LECTURE NOTES

SUBJECT- ENGG CHEMISTRY BT101

UNIT NO-1

LECTURE NO -1

UNIT-1

Water -Analysis & Its Industrial Applications treatment

Water is Nature's most wonderful, Abundant and useful compound. For the Existence of the human Beings, animals and plants water is rated to be of the greatest importance without food, human can survive for a number of days, but water is such an essential that without it one can't survive.

Water is not only essential for the lives of animals and plants but also occupies a unique position in industries, probably, its most important age as an engineering material is the steam generation.

Classification of water

Water is classified into two categories depending upon its behavior towards soap solution

There are: soft and hard water

(a) Soft water : water which produces lather with soap solution easily is called soft water e.g. Distilled water and rain water
(b) Hard water : water which does not produce lather with soap solution easily is called hard water e.g. river water sea water tap water

SOURCES OF WATER

The main sources of water are:

(i) Surface water. It includes flowing water (streams and rivers) and still water (lakes , ponds and reservoirs) .

(ii) Underground water. It includes water from wells and springs.

(iii) Rain water.

(iv) Sea water.

LECTURE NO -2

IMPURITIES IN WATER

The following types of impurities are present in water:

(i) Suspended impurities . These impurities impart turbidity, colour and odour to water. It may be inorganic (clay and sand) or organic (oil globules, vegetable and animal matter) in nature.

(ii) Colloidal impurities. Products from organic waste, finely divided silica and clay etc. are colloidal impurities.

(iii) Micro - Organisms. They include bacteria, fungi and algae. Many micro - organisms make water unfit for human consumption. They cause various diseases. These disease - producing micro - organisms are introduced in to water by animal or vegetable waste through sewage flowing in to the river.

(iv) Dissolved impurities. The presence of dissolved salts like carbonates, bicarbonates, chlorides and sulphates of calcium, magnesium, iron and sodium make water hard. Dissolved gases like O_2 and CO_2 are also dissolved impurities.

Sources of Impurities in Water Following are the sources of impurities in water:

(a) Gases (e.g. O_2 and CO_2) are picked up from the atmosphere by rainwater .

(b) Decomposition of plant and animal residues introduce organic impurities in water.

(c) Water takes impurities when it comes in contact with ground, soil or rocks.

(d) Impurities are also introduced in water when it comes in contact with sewage or industrial waste.

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LECTURE NO -2

Hardness of Water:

Hardness in water is that characteristic, which prevents the lathering of soap. This is due to the presence of certain salts of Calcium, Magnesium and other heavy metals dissolved in it. A sample of hard water, when treated with soap does not produce lather, but on the other hand forms a white curdy precipitate. The precipitated is formed due to the formation of insoluble soaps of calcium and magnesium.

$2C_{17}H_{35}COONa + CaCl_2 \longrightarrow (C_{17}H_{35}COO)_2Ca + 2\ NaCl$

Sodium Stearate + hardness calcium Stearate (insoluble)

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

TYPES OF HARDNESS

Temporary hardness : Temporary hardness is caused by the presence of dissolved bicarbonates of calcium, magnesium and other heavy metals and carbonates of iron This can be removed by boiling.

Salts of mainly responsible for temporary hardness are $Mg(HCO_3)_2$ and $Ca(HCO_3)_2$.

$$Ca(HCO_3)_2 \longrightarrow CaCO_3 + H_2O + CO_2$$

Calcium bicarbonates

$$Mg(HCO_3)_2 \xrightarrow{\text{Heating}} Ma(OH)_2 + 2CO_2$$

Magnesium bicarbonates

Permanent hardness :

Permanent hardness is due to presence of chlorides & sulfates of dissolved calcium, magnesium, iron & other heavy metals.

The salts responsible for permanent hardening are $CaCl_2$, $MgCl_2$,$CaSO_4$, $MgSO_4$, $FeSO_4$, $Al_2(SO_4)_3$. Permanent hardness cannot be removed by boiling. This is also known as non –carbonate or non – alkaline hardness.

The sum of temporary and permanent hardness is referred as total hardness of water. Although hardness of water is never presence in the form of $CaCO_3$ as it is insoluble in water hardness of water is conveniently expressed in terms of equivalents of $CaCO_3$.

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The hardness is expressed in terms of equivalent calcium carbonate.
The reason for choosing $CaCO_3$ as standard for report in hardness is ease in calculations on its molecular weight is exactly 100.

Units of Hardness :

1. **Parts Per Million (ppm)**

Parts of CaCO3 equivalent hardness per 106 parts of water.
1 ppm = 1 part of CaCO3 equivalent hardness in 106 parts of water.

2. **Milligrams per litre :- (Mg/l)**

Number of milli grams of Calcium Carbonate equivalent hardness present in 1 litre of water.

1 mg / L = 1 mg of $CaCO_3$ equivalent hardness present in 1 liter of water.
1 L = 1 Kg = 1000 g = 1000 x 1000 mg = 106mg.
1 mg /L = 1 mg of $CaCO_3$ eq. per 106mg of H2O = ppm

3. **Clarke's degree : (°cl)**

No. of grains (1/70000) of CaCO3 equivalent hardness per 70,000 parts of water.
1°Clarke = 1 grain of CaCO3eq hardness per gallon of water.
= 1 part of CaCO3of hardness per 70,000 parts of water.

4. **Degree French (°Fr)**

It is in the parts of CaCO3 eq hardness per 105parts of water.

Relation between various units of hardness:
1 ppm = 1 mg /L = 0.1 °Fr = 0.07°CL
1 mg /L = 1ppm = 0.1 °Fr = 0.07°CL
1 °cL = 1.433 °Fr = 14.3 ppm = 14.3 mg /L
1°Fr = 10 ppm = 10 mg /L = 0.7 °CL

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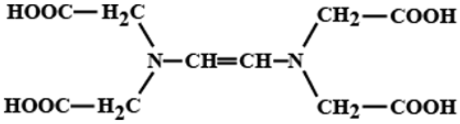
Estimation of hardness of water by EDTA Method:

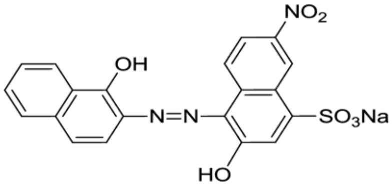
This is a complexometric method. Ethylene diamine tetra acetic acid (EDTA) in the form of its sodium yields the anion.



Ethylene diamine tetra acetic acid (EDTA)

Principle of EDTA titrations:

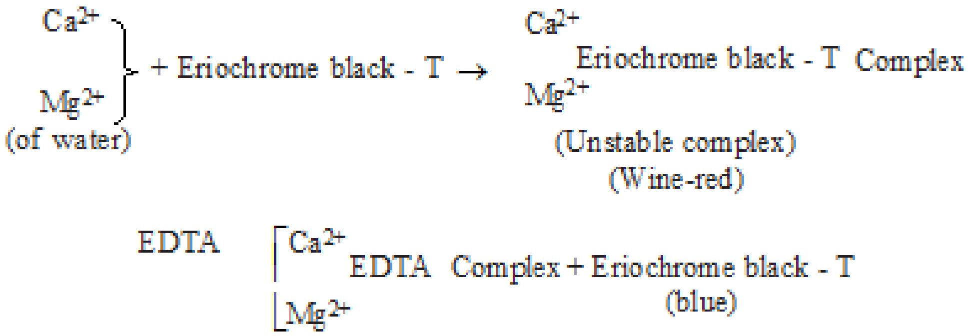
The quick, complete and 1:1 interaction of metal ions with EDTA leading to the formation of stable complex is the basis for complex metric titrations.



Erochrome Black -T

Theory: The hard water is buffer to a pH value of 10 using NH_4OH-NH_4Cl buffer and few drops of EBT indicator solution are added. EBT forms a weak complex with metal ions that has a wine-red colour.

During the course of titration of water sample against EDTA, first EDTA combines with free Ca2+ or Mg2+ ions to give very stable and colour less metal-EDTA Complex. After all the free metal ions are consumed, the next drop of added EDTA solution displaces the indicator to form Metal-EBT complex.



$$\left.\begin{matrix} Ca^{2+} \\ Mg^{2+} \end{matrix}\right\} + \text{Eriochrome black - T} \rightarrow \begin{matrix} Ca^{2+} \\ Mg^{2+} \end{matrix} \text{Eriochrome black - T Complex}$$

(of water) (Unstable complex) (Wine-red)

$$\text{EDTA} \quad \left[\begin{matrix} Ca^{2+} \\ Mg^{2+} \end{matrix}\right. \text{EDTA Complex} + \text{Eriochrome black - T}$$

(blue)

At the equivalence point, there is change in colour from wine-red to blue.

Procedure:

Step – 1: Standardisation of EDTA solution:

The burette is filled with EDTA solution after washing and rinsing. Pipette out 50mL of standard hard water (1mL of it must contain 1mg of $CaCo_3$) into a 250mL conical flask, 10mL of buffer solution and 2-3 drops of EBT indicator are added and titrated against EDTA solution until the wine-red colour changes to blue. Let the volume of EDTA solution consumed be V_1 mL.

Step – 2: Determination of total hardness of water:

As per the same procedure (Step-1), 50mL of the unknown water sample is titrated against EDTA. Let the volume of EDTA solution consumed be V_2 mL.

Step -3: Determination of permanent hardness of water:

250mL of the water sample is taken in a 500mL beaker and boiled it till the volume is reduced to about 50mL. [The step causes all the bicarbonates to decompose respectively into insoluble $CaCO_3$ and $Mg(OH)_2$]. Filter and wash the precipitate with distilled water and quantitatively collect the filtrate and washings in a 250mL conical flask and made up the volume to 250mL with distilled water. 50mL of this water sample is titrated against EDTA solution as in Step-1. Let the volume of EDTA solution consumed be
V_3mL.

Calculations:

Step – 1: Standardisation of EDTA Solution:
V_1mL of EDTA = 50mL of standard hard water
= 50mg of $CaCO_3$ (1mL contains 1mg of $CaCO_3$)
1mL of EDTA = 50 / V_1 mg of $CaCO_3$ equivalent hardness.

Step -2: Determination of total hardness of water:
50mL of unknown hard water sample = V_2mL of EDTA
= V_2 x 50 / V_1mg of $CaCO_3$ eq.
Step-3: Determination of permanent hardness of water:
50mL of boiled water = V_3mL of EDTA
=V_3 x 50/V_1mg of $CaCO_3$ eq.
Step-4: Determination of temporary hardness:

Alkalinity

The alkalinity of water is attributed to the presence of the (i) caustic alkalinity (due to OH and CO^2 ions) , and (ii) temporary hardness (due to HCO , ions) . These can be estimated separately by titration against standard acid, using phenolphthalein and methyl orange as indicators.
The determination is based on the following reactions:

i) [OH] + [H +] → H_2O
ii) [$CO3^1$] + [H +] → [HCO3]
iii) [HCO3] + [H+] → $CO_2 + H_2O$

The titration of the water sample against a standard acid upto Phenolphthalein [P] end point marks the completion of reaction 1 and 2 only and the titration of water sample against standard acid to methyl orange [M] end point marks . The completion of reaction 1 , 2 and 3. Hence the total amount of acid used represent the total alkalinity.
P = OH^- and ½ $CO_2{}^{2-}$
M = OH^- , CO_2^{2-} and HCO_3^-
with respect to the constituents (ions) causing alkalinity in water the following situations may present

1. OH^-
2. $CO\ 3^{2-}$
3. HCO_3^-
4. OH- + CO_3^{2-}
5. $CO_3{}^{2-} + HCO_3{}^-$

   The possibility of OH ion and HCO_3- , ion together is ruled out because, they combine to form CO_2^2- ions .
   OH + HCO_3^- → CO_3^2- + H_2O
   On the basis of same reason, all the three ions cannot exit together

Discussion

1. When P = M , alkalinity is due to OH ion
   Total Alkalinity = M
2. When P = $\frac{1}{2}$ M , alkalinity is due to CO_2^2 ion
   Total Alkalinity = 2P
3. When P = 0 , alkalinity is due to HCO_3^- , ion
   Total Alkalinity = M

4. When $P > \frac{1}{2}M$, alkalinity is due to OH & CO_2^{2-} ion
Total Alkalinity = OH = 2P - M
$CO^2 = 2 (M - P)$

5.When P < ½ M , alkalinity is due to CO_2 & HCO
Total Alkalinity = $CO_2^2 = 2P$
$HCO_2 = M - 2P$

$OH + HCO3 + CO_2 \rightarrow CO3^{2-} + H_2O$

Procedure

Pipette out 100 ml of water sample in a clean titration flask . Add to it 2 to 3 drops of a phenolphthalein indicator . Run in N / 50 H_2SO4 (from a burette) , till the pink color is just discharged . Then to the same solution , add 2 or 3 drops of methyl orange . Continue the titration, till the pink colour reappears.

Calculations

i) 100 ml of water up to phenolphthalein end point = V_1 ml of N / 50 HCI
$N_1V_1 = N_2V_2$
$N_1 x 100 = N / 50 x V_2$
$N_2 = N / 50 x V_1 / 1000$

$= V_1 / 5000 \; N_2 = V_1 / 5000 x 1000 \times 50 \; Np = 10V_1$ mg / l

i) 100 ml of water up to methyl orange end point = $(V_1 + V_2)$ ml of N / 50 HCI
$N_2V_2 = N3V3$
NM. X 100 N / 50 $(V_1 + V_2)$ = NM = N / 5000 $(V_1 + V_2)$ 1L (1000 ml) = $(V_1 + V_2) / 5000 x 1000$

For CaCO3 equivalent = $(V_1 + V_2) \times 1000 x 50/5000 = 10 (V_1 + V_2)$ mg / l

The following values give the type of hard water:

Hardness mg/lit as $CaCO_3$	Hardness (mg/lit Type of water
0 - 75	Soft water
75 - 150	Moderately hand water
150 - 300	Hard water
above 300	Very hard water

LECTURE NOTES

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UNIT NO-2

LECTURE NO -1

BOILER TROUBLE

For steam general, Boilers are most invariably employed. If the hard water is fed directly to the boilers there arise many troubles. In boilers, water evaporates continuously and the concentration of the dissolved salts increases progressively.

When the concentration of the dissolved salts reach saturation point, they are thrown out of water in the form of precipitates on the inner walls of the boiler.

Sludge:

It is a soft, loose and slimy precipitate formed within the boiler. It is formed at colder portions of the boiler and collects in the system where the flow rate is slow or at bends. It can be removed very easily by a wire brush. It is formed by the substances that have greater solubility values in hot water than in cold water.
Ex: $MgCO_3$, $MgCl_2$, $CaCl_2$, $MgSO_4$ etc.

Disadvantages:
1) Sludge are poor conductors of heat, hence there is wastage of portion of the heat generated.
2) If sludge is formed along with scales, then sludge gets entrapped in the scales and both get deposited as scales.
3) Excessive sludge formation disturbs the working of the boiler.

Preventive measures:

1) By using softened water
2) By frequently ‘blow-down operation’ (drawing off a portion of the concentrated water).

(a) Sludge in boiler (b) Scale in boiler

Sludges and scales in boiler

Scales:

Definition: Scales are hard deposits firmly sticking to the inner surfaces of the boiler.
The scales are difficult to remove, even with the help of hammer and

chisel and are the main source of boiler troubles.

Formation: The scales may be formed inside the boiler due to –

1) Decomposition of calcium bicarbonate:

$Ca(HCO_3)_2 \longrightarrow CaCO_3 \downarrow + H_2O \uparrow + CO_2$
Scale

The scale consisting of mainly $CaCO_3$ is soft and is the main cause of scale formation in low-pressure boilers. Whereas in high-pressure boilers, $CaCO_3$ is soluble due to the formation of $Ca(OH)_2$.

$CaCO_3 + H_2O \longrightarrow Ca(OH)_2 + CO2 \uparrow$
Soluble

2) Deposition of calcium sulphate:

The solubility of $CaSO_4$ in water decreases with increase in temperature.
$CaSO_4$ is soluble in cold water and almost insoluble in hot water [may be due to increased ionization at high temperature so Ksp<Kionic product & less availability of water molecules for salvation at high temperature.] $CaSO_4$ gets precipitated as hard scale on the hotter parts of the boiler. This type of scale causes troubles mainly in high-pressure boilers. $CaSO_4$ scale is quite adherent and difficult to remove even with the help of hammer and chisel.

3) Hydrolysis of magnesium salts:

Dissolved magnesium salts get hydrolysed forming magnesium hydroxide precipitate that forms a soft type of scale.

$MgCl_2 + 2H_2O \longrightarrow Mg(OH)_2 \downarrow + 2HCl \uparrow$
Scale

4) Presence of silica:
Even if a small quantity of SiO_2 (silica) is present. It may deposit as calcium or magnesium silicate ($CaSiO_3$ and / or $MgSiO_3$). These deposits adhere very firmly on the inner side of the boiler surface and are very difficult to remove. One important source of silica in water is the sand filter.

Disadvantages:

1) Wastage of Fuel: Scales have low thermal conductivity so the rate of heat transfer from boiler to inside water is greatly reduced. In order to provide a steady supply of heat to water, excessive or, over heating is done and this causes increase in the consumption of fuel. The wastage of fuel depends on the thickness and the nature of scale.

Ex:

Thickness Of scale(mm)	0.325	0.625	1.25	2.5	12
Wastage of fuel	10%	15%	50%	80%	150%

2) Lowering of boiler safety: Over-heating of boiler is done in order to maintain a steady supply of steam due to the formation of scales. This makes the boiler material softer and weaker. This causes the distortion of the boiler tube and also makes the boiler unsafe.
3) Decrease in efficiency: Scales may deposit in the valves and condensers of the boiler and choke them partially. This results in decrease in the efficiency of the boiler.
4) Danger of explosion: When thick scales crack due to uneven expansion, the water comes suddenly in contact with over-heated portion and large amount of steam is formed instantaneously. This results in the development of sudden high-pressure that may cause explosion of the boiler.

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LECTURE NO -3

Removal of scales:

If the scales are loosely adhering, they can be removed by scraper or piece of wood or wire brush.

- If the scales are brittle, they can be removed by thermal shocks i.e, heating the boiler and then suddenly cooling with cold water.

- If the scales are loosely adhering, they can be removed by frequent blow-down operation.

- If the scales are adherent and hard, they can be removed by adding chemicals.

Ex: a) $CaCO_3$ scales can be removed by dissolving in 5-10% HCl.
b) $CaSO_4$ scales can be removed by adding EDTA, since the Ca-EDTA complex is highly soluble in water.

Prevention of scale formation:

1) External treatment: The treatment includes efficient ‘softening of water’ (removing hardness-producing constituents of water)
2) Internal treatment: In this process, an ion is prohibited to exhibit its original character by ‘Complexing’ or converting into other more stable salt by adding appropriate reagent.

a) Colloidal conditioning b) Phosphate conditioning
c) Carbonate conditioning d) Calgon conditioning
e)Treatment with sodium aluminate ($NaAlO_2$)
f)Electrical conditioning g)Radioactive conditioning
h) Complexometric method.

Differences between sludges and scales:

Sludges	Scales
1. Sludges are soft, loose and slimy precipitate 2. Sludges are non-adherent deposits and can be removed easily. 3. Sludges are formed by substances like $CaCl_2$, $MgCl_2$,$MgSO_4$,$MgCO_3$,etc, 4. Formed at comparatively colder portions of the boiler 5. Decrease the efficiency of boiler but are less dangerous 6. Can be removed by blowdown operation.	1. Scales are hard deposits 2. Scales stick firmly to the inner surface of boiler and are very difficult to remove. 3. Scales are formed by substances like $CaSO_4$, $Mg(OH)_2$ etc., 4. Generally formed at heated portions of the boiler. 5. Decrease the efficiency of boiler and chances of explosions are also there. 6. Cannot be removed by blowdown operation.

For steam general, Boilers are most invariably employed. If the hard water is fed directly to the boilers there arise many troubles such as

1. **Scale & Sludge formation**:

Scale is hard deposits which stick very firmly to the inner surfaces of the boiler sludge is soft loose and slimy precipitate formed within the boiler

2. **Caustic Embrittlement**: (Inter crystalline cracking of boiler metal)

Caustic embrittlement is the phenomenon during which the boiler material becomes brittle due to the accumulation of caustic substances. This type of boiler corrosion is caused by the use of highly alkaline water in the high pressure boiler.
During softening by lime-soda process, free Na_2CO_3 is usually present in small portion in the softened water.
In high pressure boilers, Na_2CO_3 decomposes to give NaOH and CO_2. The NaOH produced makes the boiler water “Caustic”.

$$Na_2CO_3+H_2O \longrightarrow 2NaOH + CO_2$$

$$Fe + 2\,NaOH \longrightarrow Na_2FeO_2 + H2 \uparrow$$

(Soluble) (Insoluble)

This caustic water flows into the minute hair-cracks, present in the inner side of the boiler, by capillary action. On evaporation of water, the concentration of dissolved caustic soda increases progressively that attacks the surrounding area, there by dissolving iron of boiler as sodium ferrate.

Embrittlement arises due to the setting up of a concentration cell.

With the iron surrounded by dilute NaOH is acting as the cathode
Where as the iron surrounded by conc.NaOH is acting as anode. The anode in the anodic part gets dissolved or corroded.

Prevention:

Caustic embrittlement can be prevented

i) By using sodium phosphate as softening reagent instead of Na_2CO_3 in external treatment of boiled water.

ii) By adding lignin or tannin to boiler water that blocks the hair-cracks in the boiler walls thereby preventing infiltration of caustic soda solution in these areas.

iii) By adding Na_2SO_4 to boiler water:

Na_2SO_4 blocks hair-cracks, thereby preventing infiltration of caustic soda solution in these. It has been observed that caustic cracking can be prevented, if Na2SO4 is added to boiler water so that the ratio. [Na2SO4] / [NaOH] is kept as 1:1, 2:1 and 3:1 in boilers working respectively at pressures upto 10, 20 and > 20 atmospheres.

3. **Boiler Corrosion**:

Boiler corrosion is ‘decay’ or ‘disintegration’ of boiler material by either chemical or electrochemical reaction with dissolved gases. It may be due to three major reasons:

Reasons for boiler corrosion:

1)Dissolved oxygen: This is the most usual corrosion causing factor., water
usually contains about 8ppm of dissolved oxygen at room temperature. Dissolved oxygen reacts with iron of boiler in the presence of water and under prevailing high temperature to form ferric oxide (rust).

$$4Fe + 2H_2O + O_2 \longrightarrow \underset{\text{Ferrous hydroxide}}{4Fe(OH)_2 \downarrow}$$

$$4Fe(OH)_2 + O2 \longrightarrow \underset{\text{Rust}}{2[Fe_2O_3.2H_2O] \downarrow}$$

Removal of dissolved oxygen:

i) By adding calculated quantity of hydrazine or, sodium sulphite or, sodium sulphide

Adding Hydrazine

$$N_2H_4+O_2 \longrightarrow N_2+2H_2O$$

This method results in inert gas and pure water, and has no side effects. So it is preferred.

Adding Sodium Sulphite

$$2Na_2SO_3+O_2 \longrightarrow 2Na_2SO_4$$

This method results in other precipitates which can have some side effects. So this method is less preferred

$$Na_2S+2O_2 \longrightarrow Na_2SO_4$$

ii) By mechanical deaeration: The process consists of spraying water over preheated perforated plates stacked in a tower. Removal of dissolved oxygen is ensured by applying high temperature and vacuum.

1. This is based on the principle that at high temperature, low pressure and high exposed area, the solubility of gases in water is decreased. So, the gases can be expelled easily.
2. Here, the water is fed into the mechanical de aerator which is provided with vacuum pump, heaters and perforated plates.
3. The out coming water will be free from dissolved gases.

2 Carbon dioxide:

Two sources of CO_2 in boiler water are –

a) Dissolved CO_2 in raw water and
b) **CO_2** formed by decomposition of bicarbonates.

$$Mg(HCO_3)_2 \longrightarrow MgCO_3 + H_2O + CO_2$$

In the presence of water, CO_2 forms carbonic acid that has a corrosive effect on the boiler material like any other

$$H_2O + CO_2 \longrightarrow H_2CO_3$$

Removal of CO_2:

i) By adding calculated quantity of ammonium hydroxide

$$CO_2 + 2NH_4OH \longrightarrow (NH_4)_2CO_3 + H_2O.$$

ii) Mechanical de-aeration along with oxygen

iii) By filtering water through line stone

$$CaCO_3+H_2O+CO_2 \longrightarrow Ca(HCO3)_2$$

But this method increases hardness.

5) ***Mineral acids***: Water containing dissolved magnesium salts ($MgCl_2$)

liberate acids on hydrolysis.

$$MgCl_2 + 2H_2O \longrightarrow Mg(OH)_2 + 2HCl$$

The liberated acid reacts with iron material of the boiler to form ferrous hydroxide which in turn is converted to rust.

$$Fe + 2HCl \longrightarrow FeCl_2 + H_2$$
$$FeCl_2 + 2H_2O \longrightarrow Fe(OH)_2 + 2HCl$$

$$2Fe(OH)_2 + O_2 \longrightarrow Fe_2O_3.\ H_2O$$

Thus, a small amount of HCl may cause extensive corrosion since HCl is produced in a chain-like manner. Presence of even a small amount of $MgCl_2$ cause corrosion of iron to a large extent.

Disadvantages of corrosion:

1) Shortening of boiler life.
2) Leakage of the joints and revents.
3) Increased cost of repairs and maintenance.

Priming and foaming:

Priming:

When steam is produced rapidly in the boilers, some droplets of the liquid water are carried along with steam. The process of ‘wet-steam’ formation is known as ‘priming’

Priming is caused by –

1) The presence of large amount of dissolved salts
2) High steam velocities.
3) Sudden boiling
4) Improper boiler design
5) Sudden increase in steam-production rate.

Priming can be avoided by-

1) Controlling rapid change in steaming velocities.
2) Proper design of boilers.
3) Ensuring efficient softening
4) Filtration of the boiler-water carried over to the boiler
5) By blowing off sludges or, scales from time to time.
6) By maintaining low water levels in boilers.

Foaming:

The formation of small but persistent foam or bubbles at the water surface in boilers, which do not break easily. Foaming is caused by the presence of an oil and alkalis in boiler-feed water

1. Foaming can be avoided by
   1) The addition of anti-foaming agents like caster oil.
   2) The removal of foaming agent (oil) from boiler water

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UNIT NO-2

LECTURE NO -5

The objective of boilers feed water treatment is firstly to avoid trouble in the boiler plant and secondly to obtain steam of sufficient purity for the steam turbine.

There are two methods of treatment of water

1. External treatment

2. Internal Treatment.

EXTERNAL TREATMENT:

1. LIME-SODA PROCESS:

In this Method, the soluble calcium and Magnesium salts in water are chemically converted into **insoluble Compounds by** adding calculated amounts of lime Ca $(OH)_2$ and soda Na_2CO_3 calcium carbonate $CaCO_3$ and magnesium hydroxide Mg $(OH)_2$. So Precipitated, are filtered off.

A) COLD LIME-SODA PROCESS:

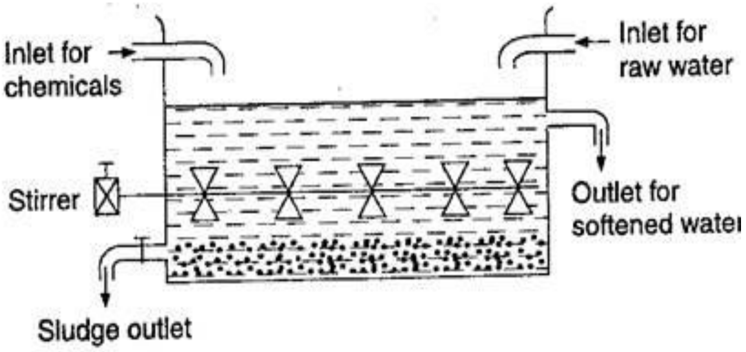
In this Method, Calculated quantity of chemical (lime and soda) is mixed with water at room temperature. At room temperature, the precipitates formed are finely divided, so they do not settle down easily and cannot be filtered easily. Consequently, it is essential to add small amounts of coagulants (Like Alum, aluminum sulphate, sodium aluminate, Etc.)Which hydrolyse to flocculent, gelatinous precipitate of aluminium hydroxide, and entraps the fine precipitates. Use of sodium aluminates as coagulant, also helps the removal of silica as well as oil, if present in water. Cold L-S process provides water, containing a residual hardness of 50 to 60 ppm.

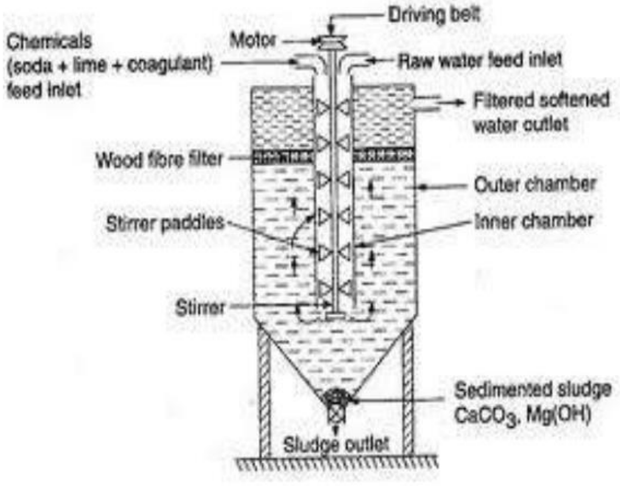
$$NaAlO_2 + 2H_2O \longrightarrow NaOH + Al(OH)_3$$

$$Al_2(SO_4)_3 + 3\,Ca(HCO_3)_2 \longrightarrow 2Al(OH)_3 + 3\,CaSO_4 + 6CO_2$$

Method:

Raw water and calculated quantities of chemicals (Lime+soda+coagulant) are fed from the top into the inner vertical circular chambers, fitted with a vertical rotating shaft carrying a number of paddles , As the raw water and chemicals flow down there is a vigorous stirring and continuous mixing, whereby softening of water takes place. As the softened ware comes into the outer chamber of the lime the softened water reaches up. The softened water then passes through a filtering media (usually made of wood fibers) to ensure complete removal of sludge. Filtered soft water finally a flow out continuously through the outlet at the top sludge settling at the bottom of the outer chamber is drawn off occasionally.

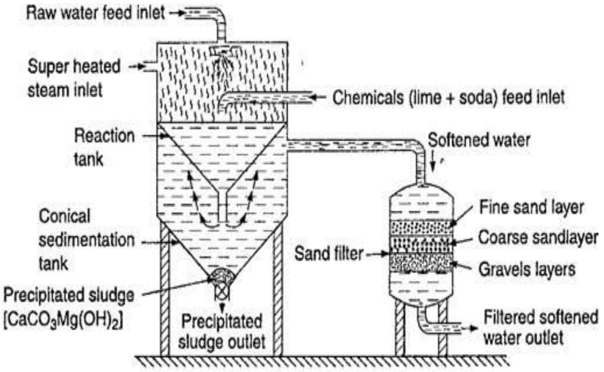




HOT LIME-SODA PROCESS:

Involves in treating water with softening chemicals at a temperature of 80 to 150 ^{0}C. Since hot process is operated at a temperature close to the boiling point of the solution, so (a) the reaction proceeds faster; (b) the softening capacity of hot process is increased to may fold; (c) the precipitate and sludge formed settle down rapidly and hence, no coagulants are needed;(d) much of the gases (Such as CO_2 and air) Driven out of the water;(e) Viscosity of softened water is lower, so filtration of water becomes much easier. This in-turn increases the filtering capacity of filters, and (f) Hot Lime-Soda Produces water of comparatively lower residual hardness of 15 to 30ppm.

Hot lime-soda plant consists essentially of three parts (a) a ‘reaction tank’ in which raw water, chemicals and steam are thoroughly mixed; (b) a ‘conical sedimentation vessel’ in which sludge settles down, and (c) a ‘Sand filter’ which ensures complete removal of sludge from the softened water.



Advantages of L.S.Process:

- (i) It is a very economical
- (ii) If this process is combined with sedimentation with coagulation, lesser amounts of coagulants shall be needed
- (iii) The process increased the pH value of the treated water, thereby corrosion of the distribution pipes is reduced
- (iv) Besides the removal of hardness, the quantity of minerals in the water are reduced
- (v) To certain extent, iron and manganese are also removed from the water.
- (vi) Due to alkaline nature of treated- water, amount of pathogenic bacteria’s in water is considerably reduced

Disadvantages of L.S.Process:

For efficient and economical softening, careful operation and skilled supervision is required

- (i) Disposal of large amounts of sludge (insoluble precipitate) poses a problem. However, the sludge may be disposed off in raising low-lying areas of the city
- (ii) This can remove hardness only up to 15ppm, which is not good for boilers.

UNIT NO-2

LECTURE NO -6

2) ZEOLITE PROCESS:

Chemical structure of sodium zeolite may be represented as Na_2O_3, X SiO_2, YH_2O where x=2-10 and y=2-6. Zeolite is hydrated sodium alumino silicate, capable of exchanging reversibly its sodium ions for hardness, producing ions in water Zeolite are two types,

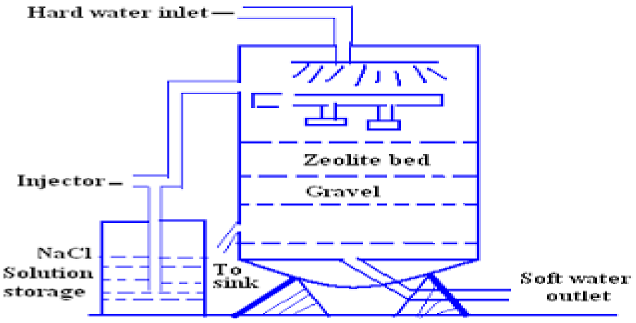
(i) Natural zeolites are non porous for Ex; Natrolite $Na_2Al_3O_3.4SiO_2.2H_2O$

(ii) Synthetic zeolites posses gel structure. Synthetic Zeolites posses higher exchange capacity than natural Zeolites

Process: - For Softening of water by Zeolite process, hard water is percolated at a specified rate through a bed of zeolite; kept in a cylinder. The Hardness causing ions (Ca^{+2}, Mg^{+2} etc.) are retained by the zeolite as CaZe and MgZe; while the outgoing water contains sodium salts. Reactions taking place during the softening process are

$$Na_2Ze + Ca(HCO_3)_2 \longrightarrow CaZe + 2NaHCO_3$$

$$Na_2Ze + Mg(HCO_3)_2 \longrightarrow MgZe + 2NaHCO_3$$



$$Na_2Ze + CaCl_2 \text{ (or } CaSO_4) \longrightarrow CaZe + 2NaCl \text{ (or } Na_2SO_4)$$

$$Na_2Ze + MgCl_2 \text{ (or } MgSO_4) \longrightarrow MgZe + 2NaCl \text{ (or } Na_2SO_4)$$

REGENERATION:

After Some time the zeolite is completely converted into calcium and magnesium Zeolites and it ceases to soften water i.e.; it gets exhausted. At this stage the supply of hard water is stopped and the exhausted zeolite is reclaimed by treating the bed with a concentrated NACL solution

$$CaZe \text{ (or } MgZe) + 2NaCl \longrightarrow Na_2Ze + CaCl_2 \text{ (or } MgCl_2)$$

The washings are led to drain and the regenerated zeolite bed thus obtained is used again for softening process

Limitations:

(i) If the supply of water is turbid in will clog the pores of zeolite led
(ii) Water contains large quantities of colored ions such as Mn^{+2} and Fe^{+2} they may be removed first because these ions produce Mn and Fe Zeolites ,which can't be easily regenerated
(iii) Mineral acids destiny the zeolite bed

ADVANTAGES:

(i) If removes the hardness almost completely
(ii) Equipment occupying a small space
(iii) Requires less time
(iv) It is quite clean

DISADVANTAGES:

(i) Treated water contains more sodium salts than in time soda process
(ii) The method only replaces Ca^{+2} and Mg^{+2} ions by Na+ ions leaves all the acidic ions

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LECTURE NOTES

SUBJECT- ENGG CHEMISTRY BT101

UNIT NO-2

LECTURE NO -7

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3) ION EXCHANGE PROCESS:

Ion exchange resins are insoluble, cross linked long chain organic polymers with micro porous structure, and the functional groups attached to the chains are responsible for the Ion –exchanging properties resigns containing acidic functional groups (-COO-,-SO_3H etc,) are capable of exchanging their H+ ions with other cat ions, which comes in their contact where as those containing basic functional groups(-NH2=NH,hydrochloride) are capable of exchanging their anions with other anions, which comes in their contact Ion exchange resins may be classified as

(i) Cat ion exchange resin(RH+) are mainly styrene-divinyl benzene copolymers, which on sulphonation or carboxylation, become capable to exchange their hydrogen ions with the cat ions in water
(ii) Anions exchange resins (ROH) are styrene-divinyl benzene or amine-formaldehyde, copolymers, which contains amino or quaternary ammonium or quaternary phosphonium or tertiary sulphonium groups as an integral part of the resin

matrix these after treatment with dilute. NaOH solutions become capable to exchange their OH-anions with anions

***PROCESS*:**

The Hard water is passed first through cat ion exchange column, which removes all the cations like Ca^{+2} etc, from it and equivalent amount of H+ ions released from this column to water, thus

$$2RH^{+} + Ca^{2+} \longrightarrow R_2Ca^{2+} + 2H^{+}$$

$$2RH^{+} + Mg^{2+} \longrightarrow R_2Mg^{2+} + 2H^{+}$$

After Cation exchange column, the hard water is passed through anion exchange column which removes all the anions like SO_4^{--}, Cl^{-} etc present in the water and equivalent amount of OH- ions are released from this column to water thus:

$$R'OH^{-} + Cl^{-} \longrightarrow R'Cl^{-} + OH^{-}$$

$$2R'OH^{-} + SO_4^{2-} \longrightarrow R'_2SO_4^{2-} + 2OH^{-}$$

$$2R'OH^{-} + CO_3^{2-} \longrightarrow R'_2CO_3^{2-} + 2OH^{-}$$

$H^{+}$and OH^{-} ions get combined to produce water molecule

$$H^{+} + OH^{-} \longrightarrow H_2O$$

The water coming out from the exchanger is deionized or demeneralised water

REGENRATION:

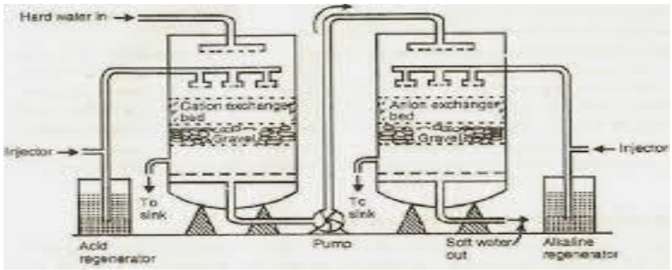
When capacities of cation and anion exchangers to exchange H+ and OH- ions respectively are lost, they are then said to be exhausted

The exhausted cat ion exchange column is regenerated by passing a solution of Diluted HCL Or Dilute H2so4. The regeneration can be represented as

$$R_2Ca^{2+} + 2H^{+} \longrightarrow 2RH^{+} + Ca^{2+}$$

The exhausted anions exchange column is regenerated by passing a solution of diluted NaoH. The regeneration can be represented as

$$R'_2SO_4^{2-} + 2OH^{-} \longrightarrow 2R'OH^{-} + SO_4^{2-}$$



Advantages:

(i) Process used to soften highly acidic or alkaline water
(ii) It produces water of very low hardness

DISADVANTAGES:

(i) The equipment is costly
(ii) If water contains turbidity out-out of the process is reduced

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LECTURE NOTES

SUBJECT- ENGG CHEMISTRY BT101

UNIT NO-2

LECTURE NO -8

INTERNAL TREATMENT:

In this process; an ion is prohibited to exhibit its original character by converting it into other more soluble salt by adding appropriate reagent. An internal treatment is accomplished by adding a proper chemical to the boiler water either to precipitate the scale forming impurities in the form of sludge, which can be removed by blow down operations, or to convert them into compounds, which will stay in dissolved form in water and they do not cause any harm .

Important Internal treatment methods are:

(i) **Colloidal conditioning:** In low pressure boilers, scale formation can be avoided by adding organic substances like Kerosene, tannin ,agar-Agar etc; which get coated over the scale firming precipitates, there by yielding coated non sticky and loose deposits

(ii) **Phosphate conditioning**: In High pressure boilers, scale formation can be avoided by adding sodium phosphate which reacts with hardness of water forming non- adherent and easily removable soft sludge

$$3CaCl_2 + 2Na_3PO_4 \longrightarrow Ca_2(PO_4)_2 + 6NaCl$$

The main phosphates employed are (a) NaH_2PO_4 (b) Na_2HPO_4 (c) Na_3PO_4

(iii) **Carbonate Conditioning**: In low pressure boilers, scale formation can be avoided by adding sodium carbonate to boiler water, then caSo4 converted into Caco3 in equipment Caco3 forms loose sludge

$$CaSO4 + Na_2CO_3 \longrightarrow CaCO_3 + Na_2SO_4$$

(iv) **Calgon Conditioning**: Involves in adding calgon $[(NaPO_3)_6]$ to boiler water then it forms soluble complex compound with caso4

$$Na_2\,[Na_4(PO_3)_6] \longrightarrow 2Na^+ + [Na_4P_6O_{18}]^{2-}$$

$$2CaSO4 + [Na_4P_6O_{18}]^{2-} \longrightarrow [CaP_6O_{18}] + 2$$

(v) **Treatment with sodium aluminate ($NaAlO_2$)** Sodium aluminate gets hydrolyzed yielding NaOH and a gelatinous precipitate of aluminium hydroxide

$$\mathbf{NaAlO_2 + 2H_2O} \longrightarrow NaOH + Al[OH]_2$$

The NaOH, so formed precipitation some of the magnesium as $Mg(OH)_2$ i.e.;

$$MgCl_2 + 2\,NaOH \longrightarrow Mg(OH)_2 + 2NaCl$$

The precipitate of $Mg(OH)_2$ and $Al(OH)_3$ produced inside the boiler entraps finely suspended and Colloidal impurities including oil drops and silica.

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LECTURE NOTES

SUBJECT- ENGG CHEMISTRY BT101

UNIT NO-3

LECTURE NO -1

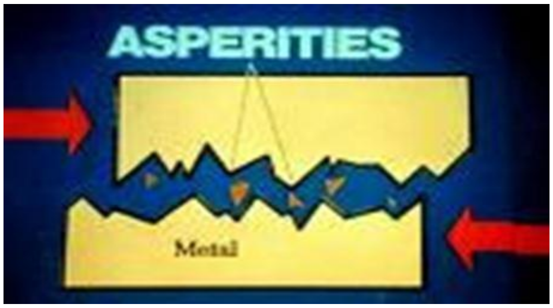
LUBRICANTS AND LUBRICATION

In machines, engines etc. where the metallic parts slide or rotate one over the other. While in direct contact, they rub against each other with the result frictional resistance is developed. Friction causes a lot of wear and tear of the concerned surfaces and hence such parts require replacements at frequent intervals. Furthermore, due to friction large amounts of energy are dissipated in the form of heat and thus causes loss in the efficiency of the machine. Moreover, the heat produced due to friction heats up and thus causes damage to the moving part.

The above ill effects of frictional resistance can be minimised by applying a thin layer of certain substances, known as lubricants, in between the moving parts.

Thus, lubricants may be defined as "the substance which reduces the friction between the two moving or sliding surfaces".

The process of applying the lubricant in between the moving or sliding surfaces is called lubrication.



FUNCTIONS OF LUBRICANTS

A lubricant performs the following functions:

1. It avoids the direct contact between the rubbing surfaces, hence it reduces wear and tear and surface deformation of the concerned parts. Thus, it reduces the maintenance, and running cost of the machine.

2. It makes the relative motion of the moving or sliding part smooth.

3. It reduces loss of energy in the form of heat, i.e., it acts as a coolant.

4. It reduces wastage of energy and hence increases efficiency of machine.

5. It reduces expansion of metal and chances of moving surfaces to be welded because of minimum liberation of frictional heat.

6. It also acts as a seal.

CLASSIFICATION OF LUBRICANTS

The lubricants may be divided into three classes depending upon their physical states:

1. Liquid lubricants
2. Semi-solid lubricants
3. Solid lubricants

1. LIQUID LUBRICANTS: The liquid lubricants are of following types:

(i) **Lubricating Oils:** Lubricating oils (or mineral oils) are derived by the fractional distillation of petroleum at a temperature of about 400°C. The lubricating oil is further redistilled under certain conditions so as to separate light oils, heavy oils and most of the road oil or asphalt. The oils are further refined to remove the unwanted materials (like wax) which may prove harmful.

(ii) **Synthetic Lubricating Oils:** Where petroleum lubricants fail to work effectively, use of synthetic lubricants is made. These synthetic lubricants are very effective under severe conditions. These lubricants are prepared chemically and are used for military jet engines, in rocket motors, submarines, atomic energy plants and under conditions of severe corrosion and of high temperature because they have better resistance to oxidation and corrosion

(iii) Fatty Oils: The oils obtained from plants and animals are known as fatty oils. The vegetable oils are obtained from seeds and nuts of many plants such as olives, peanuts, corn, palm and soya-beans etc. Animal oils are obtained from the tissues, kidneys and livers of animals. These oils have considerable industrial importance. These oils are greasy and insoluble in water and hence are used for lubrication purposes. Some of the vegetable and animals oils are given below:

(a) Vegetable Oils Commonly used vegetable oils are: (i) Olive oil, (i) Palm Oil, (iii) Castor Oil, (iv) Rape-seed oil or Colza oil (v) Hazel nut oil.

(b) Animal Oils: Commonly used animal oils are: (i) Whale oil (ii) Lard oil (iii) Tallow oil and (iv) Neats foot oil.

These vegetable and animal oils are used for lubrication of guns, sewing machines, scientific instruments, watches, clocks and other delicate instruments.

(iv) Blended Oils: A single oil is rarely a good lubricant. So to get lubricants of desired good qualities, blending of oils is done. Generally fatty oils are mixed with mineral oils for effective lubrication. The mixture is known as **Blended oil or Compound oil.** The 122 addition of fatty oil to a mineral oil develops certain lubricating properties which a possessed by the later.

2. SEMI-SOLID LUBRICANTS OR GREASES

Greases are semi-solid lubricants consisting of a soap dispersed in liquid lubricating oil. The liquid lubricant may be petroleum oil or synthetic oil. The main function of soap in grease is as thickening agent so that grease sticks firmly to the metal surfaces. Grease is used when

(i) Oil can't remain in place, due to high load, low speed, sudden jerks etc.

(ii) In hearing and gears that work at high temperature.

(iii) In situations where dripping of oil is undesirable
(iv) In situations where bearing needs to be sealed against entry of dust, dirt or moisture.

Greases have higher frictional resistance than oils and can support much heavier loads at low speeds. But greases have a tendency to separate into oils and soaps. Depending upon the nature of soap present in the grease, greases are classified as follows:

(i) **Calcium-base greases:** These are emulsions of petroleum oils with calcium soaps. These are water resistant but can be used upto 80°C.

(ii) **Soda-base greases:** These are emulsions of petroleum oils with sodium soaps. They are soluble in water and can be used upto 175°C.

(iii) **Lithium base greases:** These are emulsions of petroleum oils with lithium soap. These are water resistant and can be used at low temperature upto 15°C.

(iv) **Axle greases:** These are prepared by adding lime or any metal hydroxide to resin and fatty oils. These are water-resistant and are suitable for less delicate equipment working under high loads and low speeds.

1. SOLID LUBRICANTS

Solid lubricants are used in the conditions when

(i) Operating conditions are such that lubricating film cannot be secured by the use of greases or lubricating oils.

(ii) The operating temperature is very high, even for a semi solid lubricant to remain in the position.

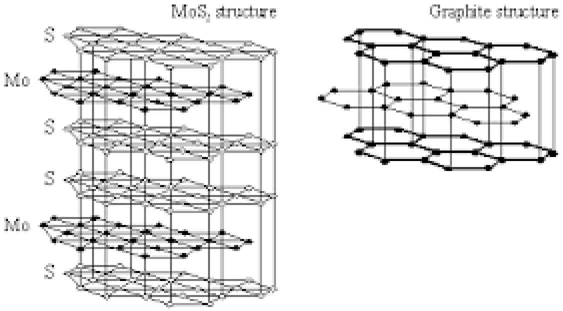
(iii) Contamination of lubricant by dust or moisture is unacceptable.

(iv) Combustible lubricants are to be avoided.

Solid lubricants are used either in the dry powder form or mixed with water or oil. The solids fill up the low spots in the surfaces of moving parts and form solid films, which have low frictional resistance. The most commonly used solid lubricants are graphite and molybdenum disulphide

(a) Graphite

(b) Molybdenum disulphide



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LECTURE NOTES

SUBJECT- ENGG CHEMISTRY BT101

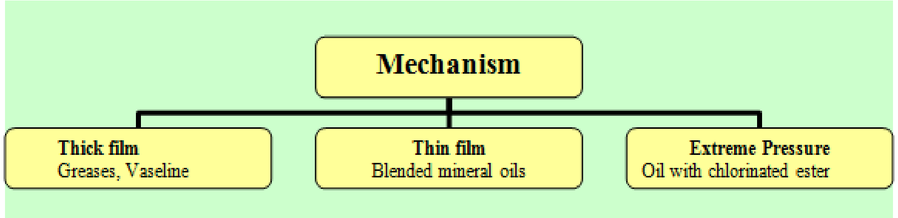
UNIT NO-3

LECTURE NO -3

MECHANISM OF LUBRICATION

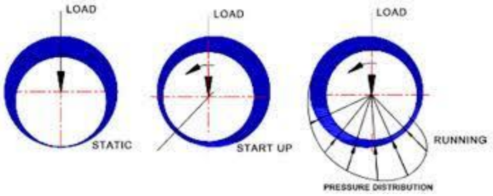
There are mainly three types of mechanism by which lubrication is done:

1. Fluid Film lubrication / HYDRODYNAMIC /THICK Film lubrication
2. Boundary Lubrication / THIN Film lubrication
3. Extreme Pressure Lubrication

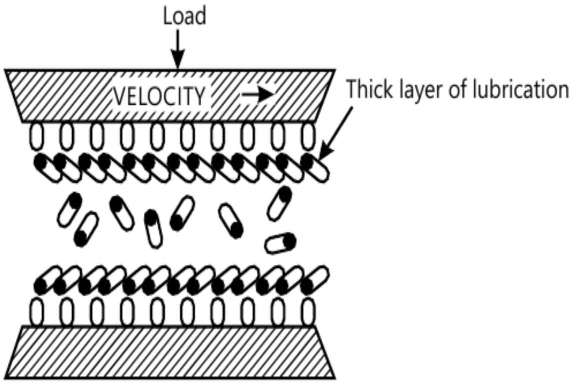


1. FLUID FILM OR THICK FILM OR HYDRODYNAMIC LUBRICATION

This type of lubrication is used when the two surfaces of the metals rotate against each other. The liquid lubricant is interposed between the two sliding surfaces which forms a film between them. The lubricant film fills the irregularities of the sliding surfaces and forms a thick layer between them so that metal to metal contact is prevented. This reduces wear and tear of the metal surfaces. The lubricant selected for the fluid film lubrication should have minimum viscosity and it should remain in place and separate the surfaces. (Film thickness is ≥**1000º A)**



Delicate instruments like watches, clocks, guns, sewing machines, scientific instruments are provided with this type of lubrication. Hydrocarbon oils are considered to be satisfactory lubricants for fluid film lubrication. In order to maintain the viscosity of the oil in all seasons of year, ordinary hydrocarbon lubricants are blended with selected long chain polymers.



Thick-film Lubrication

2. **BOUNDARY LUBRICATION OR THIN LAYER LUBRICATION**

Boundary lubrication is done for those cases in which the continuous thick film of lubricant cannot persist and direct metal to metal contact is possible. This happens when

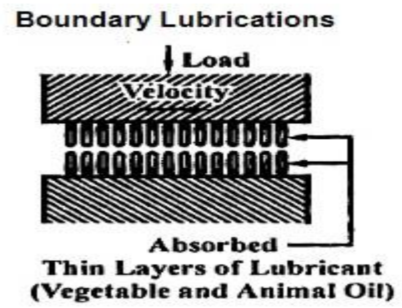
(i) A shaft starts moving from rest

(ii) The speed is very low

(iii) The load is very high and

(iv) The viscosity of the lubricant oil is very low.

In such conditions, boundary lubrication is done, in which the oil lubricants are filled in, between the sliding or moving metallic surfaces which is adsorbed on both the metallic surfaces by any physical or chemical means and cannot be removed easily. These adsorbed lubricants form two thin layers between the sliding metallic surfaces and avoids direct metal to metal contact. As a result, the frictional resistance between the moving or sliding metallic surfaces gets reduced.



For boundary lubrication the greases or solid lubricants like graphite or molybdenum disulphide may be used. But the most useful materials are long chain organic compounds such as fatty acids

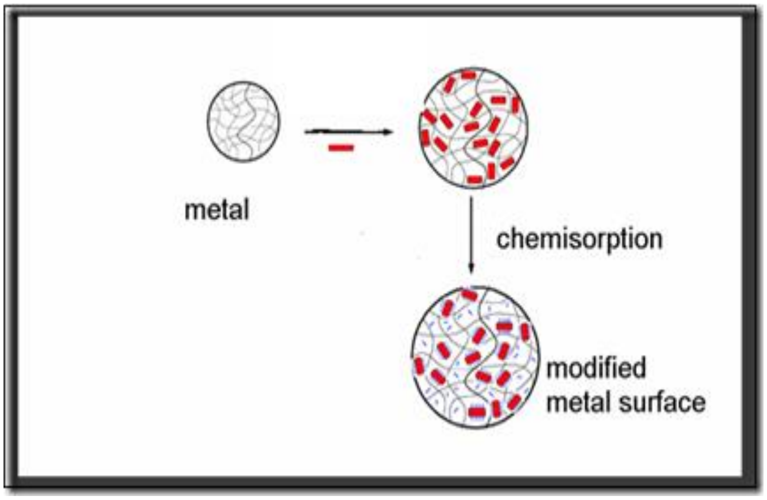
SUBJECT- ENGG CHEMISTRY BT101

UNIT NO-3

LECTURE NO -4

3. EXTREME PRESSURE LUBRICATION

When the fast moving or sliding metallic surfaces are under very high pressure and speed, they produce large amount of heat. As a result temperature becomes very high. The ordinary liquid lubricants decompose or even vaporise at such a high temperature and they fail to stick over-the metallic surfaces. In these conditions, to provide effective lubrication, special additives called extreme pressure additives are added to the mineral oils. The extreme pressure additives are the organic compounds possessing active radicals or groups such as chlorine, sulphur or phosphorus etc. These groups react with metal to form their respective compounds e.g., metallic chlorides, sulphides or phosphides. The reactions which take place are :



$RS_x + Fe \longrightarrow FeS + R\,S_{x-1}$

Organic Iron Iron sulphide

compound

$FeS + R'Cl_Y \longrightarrow FeCl_2 + R'\,Cl_{Y-2} + S$

Iron Chloride

$S + Fe \rightarrow Fe\,S$

Iron sulphide

These metallic compounds possess high melting points (e.g. iron chloride and iron sulphide melts respectively at 650°C and 1100°C). They form a film on the metal surface, which acts as a lubricant and can withstand extreme pressure and extreme temperature conditions.

CHARACTERISTICS OF A GOOD LUBRICANT

A good lubricant should possess following characteristics.

1. It should have proper viscosity and viscosity index.
2. It should have high melting point.
3. It should have low freezing point.
4. It should be stable to heat and should not decompose at high temperatures.
5. It should not stick to moving machine parts and may not result in jamming of machine parts.
6. It should be resistant to oxidation.
7. It should not possess corrosive properties.

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LECTURE NOTES

SUBJECT- ENGG CHEMISTRY BT101

UNIT NO-3

LECTURE NO -

PROPERTIES OF LUBRICANTS

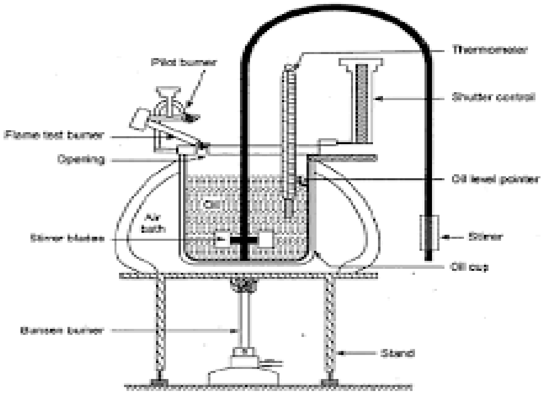
A large number of substances are available which are used as lubricants in different types of machines. One type of lubricant may be suitable for one type of machine but not for the other. So in the selection of lubricants their properties must be taken into consideration for proper lubrication. Some of the important properties of lubricants which are usually tested are given below.

1. Flash and Fire Points: Flash point of a lubricant is ***the lowest temperature at which the oil gives enough vapours which burn for a moment when a small flame is brought near it.***

Fire point is ***the lowest temperature at which the lubricating oil gives enough vapours which catchès fire and burn continuously when a flame is brought near to it.***

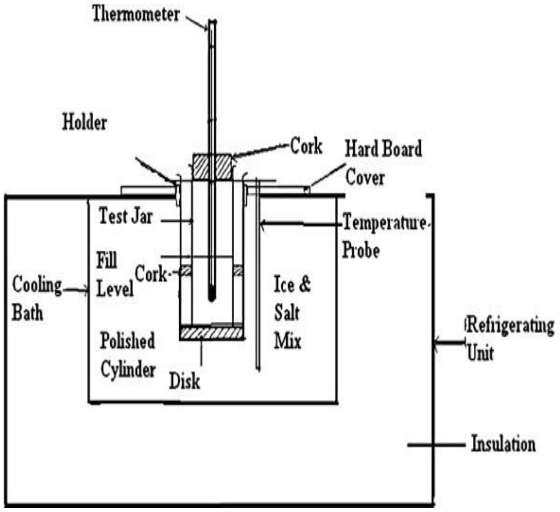
Significance

A good lubricant should have high flash and fire points at least above the temperature at which it is to be used. A lubricant having low flash and fire points is not safe to use because due to rubbing of sliding or moving surfaces of the machine in contact, large amount of heat is produced even in the presence of lubricant and sometimes the lubricating oils catch fire which may cause the damage of life and machine.



Flash and fire points of an oil can be determined by using Pensky martins flash & fire point apparatus.

2. **Cloud Point and Pour Point:** When an oil is cooled slowly, the temperature at which it becomes cloudy or hazy in appearance is called its cloud point. The temperature at which the oil ceases to flow on cooling is called its pour point.



Significance

Cloud and pour-points indicate the suitability of lubricants in cold conditions. Lubricant used in a machine working at low temperatures should possess low pour point, otherwise the lubricant will solidify and will cause jamming of the machine.

For example, refrigerator plants and air-craft engines, which may be operated at sub- zero temperatures, need lubricants with low pour-point. The presence of waxes in the lubricating oil raises the pour point.

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LECTURE NOTES

SUBJECT- ENGG CHEMISTRY BT101

UNIT NO-3

LECTURE NO -6

3. Emulsification: It is also an important property usually tested for selecting a good lubricant. ***Certain lubricating oils have property of mixing up with water to form intimate mixture under high pressure. This intimate mixture formed is called as emulsion.***

Significance

This emulsion formed has the tendency to pick up dirt, particles of grit and other matter present in the surrounding atmosphere. Due to the collection of such solid particles of the matter between the sliding surfaces, the lubricating system is spoiled and no longer smooth and thus wearing of the metallic surface begins. So a lubricant which has properties of forming such emulsion is not considered as good. A good lubricant is that which does not form any emulsion or if it forms, then the emulsion should break off quickly.

4. Viscosity: Viscosity is the most important property which is considered while selecting a good lubricant for particular application.

It may be defined as the property of a liquid or fluid by virtue of which it offers resistance to its own flow.

When a liquid flows on a surface at a steady rate, its flow actually consists of a flow of series of parallel layers moving one above the other. Each layer moves with different velocity, the top layer moves faster than the next lower layer due to internal resistance (viscous drag).

Let us consider a flowing liquid whose two adjacent layers separated by a distance d moves with a relative velocity difference V, the force per unit area F, required to maintain this velocity difference is represented by

$$F = \frac{nV}{d} \qquad (1)$$

where n is constant called as coefficient of viscosity.

In case d = 1 cm and V = l cm/ sec., then F = n.

Hence coefficient of viscosity may be defined as the force per unit area required to maintain a unit velocity gradient between two parallel layers. In C.G.S. system, the unit of viscosity is poise or centipoise ; 1 centipoise poise= 1/100 poise.

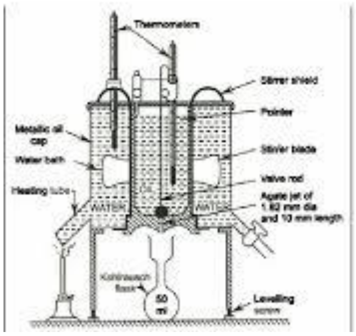
In equation (i), if F = 1 dyne,

V = 1cm/sec

and d = 1cm,

then n = 1 poise.

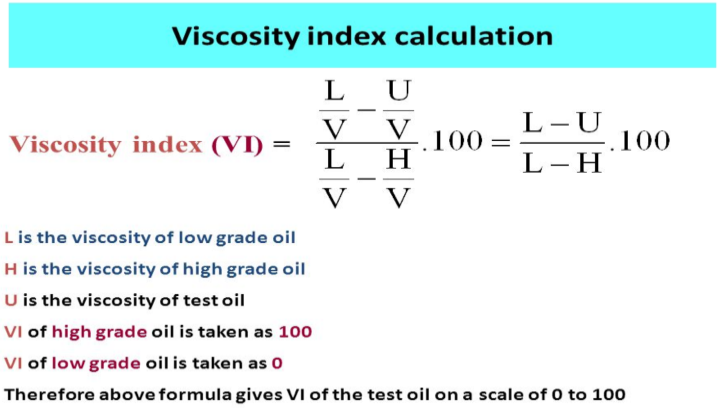
Viscosity is measured by determining time of the flow of a given quantity of liquid from a given height through a calibrated capillary tube under its own weight and the time of flow in seconds is noted. The time in seconds is proportional to true viscosity. One apparatus is Redwood viscometer, which is used for measuring viscosities of lubricating oils.



Significance

Viscosity is an important property of a lubricant for its selection. Generally, lubricants of low viscosity are used for bearings subjected to high speed and low pressure, while for low speed and high pressure bearings, lubricants of high viscosity are used. For light machinery like sewing machines, guns, watches, scientific equipments, light lubricating oils having low viscosity are used. For heavy machinery like trucks, lathes, concrete mixers, thick liquids of high viscosity are used.

Viscosity Index: Viscosity of liquids decreases with increasing temperature as a result the lubricating oil becomes thinner as the operating temperature increases. Thus, the rate of change of viscosity of a liquid with temperature is known as viscosity index. In general, low viscosity index means that the viscosity of on oil falls rapidly with the increase in temperature, while high viscosity index indicates that the viscosity of the oil is affected only slightly with temperature. A good lubricant is that whose viscosity does not change much with temperature or it should have high viscosity index.



Viscosity index calculation

$$\text{Viscosity index (VI)} = \frac{\frac{L}{V} - \frac{U}{V}}{\frac{L}{V} - \frac{H}{V}} .100 = \frac{L-U}{L-H} .100$$

L is the viscosity of low grade oil

H is the viscosity of high grade oil

U is the viscosity of test oil

VI of high grade oil is taken as 100

VI of low grade oil is taken as 0

Therefore above formula gives VI of the test oil on a scale of 0 to 100

SAGAR INSTITUTE OF RESEARCH AND TECHNOLOGY-EXCELLENCE

LECTURE NOTES

SUBJECT- ENGG CHEMISTRY BT101

UNIT NO-3

LECTURE NO -7

CLOUD AND POUR POINTS

The cloud point of a petroleum oil is the temperature at which solidifiable compounds, like paraffin wax, present in the oil begin to crystallize or separate from solution , when the oil is cooled under specified conditions .

At the Cloud point, oil becomes cloudy or hazy in appearance . Naphthenic type of oils that are quite wax - free show no cloud points .

The pour point of a petroleum oil is the temperature at which the oil ceases to flow or pour,

Significance

Cloud and pour - points indicate the suitability of lubricants in cold conditions. Lubricants used in a machine working at low temperature should possess low pour - point; otherwise solidification of lubricant will cause jamming of the machine, see Fig Pour point is of importance in establishing the lowest temperature at which a diesel fuel is still sufficiently fluid to be pumped or transferred. An oil with a low pour point should be selected whenever the oil must remain fluid at low temperatures.

Determination of Cloud and Pour Points

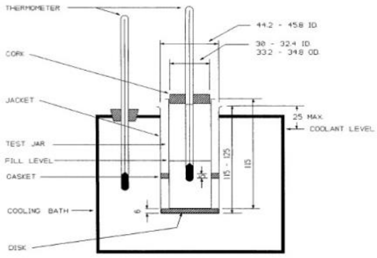
These determinations are carried out with the help of apparatus shown in Fig . The apparatus consists of a flat - bottomed tube (about 2 cm high and 3 cm in diameter) enclosed in an air -jacket. The air - jacket is surrounded by freezing mixture (ice + NaCl) contained in a jar .

To determine cloud point , a sample of the lubricating oil (moisture free) is poured into a test jar and cooled in progressive steps . When inspection first reveals at distinct cloudiness or haze at the bottom of the test jar, the temperature is recorded as the cloud point. To determine pour point, a sample of oil is cooled in flat - bottomed tube

(i.e. , test jar) under specified conditions ; the temperature is observed in increments of 5 ° F until no . Movement is observed at the surface of the oil when the tube is held in a horizontal position for 5 seconds. This temperature is recorded as the solid point. By definition the pour point is 5 ° F above this temperature .

Significance .

Cloud point is useful for estimating the temperature at which filter screens in the fuel intake system of diesel engines might become clogged because of wax separation. Filterability depends on type of wax, micro crystalline or amorphous . The amorphous wax is sticky in nature and would more easily clog filter screens. Pour point values of petroleum and non - petroleum lubricants are significant as many operations must function in sub - freezing condition .



ANILINE POINT

Aniline point is defined as : " The minimum equilibrium solution temperature for equal volume of aniline and oil sample . " It is determined by thoroughly mixing equal volumes of oil sample and aniline in a test tube and heating the mixture until a homogeneous solution is obtained . Then , the tube is allowed to cool at a controlled rate . The temperature at which the oil and aniline phases separate out is recorded as the aniline point .

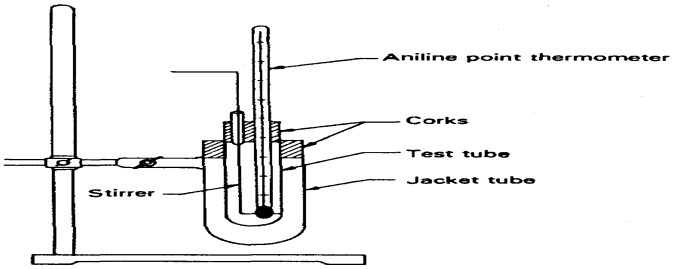
Significance

A lower aniline point of an oil means a higher percentage of aromatic hydro carbons in it. Since aromatic hydrocarbons have a tendency to - dissolve natural rubber and certain types of synthetic rubber Thus , higher the percentage of aromatic hydrocarbon or lower the aniline point of a oil , more are the chances of deterioration of an oil when it comes in contact with rubber sealing’s , packing , etc. Consequently, low aromatic content in the lubricants or their higher aniline point is desirable .

Determination of Aniline Point

(i) Dry the clean aniline point apparatus at 100-110 ° C by keeping it in electric oven .

(ii) Take 5 mL of pure aniline . Keep it in contact with KOH pellets . After some time , filter it to get dry aniline . Carefully handle aniline as it is highly toxic .



SAPONIFICATION NUMBER OR KOETTSDOERFER NUMBER

Saponification number is defined as " The number of milligrams of potassium hydroxide required to saponify the fatty material present in one gram of the oil " .

$$\text{Saponification value} = \frac{\text{Weight in mg of KOH}}{\text{Weight in g of oil}}$$

Saponification number is determined by refluxing a known quantity of oil with a known excess of potassium hydroxide solution and titrating the unused alkali against an acid .

Let mol wt of oil or fat =M

Here M gms of oil or fat require 168000 milligrams of KOH for saponification

Therefore one gram of fat or oil will require = 168000/M milligrams of KOH

Significance :

(i) As the saponification number is inversely proportional to molecular weight of oil or fat (M) hence average molecular weight of oil or fat can be found ; the smaller the saponification value , the higher the molecular weight .

(ii) It also indicates the average length of the carbon chains of the fatty acid components .

(iii) Saponification number also gives an estimate of non - fatty impurities present in oil or fat . Thus , we can find the extent of adulteration in an oil or fat .

(iv) As soap is formed in the product so saponification number also gives the actual amount of alkali required by triglyceride for its conversion to soap .

(v) Mineral oils do not undergo saponification but animal and vegetable oils undergo saponification . Hence , this test gives an indication of the amount of animal and vegetable oils added to mineral oils to improve oiliness . This test also helps us to ascertain whether the oil under study is animal / vegetable or mineral or compounded oil .

ACID NUMBER

Lubricating Oil's acidity or alkalinity is determined in terms of neutralization number. The neutralization number represents either the Total Acid Number (TAN) " The number of milligrams of potassium hydroxide (KOH) needed to neutralize any acid in one gram of oil " or the Total Base Number (TBN) . The number of milligram of hydrochloric acid (HCI) needed to neutralize any base in one gram of oil . Determination of TAN is more common and its tests procedure is given below :

Reagents :

(i) 0.1 N alcoholic HCl solution ,

(ii) 0.2 N alcoholic KOH solution ,

(iii) Titration solvent : Made by mixing 500 mL of toluene and 5 mL of distilled water with 495 mL of isopropyl alcohol .. (C3H8O)

(iv) Para Naphtholbenze ($C_{27}H_{18}O_2$) indicator solution made by adding 1 gm of dry indicator powder in 100 ml of isopropyl alcohol.

Test procedure : (1) Into 300 mL conical flask , take a weighed amount of the sample (20 gm sample for light coloured oil or 2 gm sample for dark - colored oil) .

(i) Add 100 mL of titration solvent and 30 drops of indicator solution to the flask , then carefully swirl the mixture until the sample is completely dissolved .

(ii) If the solution turns yellow - orange or deep orange in colour , it mean the oil sample was acidic [But if it assumes green or green - blue colour , it means the oil sample was basic , then titration should be done with alc . HCI] .

(iii) Slowly add the alc . KOH solution from the burette drop by drop with careful swirling until the green or green - blue end point is reached which persist for atleast 15 s [The colour change is reversed if alc . HCI is the titrating agent] .

(iv) Read from the burette the number of mL of solution required to reach the end point .

Calculations .

Neutralization number = Total mL of titrating solution x 5.61/ Weight of sample used

Significance .

This test shows relative changes in an oil due to oxidation. Comparing the TAN or TBN with the values of a new oil will indicate the development of harmful products or the effect of additive depletion. In fact, acid number greater than oil is usually taken as an indication of oxidation of the oil. This will, consequently lead to corrosion, besides gum and sludge formation.