UNIT-4

Eng. chemistry (RAS-102)

Lecture NO-23

(Hardness of Water, Disadvatages of Hard water)

Water is a universal solvent and have sp^3 hybridization.

Hardness of water - The water which does not form lather easily with Soap is known as hard water. (Soaps are the Sodium or potassium salts of higher fatty acids). water which form lather with soap is known as soft water.

Cause of Hardness -

Hardness of water is due to the presence of dissolved salts of calcium (Ca), Magnesium (Mg) and other heavy metals. These react with soluble sodium Soap to form insoluble salts of Ca & Mg.

$$\underset{\text{sod. stearate}}{2C_{17}H_{35}COONa} + CaSO_4 \longrightarrow \underset{\text{Calcium stearate}}{(C_{17}H_{35}COO)_2Ca} + Na_2SO_4$$

$$2C_{17}H_{35}COONa + MgCl_2 \longrightarrow \underset{\text{Magnesium stearate}}{(C_{17}H_{35}COO)_2Mg\downarrow} + 2NaCl$$

Thus the precipitate formed is the insoluble soap of Ca & Mg. Hence a large quantity of Soap is required to produce lather with hard water.

Types of Hardness - Hardness of water is of two types-

1. Temporary Hardness
2. Permanent Hardness.

1. **Temporary hardness** or **Carbonate hardness** -

It is due to the presence of dissolved salts of bicarbonates of Ca, Mg & other heavy metals and the Carbonates of Iron.

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Removal - It can be removed by followïng two ways -

(1) By Boiling of water -

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

Ca. bicarbonate. Cal. carbonate (insoluble)

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

Mag. bicarbonate. Mag. hydroxide (insoluble)

2. By adding slaked lime - A precipitate of $CaCO_3$ is formed. This is called lime softening.

$Ca(HCO_3)_2 + Ca(OH)_2 \rightleftharpoons 2CaCO_3 + 2H_2O$

Calcium Bicarbonate. slaked lime Calcium Carbonate.

2. Permanent hardness or non-Carbonate hardness -

This hardness is due to the presence of chlorides and sulphates of calcium (Ca), Magnesium (Mg) and other heavy metals like Iron (Fe). It cannot be removed by boiling. It can be removed by following chemical Methods -

- Lime-soda method
- Ion-exchange Resin method
- Zeolite Method
- Calgon Method

Disadvantages of hard water -

Industry

- → Hard water shows soap consuming capacity as the cleaning properties of soap is depressed and lot of soap is washed in bathing and wasing.
- → It causes various boiler troubles in industries like -
  - Sludge & scale formation
  - Boiler Corrosion.
- → it gives side reactions in some industrial processes.

humans

- → It is not good for drinking purpose, if salts are in excess.
- → Excess hard water (saline water) can cause dehydration.
- → It can cause kidney stone.

*Questions asked in University examinations.

* Define the term hardness and give their types also.

* What is hardness. Give their disadvantages.

* Define Carbonate and non-carbonate hardness.

* Give the salts responsible for various hardness.

Eng. chemistry (RAS-102)
Lecture No. 24

(Units & Calculation of Hardness)

Hardness in terms of equivalents of $CaCO_3$ (Degree of hardness)

Hardness is always calculated in terms of equivalent of $CaCO_3$, although $CaCO_3$ is not responsible for any type of hardness. There are two basic reasons for choosing $CaCO_3$ as standard -

(i) Calculations become easy as its molecular weight is exactly 100 (and eq. wt. is 50).

(ii) It is the most insoluble salt that can be precipitated in water treatment.

$$\boxed{\text{The equivalents of } CaCO_3 = \frac{\text{Mass of hardness Producing substance} \times \text{Eq. wt. of } CaCO_3}{\text{eq. wt. of hardness producing Substance.}}}$$

UNITS of Hardness -

1. Parts per million (PPM) -

1 PPM = 1 part $CaCO_3$ equivalent hardness per 10^6 parts of water.

2. Milligrams per litre (mg/L)

1 mg/L = 1 part $CaCO_3$ equivalent hardness per 10^6 parts mg of water.

$$\boxed{1\ mg/L = 1\ PPM}$$

(3) Degree french (°Fr) -

1°Fr = 1 part $CaCO_3$ equivalent hardness present per 10^5 parts of water.

(4) Degree clark (°Cl) -

1°Cl = 1 part $CaCO_3$ equivalent hardness present for 70,000 parts of water.

Relation between Various units -

1 PPM = 1mg/L = 0.1°Fr = 0.07°Cl

1°Fr = 10 ppm = 10mg/L = 0.7°Cl.

1°Cl = 14.3 ppm = 14.3mg/L = 1.43°Fr.

Atomic Mass of Various Elements -

Element Mass.

H = 1

C = 12

N = 14

O = 16

S = 32

Cl = 35.5

Ca = 40

Mg = 24

Fe = 56

Al = 27

Na = 23

Molecular weight and Equivalent Weight of Various Salts -

Salts	Molecular Mass	equivalent weight
Salts of Ca.		
$Ca(HCO_3)_2$	162	81
$CaSO_4$	136	68
$CaCl_2$	111	55.5
$CaCO_3$	100	50
Salts of Magnesium		
$Mg(HCO_3)_2$	146	73
$MgSO_4$	120	60
$MgCl_2$	95	47.5
$MgCO_3$	84	42
$Mg(NO_3)_2$	148	74
Other salts/gases/Acids.		
$NaAlO_2$	82	82
$Al_2(SO_4)_3$	342	57
$FeSO_4 \cdot 7H_2O$	278	139
HCl	36.5	36.5
H_2SO_4	98	49
CO_2	44	22
Ions.		
HCO_3^-	61	61
CO_3^{--}	60	30
OH^-	17	17
H^+	1	1
Ca^{++}	40	20
Mg^{++}	24	12

Numerical -

A sample of water has hardness 304 ppm $CaCO_3$ equivalent. find the hardness in terms of °cl, °fr and mg/L.

Hardness in terms of °cl

1 ppm = 0.07°cl

304 ppm = 304 × 0.07°cl

= 21.28°cl

Hardness in terms of °fr

1 ppm = 0.1°fr

304 ppm = 304 × 0.1°fr

= 30.4°fr

Hardness in terms of mg/L

1 ppm = 1 mg/L

304 ppm = 304 mg/L

$$\boxed{\begin{aligned} 304 \text{ ppm} &= 304 \text{ mg/L} \\ &= 30.4^\circ fr \\ &= 21.28^\circ cl. \end{aligned}}$$

* Questions asked in university examination.

* Convert the total hardness of water sample in ppm from °cl & °fr.
(i) 2.42°cl (ii) 3.6°Fr.

Ans (i) 34.57 ppm
(ii) 36 ppm

* Why hardness is calculated in terms of $CaCO_3$ equivalents. Give various units of hardness.
[2016 even sem]

UNIT-4

Eng. chemistry (RAS-102)

Lecture - 25

(Calculation of hardness)

* A water sample contains 248 mg $CaSO_4$ per litre. Calculate the hardness in terms of $CaCO_3$ equivalent.

Mass of hardness producing substance = 248 mg.

$$\text{equivalents of } CaCO_3 = \frac{\text{Mass of hardness producing substance} \times \text{eq. wt of } CaCO_3}{\text{eq. wt. of hardness producing Substance.}}$$

$$= \frac{248 \times 100/2}{136/2} = \underline{\underline{182.35 \text{ ppm.}}}$$

* A sample of water on analysis was found to contain the following impurities -

Impurity	Quantity	Mol. wt.
$Ca(HCO_3)_2$	4	162
$Mg(HCO_3)_2$	6	146
$CaSO_4$	8	136
$MgSO_4$	10	120

Calculate the temporary, Permanent and total hardness of water in ppm, °Fr and °Cl.

Impurities	Amount (mg/L)	Equivalents of $CaCO_3$	Types of hardness
$Ca(HCO_3)_2$	4	$\frac{4 \times 100/2}{162/2} = 2.46$ mg/L	Temporary
$Mg(HCO_3)_2$	6	$\frac{6 \times 100/2}{146/2} = 4.10$ mg/L	Temporary
$CaSO_4$	8	$\frac{8 \times 100/2}{136/2} = 5.88$ mg/L	Permanent
$MgSO_4$	10	$\frac{10 \times 100/2}{120/2} = 8.33$ mg/L	Permanent

Temporary hardness = $CaCHCO_3)_2 + Mg(HCO_3)_2$
= 2.46 + 4.10
= 6.570 mg/L

Permanent hardness = $CaSO_4 + MgSO_4$
= 5.88 + 8.33
= 14.215 mg/L

Total hardness = 6.578 + 14.215
= 20.793 mg/L

Hardness	ppm	°fr	°cl
Temporary	6.578	0.6578	0.460
Permanent	14.215	1.4215	0.995
Total	20.793	2.0793	1.4555

1PPM = 1 mg/L = 0.1°fr = 0.07°cl.

*** Questions asked in University examination.**

what is the carbonate and non-carbonate hardness of a sample of water which has the following impurities per-litre.

25 $Ca(HCO_3)_2$ = 40.5 mg/L ; 30 $CaCl_2$ = 33.3 mg/L
$Ca(NO_3)_2$ = 41.0 mg/L KNO_3 = 101 mg/L
40 $MgCO_3$ = 33.6 mg/L

* KNO_3 & $Ca(NO_3)_2$ does not produce hardness.

Non Carbonate	= 30 ppm.
Carbonate	= 65 ppm

Eng. chemistry (RAS-102)   UNIT-IV

Lecture NO-27

(Lime-soda method)

(1) **Lime soda process (L-S process)** - In this process soluble hardness causing impurities are chemically converted into insoluble precipitates which may be removed by settling and filtration.

For this purpose, hard water is treated with lime, $Ca(OH)_2$, followed by soda ash (Na_2CO_3). Ca^{2+} ions are removed as $CaCO_3$ and Mg^{2+} ions are removed as $Mg(OH)_2$. Reactions are as follows -

Lime removes the following hardness-

a) It removes temporary hardness.

$$Ca(HCO_3)_2 + Ca(OH)_2 \longrightarrow 2CaCO_3\downarrow + 2H_2O$$
$$Mg(HCO_3)_2 + 2Ca(OH)_2 \longrightarrow Mg(OH)_2\downarrow + 2CaCO_3 + 2H_2O$$

(b) It removes the permanent magnesium hardness

$$MgCl_2 + Ca(OH)_2 \longrightarrow Mg(OH)_2\downarrow + CaCl_2$$
$$MgSO_4 + Ca(OH)_2 \longrightarrow Mg(OH)_2\downarrow + CaSO_4$$

(c) It removes dissolved iron and Al salts:

$$2Fe(OH)_2 + H_2O + O \longrightarrow 2Fe(OH)_3\downarrow$$
$$FeSO_4 + Ca(OH)_2 \longrightarrow Fe(OH)_2\downarrow + CaSO_4$$
$$Al_2(SO_4)_3 + 3Ca(OH)_2 \longrightarrow 2Al(OH)_3 + 3CaSO_4.$$

(d) It removes Free mineral acids.

$$2HCl + Ca(OH)_2 \longrightarrow CaCl_2\downarrow + 2H_2O$$
$$H_2SO_4 + Ca(OH)_2 \longrightarrow CaSO_4\downarrow + 2H_2O$$

(e) It removes dissolved CO_2 & H_2S.

$$Ca(OH)_2 + CO_2 \longrightarrow CaCO_3\downarrow + H_2O$$
$$Ca(OH)_2 + H_2S \longrightarrow CaS\downarrow + 2H_2O$$

(f) Soda removes all soluble calcium permanent hardness.

$$CaCl_2 + Na_2CO_3 \longrightarrow CaCO_3\downarrow + 2NaCl$$
$$CaSO_4 + Na_2CO_3 \longrightarrow CaCO_3\downarrow + Na_2SO_4$$

Eng. Chemistry (RAS-102) UNIT-4

Lecture NO. 28

(Methods of L-S process)

Lime-soda Method is of two types-

(i) Cold Lime-soda process

(ii) Hot Lime soda process.

(i) cold lime-soda process – The hard water is first analysed and then feed into the inner vertical circular chamber fitted with a stirrer. Now, a calculated quantities of lime and soda ash are added into the tank. Also, a small amount of coagulant, $Al_2(SO_4)_3$, is added, which entraps the fine precipitate of $Al(OH)_3$ thereby causing easy filteration. It also removes silica and oil if present in water.

$$\underset{\text{Sod. aluminate (Coagulant)}}{NaAlO_2} + 2H_2O \longrightarrow NaOH + Al(OH)_3\downarrow$$

$$\underset{\text{Aluminium sulphate (Coagulant)}}{Al_2(SO_4)_3} + 3Ca(HCO_3)_2 \longrightarrow 2Al(OH)_3\downarrow + 3CaSO_4 + 6C$$

water becomes soft due to Vigorous stirring and mixing. The heavy sludge settles down in the outer chamber and softened water reaches up. The softened water is then passed through filtration unit and finally filtered soft water flows out through the outlet at the top. This process provid water containing residual hardness of 50-60 ppm

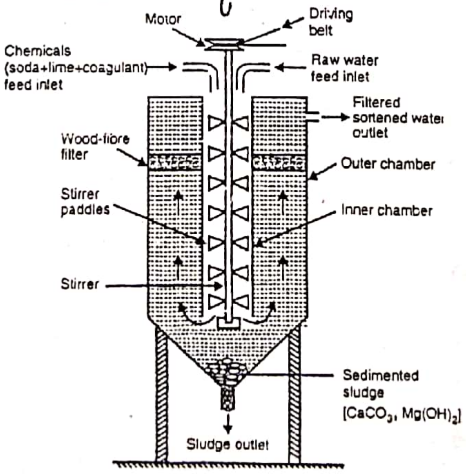


Fig. 3. ~~Continuous~~ cold lime-soda softener.

(ii) **Hot lime soda process** – In this process hard water and softener chemicals are heated near about the boiling point of water. The reaction are much faster and the precipitation is almost complete. While in cold L-S-process, the reaction takes place at room temperature due to which partial softening of water takes place. In hot L-S process, the participation occurs more quickly and also settle down rapidly. So no coagulations ~~are~~ is needed in this process.

The apparatus used in this process contains a reaction cum settling tank and a filter. Reaction tank has three separate inlets for hard water, chemicals and steam. All the three are throughly mixed in the reaction tank. Now the reaction content from the reaction tank comes to the conical sedimentation tank, in which sludge settle down.

Filter has layers of fine and coarse sand which acts as filter and ensures complete removal of sludge from the softened water.

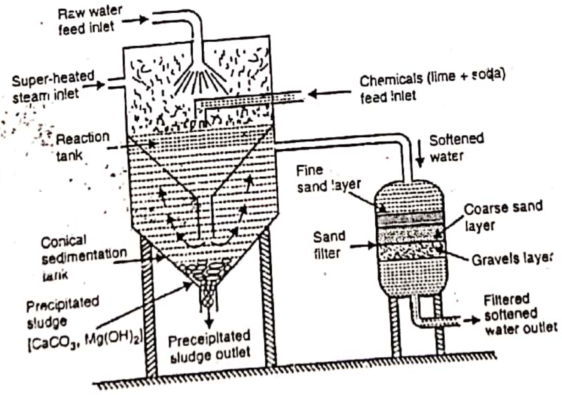


Fig. 4. ~~Continuous~~ hot lime-soda softener.

Hot lime-soda process.

Advantages of L-S process -

1. It is very cheap and economical.
2. Lesser amount of coagulants will be required, if this process is combined with sedimentation and coagulation.
3. Fe & Mn (upto some extent) are also removed from water.
4. It helps in reducing the total mineral content of water.
5. It leads to an increase in the pH value of water, thus reducing the corrosion of the distribution pipes.

Disadvantages of L-S process -

1. Carefull operation and skilled supervision is required to get good results.
2. Formation of large amount of sludge creats its disposal problem.
3. This process cannot produce water having zero hardness
4. Softened water from L-S softeners is not good for boilers.

Advantages of Hot L-S process -

1. This process takes about 15 minutes whereas cold process takes several hours for completion.
2. No coagulation is required because the precipitate and sludge formed settle down quickly.
3. Residual hardness is much less than cold process
4. Less chemicals are required
5. Most of the dissolved gases like CO_2 and O_2 are also removed.
6. Filtration becomes much easier as the viscocity of the water becomes low.

Comparision between Cold L-S process and hot L-S process

Cold L-S process	Hot L-S process
1. Reactions take place at slower rate.	1. Reactions take place at faster rate.
2. Coagulants are added to settle down the precipitate	2. Coagulants are not requir
3. Temporary hardness is removed by adding lime.	3. Temperary hardness is removed by boiling and hence lime consumption is less.
4. No fuel consumption.	4. A steam is used, so there is fuel consumption.
5. It takes longer time (few hours)	5. It takes lesser time. (few minutes)
6. The residual hardness is about 50-60 ppm.	6. The residual hardness is about 15-30 ppm.

Calculation of Lime-soda Requirement

∵ 100 parts by mass of $CaCO_3 \equiv 74$ parts of $Ca(OH)_2$

and 100 parts by mass of $CaCO_3 \equiv 106$ parts of Na_2CO_3

$$\therefore \text{Lime requirement} = \frac{74}{100}\left[\text{Temp. } Ca^{2+} + 2\times \text{temp}(Mg^{2+}) + Al^{3+} + Fe^{2+} + CO_2 + H^+ (HCl \text{ or } H_2SO_4) + HCO_3^- - NaAlO_2\right]$$

(All in terms of $CaCO_3$ equivalen × vol^m of water × 100/% purity)

$$\text{soda requirement} = \frac{106}{100}\left[\text{Perm.}(Ca^{2+} + Mg^{2+} + Al^{3+} + Fe^{2+}) + H^+ (HCl \text{ or } H_2SO_4 - HCO_3^-\right]$$

All in terms of $CaCO_3$ equivalent × vol^m of water (lit) × 100 / % purity

Note: substances like KCl, $NaCl$, SiO_2, Na_2SO_4, Fe_2O_3 etc. do not contribute any hardness and therefore, these do not consume any lime or soda. These should not be taken into consideration for calculating the lime and soda requirement.

* Calculate the amount of lime and soda required for the treatment of 20,000 litres of ~~amount~~ water whose analysis is a follows–

$Ca(HCO_3)_2 = 40.5$ ppm, $Mg(HCO_3)_2 = 36.5$ ppm, $CaSO_4 = 34$ ppm, $MgSO_4 = 30$ ppm, $CaCl_2 = 27.75$ ppm

Salt	Amount (ppm)	$CaCO_3$ equivalent	Requirement
$Ca(HCO_3)_2$	40.5	$\frac{40.5 \times 100/2}{162/2} = 25$	L
$Mg(HCO_3)_2$	36.5	$\frac{36.5 \times 100/2}{146/2} = 25$	2L
$CaSO_4$	34	$\frac{34 \times 100/2}{120/2} = 25$	S
$MgSO_4$	30	$\frac{30 \times 100/2}{120/2} = 25$	L+S
$CaCl_2$	27.75	$\frac{27.75 \times 100/2}{111/2} = 25$	S

Lime required $= \frac{74}{100}[(Ca(HCO_3)_2 + 2Mg(HCO_3)_2 + MgSO_4]$ all in terms of $CaCO_3$ equ $\times \frac{\text{Vol. of Water}}{10^6}$ kg.

$$= \frac{74}{100}[25 + 2\times 25 + 25] \times \frac{20,000}{10^6}.$$

$$\boxed{\text{Lime required} = 1.48 \text{ kg}}$$

Soda required $= \frac{106}{100}[CaSO_4 + MgSO_4 + CaCl_2]$ all in terms of $CaCO_3$ equivalent $\times \frac{\text{Vol. of Water}}{10^6}$ kg.

$$= \frac{106}{100}[25 + 25 + 25] \times \frac{20,000}{10^6}$$

$$\boxed{\text{Soda required} = 1.59 \text{ kg.}}$$

Eng. chemistry (RAS-102)

Lecture NO-29

(Numericals on Lime-soda process)

Before calculating the quantity of lime and soda, we should know the requirement of salts.

Salts —— Requirement.

$CaCO_3$ —— L

$MgCO_3$ —— 2L

$Ca(HCO_3)_2$ —— L

$Mg(HCO_3)_2$ —— 2L

CO_2 —— L

H_2S —— L

KCl, $NaCl$, SiO_2, Fe_2O_3, Na_2SO_4 } Does not require Lime & soda

$CaCl_2$ —— S

$CaSO_4$ —— S

Ca^{++} —— S

$MgSO_4$ —— L+S

$MgCl_2$ —— L+S

Mg^{++} —— L+S

$AlCl_3$ —— L+S

$Al_2(SO_4)_3$ —— 3(L+S)

Fe^{++} —— L+S

$FeSO_4$ —— L+S

HCl —— (L+S)/2

H_2SO_4 —— L+S

H^+ —— L+S

$(Na/K)HCO_3^-$ —— (L−S)/2

$NaAlO_2$ —— −L

UNIT-4

Eng. chemistry (RAS-103)
Lecture NO-30

(Numericals on Lime·Soda Method)

Calculate the quantity of lime (74% pure) and soda (90% pure) required for softening 50,000 litres of water containing

$Mg(HCO_3)_2 = 50 mg/L$ $MgCl_2 = 6 mg/L$
$Ca(HCO_3)_2 = 81 mg/L$ $CO_2 = 44 mg/L$
$HCl = 73 mg/L$ $Al_2(SO_4)_3 = 57 mg/L$
$Fe_2O_3 = 40 mg/L$

Constituent	Amount (mg/L	equivalents of $CaCO_3$	Requirement
1. $Mg(HCO_3)_2$	50	$\frac{50 \times 100/2}{146/2} = 34.26$	2L
2. $Ca(HCO_3)_2$	81	$\frac{81 \times 100/2}{162/2} = 50$	L
3. $MgCl_2$	6	$\frac{6 \times 100/2}{95/2} = 6.31$	L+S
4, HCl	73	$\frac{73 \times 100/2}{36.5/1} = 100$	(L+S)/2
5. CO_2	44	$\frac{44 \times 100/2}{44/2} = 100$	L
6. $Al_2(SO_4)_3$	57	$\frac{57 \times 100/2}{342/3} = 25$ 50	3(L+S)
7. Fe_2O_3 —	Does not consume Lime & soda.		

Lime required $= \frac{74}{100}\left[Ca(HCO_3)_2 + 2Mg(HCO_3)_2 + MgCl_2 + \frac{HCl}{2} + CO_2 + 3Al_2(SO_4)_3\right] \times \frac{\text{Vol. of water}}{10^6} \times \frac{100}{\%\ \text{purity}}$

$= \frac{74}{100}\left[50 * 2 \times 34{\cdot}26 + 6{\cdot}31 * \frac{100}{2} + 100 + 3\times25\right] \times \frac{100}{74} \times \frac{50{,}000}{10^6}]$

$= \frac{74}{100}\left[349{\cdot}83\right] \times \frac{100}{74} \times \frac{50{,}000}{10^6}$

21.24 kg

$= \frac{1749{\cdot}15 \times 10^4}{10^6}$

$\boxed{\text{Lime required} = 17{\cdot}49\ \text{kg}}$ 12.40 kg.

Soda required $= \frac{106}{100}\left[MgCl_2 + \frac{1}{2}HCl + 3Al_2(SO_4)_3\right] \times \frac{100}{\%\ \text{purity}} \times \frac{V}{10^6}$ kg

$= \frac{106}{100}\left[6{\cdot}31 + \frac{100}{2} + 3\times25\right] \times \frac{100}{90} \times \frac{50{,}000}{10^6}$ kg.

$= \frac{106}{100}\left[131{\cdot}31\right] \times \frac{100}{90} \times \frac{50{,}000}{10^6}$ kg.

$= \frac{13918{\cdot}86 \times 5 \times 10^4}{90 \times 10^6}$ kg.

12.145 kg

$= \frac{773{\cdot}27}{10^2}$

$\boxed{\text{Soda required} = 7{\cdot}7327\ \text{kg.}}$

Lecture NO-31

(Zeolite Process or Permutit process)—

Zeolite is derived from two greek words (Zein + lithos) which means boiling stone. Chemically zeolite is a sodium aluminium orthosilicate, i.e $Na_2Al_2SiO_8 \cdot xH_2O$. The artificial zeolite is called permutit, having a general formula:
$Na_2O \cdot Al_2O_3 \cdot xSiO_2 \cdot yH_2O$ (where x = 2–10 & y = 2–6)
Permutit may be obtained by fusing Na_2CO_3, Al_2O_3 & SiO_2 in a proper ratio. It acts as a base exchanger when brought in contact with water containing cations.

In this process, hard water is perlocated at a specified rate through a bed of zeolite, present in a cylindrical zeolite unit.

Zeolite holds sodium ions loosely and can be simply represented as Na_2Ze.

The hardness-causing ions (Ca^{2+}, Mg^{2+} etc) are removed by the zeolite as CaZe & MgZe respectively, while the outgoing water contains sodium salts.

$$Na_2Ze + Ca(HCO_3)_2 \longrightarrow CaZe + 2NaHCO_3$$
$$Na_2Ze + Mg(HCO_3)_2 \longrightarrow MgZe + 2NaHCO_3$$
$$Na_2Ze + CaCl_2 \longrightarrow CaZe + 2NaCl$$
$$Na_2Ze + CaSO_4 \longrightarrow CaZe + Na_2SO_4$$
$$Na_2Ze + MgCl_2 \longrightarrow MgZe + 2NaCl$$
$$Na_2Ze + MgSO_4 \longrightarrow MgZe + Na_2SO_4$$

Regeneration– After some time, the zeolite is completely converted into Ca & Mg zeolites and it gets exhausted. Now, the supply of hard water is stopped and the exhausted zeolite is treated with a concentrated brine (10 % NaCl) solution.

$$CaZe + 2NaCl \longrightarrow Na_2Ze + CaCl_2$$
$$MgZe + 2NaCl \longrightarrow Na_2Ze + MgCl_2$$

Eng. chemistry (RAS-102)

Lecture NO-32

(Numericals on Zeolite Method)

The hardness of 1000 litres of a sample of water was removed by passing it through a zeolite softener. The zeolite softener then required 30 litres of sodium chloride solution containing 1.5 gm/litre of NaCl for regeneration. Find the hardness of water sample. [2008-09]

NaCl contained in 30L of NaCl Sol^n

$= 1.5\ gm/L \times 30L$

$= 45\ gm$ NaCl.

equivalents of $CaCO_3 = \frac{45 \times 100/2}{58.5/1}$

$= 38.46$ equivalents of $CaCO_3$.

1000 litres of water $= 38.46$ gm equivalents of $CaCO_3$.

1L of water $= \frac{38.46}{1000} \times 10^3\ mg/L$

$= 38.46$ ppm.

Hardness of water is 38.46 ppm.

Eng. chemistry (RAS-102) UNIT-4

(Lecture NO-34)

3. **Calgon process-** Calgon is the trade name. chemically it is sodium hexametaphosphate having formula $(NaPO_3)_6$ or $Na_2(Na_4P_6O_{18})$

Ca^{2+} ions and Mg^{2+} ions present in hard wate react with calgon to give complex negative ions as $[Ca_2P_6O_{18}]^{2-}$ or $[Mg_2P_6O_{18}]^{2-}$

$$Na_2[Na_4P_6O_{18}] \rightleftharpoons 2Na^+ + [Na_4P_6O_{18}]^{2-}$$

$$\underset{\text{In hardwater}}{2Ca^{2+}} + \underset{\text{Calgon}}{[Na_4P_6O_{18}]^{2-}} \longrightarrow 4Na^+ + [Ca_2P_6O_{18}]^{2-}$$

$$\underset{\text{In hardwater}}{2Mg^{2+}} + \underset{\text{calgon}}{[Na_4P_6O_{18}]^{2-}} \longrightarrow 4Na^+ + [Mg_2P_6O_{18}]^{2-}$$

Since, the formation of the complex negative ion decreases, the concentration of the calcium ions, hence reducing the hardness of water. calgon not only prevents the ~~prevents the~~ precipitation of soap as calcium salts of higher fatty acids (calcium soaps) but actually dissolves such soaps. It has, therefore found wide use in laundry for removing calcium Soap which otherwise encrusts the washed taxtiles.

4. **With Ion exchange Resins-** Recently ion-exchange resin is used to remove all minerals from water. In this method, hard water is allowed to flow through a tank partly filled with the granules of a resin 'x' which absorbs positive ions (like Ca^{2+} or Mg^{2+} ions). water flowing out of this tank does not contain any ions like Ca^{2+}, Mg^{2+} i.e it is soft water.

Cation exchange Resin - 'x' consist of giant organic molecules. These organic molecules arranged in the form of a porous frame work having acidic groups (carboxyl groups, COOH). Ca^{2+} & Mg^{2+} ions present in hard water are removed by these acidic frameworks and H$^+$ ions are added to water.

Dia

$$\underset{\text{Resin 'x'}}{2RCOOH} + \underset{\text{In hard water.}}{Ca^{2+}} \longrightarrow (RCOO)_2Ca + 2H^+$$

After use, the giant molecules of resin x can regenerated by passing a moderately concentrate **solution** of sulphuric acid through it :

Regeneration–

$(RCOO)_2Ca + H_2SO_4 \longrightarrow 2RCOOH + Ca^{2+} + SO_4^{2-}$

If the water is further passed through ~~another resin~~ 'y' which absorbs negative ions. After this treatment the water is completely demineralized and is as good as distilled water.

Anion exchange Resin–

Resin y contains grains of giant organic molecules (substituted NH_4OH) with basic groups (OH.

The electronegative ions present in the incomi water are held by the ammonium ions of the frame work.

$(RNH_3)OH + Cl^- + H^+ \longrightarrow (RNH_3)Cl + H_2O$

Resin y

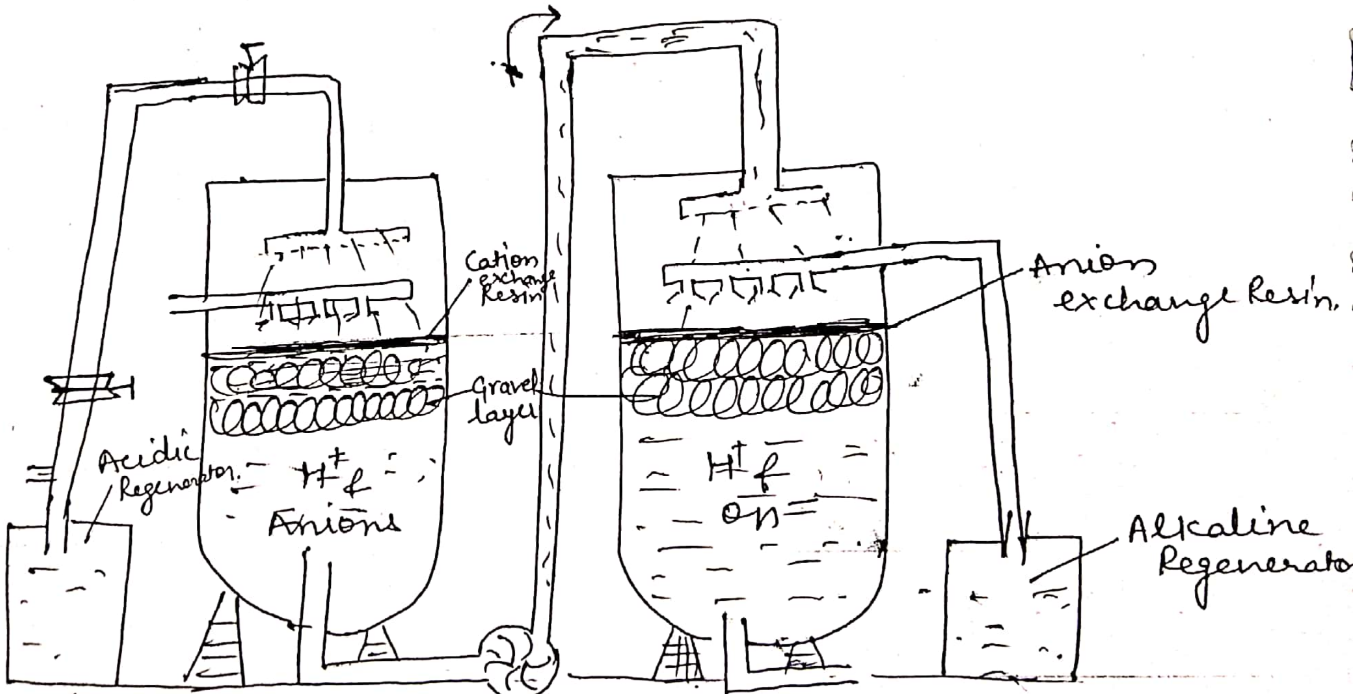
$(RNH_3)OH + SO_4^{2-} + 2H^+ \longrightarrow (RNH_3)_2SO_4 + 2H_2O$

Thus the outgoing water contains practically no ions and can be used in place of distilled water.

Resin y can be regenerated by treating with moderately concentrated solution of caustic soda.

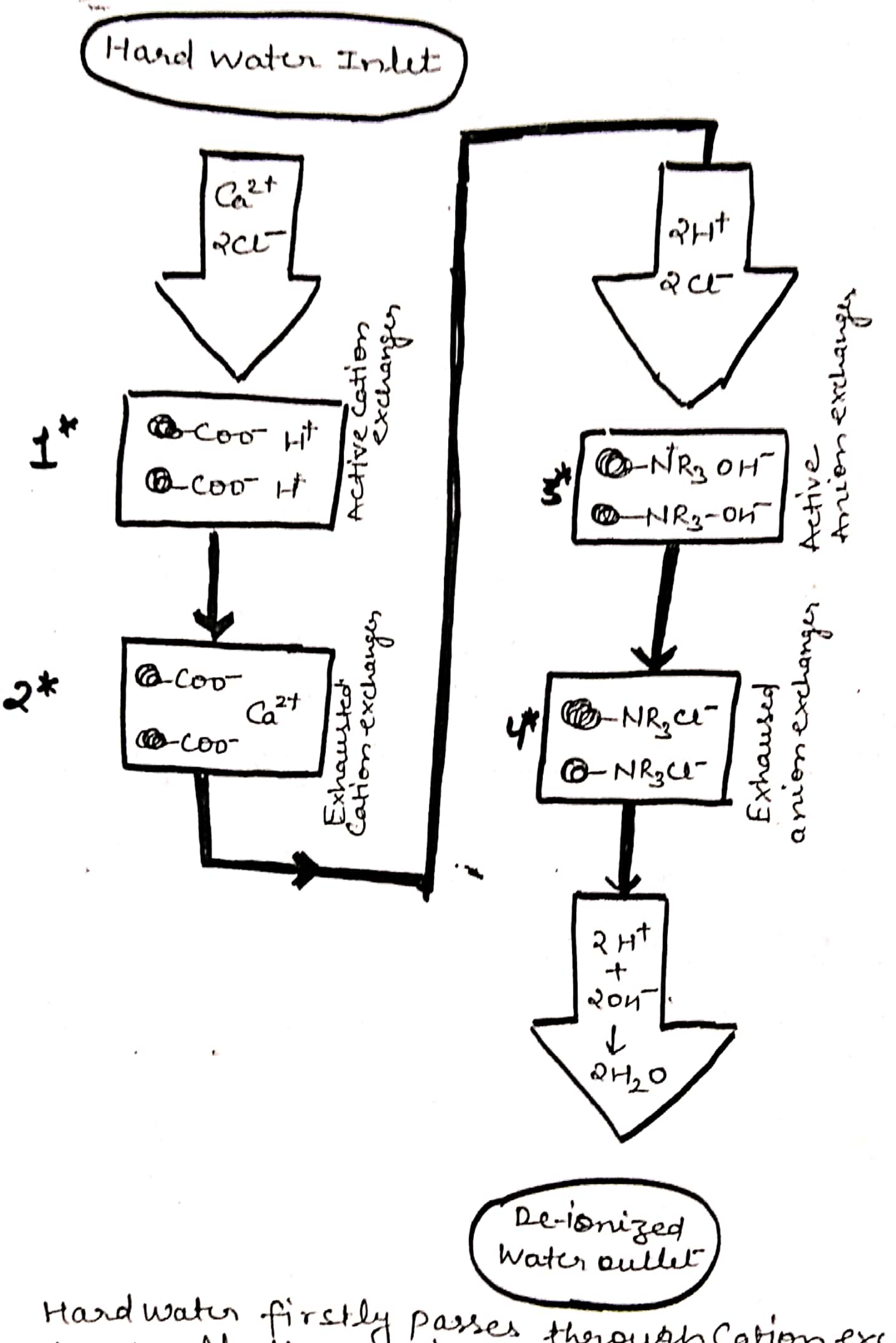
Regeneration

$(RNH_3)Cl + NaOH \longrightarrow (RNH_3)OH + Cl^- + Na^+$



Ion exchange Resin Method
(Demineralization Method)

Working of Ion exchange Resin Method -



Hard Water firstly passes through Cation exchange resin, where all the Cations are exchanged with H^+ ions. then this water having H^+ and anions are passed through anion exchange Resin where all the anions are exchanged with OH^- ion. Resins are regenerated for further Softening Purpose.

Advantages of Ion exchange Resin -

(i) This process can be used to soften highly acidic or alkaline waters.

(ii) It produces water of very low hardness (2ppm). 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.

*· Questions asked in university examinations.

* Describe 'treatment of water with Ion exchange Resin Method.

* Explain Principle, working and advantages & disadvantages of Ion-exchange Resin Method.

UNIT-4

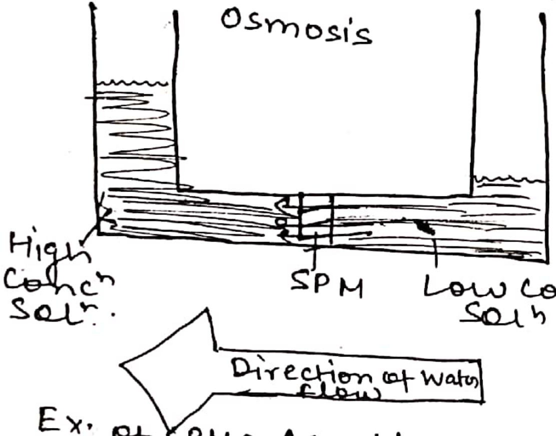
Eng. chemistry (RAS-102)

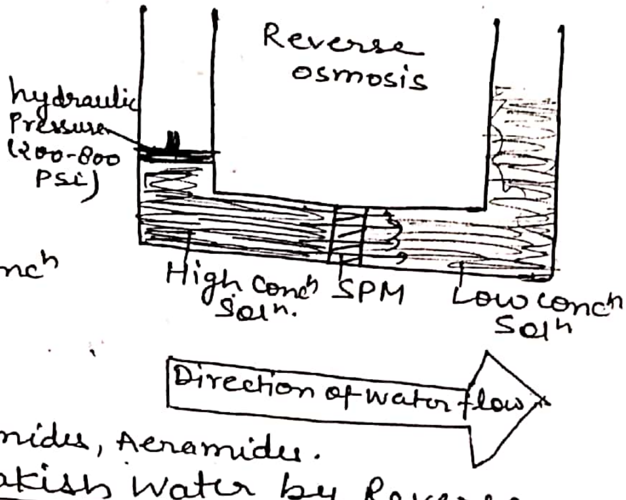
Lecture NO-35

(Reverse Osmosis)

"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 concentration are separated by a semi-permeable memberane (SPM)." The driving force responsible for the flow is known as osmotic pressure.

If a hydraulic pressure in excess of osmotic pressure is applied on the concentrated side, the flow of solvent reverses as it forced to move from concentrated side to dilute side across the memberane. This process is known as Reverse osmosis.

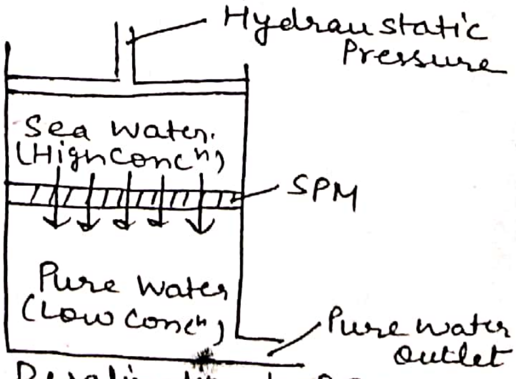




Ex. of SPM - Acrylics, Polyamides, Aeramides.

Desalination of brakish water by Reverse Osmosis method -

Sea water has brakish taste due to the presence of excess of salts. Sea water is not drinkable. But by desalination (Removal of salts) method it can be converted into pure water.



Desalination by R.O method.

Advantages-

(i) It is simple and reliable process.
(ii) It operates comparatively at low temperature.
(iii) Capital and operating costs are low.
(iv) colloidal SiO_2 Can be removed by Reverse osmosis method, which Can not be removed by Ion-exchange method.

Application-

(i) Treatment of water
(ii) Desalination.
(iii) for Dialysis in hospitals.

Questions asked in university examinations.

- * Define the term Reverse osmosis.
- * Explain the desalination of Brakish water by reverse osmosis method.

Eng. chemistry (RAS-102)

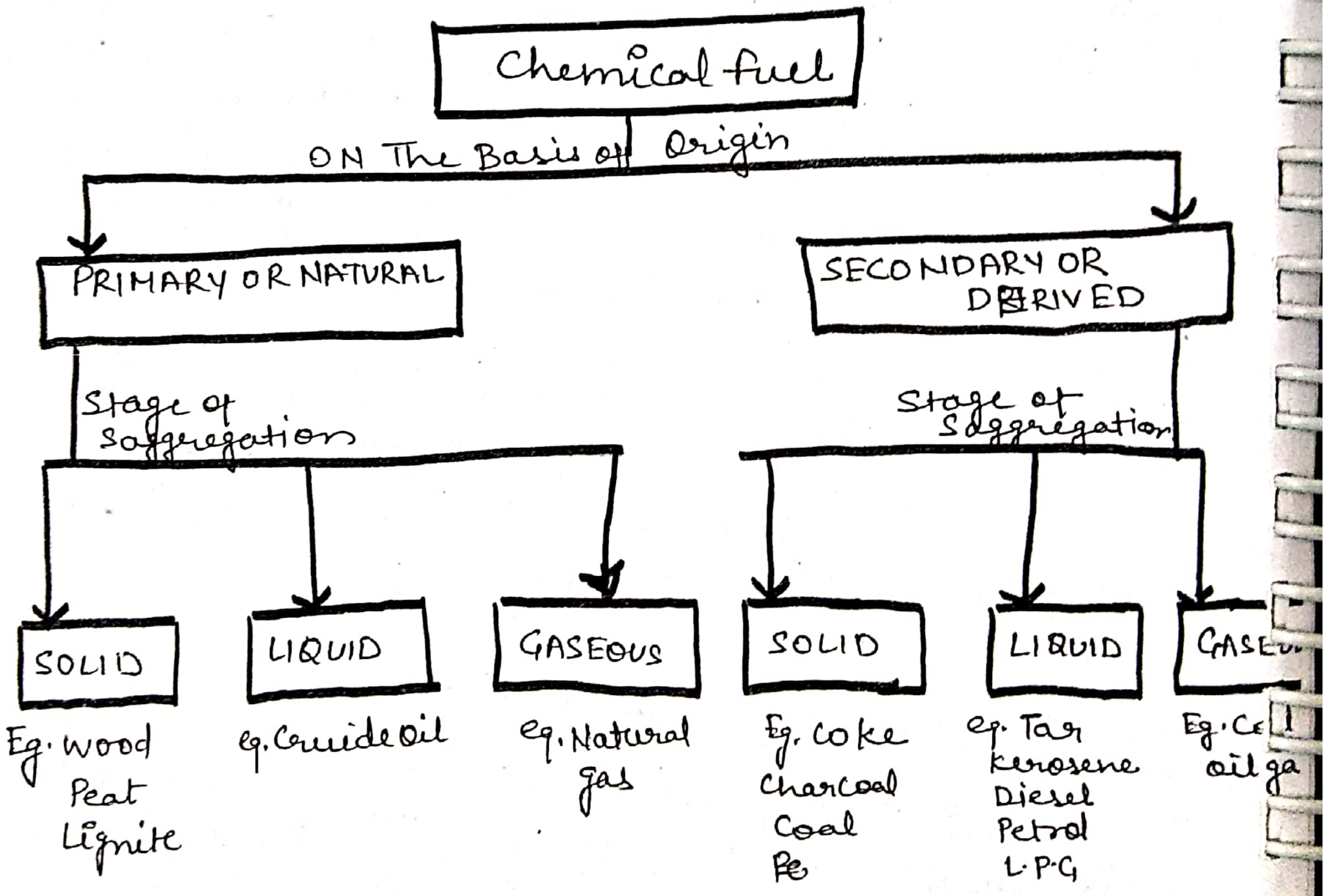
Lecture NO-38

(Fuels, classification of fuels)

fuel is a combustible substance, containing carbon as main constituent, which on proper burning gives large amount of heat, which can be used economically for domestic and indust purpese.

$$\text{fuel} + O_2 \longrightarrow \text{Products} + \text{Heat}.$$

classification of fuel-



Properties of Good fuel-

(1) A Good fuel should have high calorific value.

(2) It should be easy to carry from one place to another.

(3) Its ignition point should be ~~high~~ Moderate.

(4) It should be cheap.

(5) It should be ecofriendly.

(6) It should have low ash component.

(7) It should have higher amount of fixed Carbon.

(8) It should be easily available.

Classification of Coal on the basis of Percentage of Carbon-

Fuel	% of Carbon
Wood	50
Peat	57
Lignite	67

fuel	% of C
Sub-Bituminous	77
Bituminous	83
Semi-Bituminous	90
Anthracite	93

Questions asked in University Questions

- * What is fuel. Give its classification.
- * What is the property of a good Fuel.
- * Give the classification of Coal on the basis of percentage of Carbon.

Flash point & fire point-

Flash point is a temperature at which Vapour of fuel will ignite in form of flash when it come in contact with fire (flash may last long for 5 sec.)

fire point is a temperature at which Vapour of fuel will ignite for long time when it come in contact with fire.

UNIT-4

Eng. chemistry (RAS-102)

Lecture NO-39

(Analysis of fuel)

In order to assess the quality of coal, following Two types of analysis are made—

(i) Proximate Analysis

(ii) Ultimate Analysis

Proximate Analysis

Proximate analysis involves the in following determinations.

Proximate Analysis

STEP-1

1. Moisture

About 1 gm of finely powdered air-drie Coal sample is weighed in crusible. The crusible placed inside an electric ho air oven at 105–110°C for 1 hour. After it, it is cooled in descicator & weighed.

$$\% \text{ of Moisture} = \frac{\text{Loss in weight}}{\text{Wt. of Coal taken}} \times 100$$

STEP 2

2. Volatile Matter

The dried sample of coal left in the Crusi in (1) is then covered with lid and placed i electric furnace (muffle furnace) at 925±2c for 7 minutes. After it, it is cooled in descicator and weighed.

$$\% \text{ of Volatile Matter} = \frac{\text{loss in weight}}{\text{Wt. of Coal sample taken}} \times 1$$

STEP-3

3. Ash

The residual coal in crusible in (2) is the heated without lid in muffle furnace at 700±50°C for 1/2 hour. Then crusible is taken out, cooled & weighed.

$$\% \text{ of Ash} = \frac{\text{Wt. of ash left}}{\text{Wt. of Coal sample taken}} \times 100$$

STEP 4

4. FIXED CARBON

% of fixed Carbon

$= 100 - \%$ of (M + VM + Ash)

~~= Wt. of Ash left × 100 / wt of coal sample taken~~

Importance of Proximate Analysis-

1. **Moisture** - Moisture lowers the effective calorific value of coal.

2. **Volatile Matter** - A high volatile matter containing coal burns with a long flame, high smoke and low calorific value. Hence lesser the volatile matter better the rank of coal.

3. **Ash** :- It reduces the calorific value of coal.

4. **fixed Carbon** - Higher the percentage of fixed carbon, greater the calorific value & quality of coal.

(ii) Ultimate Analysis

In Ultimate Analysis following determinations takes place -

Ultimate Analysis

1. % of C & H

About 1-2 gm of accurately weighed coal sample is burnt in a current of oxygen in a combustion apparatus. C, and H are converted into CO_2, & H_2O respectively and are absorbed in KOH & $CaCl_2$ tubes respectively. The increase in weight of these are determined.

$$\% \text{ of } C = \frac{12}{44} \times \frac{\text{Increase in wt. of KOH tube}}{\text{weight of coal sample taken}} \times 100$$

$$\% \text{ of } H = \frac{2}{18} \times \frac{\text{Increase in wt. of } CaCl_2 \text{ tube}}{\text{weight of coal sample taken}} \times 100$$

2. % of Nitrogen

(Kjeldahl's method)

About 1 gm of accurately weighed powdered coal is heated with conc. H_2SO_4 along with K_2SO_4. Now it is treated with excess of KOH and liberated Ammonia then absorbed in known volume of standard Acid solution. The Unused Acid then determined by back titration.

$$\% \text{ of Nitrogen} = \frac{1.4 \, \text{Vol. of Acid used} \times \text{Normality}}{\text{weight of Coal sample taken}}$$

3. % of Sulphur

After Combustion Sulphur is converted into Sulphate. It is treated with Barium chloride, then $BaSO_4$ is precipitated.

$$\% \text{ of sulphur} = \frac{32}{233} \times \frac{\text{wt. of } BaSO_4}{\text{wt. of coal sample taken}} \times 100$$

4. % of oxygen

Percentage of O = 100 − (% of C+H+S+N+Ash)

* % of Ash will be determined as in proximate Analysis

Eng. chemistry (RAS-102)

Lecture NO-40

(Numericals on Analysis of Coal).

* A sample of Coal was analyzed for the Content of moisture, volatile matter and ash from following data, calculate the percentage of the above quantities.

(i) Weight of Coal taken = 2.5 gms

(ii) Weight of coal after heating at 100°C = 2.365 gms.

(iii) Weight of coal after heating covered crusible at 950±20°C = 1.165 gm.

(iv) constant weight obtained at the end of experiment = 0.460 gms.

Solⁿ

$$\% \text{ of Moisture} = \frac{\text{Loss in weight}}{\text{Weight of coal sample}} \times 100$$

$$= \frac{(2.5 - 2.365)}{2.5} \times 100$$

$$= \frac{0.185}{2.5} \times 100$$

$$\boxed{\text{Moisture} = 5.4\%}$$

$$\% \text{ of volatile Matter} = \frac{\text{Loss in wt. due to volatile Matter}}{\text{Weight of coal taken}} \times 1$$

$$= \frac{2.365 - 1.165}{2.5} \times 100$$

$$= 48\%$$

$$\% \text{ of Ash} = \frac{\text{Wt. of ash left}}{\text{Wt. of Coal taken}} \times 100$$

$$= \frac{.460}{2.5} \times 100 = 18.4\%$$

Lecture NO-43

Calorific Value & Determination of calorific value (Bomb calorimeter)

Calorific value -

"The total quantity of heat liberated, when a unit mass (or volume) of fuel burnt completely."

Calorific value is of two types -

(i) Higher or Gross Calorific value.
(ii) Lower or Net Calorific Value.

(i) **Higher or Gross calorific value (GCV)** - "The total amount of heat produced, when unit mass/volume of the fuel has been burnt completely and the products of combustion have been cooled to room temperature."

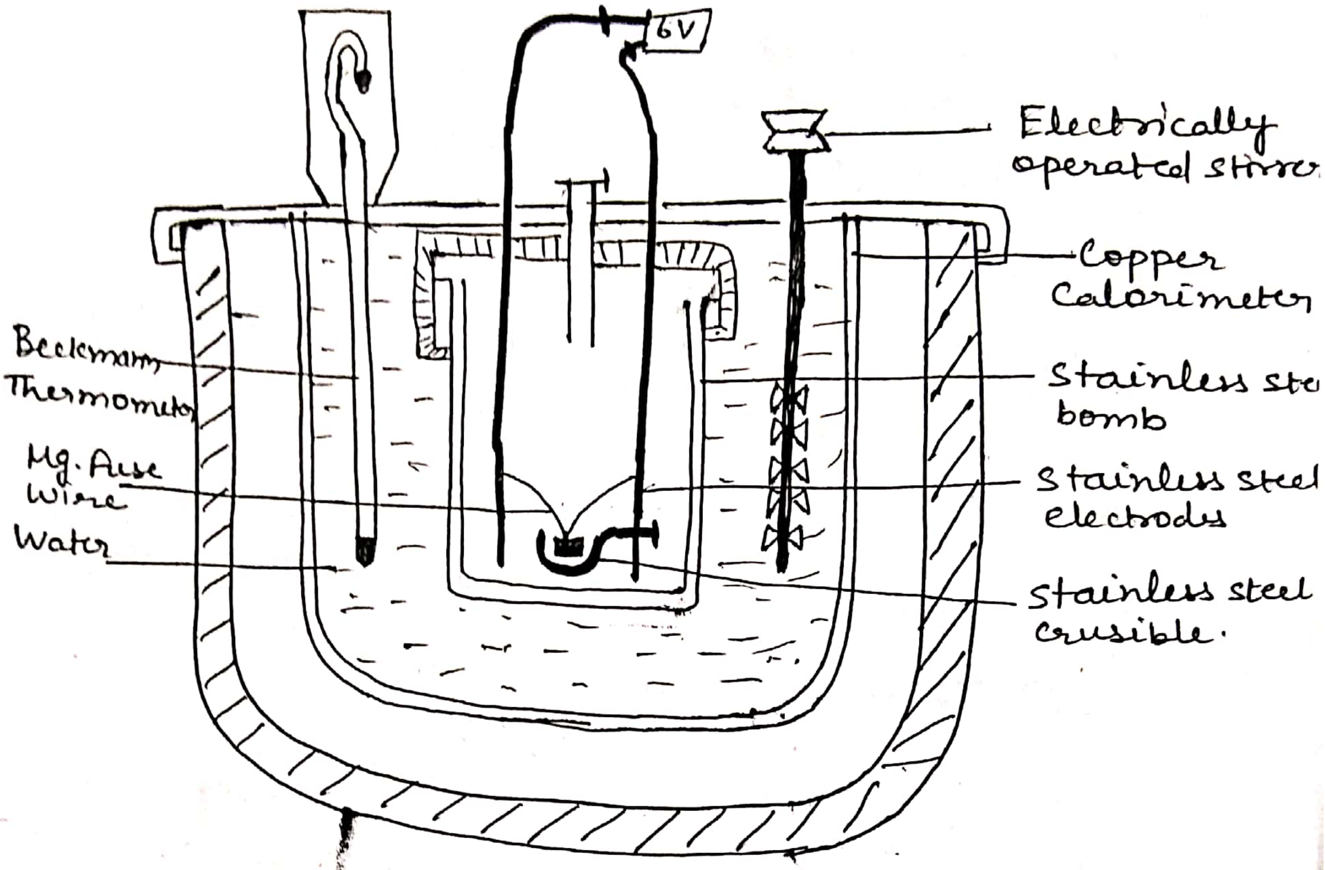
(ii) **Lower or Net Calorific Value (LCV)** - "The net heat produced, when unit mass/volume of the fuel burnt completely and products are permitted to escape."

LCV = HCV - Latent heat of Water Vapour formed
= HCV - Mass of hydrogen × 9 × Latent heat of steam.

Units of Calorific value -

(1) **Calorie** - Calorie is the amount of heat required to raise the temperature of water (1gm) through one degree centigrate.

(2) **Kilo Calorie** - is the amount of heat required to raise the temperature of 1 kg. water up to 1°C.



Bomb-calorimeter

Working - A known mass of the given fuel is ~~taken~~ in an clean crusible. The crusible is then supported over the ring. A fine magnesium wire, touching the fuel sample, is then stretched across the electrodes. The bomb lid is tightly screwed and bombfilled with oxygen to 25 atmospheric pressure. The bomb is then lowered into copper calorimeter, containing a known mass of water. The stirrer is worked and initial temperature of water is noted. The electrodes are then connected to 6-V battery and circuit completely. The sample burns and heat is liberated. Uniform stirring of water is continued and maximum temperature attained is recorded.

* Question

* How will you calculate calorific value of a solid fuel, Explain briefly.

Calculations-

Let x = mass of fuel sample taken in gm.

W = mass of water in calorimeter

w = water equivalent in g of calorimeter, stirrer, thermometer, bomb etc.

t_1 = initial temperature of water.

t_2 = final (maximum) temperature of water

L = higher calorific value in cal/g.

Heat liberated by burning of fuel = xL

heat absorbed by water and apparatus = $(W+w)(t_2-t_1)$

heat liberated by the fuel = Heat absorbed by water

$$xL = (W+w)(t_2-t_1)$$

$$\boxed{HCV\,(L) = \frac{(W+w)(t_2-t_1)}{x}}$$ cal/g. or (kcal/g)

$$\boxed{LCV = HCV - 9H \times 587}$$ cal/g (or kcal/g)

Formula with corrections-

$$\boxed{L = \frac{(W+w)(t_2-t_1+C_C)-(C_A+C_F+C_{CT})}{x}}$$

where C_C = Cooling correction

C_A = Acid correction

C_F = fuse wire correction

C_{CT} = Cotton thread correction.

Eng. Chemistry (RAS-102) UNIT-4

Lecture NO-44

Numericals based on Calorific value -

* On burning 0.83 g of a solid fuel in a bomb Calorimeter, the temperature of 3500 g of water increased from 26.5°C to 29.2°C. Water equivalent of Calorimeter and latent heat of steam are 385.0 g and 587.0 Cal/g respectively. If the fuel contains 0.7 % hydrogen, calculate its gross and net calorific value.

Sol^n $x = 0.83$ gm $t_1 = 26.5°C$ $t_2 = 29.2°C$

$W = 3500$ gm $w = 385$ $H = .7\%$

Latent heat of steam $= 587$

$$HCV\ (GCV) = \frac{(W+w)(t_2-t_1)}{x}$$

$$= \frac{(3500+385)(29.2-26.5)}{.83}$$

$$= 12{,}637\ \text{Cal/g}$$

$$LCV\ (NCV) = GCV - 0.09H \times \text{Latent heat of steam}$$

$$= 12637 - 0.09 \times .7 \times 587$$

$$= 12601\ \text{cal/g}$$

* The following data is obtained in bomb calorimeter experiment:

Weight of crucible = 3.649 gm.

Weight of crucible + fuel = 4.678 gm.

Water equivalent of Calorimeter = 570 gm. (w)

Water taken in calorimeter = 2200 gm. (W)

Obseved rise in temperature = 2.3°C (t_2-t_1)

Cooling correction = 0.047°C (C_c)
Acid correction = 62.6K. (C_A)
fuse wire correction = 3.8 K. (C_F)
Cotton thread correction = 1.6 Cal. (C_{CT})
Calculate the gross and net calorific value of fuel; if fuel contains 0.5% H.

Sol^n

$$x = 4.678 - 3.649 \text{ gm.}$$

$$x = 1.029 g$$

$$HCV = \frac{(W+w)(t_2 - t_1 + C_c) - (C_A + C_F + C_{CT})}{x}$$

$$= \frac{(2200+570)(2.3+0.47) - (62.6+3.8+1.6)}{1.029 \text{ gm}}$$

$$= 6251.88 \text{ Cal/gm.}$$

$$NCV = HCV - .09 \times H \times \text{Latent heat of steam.}$$

$$= 6251.88 - .09 \times .5 \times 587$$

$$= 6251.88 - 26.415$$

$$= 6225.46 \text{ Cal/gm.}$$

HCV = 6251.88 Cal/g
LCV = 6225.46 Cal/gm

Eng. chemistry (RAS-102) UNIT-4

Lecture-45

Determination of calorific value (Dulong's Method)

According to Dulong's formula

$$\boxed{HCV = \frac{1}{100}\left[8080C + 34500\left(H - \frac{O}{8}\right) + 2240S\right] \text{ Kcal/k}}$$

$$\boxed{LCV = HCV - .09 \times H \times \text{Latent heat of steam}}$$

where all elements, C, H, O, S are in %, their calorific values are

C = 8080 Kcal/kg.
H = 34500 Kcal/Kg.
S = 2240 kal/kg.

* Calculate the gross and net calorific value of coal having the following compositions, Carbon = 85%, hydrogen = 8%, Nitrongen = 2%, ash = 4%, Latent heat of steam = 587 Cal/g; S = 1%

Sol

Solⁿ

$$HCV \text{ or } (GCV) = \frac{1}{100}\left[8080C + 34500\left(H - \frac{O}{8}\right) + 2240S\right] \text{ Kcal/kg.}$$

C = 85%. H = 8%; $O = 100 - (C + H + N + \overset{+S}{ash})\%$
S = 1%

$O = 100 - (85 + 8 + 2 + 4 + 1)$

$O = 0\%$

$$GCV = \frac{1}{100}\left[8080 \times 85 + 34500\left(8 - \frac{0}{8}\right) + 2240 \times 1\right]$$

$$= 9650.4 \text{ Kcal/Kg.}$$