

Unit 4

Corrosion

Corrosion → It is the process in which degradation or deterioration of Metal from its surface due to the unwanted chemical with its environment

Example → a) - Rusting of Iron

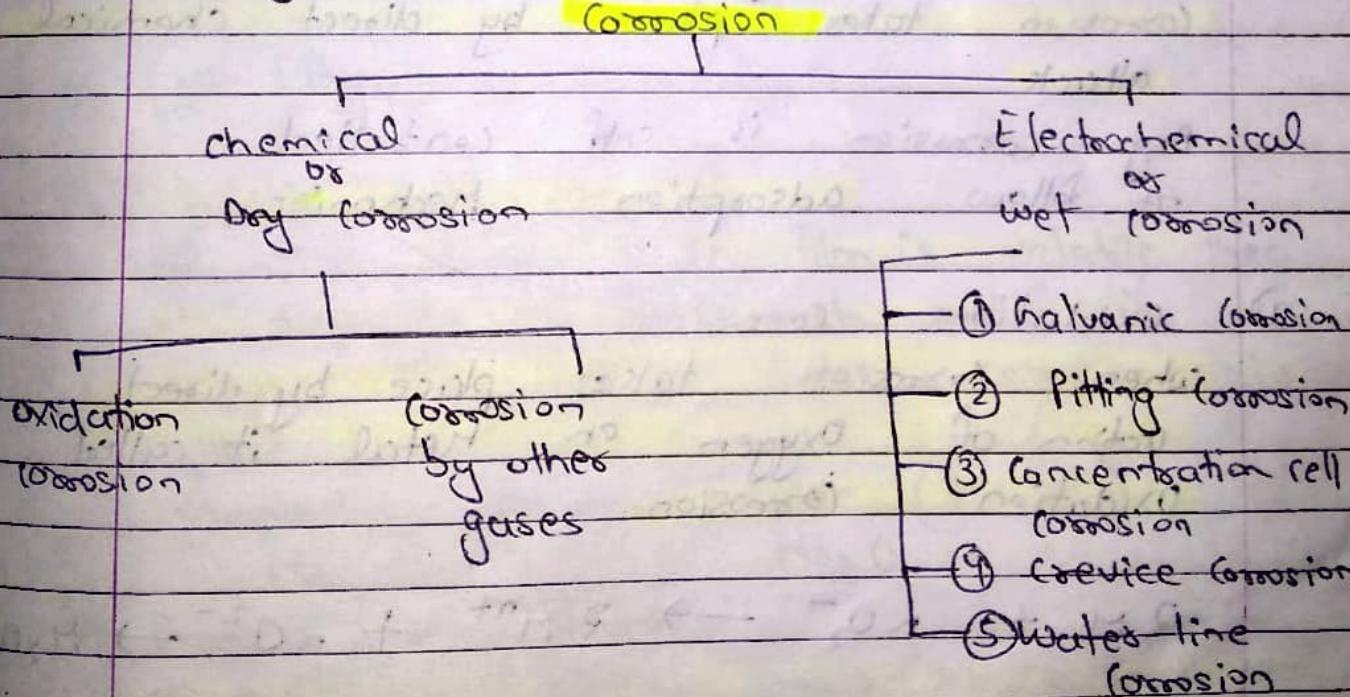
b) formation of green coating on surface of copper

c) tarnishing of corrosion

Consequences of corrosion

- 1) It causes contamination of potable water
- 2) It may cause leakage of inflammable gas from the corroded pipe line resulting into fire hazard and leakage of toxic product.

Theory of Corrosion



Dry Corrosion

- 1) Slow Process
- 2) Occur in absence of Moisture
- 3) Involves direct attack of chemicals on the metal surface
- 4) Process of corrosion is uniform

~~Wet~~

- 5) Corrosion product are produced at Site of corrosion

Wet Corrosion

- 1) Rapid Process
- 2) Occur in presence of conducting Medium
- 3) Involves formation of electrochemical cells.
- 4) Depend on the size of the anodic Part of the Metal
- 5) Corrosion occur at anode but rust is deposited at cathode

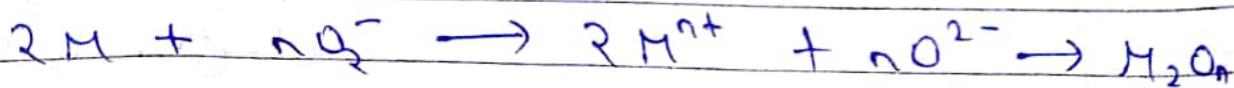
A) Chemical or dry corrosion

Corrosion takes place by direct chemical attack

Dry corrosion is self controlled
It follows adsorption Mechanism

B) Oxidation + corrosion

When corrosion takes place by direct action of Oxygen on Metal it called
Oxidation corrosion



Role of nature of oxide formed in oxidation corrosion.

Nature of oxide film formed plays an important part of in corrosion process. If the thickness of the oxide layer is less than 300 \AA then such layer is called a film.

According to the nature of these are following types of film.

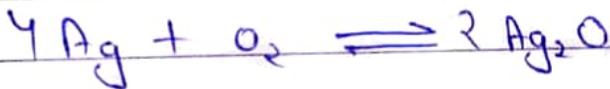
1) Stable film

Thick film and adhere to metal surface tightly this form protective coating over the metal and prevent further oxidation or corrosion.

eg \rightarrow Al, Cr, Sn, Pb.

2) Unstable film

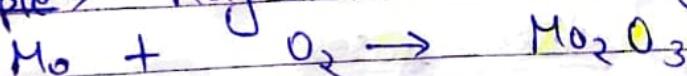
This film is decomposed back into metal and oxygen so it is called unstable and hence do not undergo corrosion like Pt, Au and Ag etc.



3) Volatile oxide film

If the metal oxide film is volatile then it evaporates \rightarrow The fresh metal is exposed air thus faster corrosion take place.

Example \rightarrow Molybdenum oxide (Mo_2O_3)



4) Porous / Non protective

If the oxide film is porous (having small pores) oxygen gas can pass & continue the corrosion.

Ex- Oxide films of iron (steel), Na, Mg, K, Cl

Pilling Bedworth Rule

The ratio of volume of oxide to the volume of metal consumed is called pilling bedworth rule.

$$\text{Pilling Bedworth Ratio} = \frac{\text{Volume of Metal Oxide}}{\text{Volume of Metal}}$$

If smaller the ratio then greater is the oxidation corrosion

case 1 Volume of oxide $>$ volume of parent metal
 (Pilling bedworth ratio is more than unity)

then the metal oxide film is non porous, protective eg - Al, Cr, Cu and W etc.

case 2 Volume of oxide $<$ volume of parent metal (Pilling bedworth ratio is less than unity)

In such case metal oxide film is porous and non-protective in nature
 eg - Na, Ca, Li & Mg

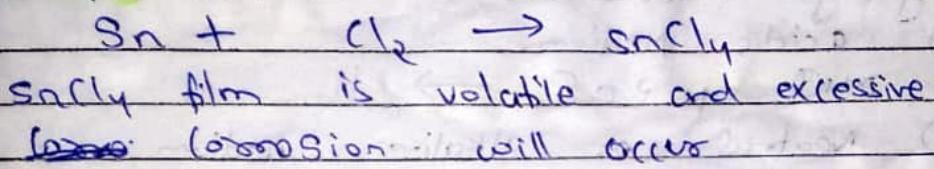
(Stable film & Non porous \Rightarrow)

Corrosion by other gases

Some gases such as Cl_2 , H_2S , SO_2 , CO_2 , Fe etc also show corrosive effects with metal. The extent of corrosion depends upon the chemical affinity b/w the metal and gas involved.

If protective film The extent of attack or corrosion is decrease eg $\text{Ag} + \text{Cl}_2 \rightarrow \text{AgCl}$
 This silver chloride film protects further corrosion.

If non-protective film The extent of attack is or corrosion is increases even destroy the whole metal



H₂S attacks on steel forming FeS layer which is porous in nature.

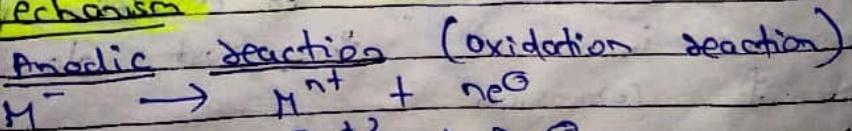
B) Electrochemical or wet corrosion

when corrosion takes place mostly in wet or moist conditions through the formation of electrochemical cell

Transfer of electron from one anodic parts of metal to cathodic through a conductive soln is called electrochemical corrosion.

Example formation of rust, the mechanism of rust formation in (i) acidic and (ii) neutral medium.

Mechanism



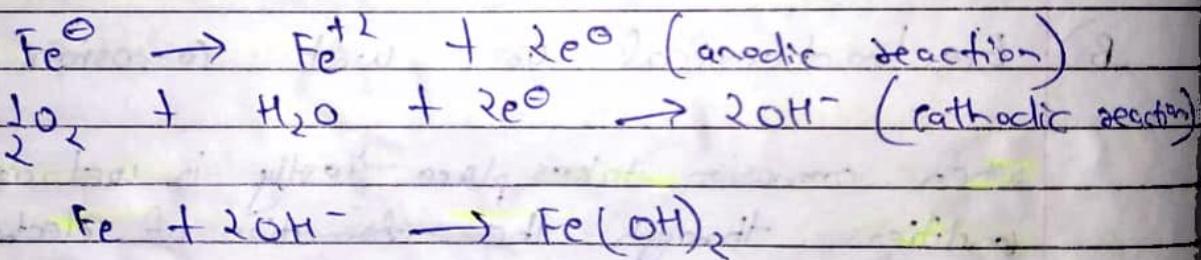
Nob Metal is destroyed or change into metallic ion corrosion takes place at anodic area But rust is deposited near cathodic area.

- ~~WR~~
- i) Cathodic reaction (Reduction Process)
- Absorption of Oxygen in presence of dissolved oxygen
- acidic Medium
 $4H^+ + O_2 + 4e^- \rightarrow 2H_2O$
 - Neutral or alkaline Medium
 $2H_2O + O_2 + 4e^- \rightarrow 4OH^-$

ii) Hydrogen evolution

- acidic Medium
 $2H^+ + 2e^- \rightarrow H_2$
- Neutral or alkaline Medium
 $2H_2O + 2e^- \rightarrow 2OH^- + H_2$

Overall reaction of rusting of iron



Types of Electrochemical

- i) Pitting Corrosion (Pit Means holes)
- Pitting corrosion is the localized corrosion which form pits and holes of a Metal surface confined to a point or small area that takes the form of cavities. Pitting corrosion is one of the most damaging form of corrosion.

Pitting factor is the ratio of depth of deepest pit resulting from corrosion divided by the average penetration as calculated from weight loss

Prevention

- i) Proper selection of Material with known resistance of to the service environment
- ii) Cathodic Protection and / or Anodic Protection
- iii) control pH, Temperature
- iv) use higher alloy (ASTM A48)

3) Differential Aeration Corrosion

Differential Aeration Corrosion takes place where there is an uneven supply of oxygen to areas of the same metal component. It is a type of electrochemical corrosion that affects Metal such as steel and iron.

2) Waterline Corrosion

It is a corrosion that happens when material is in contact with water. Waterline corrosion occurs when one portion of a base material is submerged in the water and another portion is in contact with the air.

This creates a differential of the amount of oxygen in contact with the material's surface above and below the waterline and results in a corrosive reaction.

4) Crevice Corrosion

use the hole or gap that is formed in both Metal & Non Metals.

Identify → It is normally confined to one metal at localized areas within or close to the joining surfaces.

5) Soil Corrosion

It is a geologic hazard that affects buried metals and concrete that is in direct contact with soil or bedrock. Soil corrosion is a complex phenomenon.

with a multitude of variables involved.
Pitting corrosion and stress corrosion are ;
result of soil corrosion which leads to
underground oil and gas transmission pipeline
failures.

In some respects corrosion in soils resembles
atmospheric corrosion in that observed
usually higher than in the atmosphere.

6) Stress Corrosion

occurs due to presence of shear stress caused
by heavy working like rolling.

It is result of combined effect of static
tensile stress & corrosive environment

Stress corrosion is a form of galvanic corrosion
where stressed areas of the materials
are anodic to the unstressed area of the
material.

Practically it can be controlled by limiting or
reducing the stress.

This form of corrosion is particularly dangerous
because it may not occur under a particular
set of conditions. The corrosion is not
clearly visible.

Example → Brass in ammonia.

~~WT~~

Concentration cell corrosion

- a) Differential aeration corrosion
- b) Pitting corrosion
- c) Water line corrosion

Concentration cell corrosion occurs when two or more areas of a metal surface are in contact with different concentrations of some SOL° .

Metal in concentration cell, oxygen concentration cells and active passive cells.

This type of corrosion cells may occur in soils when a metal is exposed to an environment containing varying levels of electrolyte either as different substances or of same substances in different amounts.

For example if one electrolyte is dilute salt SOL° other concentrated salt SOL° then a concentration cell formed.

This takes place when it one factor determine an electrode potential is the electrolyte concentration.

Dissolved salts can be quite complex mixtures.

Include Ca , Mg , other metals and
~~or~~ may be sulfates, chlorides.

The role of these salts are greatly.

Galvanic (or Bimetallic) corrosion

It is also known as bimetallic corrosion is an electrochemical process whereby one metal corrodes in preference to another metal that it is in contact with through an electrolyte.

Galvanic corrosion is caused when two dissimilar metals are electrically connected with each other and are exposed to an electrolyte. The two

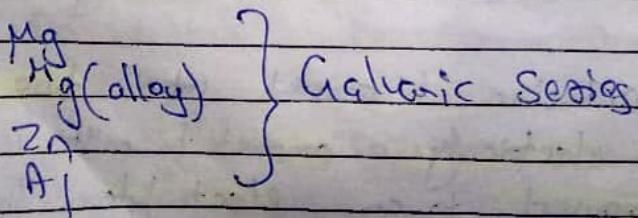
Metallic parts constitute a galvanic cell in which the metal with the lower electrochemical potential will get corroded.

Larger the potential difference b/w metals greater will be corrosion.

$\text{Ex} \rightarrow \text{Zn & Cu}$ are in contact with each other in presence of electrolyte then zinc which is higher in electrochemical series forms the anode and gets dissolved (corroded) while Cu which is lower in electrochemical series acts as cathode and is protected.

Prevention

- Selecting materials with similar corrosion potentials
- Installing a sacrificial anode that is anodic to both metals
- Separating the two materials by inserting a suitably sized spacer.
- Breaking the electrical connection by insulating the two metals from each other
- Applying coating to both materials



WZ factor affecting corrosion

Purity of Metal

Physical state of Metal

Nature of oxide film

Relative areas of cathode & anode

Position of Metal in Galvanic Series

Environmental factors

Temperature

pH

Effect of Velocity

Presence of impurities in atmosphere

Prevention of corrosion

- Material Selection
- Modifying the environment
- protection by proper designing
- use of protective coatings
- Modification of properties of Metal

Passivity

Passivity is the phenomenon by which a Metal or alloy

is a process in which corrosion resistivity increases. It is coating of a material so it becomes passive towards corrosion or less affected by corrosive environment

why it is done

ex) stainless steel. Fe (x) Ni C is it

used of operation equipment like Scissor etc so corrosion not happens.

stainless steel की functionality देखा जाएगी।

Manufacture stainless steel, then

Step 1 clean

Step 2 Passivation bath \rightarrow HNO_3 , then water for some time.

Step 3 Testing $\xleftarrow{\text{Water testing}}$ Salt testing

Protective Measures of Corrosion

1) Surface coating Method

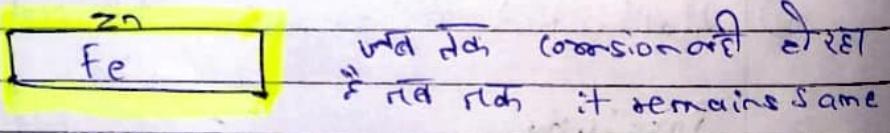
Protecting the surface of an object by the application of coating by different Methods.

Type of Coating

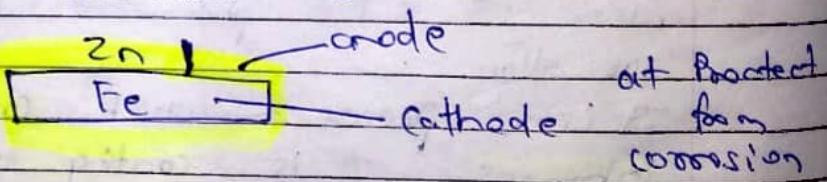
a) Anodic coating \rightarrow ~~Iron~~ Metal not Protected
~~जारी है~~ called Base Metal. जिसे ब्यूट

coating की विनि \geq More active metal of
Means which have low electrode potential \Rightarrow

Galvanization Coating of zinc is applied to
Iron



But when cracks occur -

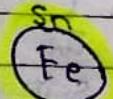


b)

Base metal applying thin layer of
tin on iron
 $Tin(Fe)$

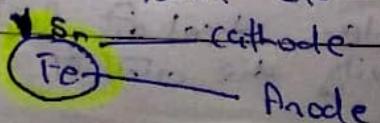
Cathodic coating (Base Metal की विनि less no. in electrochemical series की जाति से coating होता है)

Tinning



Sn is Noble element and
when it expose or in contact with
air it does not react and
protect from corrosion

When cracks occur



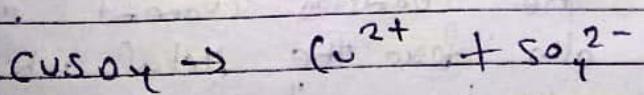
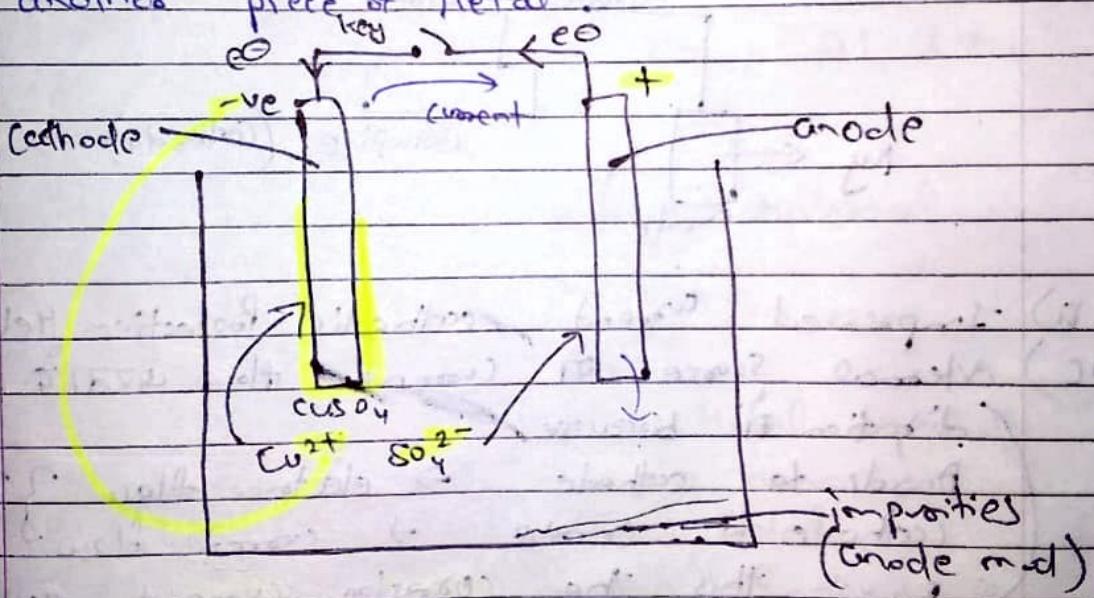
Methods of Coating

- 1) Hot dipping \rightarrow Base Metal के impurities removed by H_2SO_4
through dry chamber मिट्टी removed
then, Zn के Melt में Base Metal 45
apply करते हैं (Some को तिण)
- 2) Metal cladding
- 3) Electro plating

Base Metal \rightarrow cathode (-ve sign)

जिसकी coating करनी है, at Anode (+ve sign)

It is a process of applying a metal coating on another piece of Metal.



SO_4^{2-} & anode +ve charge ion $CuSO_4$ को लेगा
पापम से & $CuSO_4$ की जलती नहीं होती।
& anode dissolve एवं रहेगा।

3) Cathodic protection Methods (Electrical protection method)

Principle → The principle involved in this method is to force the metal to be protected to behave like a cathode thereby corrosion does not occur.

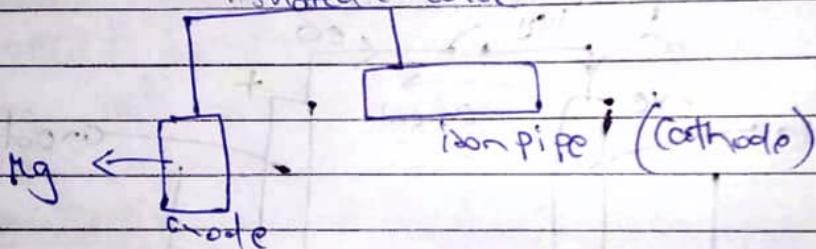
Two Methods

- Sacrificial Anodic Protection
- Impressed current Method.

i) Sacrificial Anodic Protection

e.g. galvanization

generally used in under ground Pipe
insulated copperwise



ii) Impressed current cathodic Protection Method.

(DC) External Source. से वर्ता का निकलना वाली ओपोसिट
direction ही because

Anode to cathode → electron flow } In cell
cathode to anode → current flow }

By using this the corrosion current may be
nullify & also force the metal which
works as anode change itself to cathode.

DC

-ve terminal
Metal जिसकी दूरी बढ़ावा देनी है
अंदर बढ़ावा देनी है

+ve terminal
the terminal
other metal (like graphite
or ऐसे)

Sacrificial Anodic Protection

→ Actve Metal at anode not at corrosion site

→ Direction of flow of current of corrosion is same as the direction of current by us as result Metal has anodic & cathodic combined layer.

The Metal to be protected is connected to a (active) More anodic Metal with a wire so that the active metal acts as sacrificial anode and undergoes corrosion protecting the cathode.

Sacrificial anode → Ag, Zn, Al & their alloys.

Prevention of corrosion through Material Selection & design.

- 1) Proper Selection of Material
- 2) Avoid contact of dissimilar metal especially if working environment is corrosive.
Ex → Wooden post join by iron Metal.
- 3) If unavoidable to choose 2 dissimilar metal than
- i) Area of Anode is larger than cathode
Anodic metal should not be painted

Proper design

- a) Design should be even if corrosion occurs it is uniform & does not result in intense corrosion.

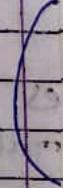
- 3) a) b) Avoid sharp bends
- c) Avoid sharp corners
- d) Surface of 2 joining should be smooth
- e) Avoid use of metal washers instead use plastic & ribbed washer
- f) Avoid use of screws, nuts, & bolts instead use welding for joints which prevent entry of gases & liquid inside

i) s

c

ge

ii)
(DC)



met

Nano Technology

→ The word signifies very small objects of range of $1 - 100 \text{ nm}$.

→ Behaviour of matter at 'nano' level is considerably different from the bulk behaviour of matter.

The physical, chemical, electrical property of Nanomaterials is different from the particles of the same material.

* → Nanostructured Materials :- of bigger size

1) zero dimension → fullerenes, Nanoparticles

2) One dimension → Carbon Nanotube, CNT fibre

3) Two dimension → graphene, Nanofilm

4) Three dimension → composite Nanomaterial.

Imp.

→ The nanoparticles have a relatively larger surface area than ordinary materials.

* → Properties of Nanomaterials :-

→ High tensile Strength

→ The properties of nanomaterials are very different from those of bulk material.

→ The nano size increases the surface area and has a marked effect on the electrical, electronic, optical and catalytic properties.

→ The properties of materials such as melting point and conductivity show a marked change.

heating point depresses by about 50% in nanoscale
and the metals change from conductors to semiconductors and also to insulators
→ Bulk gold is golden in colour; it is lustrous, ductile, good conductor of heat and electricity, is chemically inert. MP 1080°C

Nanogold on the other hand, It is never golden; it has a variety of colours depending upon the shape and size of the nanoparticle. It is not a metal but a semiconductor that melts at low temperature. (-940°C)

Nanogold acts as good catalyst.

* Applications of Nano Technology :-

- i) Energy Storage
- ii) Defense & Security
- iii) Metallurgy & Minerals
- iv) Electronics
- v) Optical Engineering & Communications
- vi) Biomedical and drug delivery
- vii) Agriculture and food
- viii) Cosmetics and paints
- ix) Biotechnology
- x) Textile

* Surface Characterization Technique,

- characterization of nanomaterials helps in understanding the physical and chemical properties of nanomaterials.
- It also helps in determining the structure at atomic and microscopic levels. Bulk properties like Shape, size, phase, electronic structure,

surface area, surface composition are determined by various characterisation techniques.

- The commonly used techniques are Brunauer-Emmet-Teller (BET) surface area analysis, Scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), Transmission electron microscopy (TEM), etc.

Brunauer-Emmet-Teller (BET) Surface Area Analysis

- This method helps in determining the surface area, pore size and pore size distribution of nanomaterials.
- This is done by Gas Sorption Method.
- Prior to determination the adsorbed foreign particles are removed from the surface of the adsorbent by heating and degassing by vacuum force.
- After cleaning the sample is brought to a constant and very low temperature usually in a dewar flask containing liquid nitrogen (77.4 K).
- Controlled doses of adsorbate gases are admitted into the evacuated sample chamber. They are first adsorbed and then desorbed.

Adsorption and desorption isotherms are obtained by subjecting the gas to a wide range of pressure. The amount of gas adsorbed or desorbed is estimated by noting the pressure variations due to adsorption or desorption of the adsorbate gas molecules on the adsorbent.

By knowing the area occupied by one adsorbate molecule, the total surface area can be determined using the adsorption model.

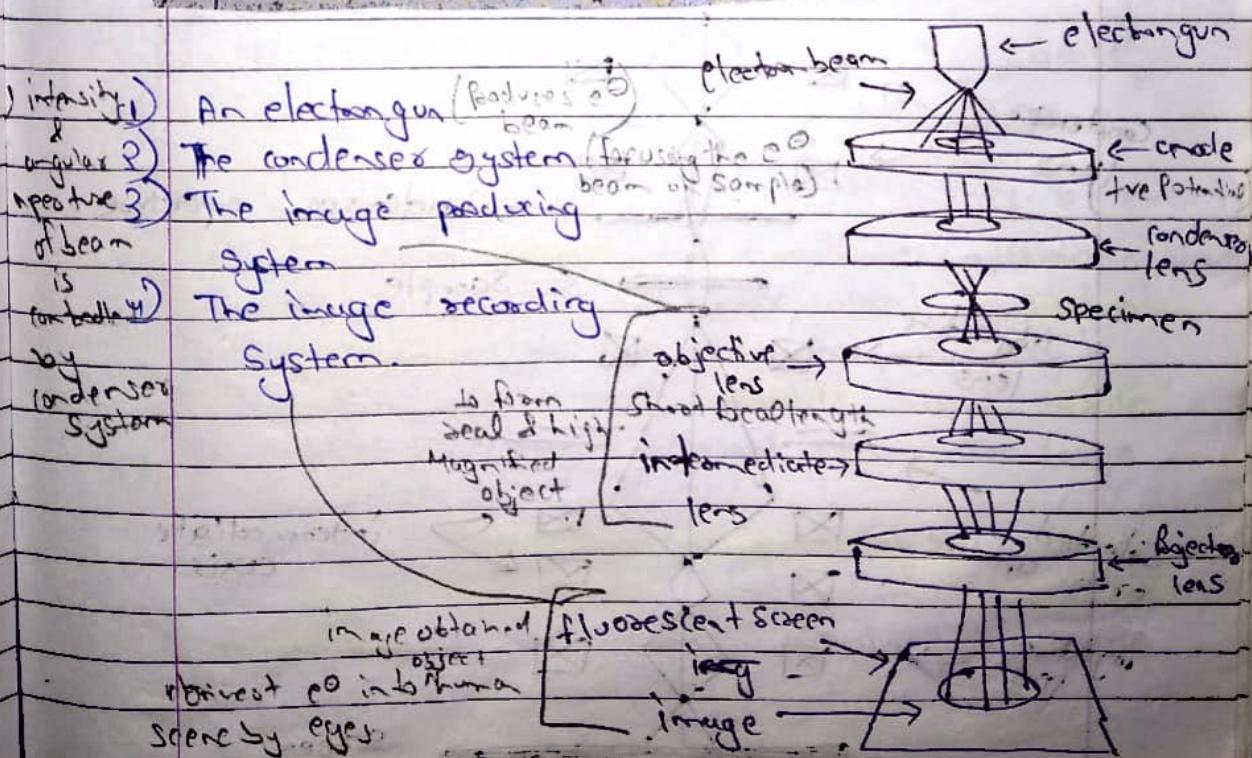
Application

- 1) Non-destructive Method
- 2) simultaneous acquisition of surface area and pore size data
- 3) surface area analysis of solid material such as Carbon black.
- 4) cement & concrete

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② Transmission Electron Microscopy (TEM) :

- This technique is used for the structural formations of solid material both by imaging and by electron diffraction.
- In TEM, a thin specimen is irradiated with an electron beam of uniform current density; the electron density is in the range of 60 - 150.
- For high-resolution TEM (HRTEM) or high voltage electron microscope (HVEM) the electron density of 200 keV - 1 MeV is used.
- The electrons emitted from the electron gun by thermionic emission from tungsten cathodes or LaB₆ rods enter the sample and are scattered as they pass through it.
- They are then focused by the objective lens and amplified by the magnifying projector to produce the desired image.



1) An electron gun (produces e⁻ beam)
 2) The condenser system (focusing the e⁻ beam on sample)
 3) The image producing system
 4) The image recording system.
 To form real & high magnified object

Advantages

- 1) very small amount of specimen is required for analysis
- 2) 3D image obtained gives more information about the specimen.

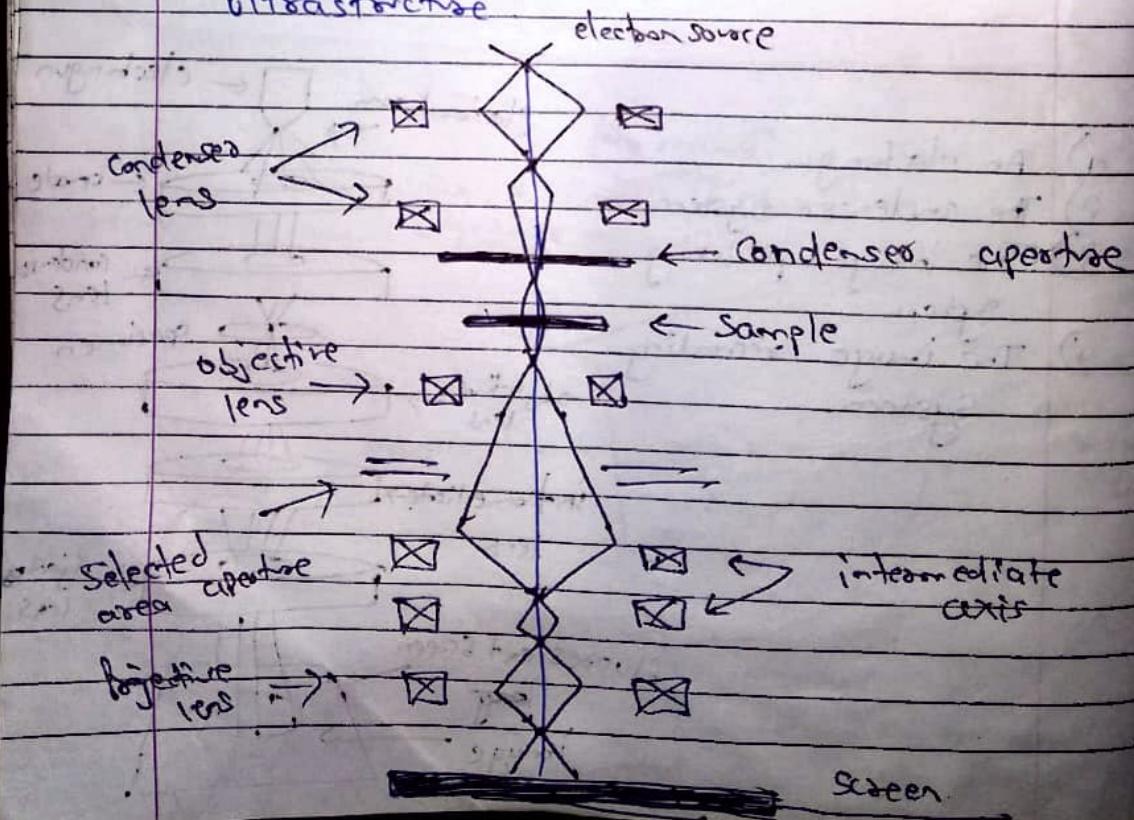
Disadvantages

- 1) High vacuum is required to maintain
- 2) large 3) expensive 4) Images are black & white

~~wt~~

Applications

- 1) TEM provide topographical, morphological, compositional and crystalline information
- 2) The images allow researchers to view samples on a molecular level, making it possible to analyze structure and texture
- 3) Cancer research studies of tumor cell ultrastructure



GREEN TECHNOLOGY AND ITS GOAL

Green technology is also called as clean technology ,it conserve the natural environment and resources.

It is a continuous process of development of materials and methods for generating energy to give non toxic products .

Expected goal of green technology

Sustainability

Cradle to cradle design

Source reduction

Innovation

Viability

Objectives of green technology

Deliver clean ,non polluting and renewable source of energy.

Optimise the use of natural resources and improve the efficiency of resource use ,specially of electricity.

Manage all the wastes generated by their reduction ,reuse and recycle .

very very Important

Twelve principles of green chemistry

Dr. RUDY GORE

1. Prevention of Waste
2. Atom Economy
3. Minimization/Prevention of Hazardous Chemical Synthesis
4. Design Safer Chemicals
5. Use of Safer Solvents and Auxiliaries
6. Design for increase in energy efficiency
7. selection of renewable feedstocks as starting material
8. Avoid of chemical derivatives
9. Use of catalysts and non stoichiometric reagents
10. Products designed should be biodegradable after use
11. Strengthening of analytical techniques for pollution prevention
12. Design of manufacturing plants to minimize the potential for accidents

It is adopted to allow process monitoring and control and minimize the formation of toxic substances

adopt that synthetic procedure which produce substance are not toxic & do not harm living organisms and environment

chemicals are designed in such a way that it do not cause severe accidents like explosions or fire release in case of accidental.



ATOM ECONOMY

Ratio of total mass of atoms in desired product to the total mass of atoms in reactants

Most of the reactant atoms becomes incorporated into the final desired product thus reducing the waste or the by products.

If a reaction may have a percentage in yield of 100% but may not be considered as green synthesis if large amounts of by products are obtained.

If percentage atom economy is 100 then the reaction is completely green synthesis

$$\text{Reaction Yield} = \frac{\text{quantity of product isolated}}{\text{theoretical quantity of product}} \times 100\%$$

$$\% \text{ yield} = \frac{\text{Actual yield}}{\text{Theoretical yield}} \times 100$$

$$\text{Atom Economy} = \frac{\text{molecular wt. of desired product}}{\text{molecular weight of all products}} \times 100\%$$

CALCULATING ATOM ECONOMY

Often, chemical reactions produce unwanted products along with the product you want.

ATOM ECONOMY is the mass of product you want as a % of the mass of all the products you make

Useful
product

Waste product

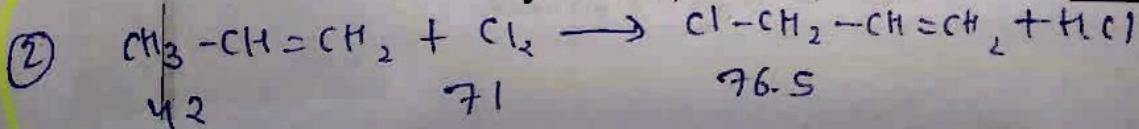


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$$\text{ATOM ECONOMY} = \frac{\text{mass useful product}}{\text{mass of all products}} \times 100\%$$

$$\% \text{ atom economy} = \frac{\text{mass useful product}}{\text{Reactant + all products}} \times 100\%$$

$$\text{Atom Economy} = 56 / (56 + 44) = 56 / 100 = 56\%$$



$$\% \text{ Atom Economy} = \frac{76.5}{42 + 71} = \frac{76.5}{113} \times 100 = 67.7\%$$

Zero waste technology

Zero waste technology - in the synthesis of chemical reaction there are no by products formed or if any by product as waste are formed they can be used as raw materials or starting material in other reaction.

Zero waste is the recycling of all materials back into the nature or the market place in a manner that protects human health and environment .

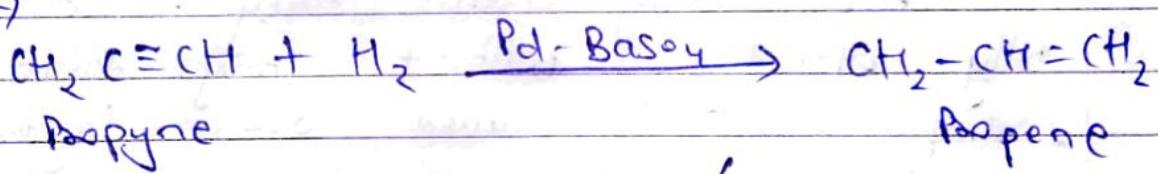
Zero Waste is a set of principles focused on waste prevention that encourages the redesign of resource life cycles so that all products are reused. The goal is for no trash to be sent to landfills, incinerators, or the ocean. Currently, only 9% of plastic is actually recycled.

7) Selection of Renewable feedstocks as starting material.

Starting Material :
Green chemistry emphasizes the need of use of raw material that is renewable & for electricity generation instead of coal (non renewable), green chemistry would suggest agricultural waste like bagasse, rice hulk (renewable feedstocks).

9) Use of catalyst and Non-stoichiometric Reagents (innocuous reagents).

use of selective catalysts is avoided.
increases (by lowering activation energy)
the specificity of the reaction and
reduce the formation of by products.



Selectivity is increased

5) Use of Softer Solvent and Auxiliaries (alternative solvents). The use of auxiliary substance used in purification and separation (for example chromatography) are generally non-volatile and toxic in nature. They required in one large volume also.

Ex -> In New drycleaning clothes, liquid carbon dioxide instead of perchlorethylene is used for dissolving grease.

5) Design for increase in energy efficiency.
Chemical reactions require lots of energy like extensive cooling of exothermic reaction, preparation of cement, glass requires high temperature ($1600 - 1800^{\circ}\text{C}$). This energy generally comes from use of fossil fuels.

Green chemistry emphasizes to develop of such chemical procedures that can be carried out at room temperature and pressure.

Energy supplied by photochemical means microwave.

4) Use of safer chemicals

The reaction product should be designed in such a way that they should be fully effective without any toxic effects. Example → CFCs cause ozone layer depletion due to release chlorine free radical.

To prevent this chemist designed hydrofluor carbon in which chlorine group replaced by hydrogen. The ozone depletion potential of this compound is far less than CFC.

8) Reduce / Avoid chemical derivatives.

Avoid extra steps in chemical reaction it causes extra detergent & generate waste.

(a) In conversion of hydroxy phenyl benzoic acid from hydroxy benzaldehyde, benzyl chloride (is hazard) is used to protect OH group.