WATER TREATMENT

In industries water is used for steam generation & as coolant mainly. Other uses are drinking, bathing , washing, sanitation
irrigation etc.

Sources of water:

A) Surface water- available as

-Rain water

-River water

-Lake water

-Sea water

Such water contains suspended impurities & pathogenic bacteria, so unfit for human consumption.

B)Underground Water- available as

-springs

-well water

It is clear due to filtering action (percolation) of soil but contains more of dissolved salts & organic impurities.

HARDNESS OF WATER

Hardness *in water is that characteristic, which "prevents the lathering of soap".* This is due to presence in water of certain salts of calcium, magnesium and other heavy metals dissolved in it. A sample of hard water, when treated with soap (sodium or potassium salt of higher fatty acid like oleic, palmitic or stearic) does not produce lather, but on the other hand forms a *white scum or precipitate.* This precipitate is formed, due to the formation of *insoluble soaps of calcium and magnesium.* Typical reactions of soap (sodium stearate) with calcium chloride and magnesium sulphate are depicted as follows :

$$\underset{\substack{\text{Sodium stearate} \\ \textit{(Sodium soap)}}}{2C_{17}H_{35}COONa} + \underset{\text{(Hardness)}}{CaCl_2} \longrightarrow \underset{\substack{\text{Calcium stearate} \\ \textit{(Insoluble)}}}{(C_{17}H_{35}COO)_2\,Ca} \downarrow + 2NaCl$$

$$2C_{17}H_{35}COONa + MgSO_4 \longrightarrow \underset{\substack{\text{Magnesium stearate} \\ \textit{(Insoluble)}}}{(C_{17}H_{35}COO)_2\,Mg} \downarrow + Na_2SO_4$$

Thus, water which does not produce lather with soap solution readily, but forms a while curd, is called ***hard water.*** On the other hand, *water which lathers easily on shaking with soap solution, is called* ***soft water.*** Such a water, consequently, *does not* contain dissolved calcium and magnesium salts in it.

(1) Temporary or carbonate hardness *is caused by the presence of dissolved bicarbonates of calcium, magnesium and other heavy metals and the carbonate of iron.* Temporary hardness is mostly *destroyed by mere boiling of water*, when bicarbonates are decomposed, yielding insoluble carbonates or hydroxides, which are deposited as a **crust** at the bottom of vessel. Thus :

$$\underset{\text{Calcium bicarbonate}}{Ca(HCO_3)_2} \xrightarrow{\text{Heat}} \underset{\substack{\text{Calcium carbonate} \\ (\textit{Insoluble})}}{CaCO_3} \downarrow + H_2O + CO_2 \uparrow$$

$$\underset{\text{Magnesium bicarbonate}}{Mg(HCO_3)_2} \xrightarrow{\text{Heat}} \underset{\text{Magnesium hydroxide}}{Mg(OH)_2} \downarrow + 2CO_2 \uparrow$$

(2) Permanent or non-carbonate hardness is *due to the presence of chlorides and sulphates of calcium, magnesium, iron and other heavy metals.* Unlike temporary hardness, permanent hardness is *not* destroyed on boiling.

EQUIVALENTS OF CALCIUM CARBONATE

The concentration of hardness as well as non-hardness constituting ions are, usually, expressed in terms of **equivalent amount of $CaCO_3$**, since this mode permits the multiplication and division of concentration, when required. *The choice of $CaCO_3$ in particular is due to its* ***molecular weight is 100*** *(equivalent weight = 50) and moreover, it is the* ***most insoluble*** *salt that can be precipitated in water treatment.* The equivalents of $CaCO_3$

$$= \frac{\begin{bmatrix}\text{Mass of hardness}\\ \text{producing-substance}\end{bmatrix} \times \begin{bmatrix}\text{Chemical equivalent}\\ \text{of } CaCO_3\end{bmatrix}}{\text{Chemical equivalent of hardness–producing substance}}$$

$$= \frac{\text{Mass of hardness–producing substance} \times 50}{\text{Chemical equivalent of hardness-producing substance}}$$

. *Calculation of equivalents of calcium carbonate.*

Dissolved salt/ion	*Molar mass*	*Chemical equivalent*	*Multiplication factor for conveting into equivalents of $CaCO_3$*
$Ca(HCO_3)_2$	162	81	100/162
$Mg(HCO_3)_2$	146	73	100/146
$CaSO_4$	136	68	100/136
$CaCl_2$	111	55.5	100/111
$MgSO_4$	120	60	100/120
$MgCl_2$	95	47.5	100/95
$CaCO_3$	100	50	100/100
$MgCO_3$	84	42	100/84
CO_2	44	22	100/44
$Ca(NO_3)_2$	164	82	100/164
$Mg(NO_3)_2$	148	74	100/148
HCO_3^-	61	61	100/122
OH^-	17	17	100/34
CO_3^{2-}	60	30	100/60
$NaAlO_2$	82	82	100/164
$Al_2(SO_4)_3$	342	57	100/114
$FeSO_4.7H_2O$	278	139	100/278
H^+	1	1	100/2
HCl	36.5	1	100/73

UNITS OF HARDNESS

(1) Parts per million (*ppm*) *is the parts of calcium carbonate equivalent hardness per 10^6 parts of water, i.e.,* 1 ppm = 1 part of $CaCO_3$ eq hardness in 10^6 parts of water.

(2) Milligrams per litre (*mg/L*) *is the number of milligrams of $CaCO_3$ equivalent hardness present per litre of water.* Thus :

$$1 \text{ mg/L} = 1 \text{ mg of } CaCO_3 \text{ eq. hardness of } 1 \text{ L of water}$$

But 1 L of water weighs

$$= 1 \text{ kg} = 1{,}000 \text{ g} = 1{,}000 \times 1{,}000 \text{ mg} = 10^6 \text{ mg.}$$

$$\therefore \quad 1 \text{ mg/L} = 1 \text{ mg of } CaCO_3 \text{ eq per } 10^6 \text{ mg of water.}$$

$$= 1 \text{ part of } CaCO_3 \text{ eq per } 10^6 \text{ parts of water} = 1 \text{ ppm.}$$

(3) Clarke's degree (*°Cl*) *is number of grains (1/7000 lb) of $CaCO_3$ equivalent hardness per gallon (10 lb) of water. Or it is parts of $CaCO_3$ equivalent hardness per 70,000 parts of water. Thus :*

$$1° \text{ Clarke} = 1 \text{ grain of } CaCO_3 \text{ eq hardness per gallon of water.}$$

or

$$1° \text{ Cl} = 1 \text{ part of } CaCO_3 \text{ eq hardness per } 70{,}000 \text{ parts of water.}$$

(4) Degree French (*°Fr*) *is the parts of $CaCO_3$ equivalent hardness per 10^5 parts of water. Thus :*

$$1° \text{ Fr} = 1 \text{ part of } CaCO_3 \text{ hardness eq per } 10^5 \text{ parts of water.}$$

(5) Milliequivalent per litre (*meq/L*) *is the number of milli equivalents of hardness present per litre.* Thus :

$$1 \text{ meq/L} = 1 \text{ meq of } CaCO_3 \text{ per L of water}$$

$$= 10^{-3} \times 50 \text{ g of } CaCO_3 \text{ eq per litre}$$

$$= 50 \text{ mg of } CaCO_3 \text{ eq per litre}$$

$$= 50 \text{ mg/L of } CaCO_3 \text{ eq} = \mathbf{50\ ppm}.$$

Relationship between various units of hardness :

1 ppm	= 1 mg/L	= 0.1° Fr	= 0.07° Cl	= 0.02 meq/L
1 mg/L	= 1 ppm	= 0.1° Fr	= 0.07° Cl	= 0.02 meq/L
1° Cl	= 1.433° Fr	= 14.3 ppm	= 14.3 mg/L	= 0.286 meq/L
1° Fr	= 10 ppm	= 10 mg/L	= 0.7° Cl	= 0.2 meq/L
1 meq/L	= 50 mg/L	= 50 ppm	= 5° Fr	= 0.35° Cl

DISADVANTAGES OF HARD WATER

(1) *In domestic use* : (*i*) **Washing :** Hard water, when used for washing purposes, does not lather freely with soap. On the other hand, it produces *sticky precipitates* of calcium and magnesium soaps. The formation of such insoluble, sticky precipitates continues, till all calcium and magnesium salts present in water are precipitated. After that, the soap (*e.g.*, sodium stearate) gives lather with water. Thus :

$$\underset{\text{Soap}}{C_{17}H_{35}COONa} + H_2O \rightleftharpoons C_{17}H_{35}COOH + NaOH$$

$$\underset{\text{Stearic acid}}{C_{17}H_{35}COOH} + \underset{\text{Soap}}{C_{17}H_{35}COONa} \longrightarrow \text{Lather.}$$

This causes a wastage of lot of soap being used. Moreover, the sticky precipitate (of calcium and magnesium soaps) adheres on the fabric/cloth giving *spots* and *streaks*. Also presence of iron salts may cause *staining of cloth*.

(*ii*) **Bathing** : Hard water *does not lather* freely with soap solution, but produces *sticky scum* on the bath-tub and body. *Thus, the cleansing quality of soap is depressed and a lot of it is wasted.*

(*iii*) **Cooking** : Due to the presence of dissolved hardness-producing salts, the boiling point of water is elevated. Consequently, more fuel and time are required for cooking. Certain foods such as pulses, beans and peas do not cook soft in hard water. Also tea or coffee, prepared in hard water, has an *unpleasant taste* and *muddy-looking extract*. Moreover, the dissolved salts are deposited as carbonates on the inner walls of the water heating utensils.

(*iv*) **Drinking** : Hard water causes bad effect on our digestive system. Moreover, the possibility of forming calcium oxalate crystals in urinary tracks is increased.

(2) ***In industrial use*** **:** (*i*) **Textile industry** : Hard water causes much of the soap (used in washing yarn, fabric, etc.) to go as waste, because hard water cannot produce good quality of lather. Moreover, precipitates of calcium and magnesium soaps adhere to the fabrics. These fabrics, when dyed latter on, *do not produce exact shades of colour*. Iron and manganese salts-containing water may cause *coloured spots* on fabrics, thereby spoiling their beauty.

(*ii*) **Sugar industry** : Water containing sulphates, nitrates, alkali carbonates, etc., if used in sugar refining, causes *difficulties in the crystallization of sugar*. Moreover, the sugar so-produced may be *deliquescent*.

(*iii*) **Dyeing industry** : The dissolved calcium, magnesium and iron salts in hard water may react with costly dyes, forming undesirable precipitates, which yield *impure shades* and give *spots* on the fabrics being dyed.

(*iv*) **Paper industry** : Calcium and magnesium salts tends to react with chemicals and other materials employed to provide a smooth and glossy (*i.e.*, shining) finish to paper. Moreover, iron salts may even affect the colour of the paper being produced.

(*v*) **Laundry** : Hard water, if used in laundry, causes much of the soap used in washing to go as *waste*. Iron salts may even cause *coloration* of the clothes.

(*vi*) **Concrete making** : Water containing chlorides and sulphates, if used for concrete making, affects the *hydration of cement* and the final *strength* of the hardened concrete.

(*vii*) **Pharmaceutical industry** : Hard water, if used for preparing pharmaceutical products (like drugs, injections, ointments, etc.,) may produce certain *undesirable products* in them.

(3) In steam generation in boilers : For steam generation, boilers are almost invariably employed. If the hard water is fed directly to the boilers, there arise many troubles such as : (*i*) *scale and sludge formation*, (*ii*) *corrosion*, (*iii*) *priming and foaming*, and (*iv*) *caustic embrittlement*.

SCALE AND SLUDGE FORMATION IN BOILERS

In boilers, water evaporates continuously and the concentration of the dissolved salts increase progressively. *When their concentrations reach saturation point, they are thrown out of water in the form of precipitates on the inner walls of the boiler. If the precipitation takes place in the form of loose and slimy precipitate,* it is called ***sludge***. On the other hand, *if the precipitated matter forms a hard, adhering crust/coating on the inner walls of the boiler,* it is called ***scale***.