Water treatment

Hardness :- Hardness is the property of water which prevents the lather formation with soap.
or
Soap consuming capacity of water

$$2C_{17}H_{35}COONa + Ca^{++} \text{ or } Mg^{++} \longrightarrow (C_{17}H_{35}COO)_2Ca\downarrow + 2Na^{+}$$

Soap (Sodium stearate) — Ca^{++} or Mg^{++} from hard water — Insoluble white ppt calcium stearate — Mg

Lather is not produced untill the cations causing the ppt of soap are completely removed

Types of Hardness :- 1. Temporary hardness
2. Permanent hardness

Temporary hardness :- It is due to the Presence of bicarbonates of Calcium, Magnesium and other heavy metals. This hardness is also known as carbonate hardness. It can be removed by boiling which converts bicarbonates into insoluble carbonates or hydroxides.

$$Ca(HCO_3)_2 \xrightarrow{\Delta} CaCO_3\downarrow + H_2O + CO_2\uparrow$$

$$Mg(HCO_3)_2 \xrightarrow{\Delta} Mg(OH)_2\downarrow + 2CO_2\uparrow$$

2. Permanent hardness :- It is due to the presence of chlorides and sulphates of calcium, magnesium and other heavy metals. This hardness is also known as non-carbonate hardness.
Permanent hardness cannot be removed by boiling. These are removed by special chemical method like
i.) Calgon process
ii) Ion-Exchange process
iii) Lime-Soda process

Units of Hardness :-

(1) Parts per million :- Parts of $CaCO_3$ equivalent hardness per million (10^6) parts of H_2O

(2) Miligrams per litre :- Number of miligrams of $CaCO_3$ equivalent hardness present in 1 litre of H_2O

1 mg/L ≡ 1 mg $CaCO_3$ equivalent hardness per litre of H_2O

1 mg/L ≡ 1 mg of $CaCO_3$ equivalent per 10^6 mg of H_2O [1 Kg H_2O = 1L of H_2O, $10^3 \times 10^3$ mg, 10^6 mg = 1L]

≡ 1 part of $CaCO_3$ equivalent per 10^6 parts of H_2O

1 mg/L ≡ 1 ppm

(3) Degree French (^{0}fr) Parts of $CaCO_3$ equivalent hardness per 10^5 parts of H_2O

1 ^{0}fr = 1 part of $CaCO_3$ equivalent hardness per 10^5 parts of H_2O

④ Clark's degree :- Parts of $CaCO_3$ equivalent hardness per 70,000 parts of water.

Relation between various units :-

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

Degree of Hardness :-

Hardness of water is expressed in terms of $CaCO_3$ equivalent because of

1. Its ($CaCO_3$) molecular weight is 100 which makes calculation easy
2. It is the most insoluble salt that can be precipitated in water treatment

$$\text{Hardness in terms of } CaCO_3 \text{ Equivalent} = \frac{\text{Strength of hardness causing substance mg/L} \times \text{Chemical Equivalent of } CaCO_3}{\text{chemical equivalent of hardness producing substance}}$$

Example A sample of water contains 204 mg of $CaSO_4$ per litre. Calculate the hardness in terms of $CaCO_3$ Equivalent

Solution :-

$$\frac{204 \times 50}{68} = 150 \text{ mg/L}$$

Hardness = 150 ppm

Calculation of $CaCO_3$ Equivalent

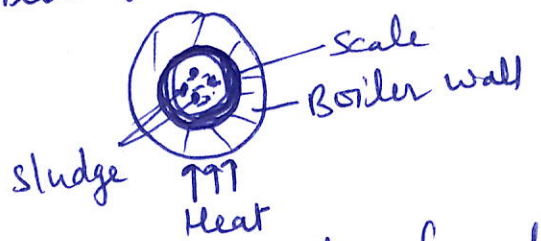
Dissolved Salt/Ion	Molar mass	chemical equivalent
$Ca(HCO_3)_2$	$162/2$	81
$Mg(HCO_3)_2$	$146/2$	73
$CaSO_4$	136	68
$MgSO_4$	120	60
$CaCl_2$	111	55.5
$MgCl_2$	95	47.5
$CaCO_3$	100	50
$MgCO_3$	84	42
HCO_3^-	61	61
CO_3^{--}	60	30
$Al_2(SO_4)_3$	342	57
$FeSO_4 \cdot 7H_2O$	278	139

Boiler troubles or Problems:- Boilers are used for steam generation in industries and powerhouses. If hard water is directly fed into the boilers it may lead to the following problems.

i) scale and sludge formation
ii) Caustic embrittlement
iii) Boiler corrosion
iv) Priming and foaming

Scale and sludge formation:- In boilers steam is generated continuously by the evaporation of water. As water evaporates continuously, the concentration of dissolved salt increases, finally the solution becomes saturated. The point at which ionic product exceeds the solubility product, they are thrown out as precipitates.

If the precipitate formed is soft, loose and floats in boiler water it is called **sludge**.



Scale and sludge formation in boiler

example:- $MgCl_2$, $MgCO_3$, $CaCl_2$, $MgSO_4$

Scale:- Scales are the hard deposits firmly sticking on the inner wall of the boiler and can't be removed easily by scrapping. **example:-** $CaSO_3$, $CaSO_4$

Disadvantages of sludge formation :-

1. Decreases the efficiency of boiler
2. Excessive sludge may cause chocking of pipe

Prevention of sludge formation :- frequent blow-down operation

Disadvantage of scale formation :-

i) Wastage of fuel
ii) Decrease in efficiency
iii) Lowering of boiler safety
iv) Danger of explosion

Removal of scale formation :-

i) Brittle scales can be removed by giving thermal shocks
ii) Hard and adherent scales can be removed by adding chemicals. ($CaCO_3$ scale can be removed by using 10% HCl solution)

Prevention of scale formation :- Scale formation can be prevented by 1.) External treatment
2.) Internal treatment

Boiler corrosion :- Loss of boiler body material or its useful properties by chemical or electrochemical interaction with its environment is known as boiler corrosion

Corrosion in boiler may be due to the following reasons

i) Presence of dissolved CO_2

ii) Presence of dissolved O_2

iii) formation of acids by dissolved salts

Caustic Embrittlement :- During the softening of water by lime-soda process, the free Na_2CO_3 decomposes to give NaOH and CO_2

$$Na_2CO_3 + H_2O \rightarrow 2NaOH + CO_2\uparrow$$

This makes the boiler water highly alkaline due to Caustic formation.

Prevention :- Caustic embrittlement can be prevented by sodium phosphate

Priming and foaming :- The process of Priming is Passage of water particle with steam from the boiler. This is caused due to the Presence of excess alkali sulphate and chlorides in water.

The foaming is persistent formation of foam of bubbles in the boiler, which do not break easily due to this the water film enclosing the steam around solid particles, passes out from the boiler along with steam. The foaming is due to the Presence of oil which greatly reduces the surface tension of water in boiler.

Prevention :- By the addition of compounds like sodium aluminate

Water Softening :- The process of removing or reducing the hardness (temporary or permanent) from water is known as softening of water.

Important method for the softening of water are :-

(1) Zeolite process (2) Ion-Exchange process

(3) Lime-soda process

All these are the external treatments

Zeolite process or Permutit process

Zeolite are hydrated sodium aluminosilicates capabable of exchanging its sodium ion reversibly with the hardness producing cations in water.

$Na_2O \cdot Al_2O_3 \cdot x SiO_2 \cdot y H_2O$

where x = 2 to 10

y = 2 to 6

Zeolites are of two types

(1) **Natural Zeolite** :- Natural zeolites are amorphous and non-porous in nature. They are derived from green sands by washing, heating and treating with NaOH

eg. Natrolite – $Na_2O \cdot Al_2O_3 \cdot 4 SiO_2 \cdot 2H_2O$

(2) **Synthetic Zeolite** :- are porous and get structure

Synthetic zeolites are prepared by heating together solution of sodium silicate, Aluminium sulphate and sodium aluminate

Q. An Exhausted zeolite softener required 500 L of NaCl solution containing 100 g/L of NaCl for regeneration. If the hardness of water is 600 ppm, calculate the volume of water softened by this softener.

$$\text{Hardness} = \frac{\text{Concentration of NaCl (g/L)} \times \text{Vol. of NaCl (L)}}{\text{Vol. of } H_2O \text{ (L)}} \times \frac{50}{58.5}$$

$$600 = \frac{100 \times 1000 \times 500}{\text{Vol. of } H_2O} \times \frac{50}{58.5}$$

$$\text{Ans.} = 7.116 \times 10^4 \text{ L}$$

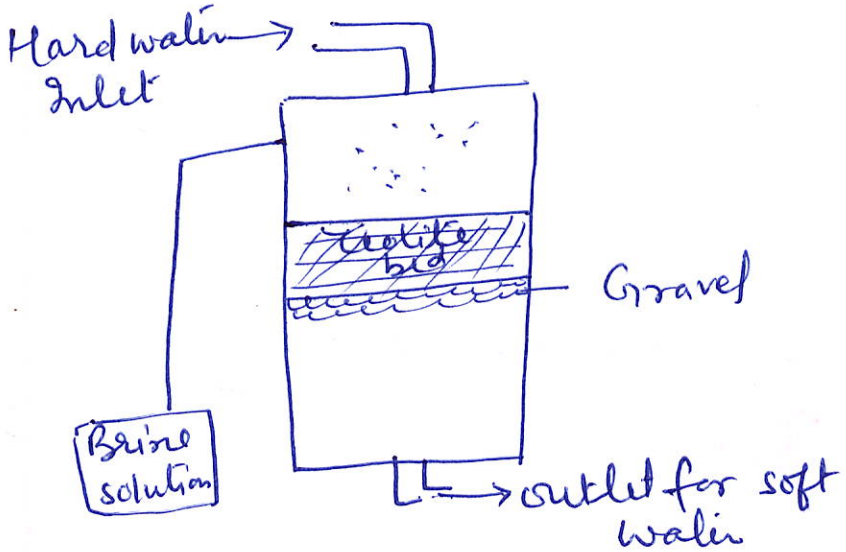
Q. A zeolite softener was 95% exhausted, when 10,000 L of hard water was passed through it, the softener required 150 L of NaCl soln. of strength 50 g NaCl/L of soln. to regenerate. What is the hardness of water.

Soln.

$$\text{Hardness} = \frac{\text{Concentration of NaCl (g/L)} \times \text{Vol. of NaCl (L)}}{\text{Vol. of } H_2O \text{ (L)}} \times \frac{50}{58.5}$$

$$= \frac{50 \times 1000 \times 150}{10,000} \times \frac{50}{58.5} = 641 \text{ mg/L}$$

Principle :- Zeolite can be represented as Na_2Z where Z represents insoluble radical frame work They hold sodium ion loosely. When hard water passed through a bed of zeolite, the hardness causing ions are retained by zeolite as CaZ or MgZ. Therefore water becomes free from the main hardness producing cations but gets more concentrated with respect to sodium salts and eventually zeolite gets exhausted.



$$Ca(HCO_3)_2 + Na_2Z \longrightarrow CaZ + 2NaHCO_3$$

$$Mg(HCO_3)_2 + Na_2Z \longrightarrow MgZ + 2NaHCO_3$$

$$MgCl_2 + Na_2Z \longrightarrow MgZ + 2NaCl$$

$$CaCl_2 + Na_2Z \longrightarrow CaZ + 2NaCl$$

$$CaSO_4 + Na_2Z \longrightarrow CaZ + Na_2SO_4$$

$$MgSO_4 + Na_2Z \longrightarrow MgZ + Na_2SO_4$$

Regeneration :- During softening, zeolite exchange its sodium ions with magnesium and calcium ions and after some time they are completely converted into Ca & Mg zeolite

and the Zeolite bed ceases to soften water i.e gets exhausted.

$$CaZ + 2NaCl \longrightarrow Na_2Z + CaCl_2$$
$$MgZ + 2NaCl \longrightarrow Na_2Z + MgCl_2$$

exhausted Zeolite — Brine solution — Reclaimed Zeolite — washings

The regenerated zeolite is again used for softening

Advantage of Zeolite process :-

1. Hardness is almost completely removed and water of about 15 ppm hardness is produced
2. It requires less time for softening
3. There is no danger of sludge formation because impurities are not precipitated

Disadvantage of Zeolite process :-

1. Only cations are replaced by sodium ions and not the acidic ions
2. Treated water contains more sodium salts than in lime - soda process

Limitations :-

① If water is turbid it will cause the clogging of pores of zeolite bed, thereby making it inactive.

② Mineral acids destroy the zeolite bed

③ Soft water obtained by zeolite process contains about 25% more dissolved solids than that obtained by lime-soda process