

- (c) Temporary hardness is also known as carbonate hardness or alkaline hardness.
- (d) Alkaline hardness is due to the presence of bicarbonate, carbonate and hydroxides of the hardness-producing metal ions. This is determined by titration with HCl using methyl orange as indicator.

## (2) Permanent Hardness

- (a) It is due to the presence of dissolved chlorides and sulphates of calcium, magnesium, iron and other heavy metals. Hence, the salts responsible for permanent hardness are :  $\text{CaCl}_2$ ,  $\text{MgCl}_2$ ,  $\text{CaSO}_4$ ,  $\text{MgSO}_4$ ,  $\text{FeSO}_4$ ,  $\text{Al}_2(\text{SO}_4)_3$  etc. [UPTU, 2000]
- (b) Unlike temporary hardness, permanent hardness is not destroyed on boiling.
- (c) It is also known as *non-carbonate* or *non-alkaline hardness*.
- (d) The difference between the total hardness and the alkaline hardness gives the *non-alkaline hardness*.



## Important Question

Q. What is carbonate and non-carbonate hardness ?

Ans. Temporary hardness due to the presence of carbonates and bicarbonates is referred to as the Carbonate Hardness (CH) and the amount of hardness in excess of CH (i.e., permanent hardness) is referred to as the non-carbonate hardness (NCH).

$$\therefore \text{Total hardness} = \text{CH} + \text{NCH}$$

Advantages and disadvantages of hard water are summarized in Table 2 below.

**Table 2** Advantages and Disadvantages of Hard Water

S. No.	Hard Water	
	Advantages	Disadvantages
1.	The taste of hard water is usually better than soft water. The label on the bottle of mineral water shows that it contains $\text{Mg}^{2+}$ and $\text{Ca}^{2+}$ ions and it tastes good.	Hard water produces scum with soap. Thus, the washed clothes look dull. Efficiency of soap decreases in hard water so economy decreases.
2.	The dissolved calcium in hard water can help to produce strong teeth and healthy bones in children.	Boiler feed water should be free from hardness otherwise even explosion can occur.
3.	In old houses, lead piping was used for distribution of water. Hard water coats these with a layer of insoluble $\text{CaCO}_3$ . This prevents any of the poisonous lead dissolving in the drinking water.	

## Degree of Hardness

Although hardness of water is never present in the form of calcium carbonate because it is insoluble in water, hardness of water is conventionally expressed in terms of equivalent amount (equivalents) of  $\text{CaCO}_3$ .



## 5 BOILER FEED WATER (WATER FOR STEAM GENERATION)

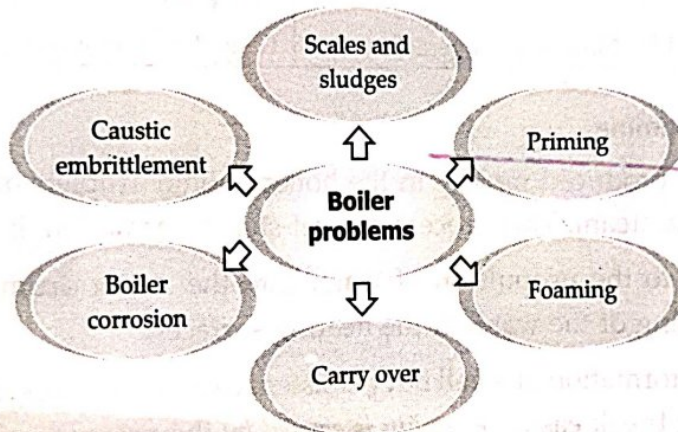
Water is mainly used in boilers for the generation of steam (for industries and power houses). For such water all the impurities are not necessarily eliminated, and only those impurities which lead to operational troubles in boilers are eliminated or kept within the tolerable limits. A boiler-feed water should correspond with the following composition :

- Its hardness should be below 0.2 ppm.
- Its caustic alkalinity (due to  $\text{OH}^-$ ) should lie in between 0.15 and 0.45 ppm.
- Its soda alkalinity (due to  $\text{Na}_2\text{CO}_3$ ) should be 0.45 – 1 ppm.

Excess of impurities, if present, in boiler feed water generally cause the following problems :

Scale and sludge formation, corrosion, priming and foaming, caustic embrittlement.

## 6 PROBLEMS CREATED BY HARD WATER IN BOILER [UPTU, 2010, 2005]



Summary of Boiler problems

### 6.1 Sludge and Scale Formation in Boilers [UPTU, 2007]

In a boiler, water is continuously evaporated to form steam. This increases the concentration of dissolved salts. Finally a stage is reached when the ionic product of these salts exceeds their solubility product and hence they are thrown out as precipitates.

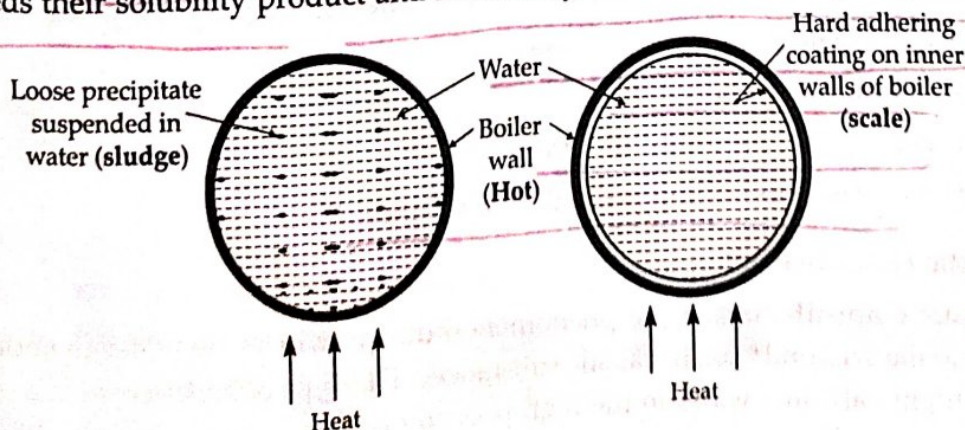


Figure 1 Sludge and scale formation in boilers.



If the precipitates formed are soft loose and slimy, these are known as *sludges* ; while if the precipitate is hard and adhering on the inner walls, it is called as *scale*.

The essential differences between sludges and scales are summarized in Table 4.

**Table 4** Differences between Sludges and Scales

S.No.	Sludges	Scales
1.	Sludges are soft, loose and slimy precipitate.	Scales are hard deposits.
2.	They are non-adherent deposits and can be easily removed.	They stick very firmly to the inner surface of boiler and are very difficult to remove.
3.	Formed by substances like $\text{CaCl}_2$ , $\text{MgCl}_2$ , $\text{MgSO}_4$ , $\text{MgCO}_3$ etc.	Formed by substance like $\text{CaSO}_4$ , $\text{Mg(OH)}_2$ , $\text{CaCO}_3$ , $\text{CaSiO}_3$ etc.
4.	Formed at comparatively colder portions of the boiler.	Formed generally at heated portions of the boiler.
5.	They decrease the efficiency of boiler but are less dangerous.	Decrease the efficiency of boiler and chances of explosions are also there.
6.	Can be removed by blow-down operation.	Cannot be removed by blow-down operation.

## 6.2 Priming and Foaming

When steam is produced rapidly in the boilers, some droplets of the liquid water are carried along-with the steam. This process of 'wet-steam' formation, is called *priming*.

*Priming* refers to the propulsion of water into the steam drum by extremely rapid, almost explosive boiling of the water at the heating surfaces.

*Foaming* is the formation of small but persistent foam or bubbles at the water surface in boilers, which do not break easily. *Foaming is caused by* the presence of an oil and alkalis in boiler-feed water. Actually oils and alkalis react to form soaps which greatly lowers the surface tension of water and thus increase the foaming tendency of the liquid.

## 6.3 Boiler Corrosion

Boiler corrosion is "decay" or "disintegration" of boiler body material either due to chemical or electrochemical reaction with its environment having  $\text{O}_2$ ,  $\text{CO}_2$  and mineral acids.

The disadvantages of corrosion are :

- (i) Shortening of boiler life,
- (ii) leakages of the joints and rivets ;
- (iii) increased cost of repairs and maintenance.

## 6.4 Caustic Embrittlement

Caustic embrittlement is the phenomenon during which the boiler material becomes brittle due to the accumulation of caustic substances. This type of boiler corrosion is caused by the use of highly alkaline water in the high pressure boiler.

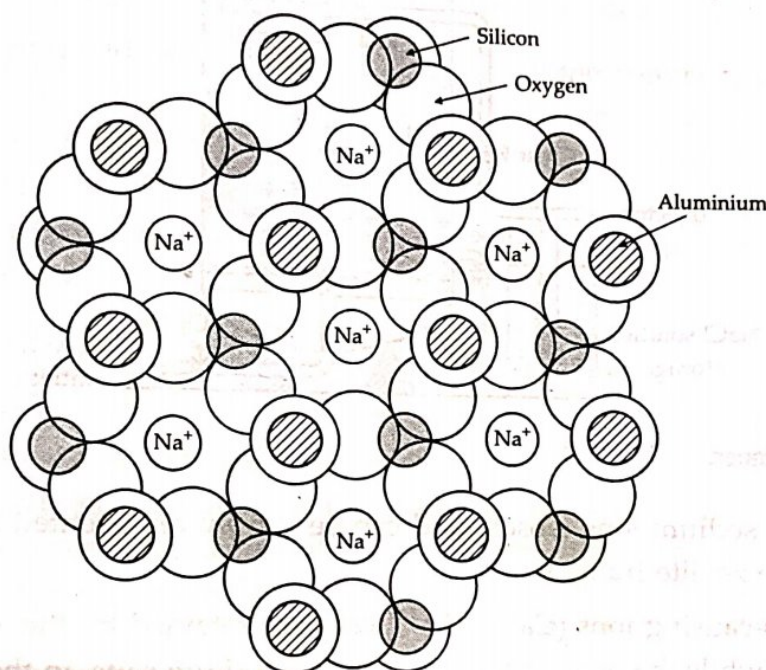
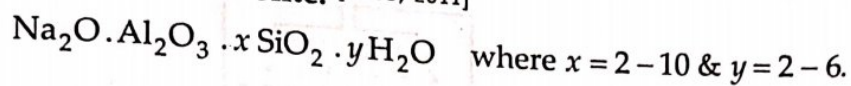


## 9 ZEOLITE OR PERMUTIT PROCESS

**Zeolites** are naturally occurring hydrated sodium aluminosilicate minerals capable of exchanging reversibly its sodium ions for hardness-producing ions in water.

Zeolites are also known as *permutits* and in Greek it means 'boiling stone'.

**The chemical formula of zeolite.** [UPTU, 2011]



**Figure 3** Structure of a naturally occurring zeolite,  $\text{NaAlSiO}_4$ . The sodium ions are loosely held in holes in the lattice.

A zeolite crystal can be considered to result from the linking of several  $\text{SiO}_4$  tetrahedra, each oxygen of a tetrahedron being shared with an adjacent one. The empirical formula is thus  $(\text{SiO}_2)_n$ . However, some of the  $\text{Si}^{4+}$  ions may be isomorphously replaced by  $\text{Al}^{3+}$  ions and in order to balance the charges an extra positive-ion such as  $\text{Na}^+$  and  $\text{K}^+$  must also be incorporated for every  $\text{Al}^{3+}$  introduced. The linking of these tetrahedra results in an open structure with cavities. The porous nature of the structure permits free movement of water molecules and ions.

Zeolites are of two *types viz.* natural and synthetic.

(i) **Natural zeolites** are non-porous, amorphous and durable for example, natrolite,  $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ .

(ii) **Synthetic zeolites** are porous and possess a gel structure. They are prepared by heating together sodium carbonate ( $\text{Na}_2\text{CO}_3$ ), alumina ( $\text{Al}_2\text{O}_3$ ) and silica ( $\text{SiO}_2$ ).

Synthetic zeolites possess higher exchange capacity per unit weight compared to natural zeolites.

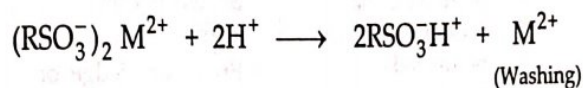


## Differences between Soft Water and Demineralised Water

	Soft Water	Demineralised Water
1.	Soft water has hardness $\leq 85$ ppm ( $\text{CaCO}_3$ eq.). Thus, soft water has more hardness than demineralised water.	Demineralised water does not have any salt (or cations & anions) present in it. So, hardness $\leq 2$ ppm.
2.	It is fit for domestic use.	It is not recommended as such for drinking purposes.
3.	It can be made by using either Lime-Soda process or Zeolite process.	It can be made either by distillation or by using cation & anion exchangers.
4.	Soft water is unfit for feeding into boilers.	It is very good for use in high-pressure boilers.

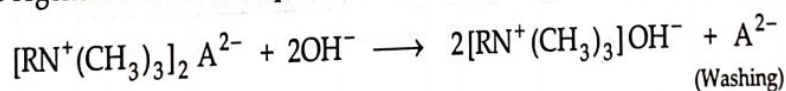
**Regeneration.** When capacities of cation and anion exchangers to exchange  $\text{H}^+$  and  $\text{OH}^-$  ions respectively are lost, they are then said to be *exhausted*.

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



The column is washed with deionized water and washing (which contains  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , etc. and  $\text{Cl}^-$  or  $\text{SO}_4^{2-}$  ions) is passed to sink or drain.

The exhausted anion exchange column is regenerated by passing a solution of dil.  $\text{NaOH}$ . The regeneration can be represented as :



The column is washed with deionized water and washing (which contains  $\text{Na}^+$  and  $\text{SO}_4^{2-}$  or  $\text{Cl}^-$  ions) is passed to sink or drain. The regenerated ion exchange resins are then used again.

**Advantages**

- (i) The process can be used to soften highly acidic or alkaline waters.
- (ii) It produces water of very low hardness (say 2 ppm). So, the treated water is very good for use in high pressure boilers.

**Disadvantages**

- (i) Capital cost is high since chemical and equipment both are costly.
- (ii) If water contains turbidity then the efficiency of the process is reduced.

In domestic water softening by ion exchange, total deionization is not necessary. Only the cations responsible for water hardness need to be removed. So, only a cation-exchanger in  $\text{Na}^+$  form is used. Its operation is reversible and regeneration is carried out using readily available, inexpensive  $\text{NaCl}$  solution (brine).



The Pros and Cons of ion-exchange, zeolite and lime-soda processes are summarized in Table 6.

**Table 6** Comparison of Ion-exchange, Zeolite (or Permutit) and Lime-soda processes

[UPTU, 2004, 2008, 2011]

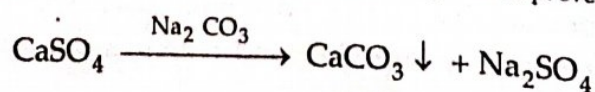
S.No.	Characteristic	Ion-exchange process	Zeolite process	Lime-soda process
1.	Requirements	Cation and anion exchangers	zeolite	Lime, soda and coagulants
2.	Exchange of ions	Exchange of both cations and anions takes place	Exchange of only cations takes place	No exchange of ions.
3.	Capital cost	Very high	High	Low
4.	Operating expenses	High	Low	High
5.	Raw water	<ul style="list-style-type: none"> <li>Should be non-turbid</li> <li>Both acidic or alkaline water can be treated</li> <li>Prior knowledge of hardness not required</li> </ul>	<ul style="list-style-type: none"> <li>Should be non-turbid</li> <li>Should not be acidic</li> <li>Prior knowledge of hardness not required.</li> </ul>	<ul style="list-style-type: none"> <li>Prior knowledge of hardness is essential</li> </ul>
6.	Automation	Possible	Possible	Not possible
7.	Residual hardness	Least (0-2ppm)	Low (0-15 ppm)	High (15-50 ppm)

#### NOTES

**1. Colloidal conditioning.** Scale formation can be avoided in low pressure boilers by adding substances like kerosene, tannin, agar-agar, etc. which get adsorbed over the scale forming precipitates, thereby yielding non-sticky and loose deposits, which can easily be removed by blow-down operation.

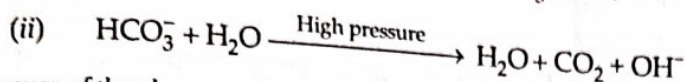
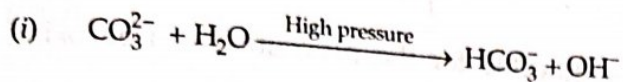
**2. Carbonate conditioning.** For a salt to be precipitated, the ions constituting the salt must be present in sufficient concentration so that the product of their concentrations (i.e., **ionic product**) exceeds a limiting value known as the **solubility product**. Thus, for a salt like  $\text{CaCO}_3$  to be precipitated, the product of the concentrations of  $\text{Ca}^{2+}$  and  $\text{CO}_3^{2-}$  must exceed the solubility product of  $\text{CaCO}_3$ , represented as  $K_{sp}^{\text{CaCO}_3}$ .

When sodium carbonate solution is added to boiler water, the  $[\text{CO}_3^{2-}]$  increases and when it becomes greater than  $K' [\text{SO}_4^{2-}]$ , only  $\text{CaCO}_3$  gets precipitated. Moreover,  $\text{CaSO}_4$  remains in solution so the deposition of scale-forming calcium sulphate is prevented.





In high-pressure boilers, scale formation cannot be avoided by adding sodium carbonate to boiler water. This is because, in high pressure boiler, the  $\text{CO}_3^{2-}$  ions undergo hydrolysis to form  $\text{OH}^-$  ions.



Because of the above two hydrolysis reactions (i) and (ii), the concentration of carbonate ions [i.e.,  $[\text{CO}_3^{2-}]$ ] gets reduced. Thus, it becomes impossible for solution to become saturated w.r.t. calcium or magnesium carbonate. As a consequence, precipitation and subsequent loose sludge formation due to  $\text{CaCO}_3$  or  $\text{MgCO}_3$  becomes impossible.

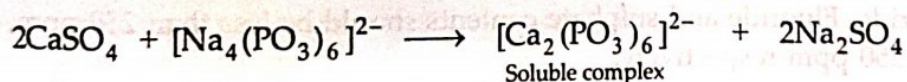
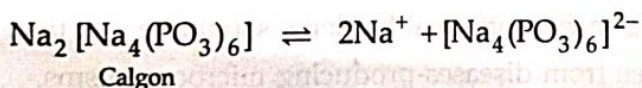
Moreover, due to hydrolysis reactions (i) and (ii), the hydroxide ion concentration [i.e.,  $[\text{OH}^-]$ ] becomes high which can lead to caustic embrittlement.

To sum up,

Carbonate conditioning is not done in high pressure boilers, because (a) it is not applicable, (b) It may lead to caustic embrittlement.

## 11 CALGON CONDITIONING [UPTU, 2007, 08]

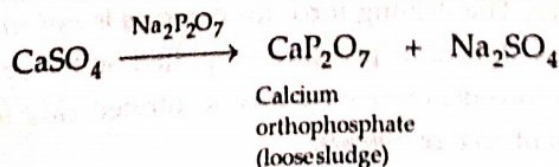
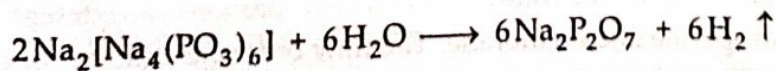
It involves in adding sodium hexa meta phosphate (also known as calgon) to boiler water to prevent the scale and sludge formation. Calgon converts the scale forming impurity (like  $\text{CaSO}_4$ ) into soluble complex compound, which are harmless to boiler.



Calgon  
( $\text{NaPO}_3$ )<sub>6</sub>

Addition of 0.5 – 5 ppm of calgon prevents scale formation in one of the following ways :

- (i) At low temperatures and pressures, it forms quite stable and soluble complexes with calcium salts,
- (ii) At high temperatures and pressures, calgon is converted into sodium ortho-phosphate which reacts with calcium salts to form calcium orthophosphate.





Calcium orthophosphate appears as loose sludge and thus can be removed by blow-down operation.

#### Limitations of Calgon Conditioning

Calgon conditioning is not applicable for the prevention of iron oxide and copper depositions.

However, iron oxide and copper depositions can be prevented by adding EDTA or its sodium salt to the boiler water. In this method, the problem causing cations are converted into complexes, which will stay in "dissolved form" in water and thus do not cause any harm.

## 12 POTABLE WATER [UPTU, 2007]

*Drinking or potable* water is fit for human consumption. The common specifications or standards prescribed and recommended for drinking water are as follows :

- (i) It should be colourless and odourless,
- (ii) It should be good in taste,
- (iii) It should not be hot,
- (iv) Its turbidity should be less than 10 ppm,
- (v) It should be free from objectionable dissolved gases like  $H_2S$ ,
- (vi) It should be free from objectionable minerals such as lead, arsenic, chromium and manganese salts,
- (vii) Its alkalinity should not be high. pH should be in the range of 7.0 – 8.5.
- (viii) It should be reasonably soft, total hardness should be less than 500 ppm.
- (ix) It should be free from diseases-producing microorganisms.
- (x) chloride, Fluoride and sulphate contents should be less than 250 ppm, 1.5 ppm and 250 ppm respectively.

## 13 REVERSE OSMOSIS

### 13.1 Principle of Reverse Osmosis [UPTU, 2006]

*Osmosis* is the phenomenon by virtue of which flow of solvent takes place from a region of low concentration to high concentration when two solutions of different concentrations are separated by a semi-permeable membrane. The flow continues till the concentration is equal on both the sides. The driving force for osmosis is *osmotic pressure*. However, if a *hydrostatic pressure* in excess of osmotic pressure is applied on the concentrated side, the flow of solvent reverses as it is forced to move from concentrated side to dilute side across the membrane. This is the basis of *reverse osmosis*.