Principles of corrosion

Corrosion may be defined as destruction of a material due to the contact with its surrounding environment.

Types of Corrosion

1. Direct or Chemical Corrosion
2. Indirect or Electrochemical Corrosion

Direct or Chemical Corrosion

In this type of corrosion, direct chemical reaction occurs between metal or alloy surface and environment and the corrosion product is deposited there.

Example

The chemical reaction between zinc metal and acid which lead to the dissolution of aluminum metal

Indirect or Electrochemical Corrosion

It is an electrochemical reaction between metals and the environment.

Electrochemical reaction

It's known as redox reaction (reduction – oxidation reaction)

Oxidation Reactions

- LOSS of electrons
- Removal of H_2 OR gain of O_2
- Take place at anode
- Oxidation Reaction ≅ Anodic Reaction
- Oxidized metal carry positive charge

Metal → Positive Ion + Electron(s)

$M \rightarrow M^{n+} + ne^-$ (n=1,2,3,…)

$Na \rightarrow Na^+ + e^-$ & $Fe \rightarrow Fe^{2+} + 2e^-$ &

$Al \rightarrow Al^{3+} + 3e^-$

Reduction Reactions

- GAIN of electrons
- Removal of O_2 OR gain of H_2
- Take place at cathode
- Reduction Reaction ≅ Cathodic Reaction
- Reduced species carried negative charge.

For strong acidic medium (pH<4) $2H^+ + 2e^- \rightarrow H_2$

For neutral or basic medium (pH= 4-10)

$1/2\ O_2 + H_2O + 2e^- \rightarrow 2OH^-$

PH-scale

It's a scale to determine the acidity or alkalinity strength

0 → 4	4 → 7	7 → 10	10 → 14
Strong acid	Weak acid	Weak base	Strong base
Sulfuric acid	Acetic acid	Ammonia	Caustic soda

Electrochemical cells

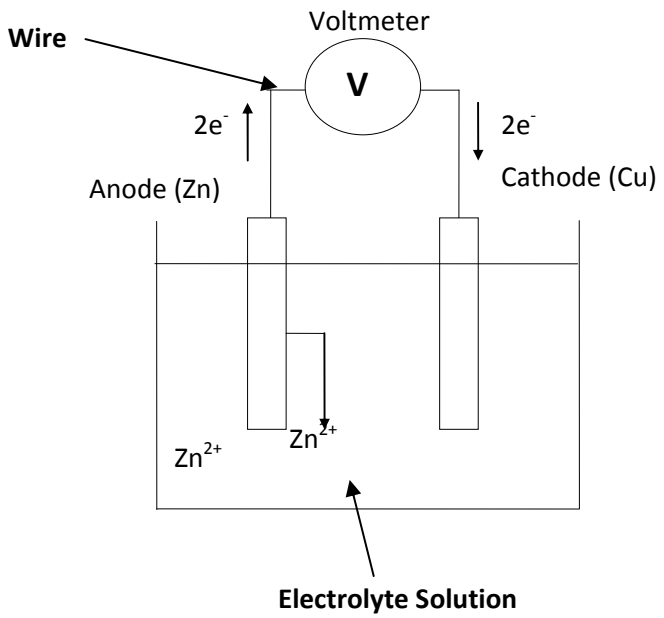
Chemical Energy ⟷ **Galvanic Cell** → / ← **Electrolytic** ⟷ **Electrical Energy**

Corrosion cell ≅ Galvanic cell

Cell formula

Anode **//** **Electrolyte** **//** **Cathode**
(Corroded Area)

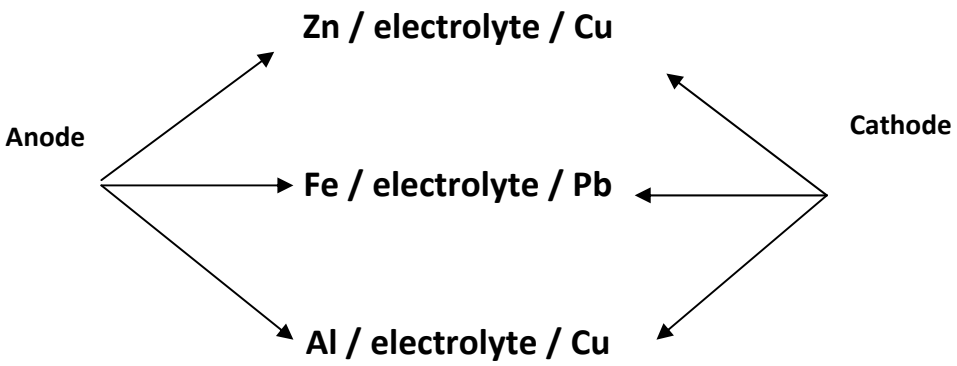
At the Anode (+)	At the Cathode (-)
Oxidation Reaction	**Reduction Reaction**
$Zn \rightarrow Zn^{2+} + 2e^-$ Two electrons will flow from the Zinc (anode) to the copper (cathode)	$2H^+ + 2e^- \rightarrow H_2$ (Hydrogen Reduction at pH<4) $1/2\ O_2 + H_2O + 2e^- \rightarrow 2OH^-$ (Oxygen Reduction pH= 4-10)



Electrolyte solution is source of ions dissolved in water.
The source of ions may be acid, base or salt.

<u>The Galvanic Cell needs:</u>

1. Potential difference between anode and cathode.
2. Suitable Electrolyte solution.
3. External conductor between anode and cathode (wire).



The Electrochemical Series (The Reactivity Series)

Metals are arranged according to their chemical reactivity

Metal	Symbol	Reactivity
Potassium	K	Most Reactive
Sodium	Na	
Calcium	Ca	
Magnesium	Mg	
Aluminum	Al	
(Carbon)	C	**Activity Decreasing**
Zinc	Zn	
Iron	Fe	
Nickel	Ni	
Lead	Pb	
(Hydrogen)	**H**	
Copper	Cu	
Mercury	Hg	
Silver	Ag	
Platinum	Pt	
Gold	Au	Least Reactive

Polarization

Definition

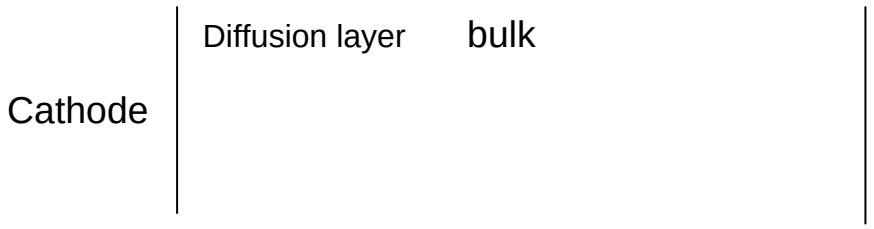
The rate of electrochemical reaction is limited by various physical and chemical factors.
The electrochemical reaction is retarded by several physical and chemical factors.
Polarization is inversely proportional to the corrosion rate.

Steps of electrochemical reaction:

1. Ion transfer from the bulk of solution to the surface through the diffusion layer (charge transfer step or mass transfer step)
2. Chemical reaction between ions and electrons. (Oxidation or reduction)
3. Material transfer from the surface of metal to the bulk of solution through the diffusion layer. (Mass transfer step).

Reduction of hydrogen:

$$2H^{+} + 2e^{-} \rightarrow H_{2(g)}$$



-the first and third steps are mass transfer steps.
-the second step is chemical reaction step.

Polarization can be conveniently divided into two type's concentration and activation polarization.

Concentration polarization:

It is refers to electrochemical reaction which are controlled by the mass transfer (diffusion) step in the electrolyte.
Condition: the transfer is slower than the chemical reaction.

Activation polarization:

It is refers to electrochemical reaction which are controlled by the chemical reaction sequence at the metal surface.
Condition: the chemical reaction is slower than the mass transfer.

Examples:

Corrosion rate in concentrated electrolyte is chemical reaction controlled.
Corrosion rate in diluted electrolyte is diffusion controlled.

Passivity

Some metals and alloys under particular environmental condition loss their chemical reactivity and become inert.

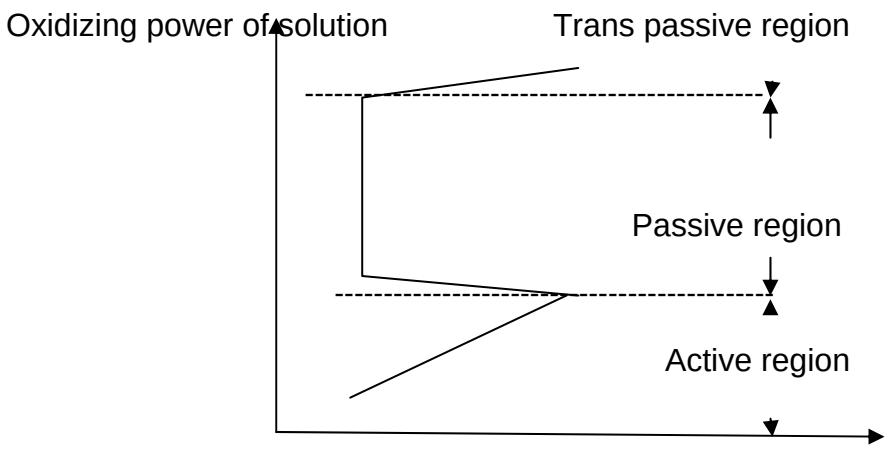
Environment	Iron	Aluminum
Air	Non passive	passive
Nitric acid (HNO_3)	passive	Non passive

Passivity depends mainly on:

1- The nature of the metal or alloy.
2- Type of the environment.

Passivity may be defined as the metal or alloy under particular environmental condition form protective layer due to the reaction between the metal and environment.

Passivity curve:



1- Active region: the behavior of metal is identical to that of normal metal where slight increase in the oxidizing power of the solution cause rapid increase in the corrosion rate.
2- Passive region: by increasing the oxidizing power the corrosion rate show sudden decrease and further increase in the oxidizing power produce no change(rate is constant).
3- Trans passive region: at very high values of oxidizing power, the corrosion rate again increase as oxidizing power increase.

Corrosive environment

Air, water, soil, gases, and acids may acts as corrosive environment.

Types of corrosive environment:

1- Air:

i. Moist and humid air is more corrosive than dry air.
ii. Hot air is more corrosive than cold air.
iii. Polluted air is more corrosive than fresh air.

2- Water:

i. Hot water is more corrosive than cold water.
ii. Salty water is more corrosive than fresh water.
iii. Polluted water is more corrosive than pure water.

3- Gases: Acidic gases (SO_x, NO_x, and H_2S.) are more corrosive than Basic gases (NH_3).

4- Acids:

Acid	mineral	organic	fatty
strength	Very strong	weak	Very weak
examples	H_2SO_4, HNO_3, H_3PO_4, HCL……	Acetic and formic acid	Animals and plant oils

5- Bases: Strong bases (sodium hydroxide, potassium hydroxide) are more corrosive than weak bases (ammonia solution).

Note: acids is most corrosive than bases.

6- Soil:

Presence of water, salts, gases, stray current, pollutants, affects the corrosion rate greatly.

Forms of corrosion

1. **Uniform corrosion**
   In such type of corrosion there is a uniform decrease in the volume of the metal due to direct contact with the surrounding environment.
   Examples
   Dissolvation of Zn, Al metal in acids and Pb metal in base.

2. **Atmospheric corrosion:**

Atmospheric corrosion take place due to direct contact between metal and atmosphere

Types of atmosphere:
1. Gas type: contain mainly oxygen gas(23% W / W) and water vapor.
2. Liquid type: contain mainly water and dissolved oxygen.

Atmospheric corrosion involve formation of metal oxide layer when metal in direct contact with its surrounding environment.

Example:
Formation of iron rust due to contact with air

$$Fe + air, H_2O \longrightarrow Fe(OH)_2 \longrightarrow Fe_2O_3$$

Iron rust (reddish brown ppt.)

Oxide layer divided into two types:

Protective	Non Protective
Non active	active
Non porous	porous
Ex: Zn, Al, Ni	Ex: Fe

Rate of atmospheric corrosion depend mainly upon:
1. Nature of metal or alloy.
2. Nature of oxide layer

Factors affecting atmospheric corrosion:

1. Type of metal or alloy.
2. Type of environment (dust, humidity, pollutant. Water vapor, gases,…)
3. Temperature(as T increase as rate increase)
4. Time: The extent of corrosion increases with increased time
5. Surface Condition:
   a. more roughness, more corrosion

b. The presence of foreign matter influence the speed of corrosion

3. **Galvanic corrosion**:

Take place due to the contact between bimetallic couple exposed to the same environment due to the potential difference.

Mechanism of galvanic corrosion:

For two different metals M_1 and M_2 when exposed to the same corrosive environment, if M_1 is more active than M_2.

Anodic reaction:

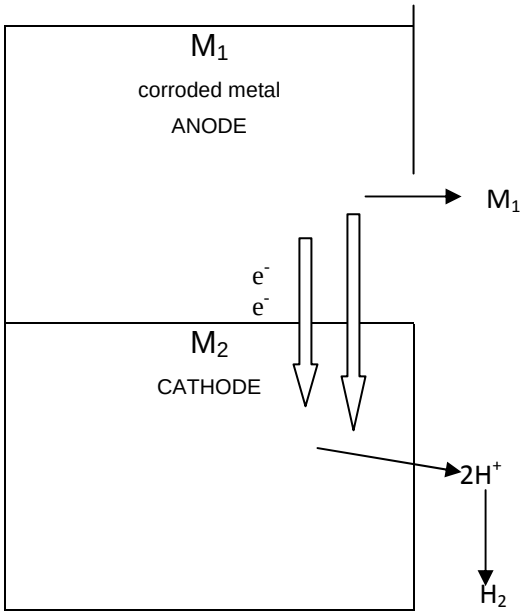
$M \rightarrow M^{n+} + ne^-$ (n=1, 2, 3, …)

Anodic metal will be corroded.

Cathodic reaction:

For strong acidic medium (pH<4) $2H^+ + 2e^- \rightarrow H_2$

For neutral or basic medium (pH= 4-10) $1/2\ O_2 + H_2O + 2e^- \rightarrow 2OH^-$



Metal (I) // electrolyte // Metal (II)

Anode **Cathode**

Application on galvanic corrosion:

1- **Metal plating:**

To protect steel tanks (or sheet) we can use Zn, Al, Cu or Pb where zinc and aluminum metal is more active than steel so, they will acts as anode and they will be corroded instead of steel, but

copper and lead are less active than steel so, they acts as Cathodic metal and the corroded metal will be the steel tanks.
I.e. to protect metal using metallic coating we must use the more active metal.

Zn plating (corroded)	**Cu plating**
Steel tank	**Steel tank (corroded)**

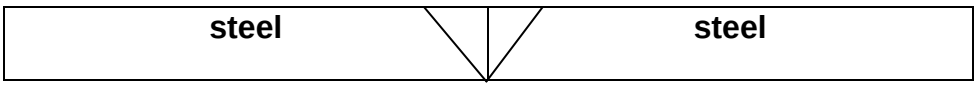
2- Welding and rivet process:

During the steel welding we may use

a- More active metal (Zn, Mg, Al…)
b- Less active metal (Cu, Pb, Au….)
c- The same metal(steel)

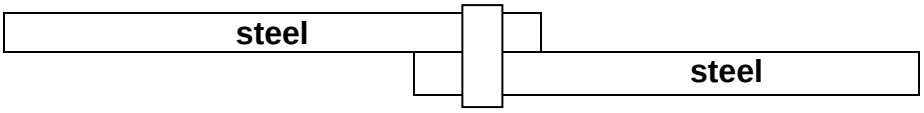
If use more active metal the welding material will be corroded, but if we use the less active the welded material will be corroded, so the best solution is to use the same metal.

Weld material



The same for the rivet, the best solution is to use the same metal.

Rivet material



Factors affecting galvanic corrosion

a. Potential Difference (P.D.)

As the P.D increases the galvanic corrosion increase

Zn	Fe	>>	Zn	Cu

Zn / electrolyte / Fe

Fast rate

Zn / electrolyte / cu

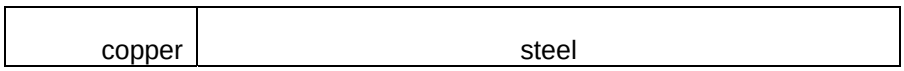
slow rate

b. Distance

As the distance increases the galvanic corrosion decrease

max corrosion rate

min corrosion rate



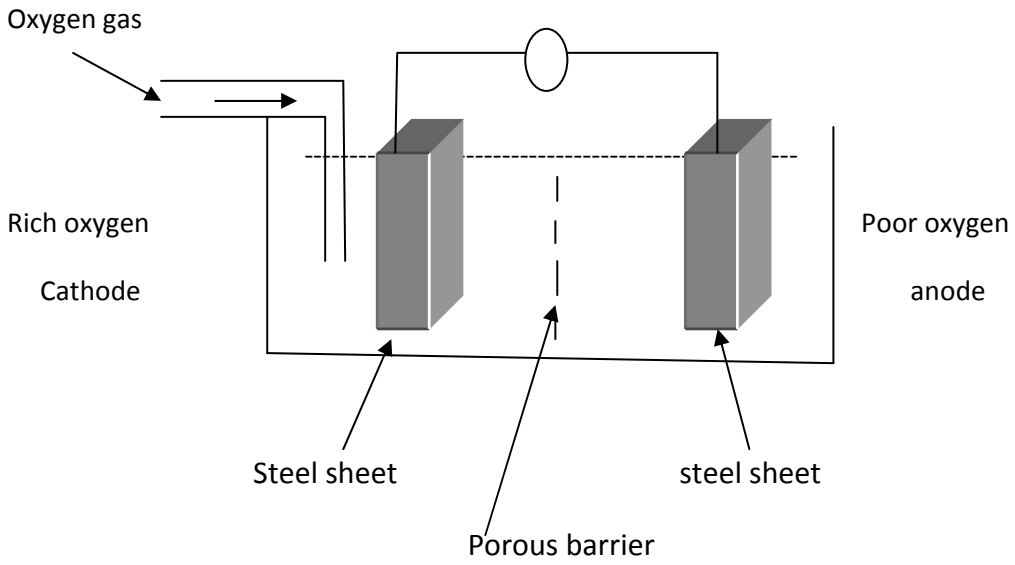
Fe / electrolyte / Cu

c. Area

As the Area increases the galvanic corrosion increase

4. Differential Aeration Corrosion

This type of corrosion tales place due to the differential in oxygen concentration on the same metal or alloy.



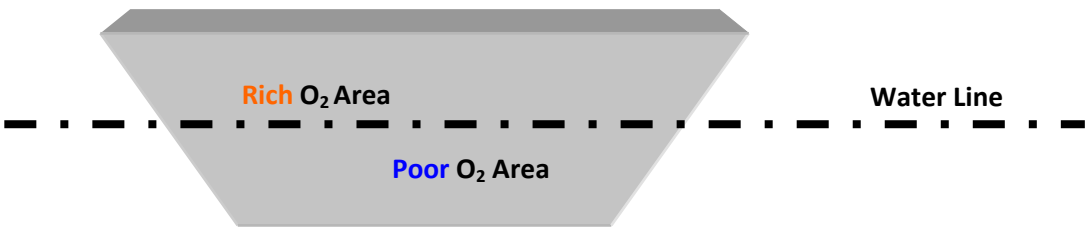
Porous barrier allow the transfer of ions only through it, so oxygen gas will not penetrate the porous membrane.

Metal (poor O_2) // electrolyte // Metal (rich O_2)

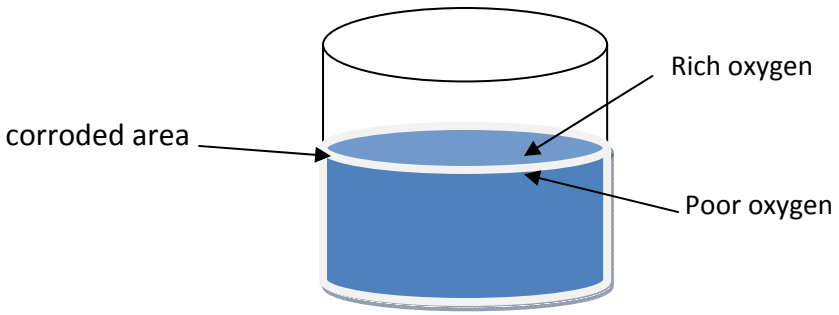
Anode (+) **Cathode (-)**

Corroded Area

Example: Ships Hull

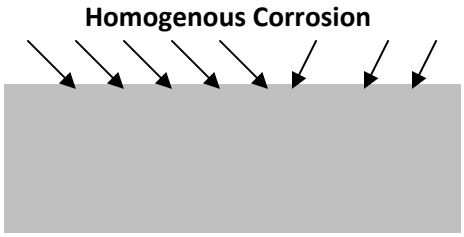


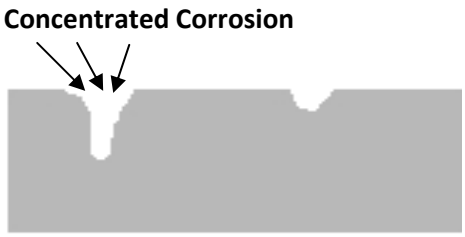
Example: storage tanks containing water.

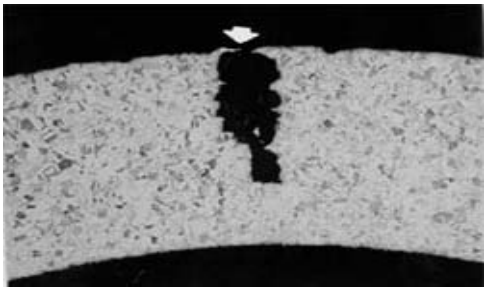


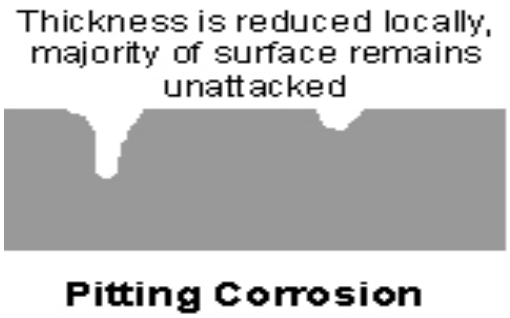
5. Pitting Corrosion

In this type, corrosion is concentrated at some places and is less in others, thus pits are formed.
Is a form of localized corrosion attack in which small pits or holes form.









Reasons of Pitting Corrosion

1. The Non-homogeneity of metal surface:
   Due to the presence of **impurities** at the metal surface

2. The Non-homogeneity of external environment

Due to the presence of **different areas in concentration**

3. Oxide Layer in not uniformly perfect
   Due to the oxide layer may be broken in a small area

6. Erosion corrosion:

It is a combination between corrosion and mechanical wear on the metal surface.
Erosion take place due to mechanical wear on metal surface
Corrosion takes place due to chemical or electrochemical reaction.

Erosion corrosion depends on:

1. **Metal surface (hardness of surface)**

Soft metal	Hard metal
Pb, Cu, Ag	Cr, high carbon steel

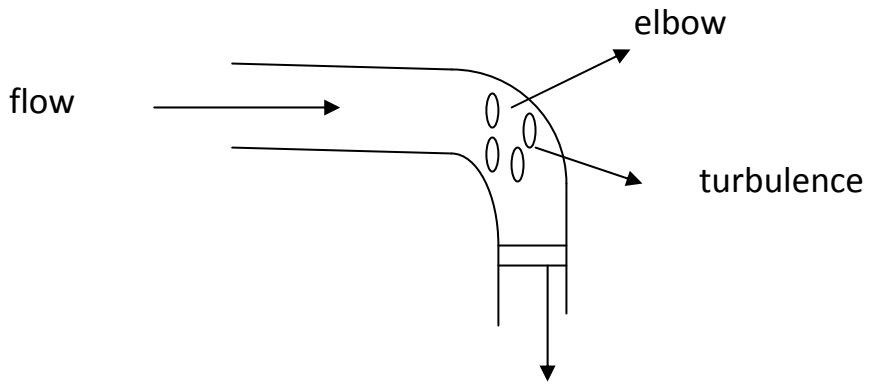
2. Environmental condition.

Factors affecting erosion corrosion:

1. **High degree of turbulent:**

Turbulent is formed due to high velocity of velocity of fluid and sudden change in direction of the fluid.

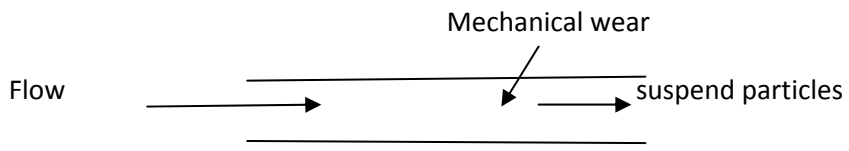
As turbulent increase as mechanical wear increase and hence the erosion will increase.



in order to decrease the turbulence effect , the thickness of tube or pipe in the turbulence area must be increase.

2. **<u>Presence of solid or suspended materials:</u>**

As suspended or solid material increase as the mechanical wear increase and hence erosion increase.



Corrosion Protection

Metal + corrosive environment = corrrosion

Protection Theory

Metal or alloy	barrier	corrosive environment

Barrier			
Sacrificial Barrier	**Inert Barrier**		**Perfect Barrier**
	Metallic	**Non-metallic**	
Metallic barrier using a more active metal than the one required to be protected Example: Steel protection by Zn, Al …	Using LESS active metal Example: for steel protection by Cu, Ag.	Example: Paints, cement, glass, ceramic, plastic, polymer, paints.	Alloys like stainless steel are protected by chromium, nickel added to the alloy. The protection is inside the grain

Protection Methods:

1. Coatings
2. Inhibitors
3. Cathodic protection

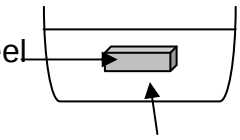
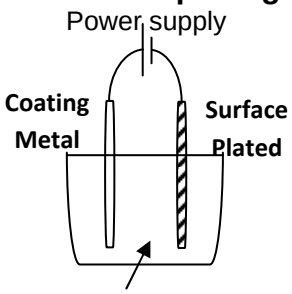
Protection Methods:

1. Coatings:

Types of coatings:

<table>
<tr><th colspan="2">1.
Metallic Coating</th><th>2.
Non – metallic Coating</th><th>3.
plastic</th></tr>
<tr><td>LESS
active metal</td><td>MORE
active metal</td><td rowspan="3">o Cement
o Carbon
o Ceramics
o Alumina(high temp)

All these materials resist corrosion.</td><td rowspan="3">o Polymer
o Epoxy
o PVC
o PVA
o PE</td></tr>
<tr><td>Cu, Pt,…
For steel protection</td><td>Zn, Mg, Al for steel protection</td></tr>
<tr><td colspan="2">1. Galvanization
(Hot dipping)

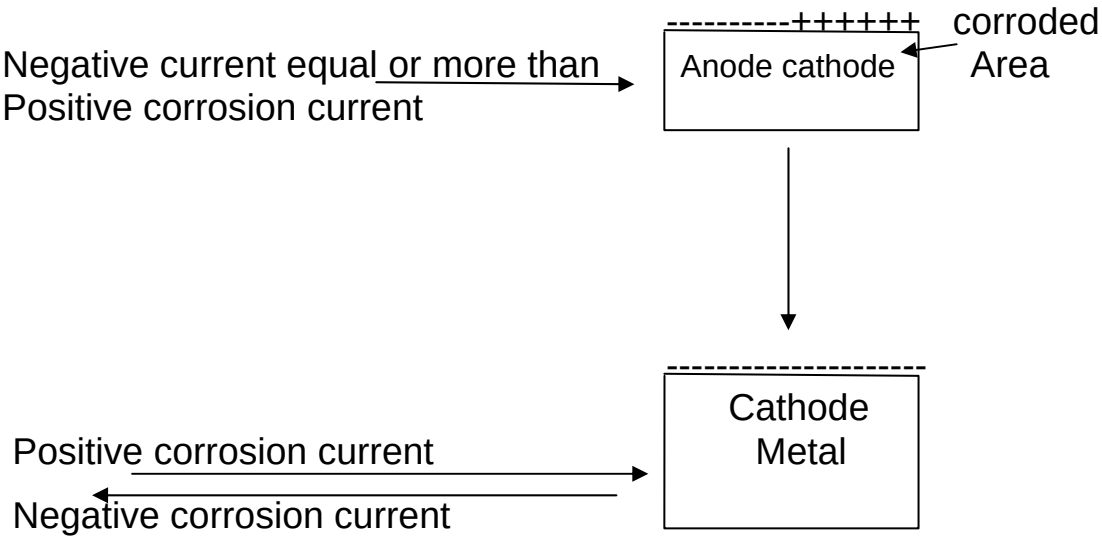
Steel
 
Hot Zn (fusion of coating) to protect steel</td></tr>
<tr><td colspan="2"></td><td>4.
Paints</td><td></td></tr>
<tr><td colspan="2">2. Electroplating
Power supply
 

Electrolyte Solution (Salt)</td><td colspan="2" rowspan="3">Paints are composed of:
1. <u>Pigments</u>
2. <u>Binder</u>
95% of paints
(polymer + oils)
3. <u>Solvent</u>
Water based solvent.
Oil based solvent</td></tr>
<tr><td colspan="2">3. Spray</td></tr>
<tr><td colspan="2">4. Vapor Deposition</td></tr>
</table>

Properties to consider the quality of coating:

i. Average thickness of coating
ii. Porosity or continuity
iii. Adherence
iv. Uniformity of thickness

3. Cathodic Protection



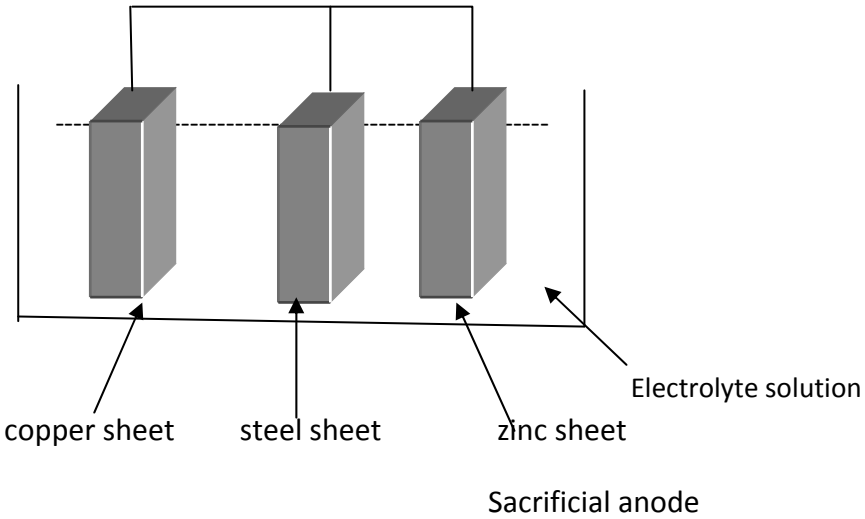
Metal protected by cathodic protection

There are two types of cathodic protection:

- Sacrificial Anode Method
- Immersed Current Method

Sacrificial Anodes Method

The main idea is connecting the metal to be protected to more active metal.



To protect steel we may use Zn, Mg, Al…….

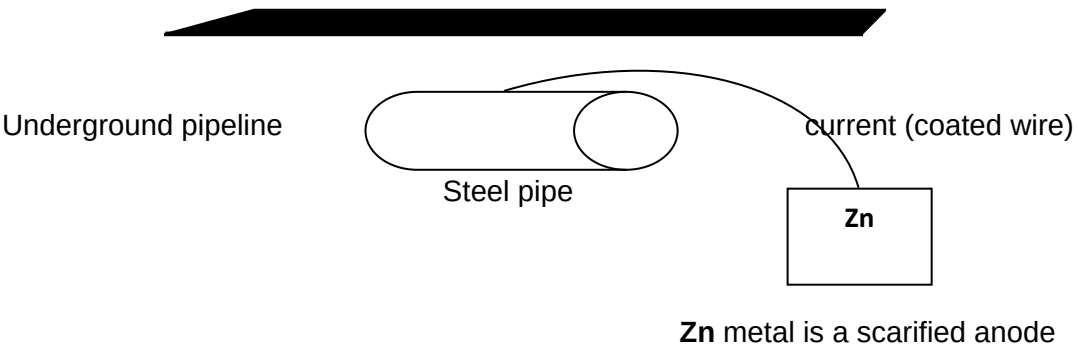
Examples*:*

Protection of Steel Structure:

- By connecting a piece of Zinc or other anodic material to the iron, in this case, the zinc or other anodic metal is termed **"Sacrificed Anode"**.
- It is called a sacrificial anode since it is consumed during the protection of the steel.

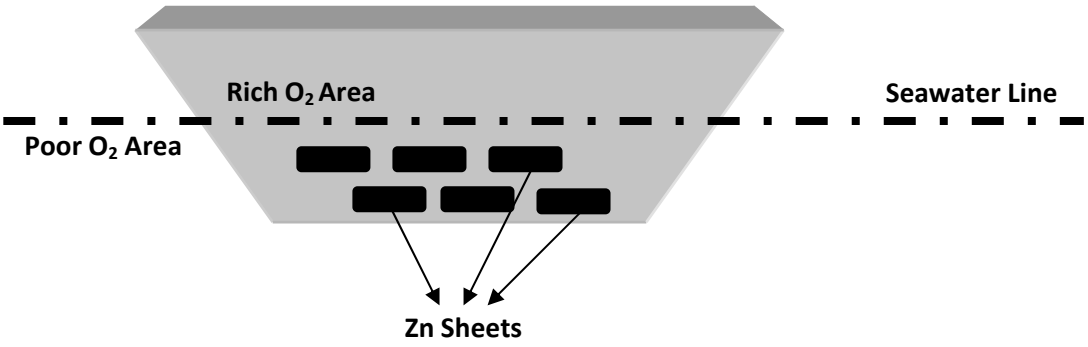
1. Cathodic protection of an underground pipeline using a zinc sacrificial anode

Ground Level



Zn metal is a scarified anode

2. <u>Cathodic protection of a ship hull using a zinc sacrificial anode</u>

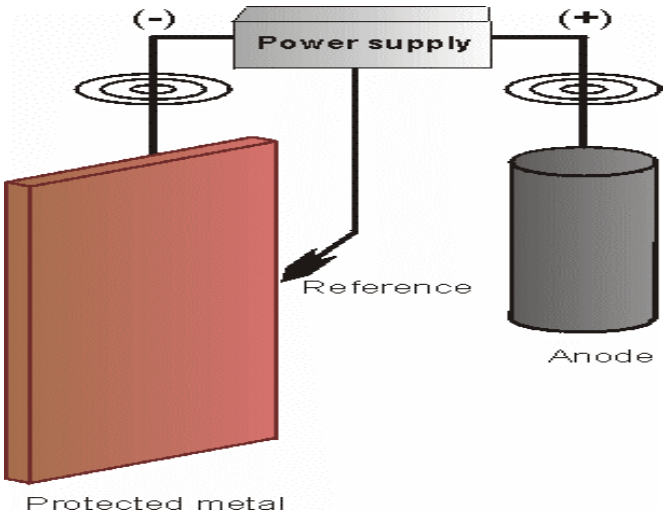


Impressed current Method

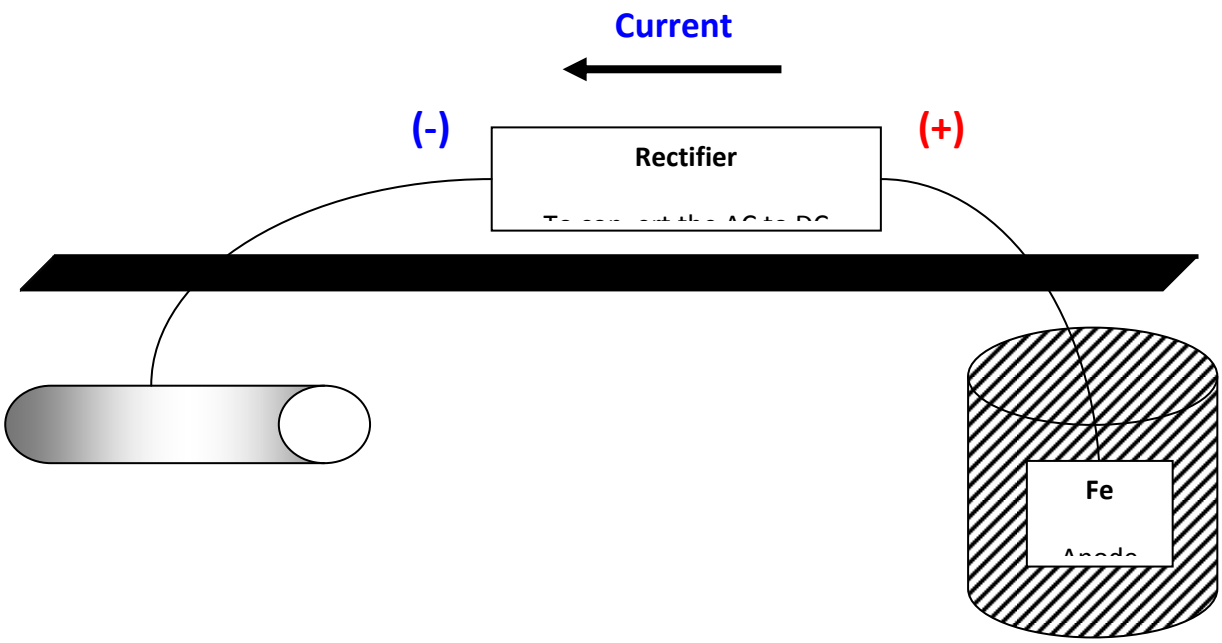
This method of protection is carried out by making the metal to be protected a cathode by connecting it to the negative pole of a DC power supply (electrolytic cell).

This is achieved by using an external power source.

- -ve is joined to the metal to be protected(cathode)
- +ve is joined to an inert anode (ground, graphite or metal scrap (Fe))



<u>Example:</u> Cathodic Protection of an underground Pipeline using Impressed Current Method



Backfill

To improve the conductivity betweeAnode and surrounding Soil

Fuel and combustion

Fuel + Oxygen $\xrightarrow{\text{flame}}$ Exhaust gases + Energy

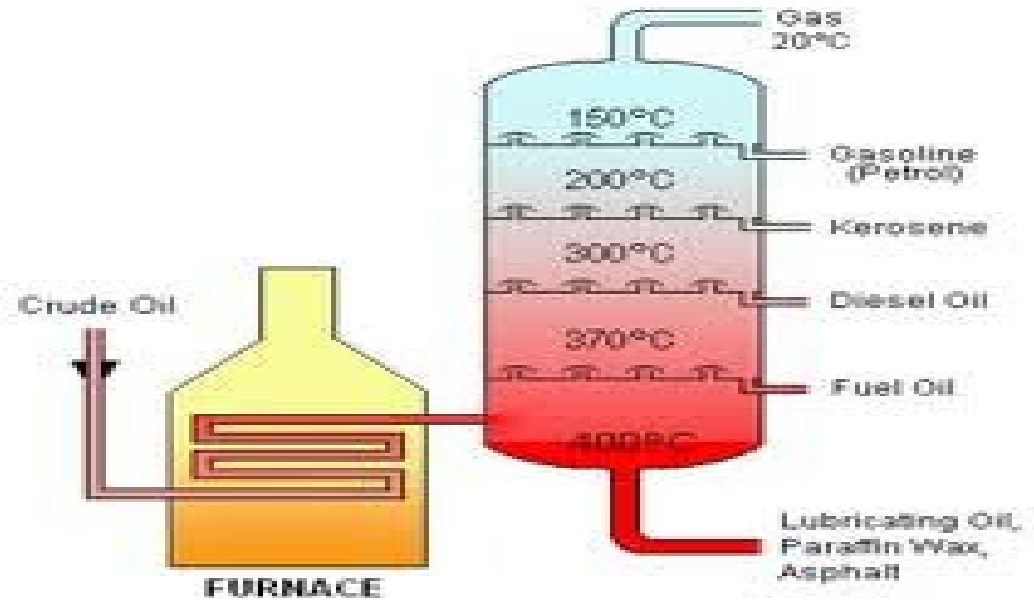
Fuel refers to organic matter and compose mainly of carbon and hydrogen.

Classification of fuels:

Solid	liquid	gases
Coal-Coke-graphite	Heavy oils (Fuel oil)	Liquefied petroleum gas(L.P.G)
	Light oils	Natural gas CH_4(N.G)

Distillation of liquid fuel:

Using distillation tower.



Composition of the petroleum oils:

Crude oil	
95% Hydrocarbons (C+H).	5% Sulfur and its compounds, dissolved gases like O_2, N_2, CO_2 and metals like V, Fe, Cu.

Hydrocarbons in the petroleum oil		
Paraffin's	**Naphthenes**	**Aromatic**
Saturated compound	Un Saturated compound	Un Saturated compound
C_nH_{2n+2}	C_nH_{2n}, Cyclo compound	Conjugated rings
CH_4, C_3H_8, C_8H_{18}	C_3H_6, C_8H_{16}	C_6H_6 benzene
Light compounds and give complete combustion	Heavy compound and give Incomplete combustion	Low heat value

Properties of liquid fuels:

1. Specific gravity (SP.gr)

It is known as relative density.

SP.gr = density of fuel at sp. Temp. / Density of water at the same Temp.

SP.gr gives a very useful indication to the properties of the fuel; a decreasing of the Sp.gr is associated with increasing the percentage of paraffin's, which indicated to a good ignition.

2. Viscosity:

Viscosity of a liquid is measured for its resistance to flow or internal friction.

Viscosity is inversely proportional to the temperature.

Viscosity units	
Dynamic viscosity	**Kinematic viscosity**
Relating to motive force	Relating to motion
= (force x distance)/ (area x μvelocity)	$K = \mu / \rho$ (ρ is density of fuel)
Unit: gm/Cm. S or Poise	Unit: Cm^2 / S or Stoke

.

Effect of viscosity:

Lower viscosity ← Viscosity scale → Higher viscosity	
Tends to incomplete combustion	Tends to incomplete combustion

3. Calorific value (C.V):

The amount of heat evolved by burning the unit mass of the fuel with oxygen.

Units : J/gm , KJ/Kg , MJ/Kg , Cal/gm , B.t.u/b

There are two methods to state the C.V:

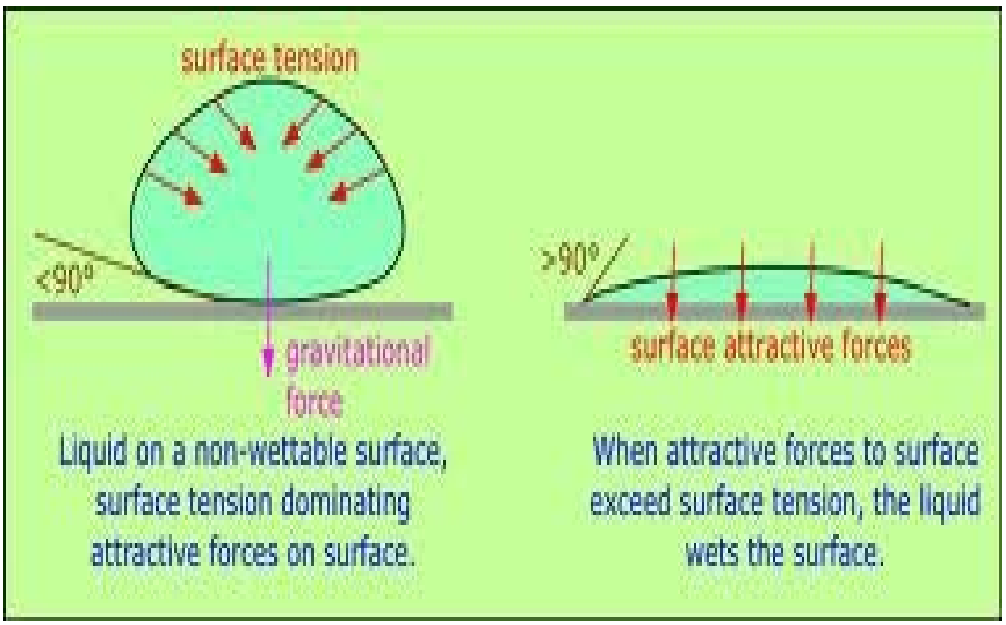
Higher C.V OR Gross C.V (H.C.V)	**Lower C.V OR Actual C.V (L.C.V)**
Its calculated value with sufficient accuracy from the empirical formula at S.T.P, Water as liquid.	Experimental value.

H.C.V ≠ L.C.V

$$H_2 + 1/2\ O_2 \longrightarrow H_2O_{(Liq)} \xrightarrow{\text{latent heat of vaporization}} H_2O_{(Vap)}$$

L.C.V = H.C.V + Latent heat of water

4. Surface tension:



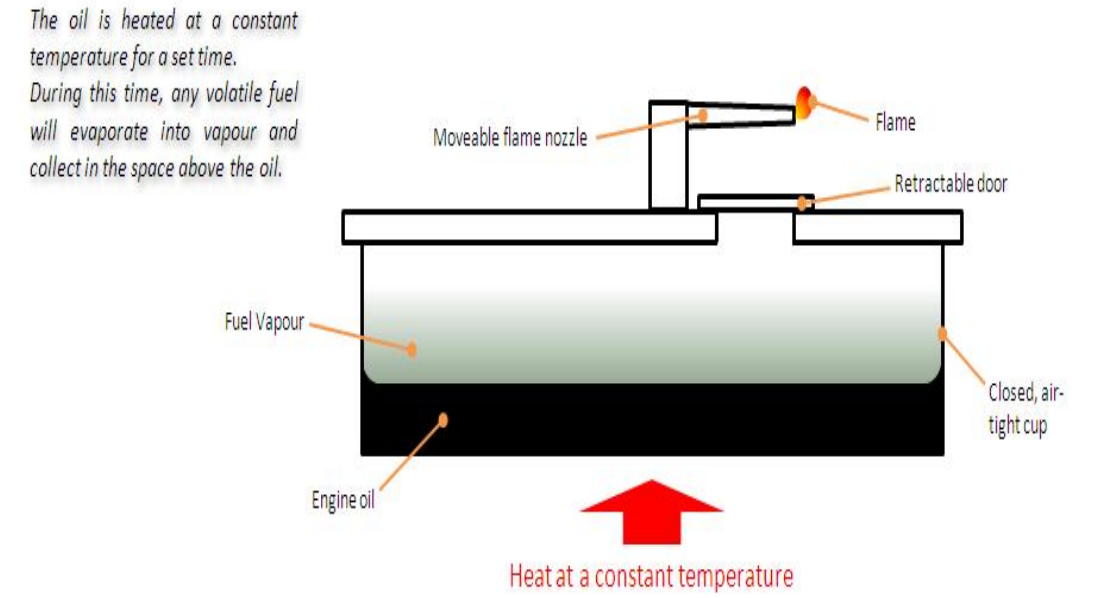
High surface tension leads to bad combustion (glass and mercury).
Low surface tension leads to good combustion (glass and water).

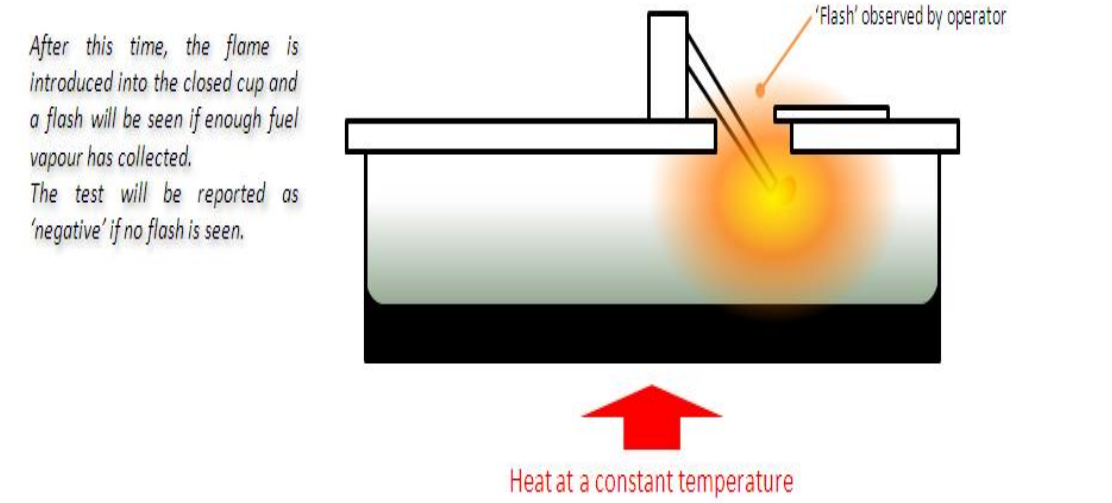
5. Pour point:

The temperature at which fuel will just flow under slandered test.

6. Flash point:

The temperature at which just enough vapors to form flammable mixture with air.





Flash point is inversely proportional to the fuel volatility.
F.pt is very useful for handling and storage of fuel.

Fuel	Flash point(C)
Gasoline	30-32
Diesel oil	60-65
Fuel oil	110-120

7. Spontenous ignition temperature (S.I.T):

The temperature at which fuel will ignite in the presence of air without flame.

S.I.T is very much greater than flash point.

S.I.T of gasoline from 260-265 C

8. Carbon hydrogen ratio:

Its give a very useful indication for the properties of fuel.

When Hydrogen decrease , its associated with increasing the Sp.gr and viscosity, but its tends to decreasing the C.V and give incomplete combustion.

9. Sulfur content:

Present in petroleum oil as free sulfur, hydrogen sulfide, mercaptens and thioether.

Presence of sulfur and its compound in fuel will lead to the formation of sulfur oxides which are acidic gases (SO_2, SO_3), and tends to air pollution and formation of strong corrosive environment.

10.Ash content:

Refers to the quantity of non combustible materials in the fuel.

Non combustible materials is inorganic material such as metals, salts, oxides)

Percent of ash in fuel is nearly 0.1%.

Ash separation is uneconomic process.