HARDNESS OF WATER

First Year B.Tech.

Engineering Chemistry, Subject Code: BCY-101/102

Unit/Module V: Water Analysis

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INTRODUCTION:

HARDNESS OF WATER: Hardness of water is the **soap consuming power of water** and hardness is the characteristics of water, which prevents the lathering of soap. Hardness in water is due to the presence of certain salt of calcium, magnesium and other heavy metals dissolved in water.

When hard water is treated with soap (i.e., sodium or potassium salt of higher fatty acids like oleic, palmitic or stearic etc.) **does not produce lather** but on other hand forms a white scum or **precipitate**. The precipitate is formed due to the formation of insoluble soaps of Ca and Mg. A typical reaction of soap (sodium stearate) with $CaCl_2$ and $MgCl_2$ may be expressed as:

$$2C_{17}H_{35}COONa + CaCl_2 \rightarrow (C_{17}H_{35}COO)_2\,Ca \downarrow + 2NaCl$$

(Sodium stearate, soap) (Hardness) (Calcium stearate, Insoluble)

$$2C_{17}H_{35}COONa + MgSO_4 \rightarrow (C_{17}H_{35}COO)_2\,Mg \downarrow + Na_2SO_4$$

(Magnesium stearate, Insoluble)

Thus, water which does not produce lather with soap readily but forms a white curd/precipitate is **called hard water**. On other hand, water which forms lather easily on shaking with soap is called **soft water**, such water consequently does not contain dissolved Ca and Mg salts.

TYPES OF HARDNESS: Hardness of water may be classified in to two types namely:

(1) **Carbonate hardness or Temporary**: is caused by the presence of dissolved carbonates, bicarbonates and hydroxides of Ca, Mg and other heavy metals.

It can be removed by water boiling.

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

$$Mg(HCO_3)_2 \xrightarrow{\Delta} \underset{\text{(Insoluble)}}{MgCO_3} \downarrow + 2CO_2 \uparrow$$

(2) **Non-carbonate hardness or Permanent**: caused by the presence chlorides and sulphates of Ca, Mg, Fe and other heavy metals. Unlike the temporary hardness, permanent hardness cannot be removed by boiling water. It needs some treatments.

EQUIVALENCE OF $CaCO_3$

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 i.e.,100**, equivalent weight i.e.,50, it is **most insoluble salt** that can be precipitated in water treatment.

Calculation of equivalents of calcium carbonate

Dissolved Salt/Ion	**Molar Mass**	**Chemical Equivalent**	**Multiplication factor for converting in to 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
$FeSO_4.7H_20$	278	139	100/278
H^+	1	1	100/2
HCl	36.5	1	100/73

Equivalence of $CaCO_3$

$$= \frac{\text{Mass of hardness producing substance x Chemical equivalent of } CaCO_3}{\text{Chemical equivalent of hardness producing substance}}$$

$$= \frac{\textbf{Mass of hardness producing substance x 50}}{\textbf{Chemical equivalent of hardness producing substance}}$$

UNITS OF HARDNESS:

(i) 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. 1ppm=1 mg per litre.

(ii) Degree Clarke(°Cl):is the no. of grains of $CaCO_3$ equivalent hardness per gallon of water or parts of $CaCO_3$ equivalent hardness per 70,000 parts of water.

1°Clarke=1 grain of $CaCO_3$ equivalent hardness per gallon of water or 1°Cl =1 part of $CaCO_3$ equivalent hardness per 70,000 parts of water

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

1°Fr=1 part of CaCO3 hardness equivalent per 10^5 parts of water

(iv) Milliequivalent per litre (meq/L): is the no. of milli equivalent of hardness present per litre .

Thus 1 meq/L=1 meq. of $CaCO_3$ per litre of water

RELATIONSHIP BETWEEN VARIOUS UNITS OF HARDNESS:

1ppm =1 mg/L = 0.1°Fr = 0.07°Cl= 0.02meq./L

1mg/L= 1ppm = 0.1°Fr = 0.07°Cl =0.02meq. /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) Domestic use

(i) **Washing:**

$C_{17}H_{35}COONa + H_2O \leftrightarrow C_{17}H_{35}COOH + NaOH$

Sodium stearate (Soap) Stearic acid

$C_{17}H_{35}COOH + C_{17}H_{35}COONa \rightarrow$ Leather

Stearic acid Soap

This causes **wastage** of lot of soap being used. Moreover, sticky precipitate adheres on fabric /cloth gives spots and streaks.

(ii**) Bathing**: Hard water produces sticky scum on bath tub and body. Thus, cleansing quality of soap is depressed and lot of soap wasted.

(iii**) Cooking:** Due to hardness producing salt boiling point of water is elevated, consequently more fuel and time required for cooking.

(iv) **Drinking**: Hard water causes bad effect on digestive system. Possibility of forming calcium oxalate in urinary tract is increased.

(2) Industrial use:

(i) **Textile industry:** precipitate of Ca and Mg soaps adhere to the fabric. When fabric dyed do not produce exact shades of colour and spoil the beauty of fabric.

(ii) **Sugar industry**: Causes difficulty in crystallization of sugar during sugar refining.

(iii) **Dyeing industry**: Dissolved Ca, Mg and Fe salts in hard water may react with dyes forming undesirable precipitate. Which yields impure shades and spot-on fabric.

(iv) **Paper industry:** Ca, Mg salts react with chemicals and materials used for smooth and glossy finish to paper and colour of paper affected.

(v**) Laundry**: hard water causes wastage of water and may even causes coloration of cloths.

(vi) **Concrete making**: Hard water used for concrete affects hydration of cement and strength of the hardened concrete.

(vii) **Steam generation in boiler**: Causes scale and sludge formation, boiler Corrosion, priming and foaming, caustic embrittlement. ***Sludge** is a soft, loose and slimy precipitate formed with in the boiler. Sludges are formed by the substances having greater solubilities in hot water than in cold water e.g. $MgCO_3$, $MgCl_2$, $CaCl_2$ and $MgSO_4$ etc.*

***Boiler corrosion**: is decay process of boiler material by a chemical or electrochemical attack by its environment*

***Caustic embrittlement**: is a type of boiler corrosion caused by using highly alkaline water in the boiler.*

(viii) **Pharmaceutical Industry**: May produce certain undesirable pharmaceutical products.

SOFTENING OF HARD WATER:

The process of removing hardness producing salts from water is known as **softening of water.** In industry, main three methods employed for softening of water.

(1) **LIME SODA PROCESS:** In this method, the soluble calcium and magnesium salts in water are chemically converted in to insoluble compounds by adding calculated amount of lime [$Ca(OH)_2$] and soda [Na_2CO_3], $CaCO_3$ and $Mg(OH)_2$ so precipitated may be filtered off.

Notes:

(i)If $Ca(HCO_3)_2$ and $Mg(HCO_3)_2$ are considered as ions (Ca^{2+} +$2HCO_3^-$) and (Mg^{2+} +$2HCO_3^-$) respectively then calculation results will be same.

(ii)Equivalent weight of $NaAlO_2$ is equal to its molar mass.

(iii)If treated water contains OH^- and CO_3^{2-} ions, then these are formed from excess eq. each of $Ca(OH)_2$ plus Na_2CO_3 and Na_2CO_3 respectively .So these excess amounts should be added to the calculations.

(iv)When impurities are given as $CaCO_3$ and /or $MgCO_3$, these should be considered due to bicarbonates of Ca and /or Mg respectively.

(v)Substance like NaCl, KCl, Na_2SO_4 , SiO_2,Fe_2O_3 etc.do not impart any hardness and therefore, these **do not consume any lime or soda**. These should not be taken in to consideration for calculating the lime and soda requirements.

Calculation of lime soda requirement

Constituent	Reactions	Need
Ca^{2+} (perm. Ca)	$Ca^{2+} + \mathbf{Na_2CO_3 \rightarrow CaCO_3} + 2Na^+$	**S**
Mg^{2+} (perm. Mg)	$Mg^{2+} \mathbf{+ Ca(OH)_2 \rightarrow Mg(OH)_2} + Ca^{2+}$ $Ca^{2+} + \mathbf{Na_2CO_3 \rightarrow CaCO_3} + 2Na^+$	**L+S**
HCO_3^- (eg. $NaHCO_3$)	$2HCO_3^- \mathbf{+ Ca(OH)_2 \rightarrow CaCO_3} + H_2O + \mathbf{CO_3^{2-}}$	**L-S**
$Ca(HCO_3)_2$ (Temp.Ca)	$Ca(HCO_3)_2 + \mathbf{Ca(OH)_2 \rightarrow 2CaCO_3} + 2H_2O$	**L**
$Mg(HCO_3)_2$ (Temp.Mg)	$Mg(HCO_3)_2 + \mathbf{2Ca(OH)_2 \rightarrow 2CaCO_3} + \mathbf{Mg(OH)_2} + 2H_2O$	**2L**
CO_2	$CO_2 + \mathbf{Ca(OH)_2 \rightarrow CaCO_3} + H_2O$	**L**
H^+(Free acids, HCl, H_2SO_4 etc.)	$2H^+ + \mathbf{Ca(OH)_2} \rightarrow Ca^{2+} + 2H_2O$ $Ca^{2+} + \mathbf{Na_2CO_3 \rightarrow CaCO_3} + 2Na^+$	**L+S**

Coagulants $FeSO_4$	Fe^{2+} + **$Ca(OH)_2$**→$Fe(OH)_2$ +Ca^{2+} $2Fe(OH)_2$ +H_2O+O_2→**$2Fe(OH)_3$** Ca^{2+} +**Na_2CO_3→$CaCO_3$**+$2Na^+$	**L+S**
$Al_2(SO_4)_3$	$2Al^{3+}$ +**3Ca(OH)2→2Al(OH)₃** +$3Ca^{2+}$ 3Ca2+ +**2Na2CO3→3CaCO3**+ 6Na+	**L+S**
$NaAlO_2$	$NaAlO_2$+$2H_2O$→**$Al(OH)_3$ +NaOH** 2NaOH is equivalent to $Ca(OH)_2$	**-L**

Now 100 parts by mass of CaCO3 are equivalent to (i) 74 parts of CaCO3 and (ii) 106 parts of Na2CO3

Hence, Lime requirement for softening

=74/100 [Temp.Ca^{2+} +2xTemp.Mg^{2+} + Perm. (Mg^{2+} +Fe^{2+} +Al^{3+}) +CO_2+H^+ (HCl or H_2SO_4) +HCO_3^- **-**$NaAlO_2$: **All in terms of $CaCO_3$ eq**.]

Soda requirement for softening

=106/100[Perm. (Ca^{2+} +Mg^{2+} +Al^{3+} +Fe^{2+}) H^+ (HCl or H_2SO_4) **–**HCO_3^- : **All in terms of CaCO3 eq**.]

TYPES OF LS PROCESS:

(i) Cold lime soda process: Calculated amount of lime and soda are mixed with water at room temp. At room temp.the precipitates formed are finely divided so they do not settle down easily and cannot be filtered easily. Hence, small amount of coagulants such as alum, aluminium sulphate, sodium aluminate etc) added which hydrolyse to flocculent, gelatinous precipitate of aluminium hydroxide and entraps the fine precipitate. Use of sodium aluminate as coagulant also helps in removal of silica as well as oil if present in water. Cold LS process provides water containing a residual hardness of **50 to 60 ppm**.

$NaAlO_2 + 2H_2O \rightarrow NaOH + Al(OH)_3\downarrow$

Sodium Aluminate

$Al_2(SO_4)_3 + 3Ca(HCO_3)_2 \rightarrow 2Al(OH)_3\downarrow + 3CaSO_4 + 6CO_2\uparrow$

Coagulant   Hard water

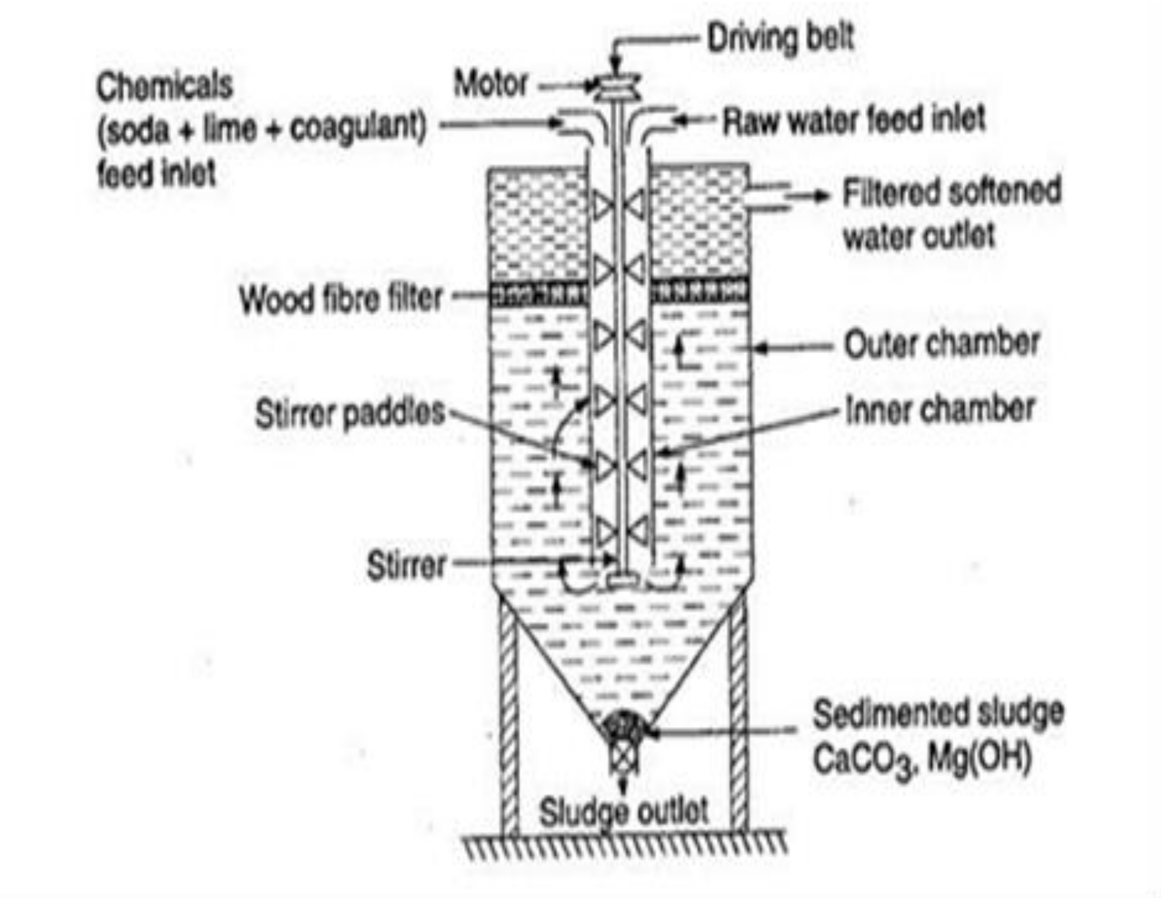

Fig. Cold lime-soda softener