Hardness in water

In water, hardness is that characteristics, which prevents lathering of soap,

This happens due to presence of Ca^{2+} and Mg^{2+} salts

Reaction of soap molecules with hardness causing salts

Hardness is due to the presence of bicarbonates, chlorides, sulfates of calcium and magnesium

$$2C_{17}H_{35}COONa + Ca(HCO_3)_2 \longrightarrow (C_{17}H_{35}COO)_2Ca\downarrow + 2NaCl$$

Sodium stearate (sodium soap)

Hardness causing salt

or $Mg(HCO_3)_2$

Insoluble Ca-stearate

$(C_{17}H_{35}COO)_2Mg$

$$2C_{17}H_{35}COONa + MgSO_4 \longrightarrow (C_{17}H_{35}COO)_2Mg\downarrow + 2Na_2SO_4$$

Sodium stearate (sodium soap)

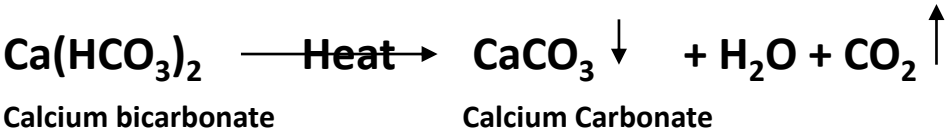
Hardness

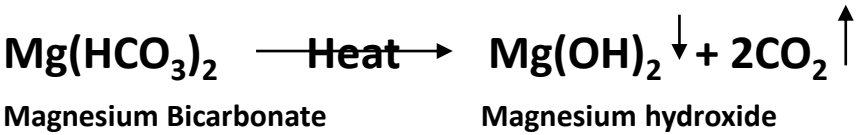
Magnesium stearate (Insoluble)

Temporary Hardness

– Temporary Hardness is caused by the presence of dissolved bicarbonate of calcium and magnesium.

It is mostly destroyed by more boiling of water, when bicarbonates are decomposed yielding insoluble carbonates.





– Calcium/Magnesium Carbonates thus formed being almost insoluble, are deposited as a scale at the bottom of vessel, while carbon dioxide escapes out.

Permanent Hardness

–Hardness which is due to the presence of dissolved sulfate or chloride of calcium and magnesium which cannot be removed by boiling is known as permanent hardness.

$CaCO_3$ equivalent hardness

$$\text{Calcium carbonate equivalent} = \frac{\text{Equivalent weight of } CaCO_3}{\text{Equivalent weight of hardness producing substances}} \times \text{Mass of hardness producing substance}$$

$$\text{Multiplication factor} = \frac{\text{Equivalent weight of } CaCO_3}{\text{Equivalent weight of hardness producing substances}}$$

Problem 1

Calculate the calcium carbonate equivalent hardness of a water sample containing 204mg of $CaSO_4$ per litre

Note : Mol. Weight of $CaCO_3$ = 100

Mol. Weight of $CaSO_4$ = 136

Solution :

$$\text{Calcium carbonate equivalent hardness} = \frac{100 \times 204}{136} = 150 \text{ mg of } CaCO_3/L$$

$$= 150 \text{ ppm}$$

Degree Of Clark (^{o}cl) :

^{o}cl is number of grains (1/7000 lb) of $CaCo_3$ equivalent hardness per gallon (10 lb) of water.

(or)

It is defined as the number of parts of $CaCo_3$ equivalent hardness per 70,000 parts of water.

$\therefore$ 1^{o}cl = 1 grain of $CaCo_3$ eq. hardness per gallon of water.

(or)

1^{o}cl = 1 part of $CaCo_3$ eq. hardness per 70,000 parts of water

$\therefore$ 1 ppm = 0.07^{o}cl

Degree Of French (^oFr) :

^oFr is the number of parts of $CaCo_3$ equivalent hardness per 10^5 parts of water.

1^oFr = 1 part of $CaCo_3$ equivalent hardness per 10^5 parts of water

$$\therefore 0.1^o\ Fr = 1\ ppm$$

Note: The hardness of water can be converted into all the four units by making use of the following interconversion formula

1 ppm = 1mg/L = 0.07^ocl = 0.1^oFr
1^ocl = 1.43^oFr = 14.3 ppm = 14.3 mg/L

Q 2. PROBLEM:

(1) A sample of water gives an analysis 13.6 mg/L of $CaSO_4$. 7.3 mg/L of $Mg(HCO_3)_2$. Calculate the total hardness and permanent hardness.

Sol:

Salt	Quantity Present (mg/L)	M.Wt	Eq. of $CaCo_3$
$CaSO_4$	13.6	136	$\frac{13.6 \times 100}{136} = 10$
$Mg(HCo_3)_2$	7.3	146	$\frac{7.3 \times 100}{146} = 5$

The Total hardness of H_2O = Temporary hardness + Permanent Hardness

= 5 + 10 = 15 mg/L

Permanent hardness = 10 ppm (or) 10 mg/L

PROBLEM

Q 3. A Sample of hard water contains the following dissolved salts per litre.

$CaCl_2$ = 111 mgs, $CaSO_4$ = 1.36 mgs, $Ca(HCO_3)_2$ = 16.2 mgs, $Mg(HCO_3)_2$ = 14.6 mgs, Silica = 40 gms, Turbidity = 10 mgs.

Calculate the temporary, permanent and total hardness of water in ppm, ^{O}cl & ^{O}Fr

Sol:

Salt	Quantity Present (mg/L)	M.Wt	Eq. of $CaCo_3$
$CaCl_2$	111 mg/L	111	$\frac{111x100}{111}$ =100
$CaSO_4$	1.36 mg/L	136	$\frac{1.36x100}{136}$ = 1
$Ca(HCO_3)_2$	16.2 mg/L	162	$\frac{16.2x100}{162}$ = 10
$Mg(HCO_3)_2$	14.6 mg/L	146	$\frac{14.6x100}{146}$ = 10

Total hardness of H_2O = Hardness of $Ca(HCO_3)_2$+ $Mg(HCO_3)_2$ interms of $CaCO_3$ equivalents

= 10 + 10 = 20 mg/L

Permanent hardness = Hardness of $CaCl_2$+ $CaSO_4$ interms of $CaCO_3$ equivalents

= 100 + 1 = 101 mg/L

<u>Conversion of hardness</u>:

1 ppm = 1mg/L = 0.07^ocl = 0.1^o Fr

Total hardness of the sample of water = 121 ppm = 121 mg/L

= 121 x 0.07 = 8.47^ocl and

= 121 x 0.1 = 12.1^o F

Permanent hardness = 101 mg/L, 101 ppm, 7.07^ocl, 10.1^o Fr

Total hardness = 20 mg/L, 20 ppm, 1.4^ocl and 2^o Fr

Water Softening methods : lime-soda process

1. Lime soda process

It is a process in which Lime ($Ca(OH)_2$) and soda (Na_2CO_3) are added to the hard water to convert the soluble calcium and magnesium salts to insoluble compounds by a chemical reaction. The $CaCO_3$ and $Mg(OH)_2$ so precipitated are filtered off and removed easily.

Calculation of lime and soda required for the softening of hard water by the lime soda process

Hardness producing substance	Chemical reaction with lime and soda	Need
Permanent Hardness		
Ca Salts	$CaCl_2 + Na_2CO_3 \longrightarrow CaCO_3\downarrow + 2NaCl$ $CaSO_4 + Na_2CO_3 \longrightarrow CaCO_3\downarrow + 2NaSO_4$ **$CaCl_2$ and $CaSO_4$ do not react with $Ca(OH)_2$**	S
Mg salts	$MgSO_4 + Ca(OH)_2 \longrightarrow Mg(OH)_2\downarrow + CaSO_4$ $CaSO_4 + Na_2CO_3 \longrightarrow CaCO_3\downarrow + Na_2SO_4$	L + S
	$MgCl_2 + Na_2CO_3 \longrightarrow MgCO_3\downarrow + 2NaCl$ $MgCO_3 + Ca(OH)_2 \longrightarrow CaCO_3\downarrow + Mg(OH)_2\downarrow$	S+ L
Temp. Hardness		
$Ca(HCO_3)_2$	$Ca(HCO_3)_2 + Ca(OH)_2 \longrightarrow 2CaCO_3\downarrow + 2H_2O$	L
$Mg(HCO_3)_2$	$Mg(HCO_3)_2 + 2Ca(OH)_2 \longrightarrow 2CaCO_3\downarrow + Mg(OH)_2 + 2H_2O$	2 L

100 parts by mass of $CaCO_3$ are equivalent to

(i) 74 parts by mass of $Ca(OH)_2$

(ii) 106 parts by mass of Na_2CO_3

Molecular weight of lime = 74

Molecular weight of soda = 106

Molecular weight of $CaCO_3$ = 100

Therefore, Lime requirement for softenening

$$= \frac{74}{100} \left[\text{T.H of } Ca^{2+} + 2 \times \text{T.H of } Mg^{2+} + \text{P.H of } Mg^{2+} \right] \times \text{Vol .of water in litre}$$

T.H = temporary hardness

P.H = Permanent Hardness

Soda requirement for softenening

$$= \frac{106}{100} \left[\text{P.H of } (Ca^{2+} + Mg^{2+} \right] \times \text{Vol .of water in litre}$$

Problem 1

Calculate the amount of lime required for softening 5,000 litres of hard water containing 72 ppm of $MgSO_4$ (mol wt = 120) Ans = 222g

Solution

Step 1 List out the given data

Given data : Hardness 72 ppm due to $MgSO_4$; water qty = 5000 litres; mol. wt. MgSO4 = 120

Step 2 calculate the $CaCO_3$ equivalent

Hardness producing substance	Quantity (ppm)	Multiplication factor	$CaCO_3$ equivalent hardness (ppm or mg/L)
$MgSO_4$	72	100/120	72 X (100/120) = 60

Step 3 calculation of lime requirement

Lime required = 74/100 (hardness due to MgSO4) x vol. of water

= 74/100 (60 mg/L) x 5000 L

= 222,000 mg

= 222 g

Problem 2

Calculate the amount of lime and soda required for softening 50,000 litres of hard water containing: $Mg(HCO_3)_2$ = 144 ppm, $Ca(HCO_3^-)_2$ = 81 ppm, $MgCl_2$ = 95ppm, $CaCl_2$ = 111ppm, Fe_2O_3 = 25ppm and Na_2SO_4 = 15ppm

Solution

Step 1 List out the given data

Given data : $MgCO_3$ = 146 ppm, $CaCO_3$ = 25 ppm, $MgCl_2$ = 95ppm, $CaCl_2$ = 111ppm, Fe_2O_3 = 25ppm

$Ca(HCO_3)_2$ = 81 ppm and Na_2SO_4 = 15ppm

Step 2 calculate the $CaCO_3$ equivalent

Hardness producing substance	Quantity (ppm)	Multiplication factor	$CaCO_3$ equivalent hardness (ppm or mg/L)
$Mg(HCO_3)_2$ $MgCl_2$ $CaCl_2$ $Ca(HCO_3)_2$	146 95 111 81	100/84 100/95 100/111 100/162	146 x (100/146) x 2 = 200 95 x (100/95) = 100.0 111 x (100/111) = 100.0 81 x (100/162) = 25.0

Step 3 calculation of lime requirement

Lime required = 74/100 ({2 x $MgHCO_3$} + $Ca(HCO_3)_2$ + $MgCl_2$ in terms of $CaCO_3$ eq) x vol. of water

= 74/100 (2 x 100.0 + 100.0 + 25.0) mg/L x 50,000 L

= 74/100 (325) mg x 50,000

= 16, 25,000 mg

Answer = 16. 25 kg

Step 4 calculation of soda requirement

soda required = 106/100 ($CaCl_2$ + $MgCl_2$ in terms of $CaCO_3$ eq) x vol. of water

= 106/100 (100/111 x 111 + 100/95 x 95) mg/L x 50,000 L

= 106/100 (200) mg x 50,000

= 10, 6,00,000 mg

Answer = 10. 6 kg