UNIT-5

GENERAL PRINCIPLES OF METALLURGY

Syllabus : Occurrence of metals, minerals and ores, Concentration of ores- levigation, magnetic separation, froth floatation, leaching, Conversion of concentrated ores to oxide- calcination and roasting, reduction of oxide to the metal, Refining of crude metal-distillation, liquation, poling, electrolysis, zone refining and vapour phase refining, Corrosion and its prevention, Alloys.

Occurrence of metals:

Generally metals occur in nature in two forms namely Free State and Combined state. Very few metals occur in nature in native form i.e occur in the free or elementary state.

Examples: Gold, platinum, silver and mercury etc.

Most of the metals occur in combined state. These metals occur in nature in the form of compound like oxides, carbonates, halides, sulphides and sulphates etc

Examples:

Oxides- Manganese as pyrolusite (MnO_3), Aluminum as bauxite ($Al_2O_3.2H_2O$) and iron as magnetite (Fe_3O_4).

Carbonates- Zinc as calamine ($ZnCO_3$), Calcium as lime stone ($CaCO_3$) and Magnesium as magnesite ($MgCO_3$).

Halides- Silver as horn silver (AgCl), Sodium as Common salt (NaCl) and Magnesium as Carnalite ($KCl.MgCl_2.6H_2O$).

Sulphides- Lead as galena (PbS), Zinc as Zinc blend (ZnS), Copper as Copper pyrites ($CuFeS_2$).

Sulphates- Calcium as gypsum ($CaSO_4.2H_2O$) and Magnesium as Epson salt ($MgSO_4.7H_2O$) etc.

Mineral: The compounds of metals occur in the earth's crust along with a rock and other impurities are called minerals. Examples of minerals: Bauxite – mineral of aluminium, Hematite (Fe_2O_3) – mineral of iron, Galena (PbS) – mineral of lead, Zinc blende (ZnS) – mineral of zinc

Ore: An ore is a mineral from which a metal can be extracted economically and profitably using available methods.

Examples of ores: Bauxite → ore of aluminium, Hematite → ore of iron, copper pyrites ($CuFeS_2$) → ore of copper, Cinnabar (HgS) → ore of mercury

In general, all ores are minerals but all minerals are not ores.

Concentration of ores:

1. Levigation: Levigation is a method used for the concentration of ores based on the difference in densities of the ore particles and the gangue (impurities).

Principle:

When a finely powdered ore is washed with a stream of water, lighter gangue particles are washed away, while the heavier ore particles settle down due to gravity.

Process:

1. The ore is first crushed and powdered.
2. The powdered ore is placed on a sloping platform or trough.
3. A stream of water is allowed to flow over it.
4. Light impurities (sand, clay, soil) are carried away by water.
5. The heavier ore particles remain behind, thus concentrating the ore.

Suitable Ores: Levigation is mainly used for ores in which the ore particles are much heavier than the gangue. Examples

Gold ore – removal of sand and soil, Tin ore (Cassiterite, SnO_2), Lead ore, Iron ores mixed with lighter impurities

Advantages:

- Simple and economical method
- No chemical reagents required
- Environment-friendly

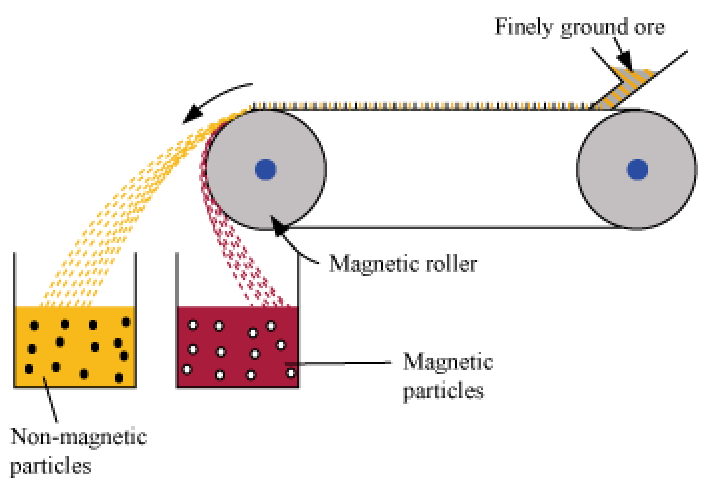
Limitations:

- Not suitable when ore and gangue have similar densities
- Fine ore particles may be lost with water

2. Magnetic separation:

Electromagnetic separation: Magnetic separation is a method used for the concentration of ores based on the difference in magnetic properties of the ore and the gangue.

If the impurities present in the ore are magnetic in nature, they are separated by electromagnetic separation. The magnetic separator consists of a leather belt moving rover two rollers, out of which one is magnetic. The powdered ore is dropped on the belt at one end at other end the magnetic impurity of the ore is attracted and falls nearer the magnetic roller in the form of a heap.



Ex: Ferromagnetic ores such as Fe_2O_3: tin stone an ore of tin containing wolframite $FeWO_4$ as a magnetic impurity. This method is used when either the ore or the gangue is magnetic. Examples

Iron ores, Magnetite (Fe_3O_4) – magnetic, Hematite (Fe_2O_3) – weakly magnetic, Chromite ($FeCr_2O_4$), Manganese ores Wolframite ($FeWO_4$) from non-magnetic impurities.

Advantages:

- Efficient and rapid process
- No chemicals required
- Low operational cost
- Environment-friendly

Limitations:

- Not suitable if both ore and gangue are non-magnetic
- Requires dry powdered ore.

<u>3. Froth floatation:</u>

The froth flotation process is a widely used method for the concentration of sulphide ores, based on the difference in surface properties (wettability) of the ore and the gangue.

Principle

Sulphide ore particles are hydrophobic (water-repellent).Gangue particles are hydrophilic (water-loving).

When air is bubbled through the ore slurry, ore particles attach to air bubbles and rise to the surface as froth, while gangue sinks.

Process

1. The ore is crushed and powdered.

2. The powdered ore is mixed with water to form slurry.

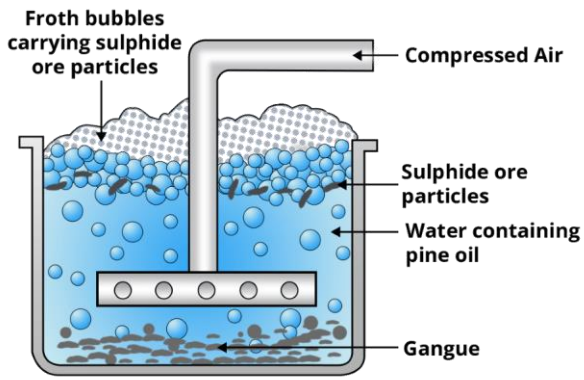
3. Small amounts of collectors (e.g., pine oil, xanthates) and frothing agents are added.

4. Air is blown through the mixture.

5. Sulphide ore particles stick to air bubbles and rise to the surface as froth.

6. The froth is skimmed off, washed, and dried to obtain concentrated ore.

7. Gangue particles remain in water.



Reagents Used:

Collectors: Make ore particles hydrophobic, Example: Pine oil, potassium ethyl xanthate

Frothers: Stabilize the froth, Example: Cresols, alcohols

Depressants: Prevent unwanted ore from floating, Example: NaCN (used to separate ZnS from PbS)

Activators: Enhance flotation of certain ores, Example: $CuSO_4$ for ZnS

Suitable Ores: Sulphide ores, such as:Zinc blende (ZnS), Galena (PbS), Copper pyrites ($CuFeS_2$)

Advantages

- Highly selective method
- Efficient for low-grade sulphide ores
- Widely used in industry-

Limitations

- Not suitable for oxide and carbonate ores
- Requires careful control of reagents

4. Leaching:

Leaching is a chemical method used for the concentration of ores, in which the ore is treated with a suitable chemical reagent that selectively dissolves the ore, leaving behind the impurities (gangue).

Principle:

The ore is dissolved in a suitable solvent, while the gangue remains insoluble. The dissolved metal is then recovered from the solution by chemical treatment.

Process (General Steps)

1. The ore is crushed and powdered.

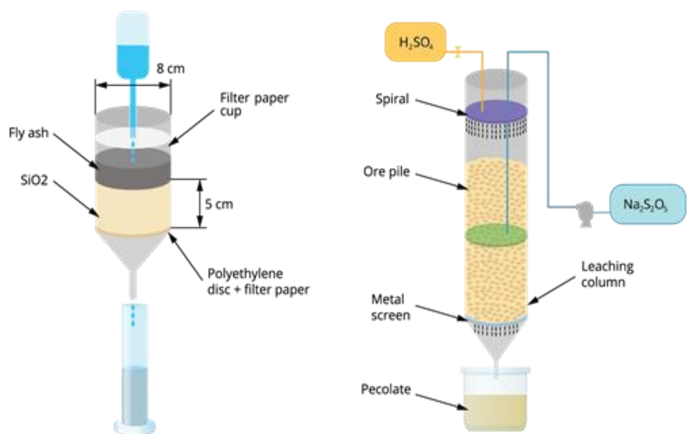
2. It is treated with a specific leaching agent.

3. The ore dissolves to form a soluble complex.

4. Insoluble gangue is filtered off.

5. The metal is recovered from the solution by precipitation or other chemical methods.

Leaching Process



Important Examples

1. Leaching of Bauxite (Aluminium Ore) – Bayer's Process

Reagent used: Hot concentrated NaOH

Reaction: $Al_2O_3 + 2NaOH + 3H_2O \rightarrow 2Na[Al(OH)_4]$

Aluminium hydroxide is precipitated by cooling and seeding. On heating, pure alumina (Al_2O_3) is obtained.

2. Leaching of Gold and Silver – Cyanide Process

Reagent used: Dilute NaCN or KCN in presence of air

Reaction: $4Au + 8NaCN + O_2 + 2H_2O \rightarrow 4Na[Au(CN)_2] + 4NaOH$

3. Leaching of Copper Ore

Reagent used: Dilute H_2SO_4, Copper dissolves as $CuSO_4$ and is later recovered by electrolysis or displacement.

Advantages

- Useful for low-grade ores
- Highly selective
- Produces high-purity metal

Limitations

- Costly chemical reagents
- Slow process
- Environmental concerns (e.g., cyanide use)

Conversion of concentrated ores to oxide -calcinations and roasting:

Calcination:

It is the process of heating the ore strongly in the absence of air without melting it. The organic matter, volatile impurities and moisture are expelled and thus the remaining mass becomes porous. Calcination is also used to remove water from hydrated oxide or carbon dioxide from a carbonate ore.

$$\underset{\text{Calamine}}{ZnCO_3} \xrightarrow{\Delta} ZnO + CO_2$$

$$\underset{\text{Bauxite}}{Al_2O_3.2H_2O} \xrightarrow{\Delta} Al_2O_3 + 2H_2O$$

$$\underset{\text{Magnesite}}{MgCO_3} \xrightarrow{\Delta} MgO + CO_2$$

Calcination is generally done in a reverberatory furnace.

Roasting:

It is a process of heating the ore strongly below its melting point in the presence of air in order to bring about its oxidation. Organic matters, volatile impurities, are removed. Non metallic impurities like s. As etc are oxidized and removed as oxides. The process is generally used in the case of sulphide ores and is carried out in a reverberatory furnace or in a blast furnace.

$$2Zns + 3O_2 \rightarrow 2ZnO + 2SO_2 \uparrow\uparrow$$

$$2PbS + 3O_2 \rightarrow PbO + 2SO_2$$

$$2\ CuFeS_2 + 3O_2 \rightarrow Cu_2S + 2FeS + SO_2$$

Reduction of oxide to the metal:

The calcined or roasted ore is then reduced to metal using various types of reducing agents depending upon the nature of the ore.

1) Smelting:

It is the process in which the oxides of metals like Zn, Pb, Fe etc. when mixed with carbon are reduced to metals by heating to a higher temperature in the presence of a flux. The flux reacts with the impurities (gangue) to from easily fusible slag.

$$Fe_2O_3 + 3C \rightarrow 2Fe + 3CO$$

$$Fe_2O_3 + 3CO \rightarrow 2Fe + 3CO_2$$

Lime stone decomposes to give calcium oxide which combines with silica to form calcium silicate.

$$CaCO3 \rightarrow CaO + CO_2$$

$$CaO + SiO_2 \rightarrow Ca\ SiO_3$$

Smelting is generally carried out in a blast furnace or a reverberatory furnace.

Flux:

The ore even after concentration contain some gangue (earthy matter as impurity) which is to be removed. There are certain substances which when mixed with furnace charge and heated combine with gangue to form a fusible material insoluble in the molten metal. Such a substance is called as flux. The type of flux used depends upon the nature of the impurity to be removed.

i) Acidic flux: it is used when the gangue is basic i.e. impurities like CaO and other metallic oxides. Eg: Silica: borax etc.

$$CaO + SiO_2 \rightarrow CaSiO_2$$

Gangue Flux Slag.

ii) Basic flux: Eg: lime stone, magnesite, haematite etc. These basic fluxes are used when the gangue is acidic impurities like silica and silicates.

$$SiO_2 + MgCO_3 \rightarrow MgSiO_3$$

Gangue Flux Slag.

Auto reduction or self reduction:

In some cases, no reducing agent is required. The sulphides of less active metals like Hg; Cu and Pb are unstable to heat. A part of the sulphide ore is converted to the oxide which then reacts with the remaining part to give the metal and SO_2, Eg: Copper

$$2Cu_2S + 3O_2 \rightarrow 2Cu_2O + 2SO_2$$

$$2Cu_2O + Cu_2S \rightarrow 6Cu + SO_2$$

In Some cases the ore is converted into metallic state during roasting, Eg: Mercury

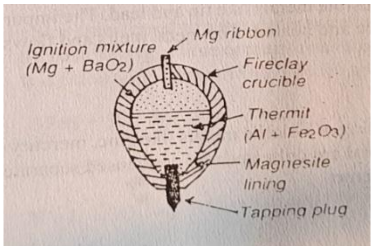
$$HgS + O_2 \rightarrow Hg + SO_2$$

Aluminothermic reduction (OR) Glod schmidts aluminothermic process:

Oxides of metals like chromium, manganese, iron which cannot be easily reduced with carbon are reduced with aluminium powder which acts as reducing agent. The charge consists of a mixture of the metallic oxide, and aluminium powder known as thermite is taken in a steel crucible and covered with an ignition mixture of magnesium powder and barium peroxide. The charge is ignited by a magnesium ribbon. The reaction is highly exothermic and the heat produced is sufficient to melt the metal. The process is used in thermite welding.

$$Fe_2O_3 + 2A1 \rightarrow A1_2O_3 + 2Fe + Heat$$

$$Cr_2O_3 + 2AI \rightarrow A1_2O_3 + 2Cr + Heat$$



Goldsmidt's Process

Electrolytic reduction:

Highly electropositive metals like Na. K. Ca. Al etc are extracted by electrolysis of their oxides, hydroxides or chlorides in fused state.

Eg: Aluminium is obtained by the electrolysis of alumina mixed with cryolite.

$$2\ Al_2O_3 \rightarrow 4Al + 3O_2$$

Refining or purification of impure metals: Generally the following methods are used to refining of metals like distillation, liquation, poling, electrolysis, zone refining and vapour phase refining.

1) Distillation:

Distillation is a method used for refining metals that have low boiling points and are volatile, while their impurities have higher boiling points and are non-volatile.

Principle:

When an impure metal is heated strongly, the metal vaporizes while the impurities remain behind. The metal vapour is then cooled and condensed to obtain the pure metal.

Process:

1. The impure metal is taken in a suitable distillation apparatus.

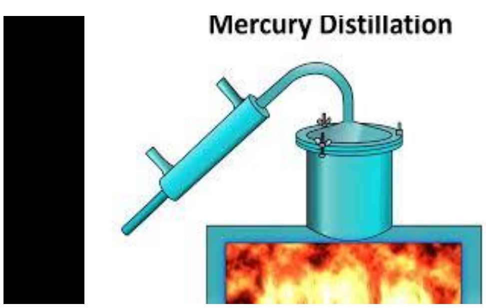
2. It is heated to a temperature above its boiling point.

3. The metal vaporizes, leaving non-volatile impurities behind.

4. The vapour is passed through a condenser.

5. On cooling, the vapour condenses to give pure metal.

The following metals are refined by distillation method like Zinc (Zn), Mercury (Hg), Cadmium (Cd)



Advantages:

- Simple and effective for volatile metals
- Produces high-purity metal

Limitations

- Applicable only to metals with low boiling points
- Not suitable for high-boiling metals
- distillation, liquation, poling, electrolysis, zone refining and vapour phase refining

2) Liquation:

Liquation is a method of refining metals that have low melting points, while their impurities have higher melting points.

Principle: When an impure metal is heated on a sloping surface to a temperature just above its melting point, the metal melts and flows away, leaving behind the solid impurities.

Process:

1. The impure metal is placed on a sloping hearth or furnace.

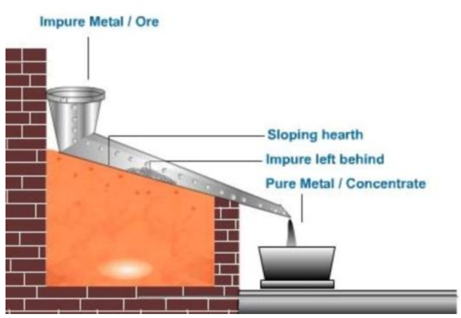
2. It is gently heated to a temperature slightly above the melting point of the metal.

3. The pure metal melts first and flows down the slope.

4. Infusible (high-melting) impurities remain on the hearth.

5. The molten metal is collected and solidified to obtain refined metal.

The following metals are refined by Liquation method like Tin (Sn), Lead (Pb) & Bismuth (Bi).



Advantages:

- Simple and economical
- Suitable for low-melting metals

Limitations:

- Not suitable for metals with high melting points
- Refining is not very high compared to other methods

3) Poling:

Poling is a refining method used to remove metal oxide impurities from molten metal's by reduction.

Principle

When green wooden poles are stirred into the molten impure metal, the reducing gases (like CO, H_2, hydrocarbons) released from the wood reduce metal oxides to pure metal.

Process:

1. The impure metal is melted in a furnace.

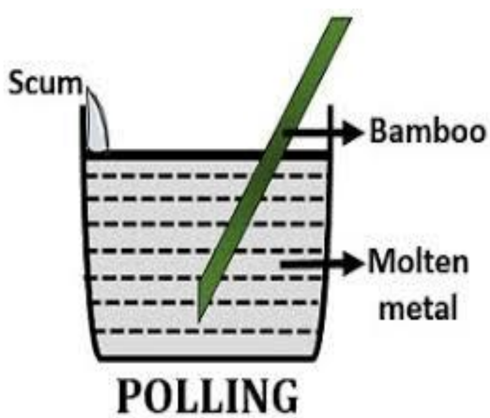
2. Green wooden poles are dipped and stirred into the molten metal.

3. Moisture and organic matter in the wood produce reducing gases.

4. These gases reduce metal oxides present as impurities.

5. The reduced metal mixes with the molten metal, and pure metal is obtained.

The following metals are refined by Poling method like Copper (Cu) (most common example) and Tin (Sn).



Advantages

- Simple and economical
- Effective in removing oxide impurities

Limitations:

- Not suitable for all metals
- Cannot remove non-oxide impurities

4) Electrolysis:
Electrolytic refining is a method used to obtain high-purity metal from an impure metal using electrical energy. It is commonly applied to metals like copper, zinc, nickel, silver, gold, and lead.

Principle

When an electric current is passed through a suitable electrolyte containing the metal ions, the impure metal dissolves at the anode and pure metal is deposited at the cathode.

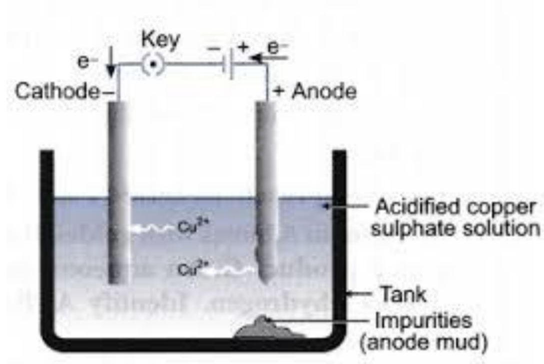
Process

1. Anode: Impure metal slab

2. Cathode: Thin sheet of pure metal

3. Electrolyte: Aqueous solution of a soluble salt of the metal

On passing electricity: Metal atoms from the anode lose electrons and go into solution as metal ions. These metal ions migrate to the cathode, gain electrons, and are deposited as pure metal. Insoluble impurities settle at the bottom as anode mud.



Electrode Reactions (Example: Copper Refining)

Electrolyte: Acidified copper (II) sulfate solution

At Anode: Cu (impure) $\rightarrow Cu^{2+} + 2e^-$

At Cathode: Cu^{2+} + 2e- $\rightarrow$Cu (pure)

Anode Mud contains precious metals like gold, silver, platinum, etc. These are recovered separately.

Advantages

- Produces very high purity metal (up to 99.9%)
- Valuable by-products recovered
- Controlled and efficient process

Limitations

- Requires electricity (costly)
- Not suitable for highly reactive metals (Na, K, Ca)
- Examples of Metals Refined by Electrolysis

The following metals are refined by Electrolysis method: vapour phase refining

Metal	**Electrolyte**
Copper	Acidified $CuSO_4$
Zinc	$ZnSO_4$
Nickel	$NiSO_4$
Silver	$AgNO_3$
Gold	$AuCl_3$
Copper	Acidified $CuSO_4$

5) **Zone Refining**:

Zone refining (also called zone melting or zone leveling) is a special method used to obtain ultra-pure metals and metalloids, particularly required in semiconductor and electronics industries.

Principle:

Zone refining is based on the fact that impurities are more soluble in the molten state than in the solid state of a metal.

When a narrow molten zone moves along a solid metal rod, impurities concentrate in the molten zone and are carried towards one end of the rod.

Process:

1. The impure metal is taken in the form of a solid rod and placed in an inert atmosphere or vacuum.

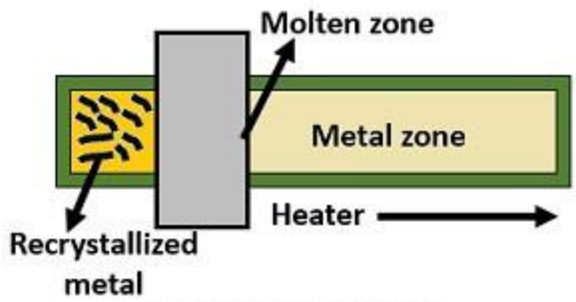
2. A circular heater melts a small region (zone) of the rod.

3. This molten zone is slowly moved from one end of the rod to the other.

4. As the molten zone travels, impurities move along with it.

5. After several passes, impurities accumulate at one end, which is cut off.

6. The remaining portion of the rod becomes highly pure metal.



ZONE REFINING

Advantages

- Produces extremely high purity metals (99.999%)
- No chemical reagents required
- Essential for electronic-grade materials

Limitations

- Slow and expensive process
- Applicable only to metals that can be melted without decomposition
- Not suitable for large-scale bulk purification

Metals Purified by Zone Refining

The following metals are refined by zone refining method like Silicon (Si), Germanium (Ge), Gallium (Ga), Indium (In), Boron (B).

6) Vapour phase refining

Vapour phase refining is a method used to obtain ultra-pure metals by converting the impure metal into a volatile compound, which is then decomposed to give pure metal.

Principle: This method is based on:

1. Formation of a volatile compound of the metal.
2. Thermal decomposition of this compound to yield pure metal.

Impurities do not form volatile compounds and are left behind.

General Steps:

1. The impure metal is heated with a suitable reagent to form a volatile compound.
2. The volatile compound is separated from impurities.
3. On heating or decomposition, the compound gives pure metal.

Important Vapour Phase Refining Processes

1. Mond's Process (Refining of Nickel)

Principle:

Nickel forms a volatile compound, nickel carbonyl ($Ni(CO)_4$), at low temperature.

Steps:

1. Impure nickel is heated with carbon monoxide at 50–60°C:

$$4Ni + 4CO \rightarrow Ni(CO)_4 \text{ (volatile)}$$

$$Ni(CO)_4 \rightarrow Ni \text{ (pure)} + 4CO$$

Purity obtained: ~99.9%

2. Van Arkel–de Boer Process (Refining of Titanium and Zirconium)

Principle:

Titanium or zirconium forms volatile iodides which decompose on a hot filament.

Steps:

1. Impure metal reacts with iodine at about 250–400°C:

$$Ti + 2I2 \rightarrow TiI_4$$

$$TiI4 \rightarrow Ti \text{ (pure)} + 2I_2$$

The following Metals are refined by Vapour Phase Method

- Nickel → Mond's process
- Titanium → Van Arkel process
- Zirconium → Van Arkel process

Advantages

- Produces very high purity metal
- Useful for metals used in electronics and aerospace
- Impurities remain completely separated

Limitations

- Costly process
- Limited to metals forming volatile compounds
- Requires precise temperature control

Corrosion and its prevention:

Corrosion is the slow deterioration of a metal due to chemical or electrochemical reaction with its environment such as air, moisture, acids, or salts.

Example: Rusting of iron in the presence of air and moisture.

Types of Corrosion

1. Dry corrosion: Occurs due to direct reaction with gases (e.g., oxidation).

2. Wet corrosion: Occurs in the presence of moisture or electrolyte (most common).

Effects of Corrosion

Weakens metal structures

Causes economic loss

Reduces efficiency and lifespan of materials

Prevention of Corrosion

Corrosion can be prevented by the following methods:

1. Protective Coatings
    - Painting
    - Oiling and greasing
    - Plastic coating
2. Metal Coating
    - Galvanization (zinc coating on iron)
    - Electroplating
    - Tinning
3. Alloying
    - Adding elements like chromium and nickel
    - Example: Stainless steel (resists corrosion)
4. Catholic Protection
    - Using sacrificial anode (Zn or Mg)
    - Used for pipelines and underground tanks
5. Use of Inhibitors: Chemicals added to slow down corrosion.

Alloys:

An alloy is a homogeneous mixture of two or more metals. Alloys can be prepared by mixing a metal with a non metal also. So an alloy can be defined as a metallic intimately mixed solid mixture of two or more different elements, atleast one of which is a metal. Alloys are homogenous in molten state but in solid state they may be either homogeneous or heterogenous. Chemically alloys may be mixtures or solid solutions of constituents in one another. When one of the metals is mercury, the alloy is called an amalgam.

Eg: Copper amalgam is an alloy of copper and mercury. Sodium amalgam is an alloy of sodium and mercury. In alloys, the chemical properties of the component elements are retained and only certain physical properties are improved, alloys are usually harder and less malleable and ductile than their constituents, have lower melting point and resists corrosion and is stable to acids.

Purpose of making alloys:

The purpose of making alloys is to develop some new property not possessed by the components individually.

i) To increase the hardness of the metal. Pure metals are generally soft while the alloys are harder. E.g: Copper increases the hardness of silver in coins. Gold is mixed with copper in making ornaments. 0.5% Arsenic is added to lead to make very strong lead bullets.

ii) To lower the melting point. In general, the alloy possess lower melting point than the original metals. For example: the wood's metal is an alloy of bismuth, lead; cadmium and tin has a melting point of only 71°c which is much lower than the melting point of any of the metals present in the alloy.

iii) To increase the tensile strength. Alloys, have greater tensile strength than the metals present in it. For example, addition of 1% carbon increases the tensile strength of pure iron by 10 times.

iv) To get good casting. Expansion of metal on solidification is the most important requirement for its use as casting material. For example. Type metal (alloy of lead and antimony); bronze (alloy of copper and tin) have good casting properties.

v) To modify colour. Aluminium-bronze which has 90% copper and 10% aluminium has a golden colour.

vi) To resist corrosion. 'ure metals are reactive and hence easily corroded by atmospheric gases, moisture etc. But alloys are more resistant to corrosion. For example stainless steel is more resistant to corrosion while iron is corroded easily even by moisture.