as carbonates, bicarbonates, chlorides, and sulfates of sodium, calcium, magnesium, and iron. Dissolved gases such as O₂ and CO₂ also come under this category.
2. **Suspended impurities:** These may be inorganic impurities such as clay and sand or organic impurities such as oil globules, animal matter, and vegetables.
3. **Colloidal impurities:** These include products from organic waste, finely divided silica, and clay.
4. **Microorganisms:** These include bacteria, fungi, and algae.

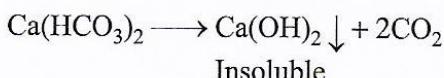
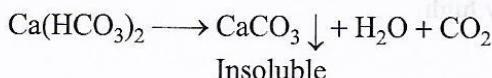
Hardness of Water

Hardness is the property of water by virtue of which it fails to form lather with soap. This is due to the presence of certain dissolved salts of calcium, magnesium, and other heavy metals such as iron, aluminum, and manganese in it. These metal ions react with the carboxylate ions of soap to form insoluble carboxylates which precipitate out as a brown sticky material known as *scum*. Carboxylate ion in soap is mainly responsible for its cleansing action. It does so by acting as a surfactant which stabilizes oil-in-water emulsion.



Water hardness may be of two types: temporary and permanent.

1. **Temporary:** It is attributed to the presence of dissolved bicarbonates of calcium, magnesium, and other heavy metals. As the name suggests, such hardness can be removed simply by boiling the water. In the process, the bicarbonates decompose to insoluble carbonates or hydroxides which subsequently settle down as a crust at the bottom of the vessel. Such hardness is also known as *carbonate hardness*.



2. **Permanent:** It is attributed to the presence of chlorides and sulfates of calcium, magnesium, and other heavy metals. It cannot be removed merely by boiling the water. This type of hardness is also known as *noncarbonate hardness*.

Note:

1. **Calcium carbonate equivalent:** The concentrations of hardness producing ions and also sometimes non-hardness producing ions are expressed in terms of calcium carbonate equivalents as this mode permits easy multiplication/division of concentrations as and when required. The choice of calcium carbonate is because its molecular mass is 100 and it is the most insoluble salt that can be precipitated in water treatment.

$$\text{Calcium carbonate equivalent} = \frac{\text{Mass of hardness}}{\text{imparting substance (mg/l)}} \times \left[\frac{\text{Equivalent mass of CaCO}_3}{\text{Equivalent mass of hardness imparting substance}} \right]$$

$$= \left[\frac{\text{Mass of hardness}}{\text{imparting substance} \times \text{Multiplication factor (mg/l)}} \right] \text{ mg/l or ppm}$$

For example,

$$\text{Calcium carbonate equivalent of HCO}_3^- = \left[\frac{\text{Mass of HCO}_3^- \times 50}{61} \right] \text{ mg/l}$$

$$\text{Calicum carbonate equivalent of CaSO}_4 = \left[\frac{\text{Mass of CaSO}_4 \times 50}{68} \right] \text{ mg/l}$$

2. **Units of hardness:** It is usually expressed in milligram per liter (mg/l) or parts per million (ppm) of calcium carbonate equivalent. It is also expressed in units such as Degree French ($^{\circ}\text{Fr}$) and Degree Clarke ($^{\circ}\text{Cl}$). For such units, we use the following conversion formulas: $1^{\circ}\text{Fr} = 10 \text{ mg/l}$ and $1^{\circ}\text{Cl} = 0.07 \text{ mg/l}$.

Example 13.1

A water sample contains 280 mg of CaSO_4 per liter. Calculate the hardness in terms of CaCO_3 equivalent.

Solution

$$\begin{aligned} \text{Hardness} &= \text{Mass of CaSO}_4 \text{ (mg/l)} \times \left[\frac{\text{Equivalent mass of CaCO}_3}{\text{Equivalent mass of CaCO}_4} \right] \\ &= \left[280 \times \frac{50}{68} \right] \text{ mg/l} \\ &= 205.88 \text{ mg/l} \end{aligned}$$

Example 13.2

How many grams of MgCl_2 dissolved per liter gives 60 ppm of hardness?

Solution

$$\text{Hardness} = \text{Mass of MgCl}_2 \text{ (mg/l)} \times \left[\frac{\text{Equivalent mass of CaCO}_3}{\text{Equivalent mass of MgCO}_2} \right]$$

$$\begin{aligned}\text{Mass of MgCl}_2 &= \frac{\text{Hardness} \times \text{Equivalent mass of MgCl}_2}{\text{Equivalent mass of CaCO}_3} \\ &= \left[60 \times \frac{47.5}{50} \right] \text{ mg/l} \\ &= 57 \text{ mg/l}\end{aligned}$$

Example 13.3

A sample of water on analysis is found to contain 4 mg/l $\text{Ca}(\text{HCO}_3)_2$, 8 mg/l CaSO_4 , and 12 mg/l of MgCl_2 . Calculate temporary, permanent, and total hardness of water.

Solution

$$\text{Hardness due to } \text{Ca}(\text{HCO}_3)_2 = \left[4 \times \frac{50}{81} \right] \text{ mg/l} = 2.47 \text{ mg/l}$$

$$\text{Hardness due to } \text{CaSO}_4 = \left[8 \times \frac{50}{68} \right] \text{ mg/l} = 5.88 \text{ mg/l}$$

$$\text{Hardness due to } \text{MgCl}_2 = \left[12 \times \frac{50}{47.5} \right] \text{ mg/l} = 12.63 \text{ mg/l}$$

Temporary hardness is due to the presence bicarbonate of calcium and is equal to 2.47 mg/l. Permanent hardness is due to the presence of sulfate of calcium (5.88 mg/l) and chloride of magnesium (12.63 mg/l) and is equal to 18.51 mg/l (i.e., 5.88 + 12.63).

Softening Methods

The process of removal of hardness producing ions/salts from water is known as softening of water. We will discuss here some important methods for water softening.

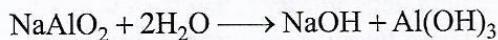
Lime-soda process

In lime-soda (LS) process, the dissolved hardness-causing salts are converted into insoluble carbonates and hydroxides by adding a calculated quantity of lime $[\text{Ca}(\text{OH})_2]$ and soda (Na_2CO_3) . The insoluble compounds so precipitated are then filtered off. The LS process can again be applied either at the room temperature or at an elevated temperature.

- Cold LS process**

Principle: In this process, calculated quantity of lime and soda are mixed with water at room temperature. The insoluble carbonates and hydroxides so formed are very fine and cannot be filtered easily. To facilitate filtration, a small amount of coagulant such as alum, aluminum sulfate, sodium aluminate, or ferrous sulfate is added. The coagulant hydrolyses to aluminum hydroxide which entraps the fine particles, thus

facilitating the easy filtering of the sludge. This process produces water containing residual hardness of ~50 ppm.



Method: Raw water and calculated quantities of lime, soda, and coagulant are introduced from the top into the inner cylindrical chamber fitted with a vertical rotating shaft attached with paddles as shown in Fig. 13.1. As the water comes down, it gets softened which then flows into the outer coaxial chamber and rises in the upward direction. Sludge or floc with relatively higher specific gravity settles down. The softened water is then allowed to pass through a filtering medium made of wood fibers to confirm the complete removal of the sludge. Finally, the soft water comes out through the outlet at the top, while the sludge is removed from the bottom periodically.

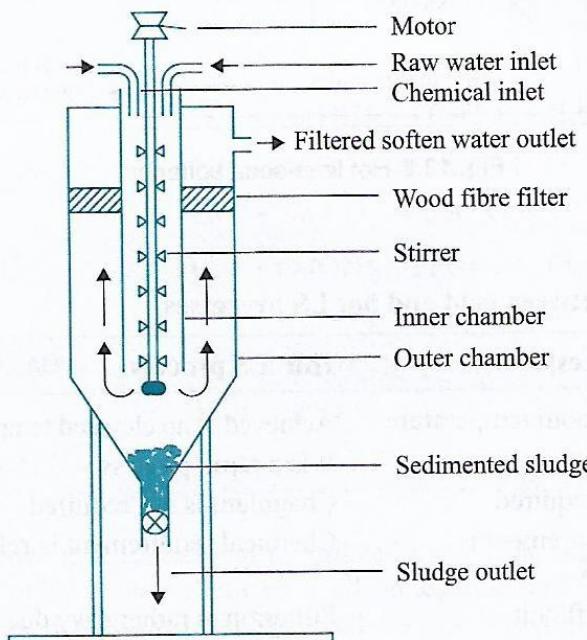


Fig. 13.1 Cold lime–soda softener

2. Hot LS method

The softening process is carried out at a temperature close to the boiling point of water. Here all the reactions are boosted up, increasing the softening process to manyfold. In the process, the sludge quickly settles down without the help of coagulant. The dissolved gases such as carbon dioxide and air are driven out easily. The filtration becomes much easier due to lower viscosity of the water. This process produces water containing residual hardness of ~15 ppm. In this process, the raw water mixed with chemicals is sprayed into superheated steam in a reaction tank as shown in Fig. 13.2. Here the plant consists of three parts:

- (i) A reaction tank in which raw water, chemicals, and steam are thoroughly mixed.
- (ii) A sedimentation tank where sludge settles down.
- (iii) A sand filter which ensures the complete removal of sludge.

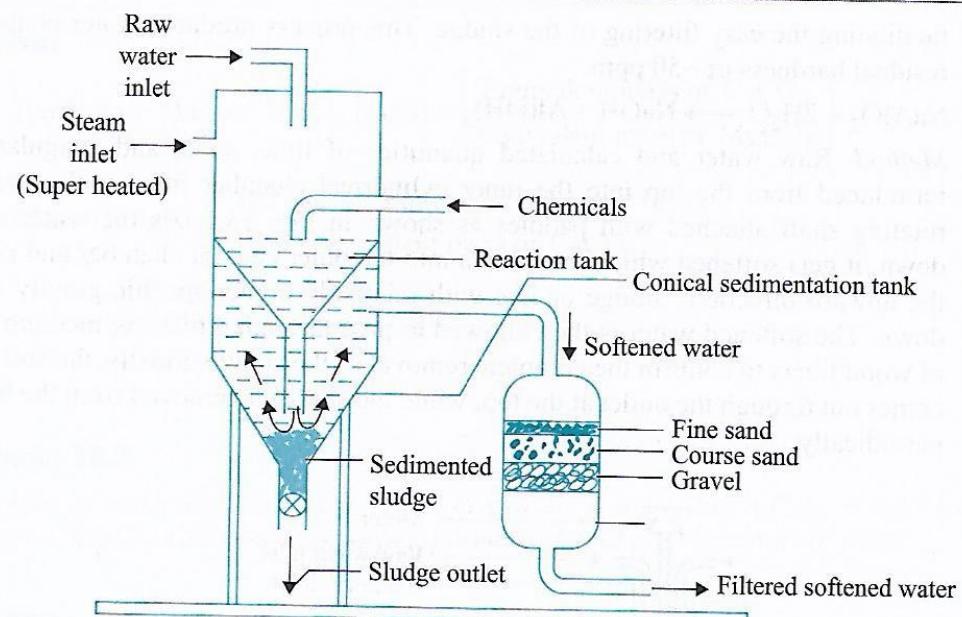


Fig. 13.2 Hot lime-soda softener

Note**1. Differences between cold and hot LS processes**

Cold LS process	Hot LS process
Achieved at room temperature	Achieved at an elevated temperature of ~100°C.
It is a slow process	It is a rapid process
Coagulant is required	Coagulant is not required
Chemical requirement is relatively high	Chemical requirement is relatively less
Filtration is difficult	Filtration is rather easy due to decrease in viscosity at elevated temperature
Residual hardness ~50 ppm (relatively high)	Residual hardness ~15 ppm (relatively small)
Dissolved gases are not removed	Dissolved gases are removed

2. Advantages of LS process

- It is economical.
- After treatment, water remains alkaline; hence, it has less corrosion tendency.
- Pathogenic bacteria are considerably reduced owing to its alkaline nature.
- Iron and manganese are also removed to some extent.

3. Disadvantages of LS process

- It needs careful operation and skilled supervision.
- Disposal of sludge is a problem.
- Softened water still contains a lot of soluble salts such as sodium sulfate which cannot be used in high pressure boilers.

4. Calculation of lime and soda requirement

A given hard water sample may contain any combination of different salts or ions. Therefore, it requires different quantities of lime and soda for effective softening. The reaction of different constituents with lime and soda is as follows.

Constituent	Reaction	Need
Temporary $[Ca^{2+}/Ca(HCO_3)_2]$	$Ca(HCO_3)_2 + Ca(OH)_2 \rightarrow 2CaCO_3 + H_2O$	L
Temporary $[Mg^{2+}/Mg(HCO_3)_2]$	$Mg(HCO_3)_2 + 2Ca(OH)_2 \rightarrow 2CaCO_3 + Mg(OH)_2 + H_2O$	2L
Permanent $[Ca^{2+} \text{ and } Mg^{2+}]$ from corresponding chlorides/sulfates	$Ca^{2+} + Na_2CO_3 \rightarrow Ca(CO_3)_2 + Na^+$ $Mg^{2+} + Ca(OH)_2 \rightarrow Mg(OH)_2 + Ca^{2+}$	S L
HCO_3^- from say $NaHCO_3$	$2HCO_3^- + Ca(OH)_2 \rightarrow CaCO_3 + CO_3^{2-} + H_2O$	L-S
CO_2	$CO_2 + Ca(OH)_2 \rightarrow CaCO_3 + H_2O$	L
H^+ [free acids like HCl , H_2SO_4 etc.]	$2H^+ + Ca(OH)_2 \rightarrow Ca^{2+} + H_2O$ $Ca^{2+} + Na_2CO_3 \rightarrow Ca(CO_3)_2 + Na^+$	L + S
$FeSO_4$ [Coagulant]	$Fe^{2+} + Ca(OH)_2 \rightarrow Fe(OH)_2 + Ca^{2+}$ $Ca^{2+} + Na_2CO_3 \rightarrow CaCO_3 + 2Na^+$	L + S
$Al_2(SO_4)_3$ [Coagulant]	$2Al^{3+} + 3Ca(OH)_3 \rightarrow 2Al(OH)_3 + 3Ca^{2+}$ $3Ca^{2+} + 2Na_2CO_3 \rightarrow 3CaCO_3 + 2Na^+$	L + S
$NaAlO_2$ [Coagulant]	$NaAl_2O + 2H_2O \rightarrow Al(OH)_3 + NaOH$	-L

Now, following formulas can be utilized to find the lime and soda required for softening of hard water. Remember, all values should be in $CaCO_3$ equivalent. The substances, such as $NaCl$, Na_2SO_4 , KCl , SiO_2 , and Fe_2O_3 , that do not consume lime and soda need not be considered.

Lime requirement for softening (mg/l)

$$= \frac{74}{100} \left[Temp. \{Ca^{2+} + 2 \times Mg^{2+}\} + Perm. \{Mg^{2+} + Fe^{2+} Al^{3+}\} + CO_2 + H^+ + HCO_3^- - NaAlO_2 \right] \\ \text{all in terms of } CaCO_3 \text{ equivalents}$$

Soda requirement for softening (mg/l)

$$= \frac{106}{100} \left[Perm. \{Ca^{2+} + Mg^{2+} + Fe^{2+} \times Al^{3+}\} + H^+ - HCO_3^- \right] \\ \text{all in terms of } CaCO_3 \text{ equivalents}$$

Example 13.4

A water sample contains the following impurities: $Ca^{2+} = 20 \text{ ppm}$, $Mg^{2+} = 18 \text{ ppm}$, $HCO_3^- = 180 \text{ ppm}$, and $SO_4^{2-} = 24 \text{ ppm}$. Calculate the amount of lime and soda needed for softening.

Solution

$$\text{CaCO}_3 \text{ equivalent of } \text{Ca}^{2+} = \left[20 \times \frac{50}{20} \right] \text{ mg/l} = 50 \text{ ppm}$$

$$\text{CaCO}_3 \text{ equivalent of } \text{Mg}^{2+} = \left[18 \times \frac{50}{12} \right] \text{ mg/l} = 75 \text{ ppm}$$

$$\text{CaCO}_3 \text{ equivalent of } \text{HCO}_3^- = \left[180 \times \frac{50}{61} \right] \text{ mg/l} = 147.54 \text{ ppm}$$

$$\begin{aligned}\text{Lime requirement for softening} &= \frac{74}{100} [\text{Perm. Mg}^{2+} + \text{HCO}_3^-] \\ &= \frac{74}{100} (75 + 147.54) \\ &= 164.68 \text{ mg/l}\end{aligned}$$

$$\begin{aligned}\text{Soda requirement for softening} &= \frac{106}{100} [\text{Prem. } \{\text{Ca}^{2+} + \text{Mg}^{2+}\} - \text{HCO}_3^-] \\ &= \frac{106}{100} (50 + 75 - 147.54) \\ &= -22.54 \text{ mg/l}\end{aligned}$$

The value is negative. This implies that soda requirement is nil.

Example 13.5

Calculate the amount of lime and soda needed for softening 50000 l of water containing following salts per liter: $\text{Ca}(\text{HCO}_3)_2 = 10 \text{ mg}$, $\text{Mg}(\text{HCO}_3)_2 = 15 \text{ mg}$, $\text{MgSO}_4 = 20 \text{ mg}$, $\text{CaSO}_4 = 18 \text{ mg}$, $\text{CaCl}_2 = 8 \text{ mg}$, and $\text{NaCl} = 4 \text{ mg}$.

Solution

Lime requirement for softening

$$\begin{aligned}&= \frac{74}{100} [\text{Temp. } \{\text{Ca}^{2+} + 2 \times \text{Mg}^{2+}\} + \text{Perm. } (\text{Mg}^{2+})] \times \text{Volume of water} \\ &= \frac{74}{100} \left[10 \times \frac{50}{81} + 2 \times 15 \times \frac{50}{73} + 20 \times \frac{50}{60} \right] \times 50000 \text{ mg} \\ &= 1605430 \text{ mg} = 1.605 \text{ kg}\end{aligned}$$

$$\begin{aligned}\text{Soda requirement for softening} &= \frac{106}{100} [\text{Temp. } \{\text{Ca}^{2+} + \text{Mg}^{2+}\} \times \text{H}^+] \times \text{Volume of water} \\ &= \frac{106}{100} \left[20 \times \frac{50}{60} + 18 \times \frac{50}{68} + 8 \times \frac{50}{55.5} \right] \times 50,000 \text{ mg} \\ &= 1967360 \text{ mg} = 1.967 \text{ kg}\end{aligned}$$

Example 13.6

Calculate the amount of lime and soda needed for softening 50000 l of water with the following analysis using 10 ppm of sodium aluminate as coagulant. Analysis result: $\text{Ca}^{2+} = 100$, $\text{Mg}^{2+} = 35$, $\text{CO}_2 = 50$, $\text{HCO}_3^- = 250$, $\text{H}^+ = 2 \text{ ppm}$.

Solution

$$\text{Lime requirement for softening (mg/l)} = \frac{74}{100} [\text{Mg}^{2+} + \text{CO}_2 + \text{H}^+ + \text{HCO}_3^- - \text{NaAlO}_2]$$

$$\text{Soda requirement for softening (mg/l)} = \frac{106}{100} [\text{Ca}^{2+} + \text{Mg}^{2+} + \text{H}^+ - \text{HCO}_3^-]$$

Substitute the values after converting into CaCO_3 equivalent as per Example 13.5.

Zeolite/permudit process

Zeolite or permudit process involves a reversible exchange of ions between the stationary ion-exchange phase, i.e., zeolite, and the external mobile liquid phase. Zeolite is hydrated sodium aluminosilicate, $\text{Na}_2\text{O}\cdot\text{Al}_2\text{O}_3\cdot x\text{SiO}_2\cdot y\text{H}_2\text{O}$, where $x = 2$ to 10 and $y = 2$ to 6 [e.g., natralite, $\text{Na}_2\text{O}\cdot\text{Al}_2\text{O}_3\cdot 3\text{SiO}_2\cdot 2\text{H}_2\text{O}$; thomsonite ($\text{Na}_2\text{O}\cdot\text{CaO}\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2\cdot 2.5\text{H}_2\text{O}$)]. Zeolites are the substances insoluble in water and can act as cation exchangers. These are commercially known as permudits and are basically classified as natural zeolites (derived from green sands by washing, heating, and then treating with NaOH) and synthetic zeolites (derived directly from a combination of silicate and sodium aluminate).

Process: In this process, raw water is introduced from the top of a steel tank packed with a thick layer of loosely packed zeolite over a layer of coarse sand and gravel (see Fig. 13.3). Zeolite can be represented by Na_2Z , where $\text{Z}: \text{Al}_2\text{Si}_2\text{O}_6\cdot x\text{H}_2\text{O}$. The following reactions take place:

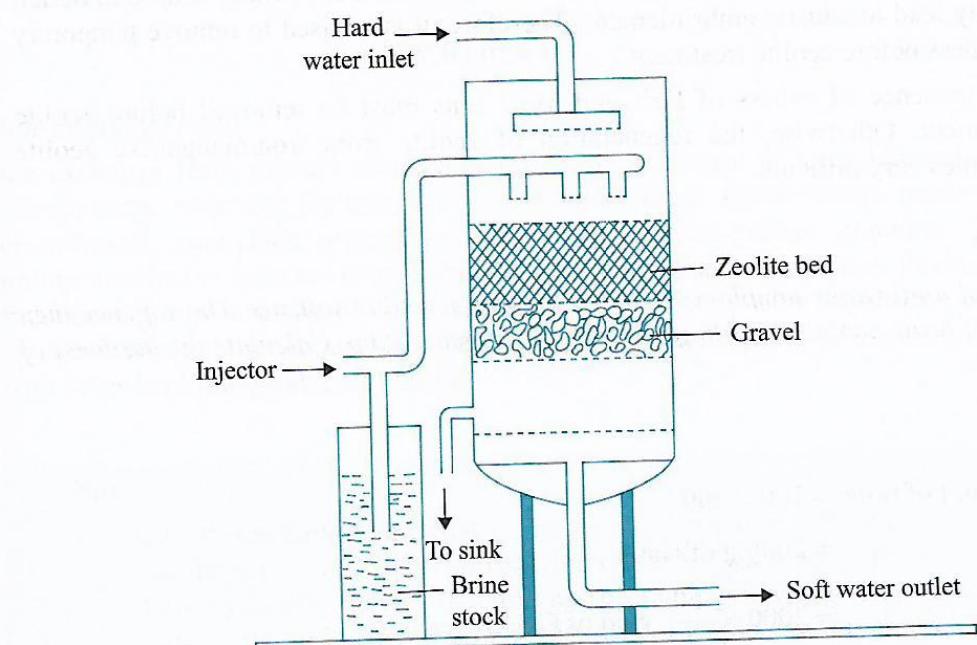
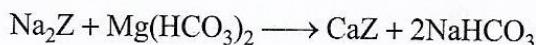


Fig. 13.3 Zeolite softener

place. The hardness causing ions are retained by zeolite as CaZ and MgZ, and the outgoing water remains rich in Na⁺ ions.



This process removes both temporary and permanent hardness. The advantage of the process is that after the exhaustion of the zeolite bed, the same can be regenerated by simply passing 10% solution of sodium chloride or brine through it.



Limitations

1. Suspended particulates present in raw water many at times clog the pores of the zeolite bed.
2. Softened water contains about 25% more dissolved solids as compared to LS process.
3. The presence of acid in water destroys zeolite; for this raw water must be neutralized before treatment.
4. Water should not be hot because zeolite tends to dissolve in it.
5. Anions are not removed in this process. Thus, bicarbonates present in hard water get converted into NaHCO₃ which goes to soft water. When such water is used in boiler, it may lead to caustic embrittlement. Therefore, it is advised to remove temporary hardness before zeolite treatment.
6. The presence of excess of Fe²⁺ and Mn²⁺ ions must be removed before zeolite treatment. Otherwise, the regeneration of zeolite from iron/manganese zeolite becomes very difficult.

Example 13.7

About 10000 l of hard water sample was passed through a zeolite softener. The softener then required 200 l of brine containing 100 g/l of NaCl for regeneration. Calculate the hardness of the water sample.

Solution

$$\text{NaCl in } 200 \text{ l of brine} = 100 \times 200$$

$$= 2000 \text{ g of NaCl}$$

$$= 2000 \times \frac{50}{58.5} \text{ g eq of CaCO}_3$$

$$= 17094 \text{ g eq of CaCO}_3$$

10000 l of water contains 17094 g eq of CaCO_3

$$\text{Now, 1 l contains} = \frac{17094}{10000} \times 10^3 \\ = 1709 \text{ mg}$$

Thus, hardness of water is 1709 mg/l.

Example 13.8

An exhausted zeolite softener was regenerated by passing 100 l of NaCl solution, having strength of 150 g/l of NaCl . Find the total volume of water that can be softened by the same softener, if hardness of water is 500 ppm.

Solution

$$100 \text{ l of } \text{NaCl} = 100 \times 150 \text{ g/l} \\ = 15000 \text{ g/l of } \text{NaCl} \\ = 15000 \times \frac{50}{58.5} \text{ g eq of } \text{CaCO}_3 \\ = 1.29 \times 10^4 \text{ g eq of } \text{CaCO}_3 \\ = 1.29 \times 10^7 \text{ mg eq of } \text{CaCO}_3$$

Now, 500 mg hardness is there in 1 l water. Therefore,

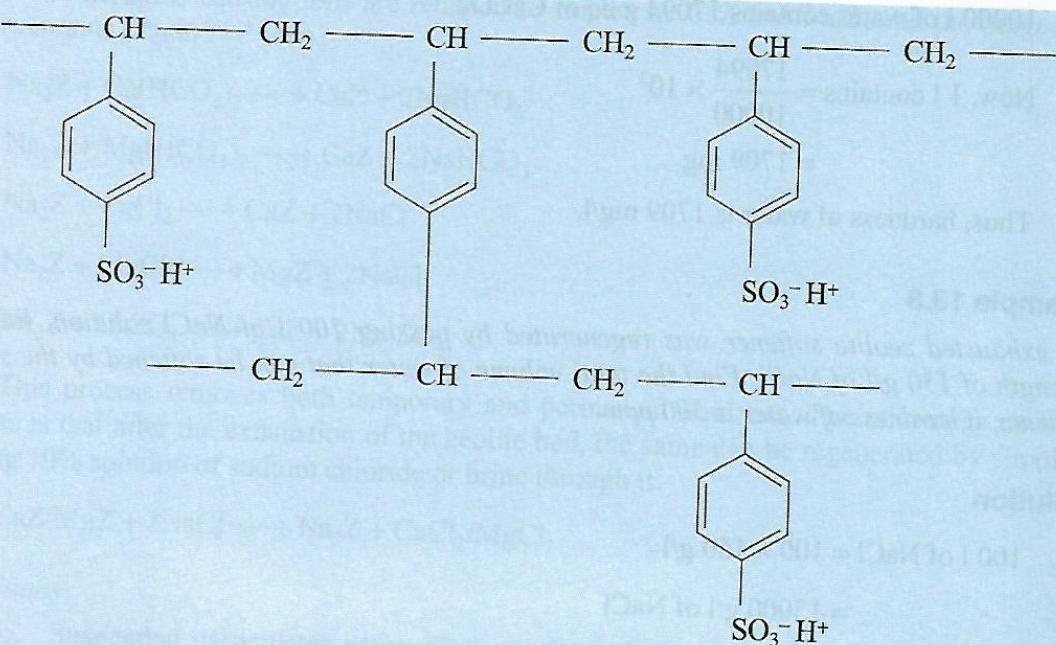
$$1.29 \times 10^7 \text{ mg hardness} = \frac{1.29 \times 10^7}{500} \text{ l of water} \\ = 25800 \text{ l of water}$$

Ion-exchange resin

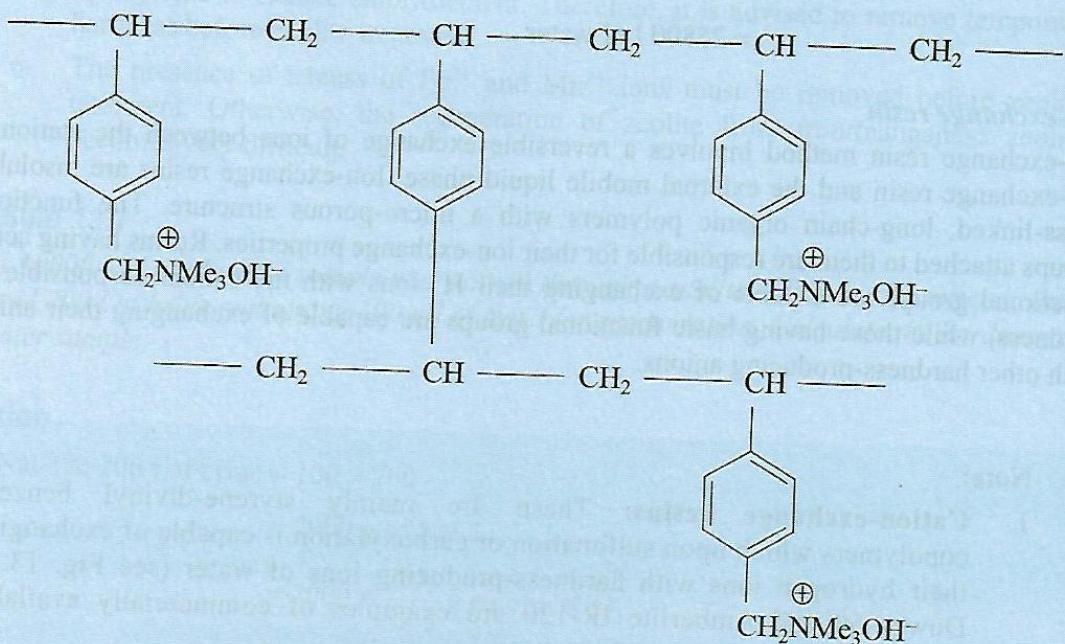
Ion-exchange resin method involves a reversible exchange of ions between the stationary ion-exchange resin and the external mobile liquid phase. Ion-exchange resins are insoluble, cross-linked, long-chain organic polymers with a micro-porous structure. The functional groups attached to them are responsible for their ion-exchange properties. Resins having acidic functional groups are capable of exchanging their H^+ ions with the cations responsible for hardness, while those having basic functional groups are capable of exchanging their anions with other hardness-producing anions.

Note:

1. **Cation-exchange resins:** These are mainly styrene-divinyl benzene copolymers which upon sulfonation or carboxylation is capable of exchanging their hydrogen ions with hardness-producing ions of water (see Fig. 13.4). Dowex-50 and Amberlite IR-120 are examples of commercially available cation exchangers.

**Fig. 13.4** Sulfonate form of cation exchanger

2. **Anion-exchange resins:** These are mainly styrene-divinyl benzene or amine-formaldehyde copolymers containing basic functional groups such as amino/quaternary ammonium/quaternary sulfonium/tertiary sulfonium groups as an integral part of the resin matrix (see Fig. 13.5). After treatment with NaOH, these resins become capable to exchange their OH⁻ ions with hardness imparting negative ions.

**Fig. 13.5** Hydroxide form of anion exchanger

Process: The hard water is first passed through the cation-exchange column as shown in Fig. 13.6. The hardness-producing cations such as Ca^{2+} and Mg^{2+} are taken up by the resin and an equivalent amount of H^+ ions are released into water. Water is subsequently allowed to pass through the anion-exchange column where hardness-producing anions such as Cl^- and SO_4^{2-} are taken up by the resin and an equivalent quantity of OH^- ions are released by the resin into water. H^+ and OH^- ions released from the exchange columns combine to produce water. Finally, the water is allowed to pass through a degasifier. It is a tower which is kept at a higher temperature by using a steam jacket and at the same time low pressure is maintained by using a vacuum pump. A high temperature and low pressure reduces the dissolved gases such as CO_2 and O_2 in water. The reactions occurring in exchange columns are as follows:

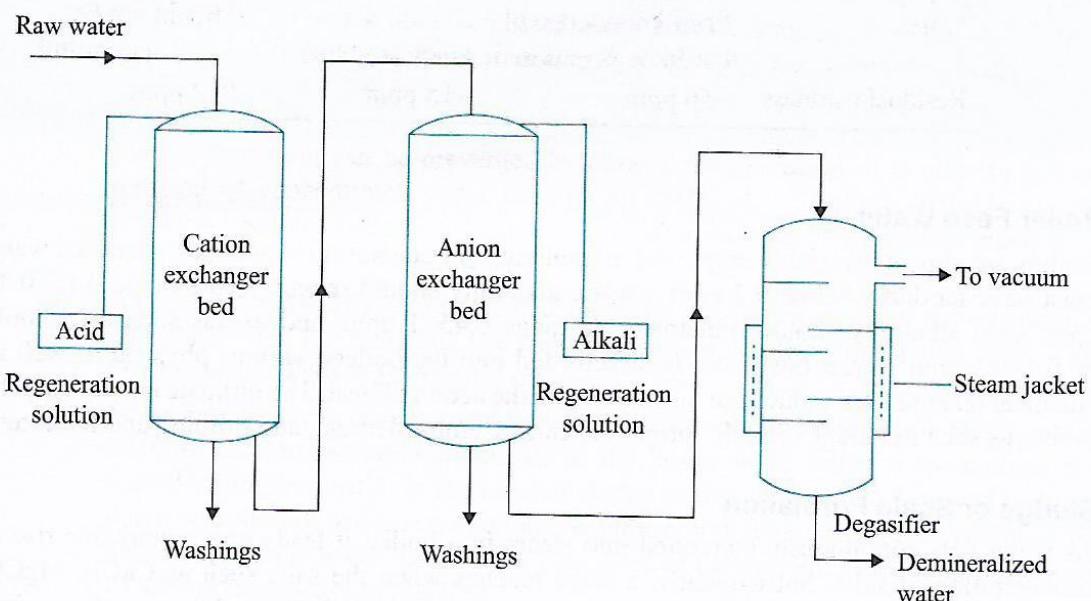
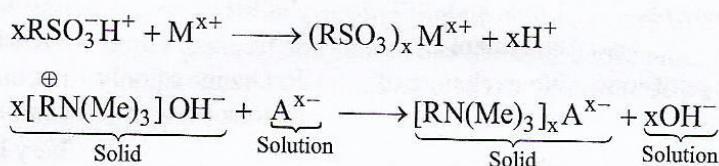


Fig. 13.6 Demineralization of water

The regeneration of exhausted cation-exchange column is possible by passing a solution of dil. HCl /dil. H_2SO_4 , while the regeneration of anion-exchange column is possible by passing a solution of dil. NaOH . After the treatment, the columns are washed by de-ionized water.

Advantages

1. The process can be utilized to soften highly acidic/alkaline water.
2. It produces water of very low hardness, say up to a residual hardness 2 ppm.

Disadvantages

1. The equipment and chemicals are costly.
2. If turbidity is >10 ppm, then efficiency is reduced substantially. Therefore, pretreatment such as coagulation and filtration must be done before this treatment.

Note:

- Mixed bed deionizer:** This consists of a single ion-exchange column containing an intimate mixture of strongly acidic and basic ion exchangers. The operation principle is same as discussed above. To regenerate such a bed deionizer, at first it is necessary to separate the two resins. These resins are then regenerated separately. Such a mixed bed deionizer is convenient to use but comparatively more expensive.
- A comparative account of different processes**

Characteristic	Lime–Soda	Zeolite	Ion-exchange
Requirements	Lime, soda, coagulant	Zeolite	Cation- and anion-exchange resins
Exchange of ions	No exchange of ions	Exchange of only cations	Exchange of both cation and anion
Capital cost	Low	High	Very high
Water	Prior knowledge of hardness is required	Should not be acidic and turbid	Should not be acidic and turbid
Residual hardness	~50 ppm	~15 ppm	0–2 ppm

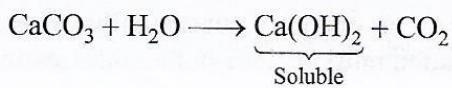
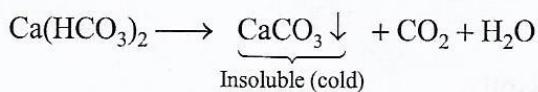
Boiler Feed Water

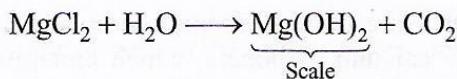
Boilers are almost invariably employed in industries for generation of steam. Boiler feed water must have hardness below 0.2 ppm, caustic alkalinity should remain in the range 0.15–0.45 ppm, soda alkalinity should remain in the range 0.45–1 ppm, and excess soda ash should be 0.3–0.5 ppm. When raw water is directly fed into the boilers, various physical as well as chemical reactions are induced in the boiler with the action of heat. The ultimate result being the problems such as sludge or scale formation, caustic embrittlement, and priming and foaming.

Sludge or Scale Formation

As water gets continuously converted into steam in a boiler, it leads to a remarkable rise in concentration of salts. Subsequently, a stage reaches when the salts such as CaCl_2 , MgCl_2 , MgCO_3 , and MgSO_4 , which have greater solubility in hot water than in cold water, change into a loose and slimy precipitate called *sludge*. It is formed at the relatively colder region of the boiler and gets deposited in the bends and tubes of the boiler where the flow rate of water is low.

If the precipitated matter forms a hard, adhering coating on the inner walls and at the bottom of the boiler, it is known as *scale*. These are formed on relatively hot surface of the boiler by salts such as CaSO_4 , CaCO_3 , $\text{Mg}(\text{OH})_2$, and Ca/MgSiO_3 , which have negative temperature coefficient of solubility. CaCO_3 is mainly formed by decomposition of corresponding bicarbonate and is a problem in low-pressure boilers. In high-pressure boilers, it is soluble because of the formation of $\text{Ca}(\text{OH})_2 \cdot \text{CaSO}_4$ creates problem mainly in high-pressure boilers. $\text{Mg}(\text{OH})_2$ is formed by the hydrolysis of dissolved magnesium salts. The reactions are as follows:



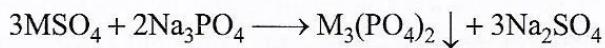
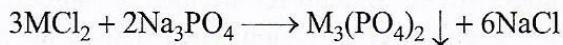


Disadvantages

1. Excessive sludge settles in the region of poor water circulation such as pipe connections, plug openings and gauge-glass connections thereby causing chocking of the pipes.
2. Sludge and scale are poor conductors of heat and therefore prevent the effective transfer of heat to water.
3. In order to provide a steady supply of heat to water, excessive or overheating is often required which increases fuel consumption. In addition, overheating also softens and weakens the boiler material and causes distortion of boiler tube. It may also result in burning out of superheated metal plates and tubes and breakdown of joints making the boiler unsafe, particularly at a high pressure.
4. Scales often crack due to their uneven expansion allowing the water to come immediately in contact with overheated metal. This suddenly results in the formation of a large quantity of steam which in turn leads to excess pressure and then to explosion.

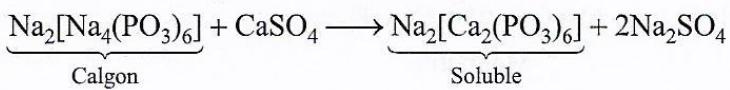
Prevention

1. Sludge formation can be prevented by *blow down operation*. It is nothing but the removal of concentrated water through an outlet at the bottom of boiler as the hardness becomes extremely high inside it. After blow down operation, *make-up* is done by the addition of fresh water.
2. It can be prevented by using softened water, i.e., treatment of water before entering into the boiler for reducing the concentration of hardness-producing ions. This process is also known as *external treatment*.
3. Scale formation can be prevented by internal treatment or conditioning that involves addition of some suitable chemicals to the boiler water either to precipitate the scale-forming impurities in the form of sludge so that they can be removed by blow down operation or to convert them into soluble compounds, which can remain in the dissolved form in water. Let us look into some of the *internal conditioning methods* which are commonly in practice.
 - (a) **Phosphate conditioning:** It is widely used in high-pressure boilers. It involves addition of sodium phosphate that reacts with calcium or magnesium salts to form soft sludge of calcium or magnesium phosphate, which can be easily removed by blow down operation. The choice of phosphate salt depends on the alkalinity of water. Na_3PO_4 is used for alkaline water, whereas Na_2HPO_4 is used in highly alkaline water, and NaH_2PO_4 is used in acidic water.

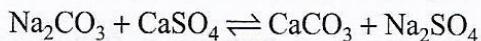


M : $\text{Ca}^{2+}/\text{Mg}^{2+}$

- (b) **Calgon conditioning:** Calgon is sodium hexametaphosphate, which can be used to convert CaSO_4 into a soluble complex.



- (c) **Carbonate conditioning:** In low-pressure boilers, sodium carbonate can be used to convert calcium sulfate into calcium carbonate, which precipitate as loose sludge and can be removed by the blow down process.



- (d) **Colloidal conditioning:** In low-pressure boilers, it is achieved by the addition of some organic substances such as kerosene, agar-agar, and tannin, which form a coating on scale-forming precipitates, thereby making them non-sticky and loose. The loose precipitates can be easily removed.

Removal of scale

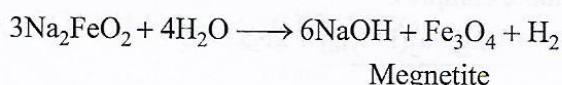
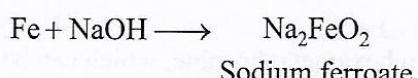
Scale can be removed by either mechanical or chemical methods. In mechanical method, it is removed by using a scraper or a wire brush. It can also be removed by giving thermal shock, i.e., heating and subsequent sudden cooling. In chemical method, it is made soluble by adding suitable chemical. For example, CaCO_3 can be removed by adding ~10% HCl.

Difference between sludge and scale

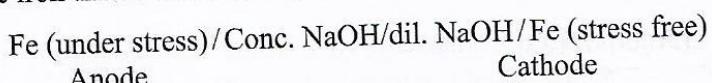
Sludge	Scale
Sludge forms soft, loose, and slimy precipitate	Scales are hard deposits
These are non-adherent deposits	These firmly stick to the inner surface of the boiler
Formed by substances such as CaCl_2 , MgCl_2 , MgCO_3 , and MgSO_4 .	Formed by substances such as CaSO_4 , CaCO_3 , Mg(OH)_2 , and Ca/MgSiO_3 .
Formed on comparatively colder portion of the boiler.	Formed on comparatively hot portion of the boiler.
They decrease the efficiency of boiler, but are less dangerous	They decrease the efficiency of boiler and chances of explosion are also there
Can be removed by blow down operation	Cannot be removed by blow down operation

Caustic Embrittlement

Caustic embrittlement is the phenomenon in which the boiler material becomes brittle due to the accumulation of caustic substances. With evaporation of water, concentration of Na_2CO_3 increases in the boiler, which is used as a water softener in the lime-soda process. Sodium carbonate upon hydrolysis yields NaOH which makes the water alkaline. This alkaline water subsequently enters into the fine cracks present in the inner walls of the boiler by capillary action. The water evaporates inside the cracks and concentration of hydroxide keeps on increasing progressively. This concentrated alkali attacks the boiler material and the iron of the boiler dissolves as sodium ferrate. This causes embrittlement of boiler parts such as rivets, bends, and joints, which remain under stress. Sodium ferrate then decomposes to magnetite, regenerating caustic soda which further enhances corrosion. The reactions are as follows:



The whole process can also be explained by taking into consideration the following concentration cell. In the cell, iron surrounded by dilute NaOH behaves anodic with respect to the iron that remains in contact with concentrated NaOH.



Prevention

Caustic embrittlement can be prevented as follows:

1. By using sodium sulfate as softening reagent instead of sodium carbonate. It also prevents infiltration of caustic soda, i.e., NaOH, by blocking the hairline cracks.
2. By adding tannin or lignin to the boiler water which can block the hairline cracks and prevent infiltration of NaOH into these areas.

Priming and Foaming

Priming refers to the carryover of varying amounts of water droplets along with the steam. This results in a lowering of the energy efficiency of the steam and leads to the deposit of salt crystals on the super heaters and in the turbines. It is caused by improper construction of boiler, excessive ratings, and sudden fluctuations in steam demand. Sometimes the presence of impurities in the boiler water also aggravates priming. When this boiler water carryover is excessive, steam-carried solids produce deposits on the turbine blades. Priming is a common cause of high levels of boiler water carryover. These conditions often lead to super heater tube failures as well. Priming is related to the viscosity of the water and its tendency to foam. These properties are governed by alkalinity, the presence of certain organic substances, and by total salinity or total dissolved solids (TDS). The degree of priming also depends on the design of the boiler and its steaming rate.

Build-up of bubbles or froth on the surface of the boiler water is known as *foaming*. It is believed that the presence of some specific substances such as alkalies, oils, fats, greases, certain types of organic matter, and fine suspended solids are particularly responsible for foaming. The suspended solids which remain collected in the surface film surrounding a bubble make it tough. The steam bubble therefore resists breaking and builds up foam. It is believed that the finer the suspended particles, the greater is their collection in the bubble.

Prevention

1. Priming can be prevented by fitting mechanical steam purifiers, low water level in boiler, ensuring softening, and timely blow down operation.
2. Foaming can be avoided by adding antifoaming chemicals such as castor oil which act by counteracting the reduction in surface tension and by removing foaming agent, i.e., oil from boiler water by addition of sodium aluminate or aluminum sulfate.

Boiler Corrosion

Boiler corrosion is decay of boiler material by a chemical or electrochemical attack by its environment. It reduces the boiler life, causes leakage in joints and rivets, and thus increases the cost of maintenance. Corrosion is attributed to the presence of dissolved oxygen, carbon dioxide, and mineral acids which are generated by the hydrolysis of dissolved salts.

1. **By dissolved oxygen:** The concentration of oxygen in water is about 8 mg/l at the room temperature. At elevated temperature, dissolved oxygen attacks the boiler material, i.e., iron.