

METALLURGY

NEET-JEE 2020



EXTRACTION **OF** METALS

WHAT IS METALLURGY?

• **Metallurgy** is a domain of materials science and engineering that studies the physical and chemical behaviour of metallic elements, their inter-metallic compounds, and their mixtures, which are called alloys.



INTRODUCTION

OCCURRENCE OF METALS

4THE MAJOR STEPS

METALLURGY OF IRON

LUSES

INTRODUCTION

For obtaining a particular metal,

We look for <u>minerals</u>, which are naturally occurring chemical substances in the earth's crust obtained by mining.

Out of many minerals only a few are viable to be used as sources of metals. Such minerals are called <u>ores</u>.

Ores are usually contaminated with earthly or undesired materials known as <u>gangue</u>.

The entire scientific and technological process used for isolation of metal from it's ores is known as <u>METALLURGY</u>.

METALS AND THEIR ORES

• Aluminium

Bauxite		
Kaolinite (a form of clay)		
• Iron Haematite		
Magnetite Siderite		
Iron pyrites		
• Copper Copper pyrites		
Malachite Cuprite		
Copper glance		
• Zinc		
Zinc blend/Sphalerite		
Calamine		

Zincite

 $AlO_{x}(OH)_{3-2x} [where O < x < 1]$ $[Al_{2}(OH)_{4}Si_{2}O_{5}]$

 $\begin{array}{c} \mathrm{Fe_2O_3}\\ \mathrm{Fe_3O_4}\\ \mathrm{FeCO_3}\\ \mathrm{FeS_2} \end{array}$

 $CuFeS_2$ $CuCO_3.Cu(OH)_2$ Cu_2O Cu_2S ZnS ZnCO₃

ZnO

METALS AND ITS EXTRACTING TECHNIQUES

Metals - in decreasing order of reactivity	Reactivity
Potassium Sodium Calcium Magnesium Aluminium	extract by electrolysis
Carbon	
Zinc Iron Tin Lead	extract by reaction with carbon or carbon monoxide
Hydrogen	
Copper Silver Gold Platinum	extracted by various chemical reactions

PYRO-METALLURGY

- **Pyro metallurgy** is a branch of extractive metallurgy.
- It consists of the thermal treatment of minerals and metallurgical ores and concentrates to bring about physical and chemical transformations in the materials to enable recovery of valuable metals.
- Pyrometallurgy is suitable for less reactive materials like iron, copper, zinc, chromium, tin, and manganese.

THE MAJOR STEPS

<u>The 3 major steps involved in extraction and</u> isolation of metals from ores are as follows:

CONCENTRATION OF ORES

EXTRACTION OF METAL FROM CONCENTRATED ORE

≻<u>REFINING OF METAL</u>

CONCENTRATION OF ORES

<u>Removal of unwanted materials from the ore is known as</u> <u>concentration</u>.

<u>On the basis of the type of ores, some of the important processes are</u> <u>given below:</u>

4 HYDRAULIC WASHING

4 MAGNETIC SEPARATION

4 FROTH FLOATATION

LEACHING

HYDRAULIC WASHING

Hydraulic washing is based on the differences in gravities of the ores and the gangue.

In this process an upward steam of running water is used to wash the powdered ore.



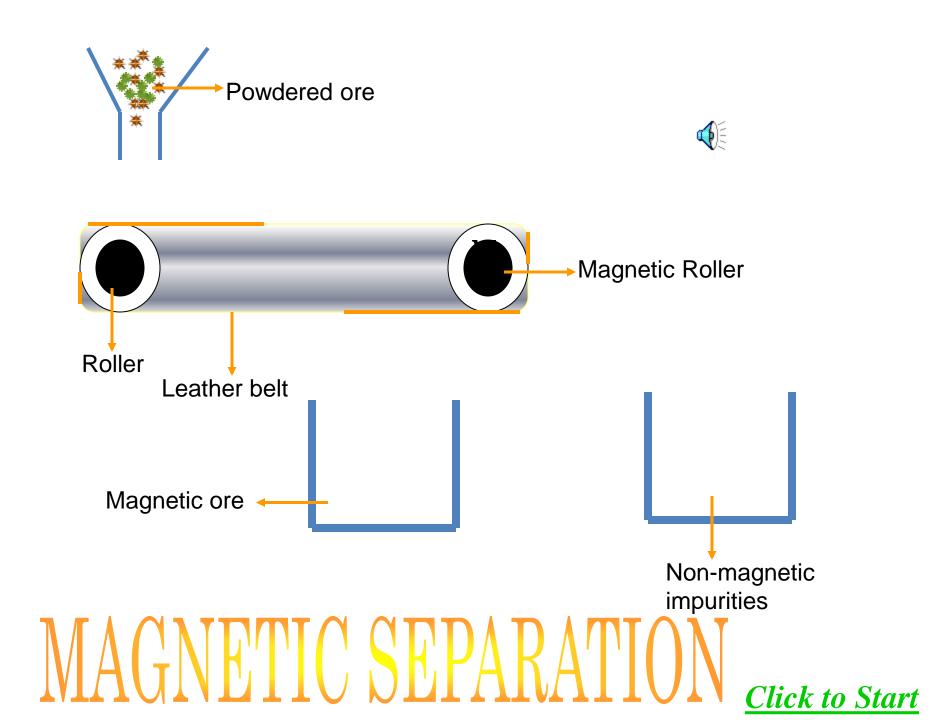
♦ The lighter gangue particles are washed away and the heavier ores are left behind.

MAGNETIC SEPARATION

Magnetic separation is based on differences in magnetic properties of the ore components.

If either the ore or the gangue is capable of being attracted by a magnetic field, then such separations are carried out.

The ground ore is carried on a conveyer belt which passes over a magnetic roller.
<u>Click here to see</u>
<u>the animation</u>



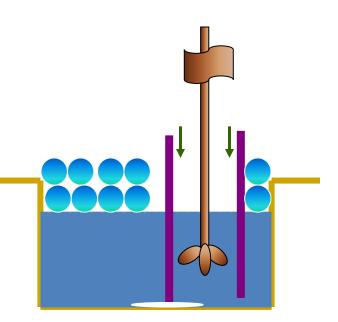
FROTH FLOATATION

This method is being used for removing gangue from *sulphide ores*.

In this process, a suspension of the powdered ore is made with water.

To it, *collectors* and *froth stabilizers* are added. The mineral particles become wet by oils while the gangue particles by water.

A rotating paddle agitates the mixture and draws air in it. As a result, froth is formed which carries the mineral particles.



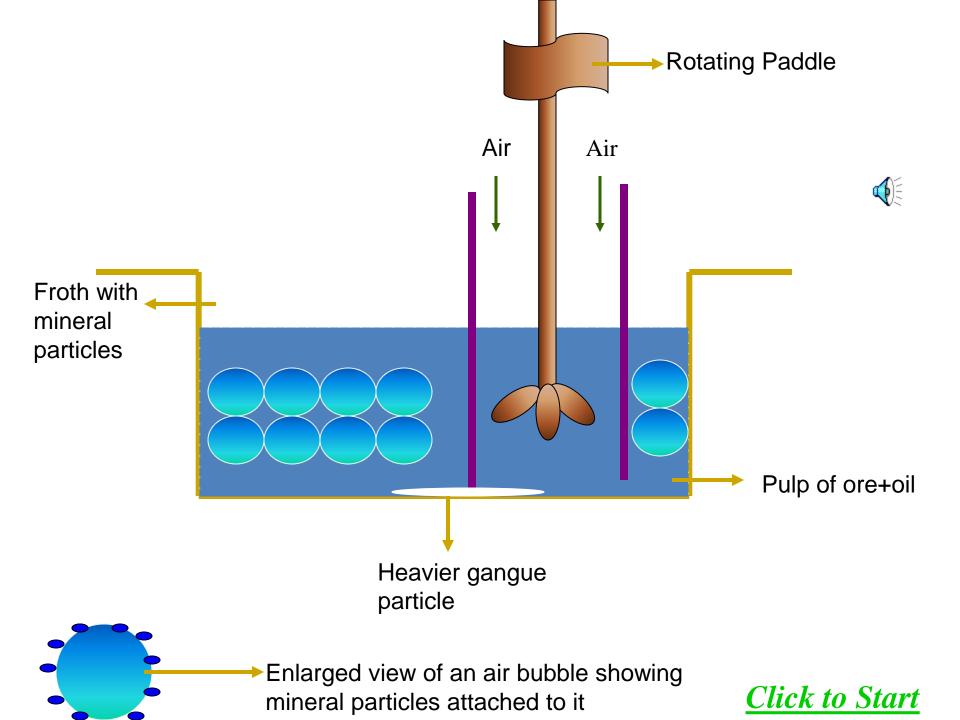
<u>Click here to see</u> <u>ANIMATION</u>

Froth Floatation method:

- Principle: The mineral particles are wetted by oil while the gangue particles are wetted by water
- This method has been in use for removing gangue from sulphide ores.
- In this process, a suspension of the powdered ore is made with water. To it collectors and froth stabilizers are added.
- Collectors- pine oil, fatty acids, xanthates, etc.-enhance non-wettability of the mineral particles
- Froth stabilizers cresols, aniline, etc. stabilise the froth.
- The mineral particles are wetted by oil while the gangue particles are wetted by water.
 A rotating paddle agitates the mixture and draws air in it. As a result, the froth is formed which carries the mineral particles. The froth is light and is skimmed off. It is then dried for recovery of the ore particles.

The role of a depressant in the floatation process

- Depressant selectively prevents one of the sulphide ore coming to froth by complexation
- NaCN is used as depressant when ore containing ZnS and PbS, it selectively prevents ZnS from coming to the froth but allows PbS to come with the froth



HYDRO-METALLURGY

• Hydrometallurgy is a method for obtaining metals from their ores. It is a technique involving the use of aqueous chemistry for the recovery of metals from ores, concentrates, and recycled or residual materials. Hydrometallurgy is typically divided into three general areas:

i. Leaching

ii.Solution concentration and purification iii.Metal or metal compound recovery This method depends on the difference in some chemical property of the metal compound present in ore and gangue.

FOR EXAMPLE :

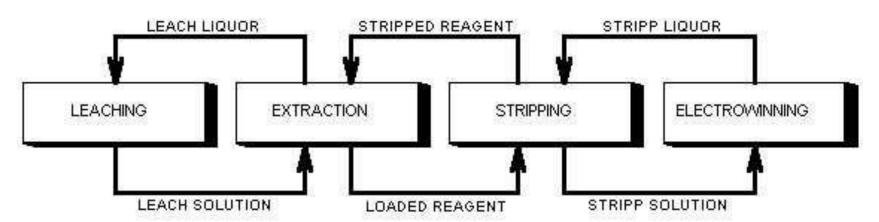
Bauxite ore is impure aluminum $oxide(Al_2O_3.2H_2O)$ containing Fe_2O_3 and SiO_2 as the gangue. The bauxite ore is treated with hot sodium hydroxide solution.

 $Al_2O_3 + 2NaOH \longrightarrow 2NaAlO_2 + H_2O$

The iron oxide and sand present in bauxite ore do not dissolve in sodium hydroxide solution, so they are separated by filtration.

SOLUTION CONCENTRATION AND PURIFICATION

- After leaching, the leach liquor must normally undergo concentration of the metal ions that are to be recovered. Additionally, undesirable metal ions sometimes require removal.
- Two major types are: i) Solvent extraction ii) Ion Exchange



METAL RECOVERY

- Sometimes, however, further refining is required if ultra-high purity metals are to be produced.
- The primary types of metal recovery processes are i) electrolysis, ii) gaseous reduction, and iii) precipitation.
- For example, a major target of hydrometallurgy is copper, which is conveniently obtained by electrolysis. Cu²⁺ ions reduce at mild potentials, leaving behind other contaminating metals such as Fe²⁺ and Zn²⁺.

Leaching Gold and Silver

 In the metallurgy of silver and that of gold, the respective metal is leached with a dilute solution of NaCN or KCN in the presence of air (for O₂) from which the metal is obtained later by replacement:

(Mac Arthur Forest Cyanide Process) $4M(s) + 8CN^{-}(aq) + 2H_{2}O(aq) + O_{2}(g) \rightarrow 4[M(CN)_{2}]^{-}(aq) + 4OH^{-}(aq) (M= Ag \text{ or } Au)$ $2[M(CN)_{2}]^{-}(aq) + Zn(s) \rightarrow [Zn(CN)_{4}]^{2-}(aq) + 2M(s)$

The role of NaCN in gold extraction

 In the metallurgy of silver and that of gold, the respective metal is leached with a dilute solution of NaCN

EXTRACTION OF METAL FROM CONCENTRATED ORE

The concentrated ore must be converted into a form which is suitable for reduction. Usually the sulphide ore is converted to oxide before reduction. Oxides are easier to reduce. Thus isolation of metals from concentrated ore involves two major steps:

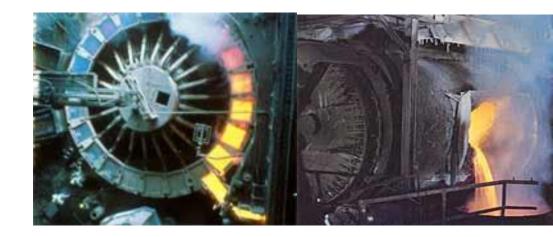
*CONVERSION TO OXIDE

CONVERSION TO OXIDE

Before reduction can be done the ore must be converted into metal oxide which can then be reduced. The concentrated ore can be converted into metal oxide by following two processes:

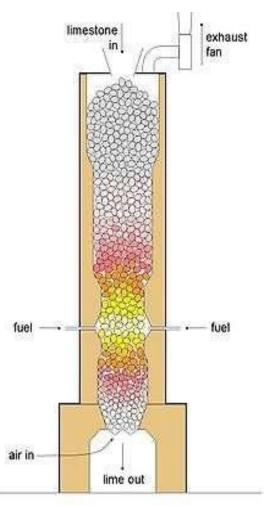
CALCINATION





CALCINATION

- Calcination is heating to high temperatures in the absence of air or oxygen.
- The main purpose of calcination of ores are to convert carbonates and hydroxides ores into oxides.
- $ZnCO_3 \rightarrow ZnO + CO_2$
- $CaCO_3 \rightarrow CaO + CO_2$
- $2Al(OH)_3 \rightarrow Al_2O_3 + 3H_2O$



Purpose of calcination

- i. Remove the volatile impurities
- ii. To remove moisture
- iii. Make the mass porous

ROASTING

- The processing of strong heating of the ore in presence of excess amount of air below its melting point.
- Purpose of roasting:
- i. To convert the sulphide into oxide and sulphate
- ii. To remove impurities like S, As, Sb.
- iii. To remove moisture
- iv. To Oxidise easily oxidisable substances

It is mainly used for sulphide oresit converts the sulphides into oxides

2ZnS+3O2 ----> 2ZnO+SO2

 $\bullet 4FeS2 + 11O2 \rightarrow 2Fe2O3 + 8SO2$

CALCINATION VS ROASTING

CALCINATION	ROASTING
It is the process of heating in absence of air	It is the process of heating in presence of air to oxidise the impurities
It is employed for carbonate ores	It is employed for sulphide ores
Calcination produces carbon dioxide along with metal oxide	Roasting produces sulphur dioxide along with metal oxide

SIMILARITIES

- •Both are processes of heating the ore below its melting point.
- •Both aim at removal of impurities in the ore.

REDUCTION OF OXIDE

The conversion of metal oxide into metal is called reduction. Depending on the nature of the metal to be extracted, the following 3 methods are used for reduction:

Reduction by heat alone

Chemical Reduction

Electrolytic Reduction



REFINING OF METALS The process of purifying impure metal is called

refining of metals.

For obtaining metals of high purity, several techniques are used depending upon the differences in properties of the metal and the impurity. Some of them are listed below:

DISTILLATION

LIQUATION

ELECTROLYTIC REFINING

ZONE REFINING

VAPOUR PHASE REFINING

CHROMATOGRAPHIC METHODS

DISTILLATION

This method is used for the purification of volatile metals like <u>zinc, cadmium</u> <u>and mercury</u> (which forms vapours easily).

- In this method, the impure metal is heated in a vessel and it's vapours are condensed separately in a receiver to get pure metal.
- The non volatile impurities are left behind.



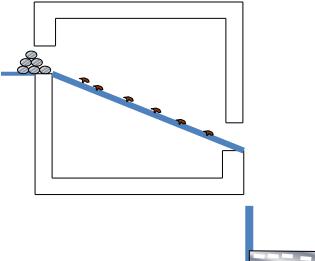
LIQUATION

The easily fusible metals like <u>tin, lead and</u> <u>bismuth</u> are refined by the process called <u>liquation.</u>

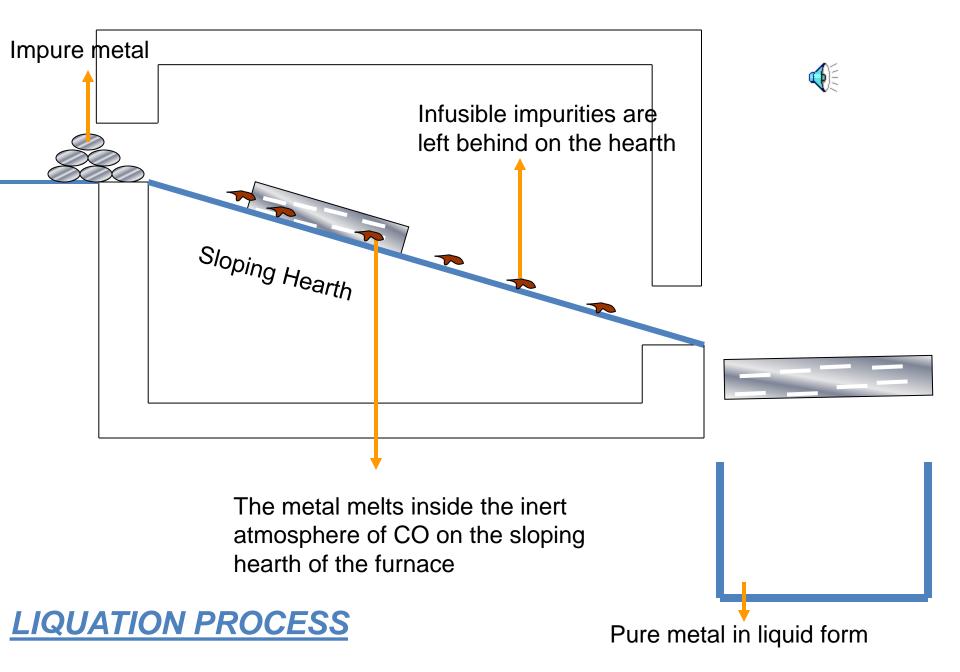
Liquation process is used where the metal to be refined is easily fusible but the impurities do not fuse easily.

In liquation process of refining metals, the block of impure metal is placed on the top side of a sloping hearth of a furnace and heated gradually.

Under these conditions, the pure metal melts and flows down to the container. The infusible impurities are left behind on the hearth.



<u>Click here to see ANIMATION</u>



ELECTRO-METALLURGY

- Electrometallurgy is the field concerned with the processes of metal electrode position There are four categories of these processes:
- Electrowinning
- Electrorefining
- Electroplating
- Electroforming
- Electropolishing

- Electrowinning, the extraction of metal from ores.
- Electrorefining, the purification of metals.
- Metal powder production by electrodeposition is included in this category, or sometimes electrowinning, or a separate category depending on application.

Refining

- Primary Refining: Refining consists of purifying an impure metal. It is to be distinguished from other processes
 like smelting and calcining in that those two involve a chemical change to the raw material, whereas in refining, the final material isidentical chemically to the original one, only it is purer.
- Electro Refining: It is the process of using electrolysis to increase the purity of a metal extracted from its ore (compound or mixture of compounds from which a metal can be extracted commercially).

Refining (contd...)

To use grey pig iron, a preliminary refining process was necessary to remove silicon. The pig iron was melted in a *running out furnace* and then run out into a trough. This process oxidised the silicon to form a slag, which floated on the iron and was removed by lowering a dam at the end of the trough. The product of this process was a white metal, known as *finers metal* or *refined iron*.

Secondary Refining

• The purposes of secondary refining are many: temperature homogenization or adjustment; chemical adjustments for carbon, sulphur, phosphorus, oxygen and precise alloying; inclusion control; degassing, and others. The equipment and processes are equally varied.

Electro-slag refining (ESR)

- The process of electro-slag refining (ESR) is well known for production of high cleanliness steels. It involves melting of an electrode by resistive heating through a slag pool, and solidification of the droplets at the bottom of the Pool.
- Steel of the desired overall chemical composition is prepared before-hand and shaped in the form of an electrode. This requires addition of the necessary ferro-alloys to the liquid steel in order to attain the aimed concentration of alloying elements.

Electrolytic refining means refining by

<u>electrolysis.</u>

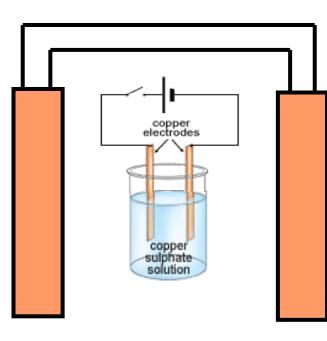
Many metals like *Cu, Zn, Ni, Ag and Au* are refined by this process. *For refining an impure metal by electrolysis :*

- A thick block of impure metal is made anode.
- A thin strip of the pure metal is made cathode.

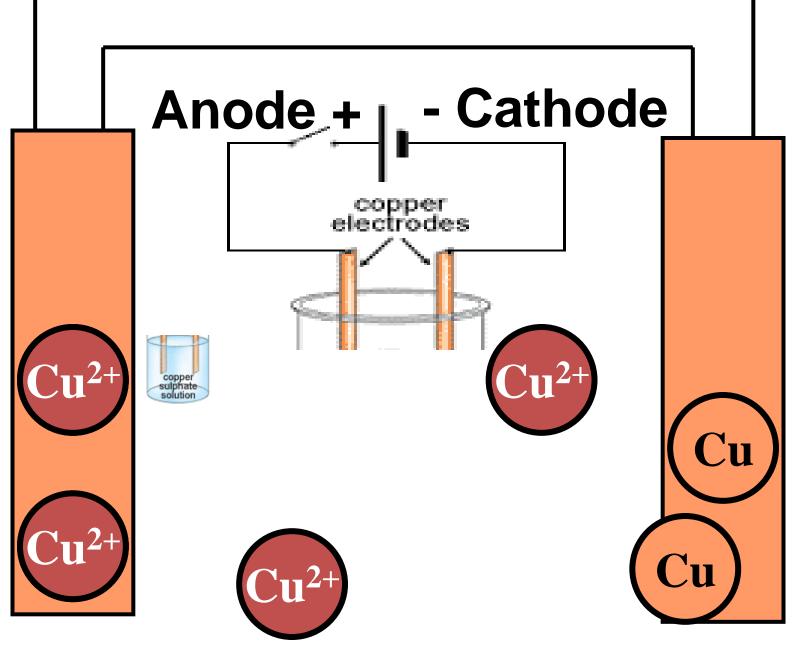
A water soluble salt (of the metal to be refined) is taken as electrolyte.

On passing the electric current, impure metal dissolves from cathode and goes into electrolyte solution and pure metal from the electrolyte deposits on the cathode

The impurities are left behind in the solution, below the anode



Click here to see ANIMATION



<u>Click to Start</u>

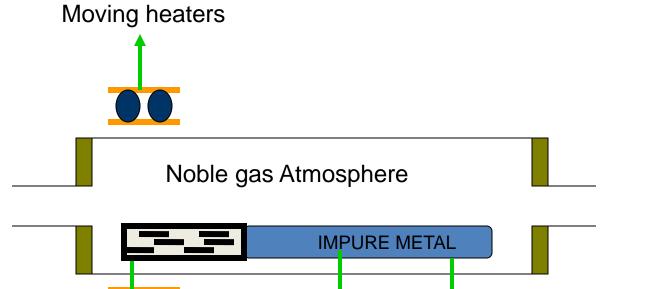
ZONE REFINING

Zone refining is based on the principle that the impurities are more soluble in melt than in the solid state of the metal.

- A circular mobile heater is fixed at one end of a rod of the impure metal.
- The molten zone moves along with the heater which is moved forward.
- As the heater moves forward, the pure metal crystallizes out of the melt and the impurities pass on into the adjacent molten zone.

At one end the impurities get concentrated.
This end is cut off.

<u>Click here to see ANIMATION</u>





 IMPURE METAL

 Impure metal

 Impure metal

 Impure metal

 Impurities



VAPOUR PHASE REFINING

In this method, the metal is converted into it's volatile compound and collected elsewhere. It is then decomposed to give pure metal.

The two requirements are:

@The metal should form a volatile compound with an available reagent,

@The volatile compound should be easily decomposable, so that the recovery is easy.

Click here for an example

Example:

Mond process for refining nickel

In this process, nickel is heated in a stream of CO forming a volatile complex, nickel tetra carbonyl

Ni + 4CO $\xrightarrow{330-350 \text{ K}}$ Ni + 4Ni(CO)₄

The carbonyl is subjected to higher temperature so that it is decomposed to give pure metal.

 $Ni(CO)_4 \xrightarrow{450-470 \text{ K}} Ni + 4CO$

Vapour phase refining:

van- Arkel method: It is used to get ultra pure metals. Zr and Ti are

purified by this process. Zr or Ti are heated in iodine vapours at about

870 K to form volatile Zrl₄ or Til₄ which are heated over tungsten filament at 1800K to give pure Zr or Ti.

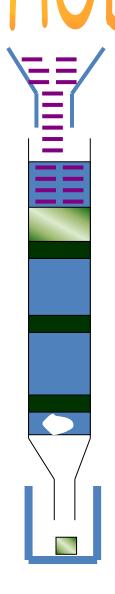
 $Ti + 2I_2 \rightarrow TiI_4 \rightarrow Ti + 2I_2$ Impurepure $Zr + 2I_2 \rightarrow ZrI_4 \rightarrow Zr + 2I_2$ Impurepure

This method is based on the principle that different components of a mixture are differently adsorbed on an adsorbent

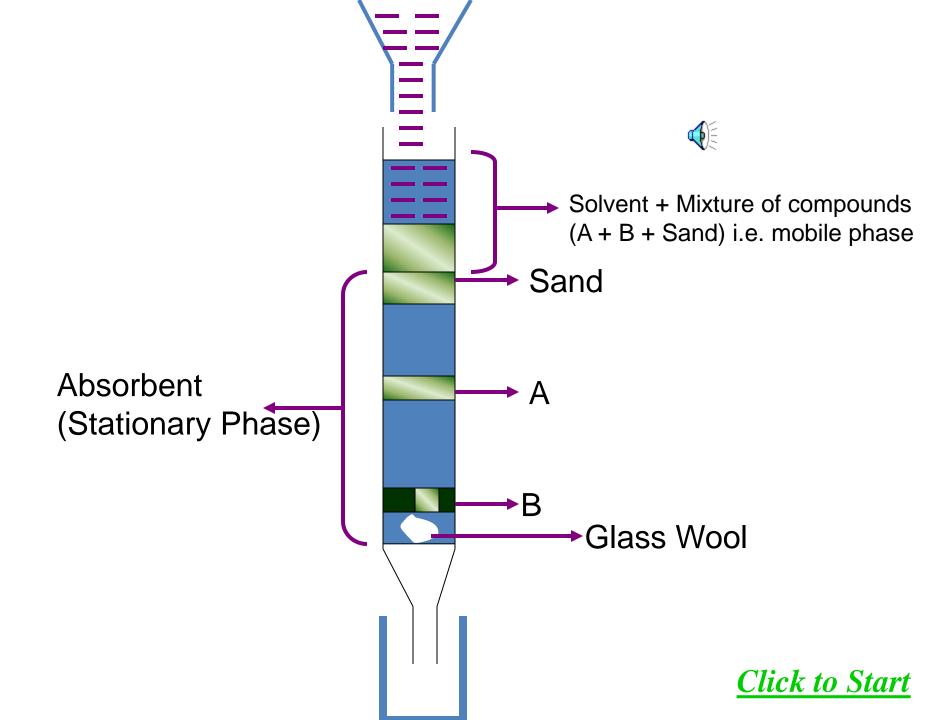
The mixture is put in a liquid on a gaseous medium which is moved through the adsorbent.

Different components are adsorbed at different levels on the column.

Later the adsorbed components are removed by using suitable solvent.



Click here to see ANIMATION



Thermodynamic aspect of metallurgy:

- $\Delta_r H \& \Delta_r S$ can not decide the feasibility of a reaction separately at constant Temperature (T) & Pressure (P)
- Ellingham Diagram decides the better reducing agent for metallurgy at different temperature
- Δ_r G decides the spontaneity of a reaction.
- Δ_rG < o or negative for a spontaneous of feasible process

(1) $\Delta G = \Delta H - T\Delta S$

- ΔG <0 or ve means the reaction is spontaneous.
- $\odot \Delta G > 0$ or +ve means the reaction is non-spontaneous.
- $\odot \Delta G = 0$ means the reaction is at equilibrium.
- ΔH is -ve for oxidation with $O_{2.}$
- For ΔS +ve at high temperature, T ΔS value increases,
- \odot So, -T Δ S in eqn. (1) becomes more -ve.
- ∆G value becomes more –ve. The reaction becomes spontaneous & vice versa

(ii)
$$\Delta_r G^{\theta} = -RT \ln K = -2.303RT \log K$$

- For a reaction: Reactants \leftrightarrows Products
- If equilibrium constant value, K is large
- T increases, $\Delta_r G^{\theta}$ values become more –ve with increase in

8

temperature & reaction becomes spontaneous.

(iii) $\Delta G^{\theta} = - nF E^{\theta}_{cell}$

If $E_{cell}{}^{\theta}\,$ is positive, $\Delta_r G^{\theta}$ values become –ve $\,$ reaction becomes spontaneous.

For a coupled reaction:

(1) $A \rightarrow B$, $\Delta G_1 > 0$ or +ve means non spontaneous reaction. (2) $C \rightarrow D$, $\Delta G_2 < 0$ or -ve means spontaneous reaction. Reactions (1) & (2) are coupled i.e.

 $A + C \longrightarrow B + D \quad \text{If } \Delta G_1 + \Delta G_2 < 0 \text{ or } -ve$

Both the reaction becomes spontaneous.

Example: (1) 2FeO \rightarrow 2Fe + O₂, $\Delta G_1 > 0 \approx$ Non-spontaneous.

(2) C + O₂ \rightarrow CO₂, $\Delta G_2 < 0 \approx$ Highly Spontaneous

(1) + (2) : <u>2FeO + C + $\mathbf{O}_2 \rightarrow 2Fe + CO_2 + \mathbf{O}_2$ </u>

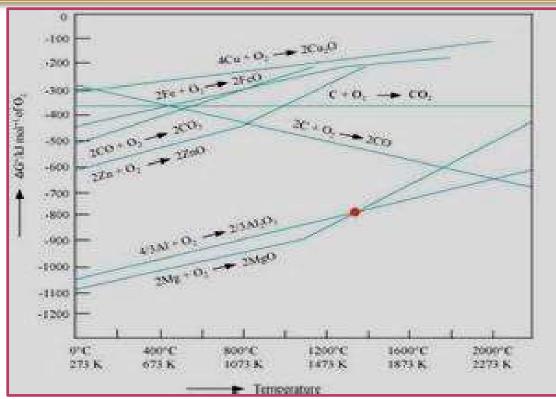
<u>Overall reaction: 2FeO + C \rightarrow Fe + CO₂</u>

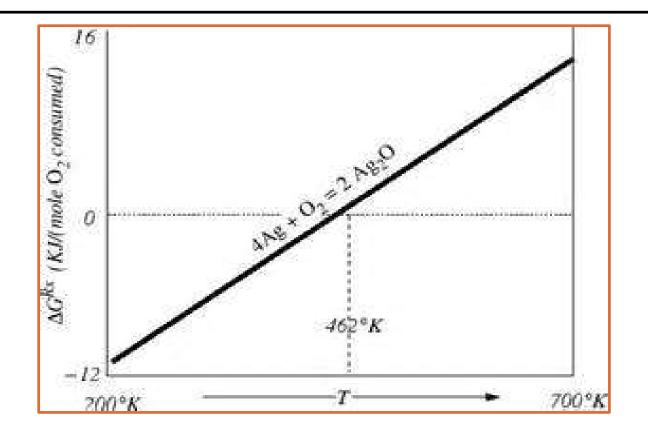
Here if $\Delta G_1 + \Delta G_2 < 0$ or –ve, so the reaction is spontaneous. This is the basis of metallurgy from Ellingham diagram.

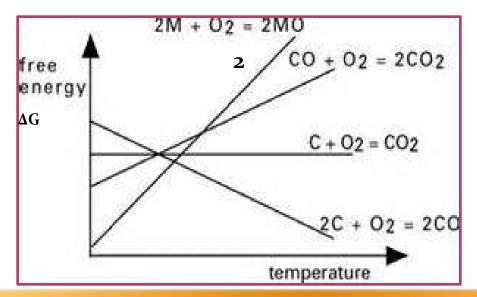
Ellingham Diagrams:

Plots of ΔG^{θ} values for 1 mole of a common reactant like O_2 , sulphur or halogen versus temperature for a number of metal & non metal to their oxide, sulphide or chloride reactions are known as *Ellingham diagram*.

If ΔG^{θ} is –ve, the thermal reduction of an ore is feasible.





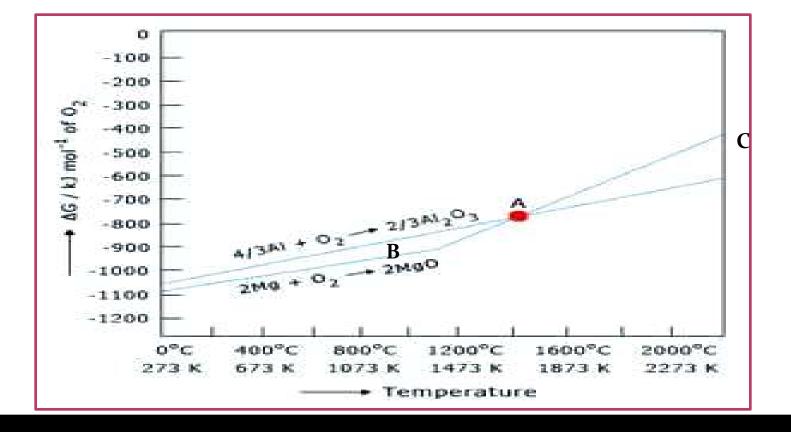


(a) ${}_{2CO}_{(g)} + O_{2(g)} \rightarrow 2CO$ Here $\Delta H = -ve$, $\Delta S = -ve$, as the temperature increases, ΔG becomes less negative or more positive, so the plot of straight line rises up.

(b) ${}_{2C_{(s)}} + O_{2(g)} \rightarrow 2CO_{(g)}$, Here $\Delta H = -ve$, $\Delta S = +ve$, as the temperature increases, ΔG becomes more negative or less positive, so the plot of straight line lowers down.

(c) $C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)}$, Here $\Delta H = -ve$, $\Delta S \approx o$, as the temperature increases, $\Delta G \approx \Delta H$ so, ΔG practically remains constant & the plot of straight line is parallel to temperature axis.

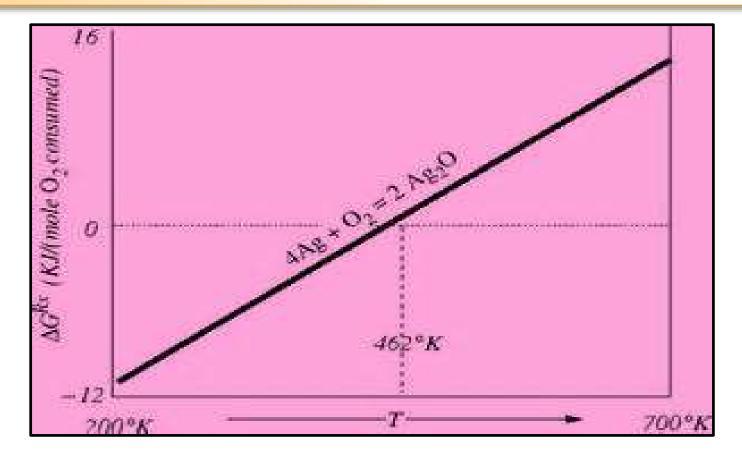
(d) ${}_{2M_{(s)}} + O_{2(g)} \rightarrow {}_{2MO(s)}$, Here $\Delta H = -ve$, $\Delta S = -ve$, as the temperature increases, ΔG becomes less negative or more positive, so the plot of straight line rises up.

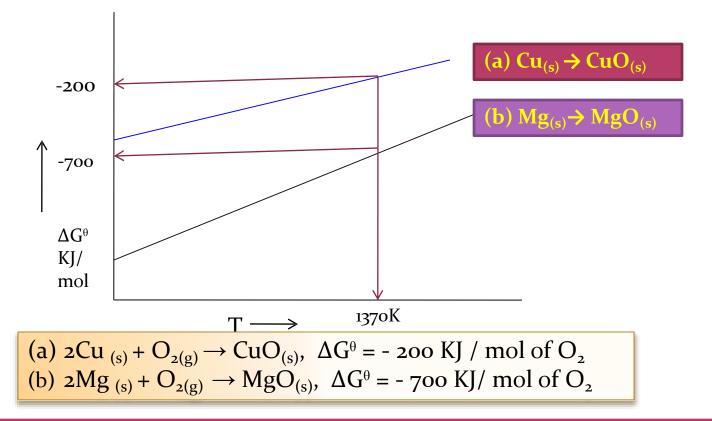


In case of reaction: $2Mg_{(s)} + O_{2(g)} \rightarrow 2MgO_{(s)}$, the straight line bends at a point **B** with more slope in straight line. This is because at the temperature corresponding to point B, the metal Mg melts, so ΔH remaining nearly same, ΔS becomes more –ve than Mg in solid state. So, -T ΔS becomes more +ve and ΔG becomes more positive. The slope of the

straight rises up further with more slope from B to C.

This graph shows that at low temperature below 462K, the ΔG^{θ} value is negative (< 0), so formation of $Ag_2O_{(s)}$ is spontaneous & $Ag_2O_{(s)}$ is stable. Above 462K, the ΔG^{θ} value is positive (> 0), so formation of $Ag_2O_{(s)}$ is non-spontaneous & $Ag_2O_{(s)}$ is unstable so $Ag_{(s)}$ is stable at high temperature.

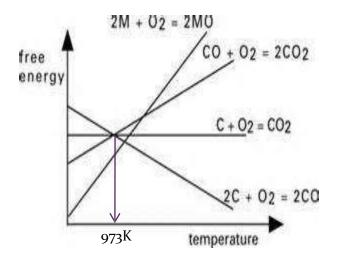




For reaction: $2Mg_{(s)} + CuO_{(g)} \rightarrow MgO_{(s)} + Cu_{(s)}$ $\Delta_r G^{\theta} = -700 - (-200) = -500 \text{ KJ}$, i.e. $\Delta_r G^{\theta} < 0$, so the above reaction is feasible, Hence, Mg can reduce CuO.

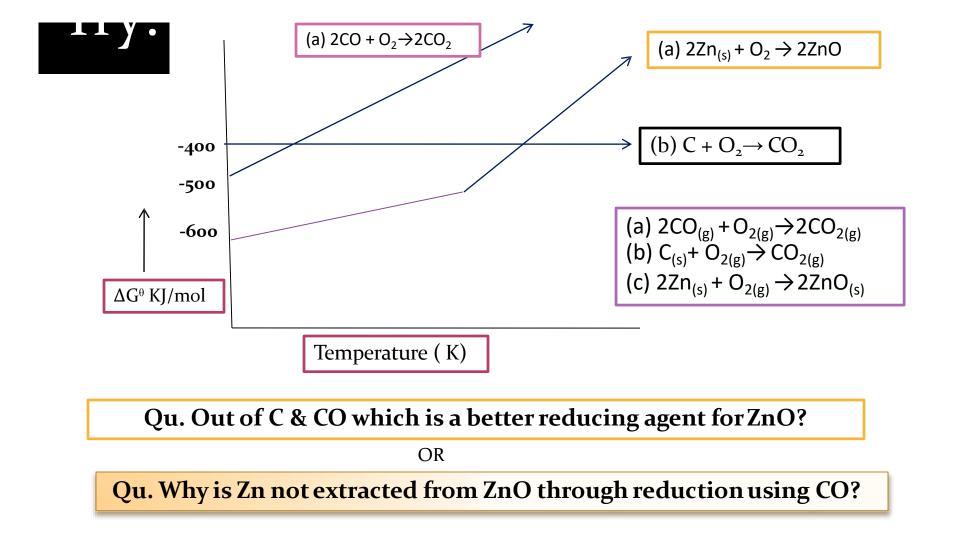
The conclusion is: **Mg is a reducing agent** (the graph lies below in Elling. Diag.) & it can reduce CuO (The graph lying above in Elling. Diagram, backward reaction)

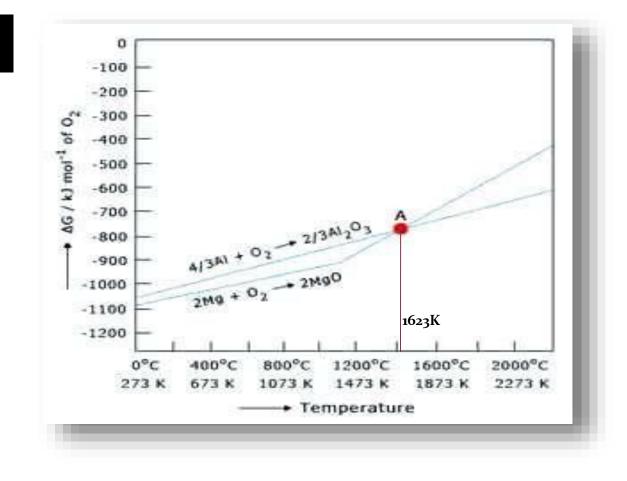
The substance (metal, Non metal or lower oxide) whose graph is below in Elling. Diagram is a better reducing agent having lower $\Delta_r G^{\theta}$ value.).



Try 1: Qu. Out of C & CO which is a better reducing agent for FeO?

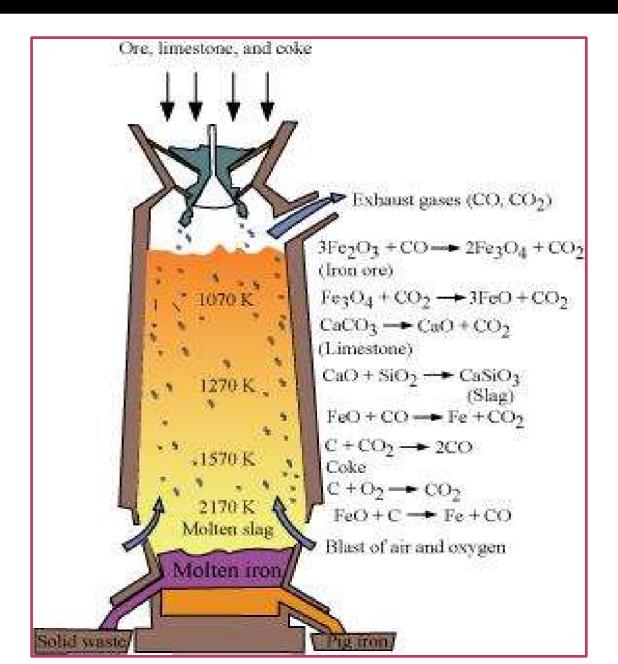
(i) In the lower part of blast furnace (higher temperature)?
 (ii) In the upper part of blast furnace (lower temperature)?
 (iii) Can MO be reduced by C or CO or both? Explain.





Iry: 3

Qu. Suggest a condition under which Mg can reduce Al₂O₃ & Al can reduce MgO? Qu. Though thermodynamically feasible, Mg can reduce Al₂O₃, yet we do not prefer this method?



Charge: Fe_2O_3 (iron ore) + C (coke) + CaCO₃ (Limestone)

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(a) CaCO₃ + heat (1070K) \rightarrow CaO + CO₂ C +O₂ (1070 K) \rightarrow CO₂ + heat

(b) C + CO₂ (2070K) \rightarrow 2CO + heat

(c) With $CO_{(g)}$ Temperature change: 1070K \rightarrow 1270K \rightarrow 1470K

 Fe_2O_3 (1070K) \rightarrow Fe_3O_4 (1270K) \rightarrow FeO (1470 K) \rightarrow Fe

(d) With C (coke) : FeO (2070K) \rightarrow Fe

(e) Slag formation: CaO (flux) + SiO₂ (gangue) (1270K)→ CaSiO₃ (Slag)

Limitations of Ellingham Diagram

(1)It does not tell anything about the kinetics of the reduction process.

(2)The concept is based on ΔG^θ whose value is calculated from 'K' from the relation: ΔG^θ = - RT In K It has presumed that all reactants & products are in equilibrium.

But this is not always true.

(3)The reactants / products may be solid. So at room temperature activation energy of reaction is high & reaction may not occur even if ΔG^θ is negative. Metallurgy Of Iron

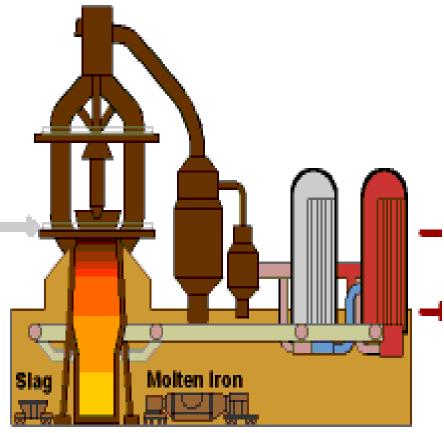


What is a Blast furnace?

•The purpose of a blast furnace is to reduce and convert iron oxides into liquid iron called "hot metal".

•The blast furnace is a huge, steel stack lined with refractory brick.

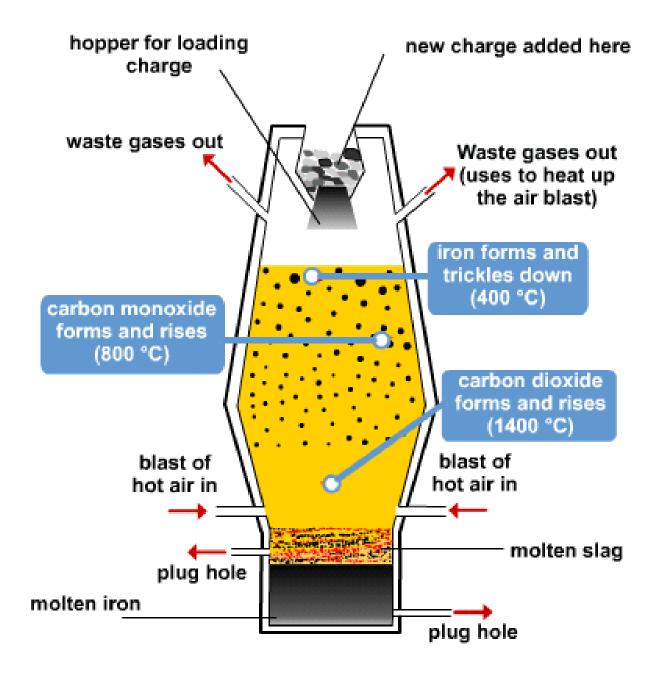
• Iron ore, coke and limestone are put into the top, and preheated air is blown into the bottom.



Blast Furnace Produces molten pig iron from iron ore.

Why does Iron have to be extracted in a Blast furnace???

- Iron Can be extracted by the blast furnace because it Can be displaced by Carbon.
- •This is more efficient method than electrolysis because it is more cost effective.





The Method



Three substances are needed to enable to extraction of iron from its ore. The combined mixture is Called the **Charge:**

- **Iron ore, haematite** often contains sand with iron oxide, Fe_2O_3 .
- Limestone (Calcium Carbonate).
- Coke mainly Carbon

The charge is placed a giant Chimney Called a **blast furnace**. The blast furnace is around 30 metres high and lined with fireproof bricks. Hot air is blasted through the bottom.

Several reactions take place before the iron is finally produced...

•Oxygen in the air reacts with coke to give Carbon dioxide:

 $C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)}$

•The limestone breaks down to form Carbon dioxide:

 $CaCO_{3(s)} \rightarrow CO_{2(g)} + CaO_{(s)}$

•Carbon dioxide produced in 1 + 2 react with more coke to produce carbon monoxide:

 $CO_{2(g)} + C_{(s)} \rightarrow 2CO_{(g)}$

• The Carbon monoxide reduces the iron in the ore to give molten iron:

 $3CO_{(g)} + Fe_2O_{3(s)} \rightarrow 2Fe_{(l)} + 3CO_{2(g)}$

• The limestone from 2, reacts with the sand to form slag (Calcium silicate):

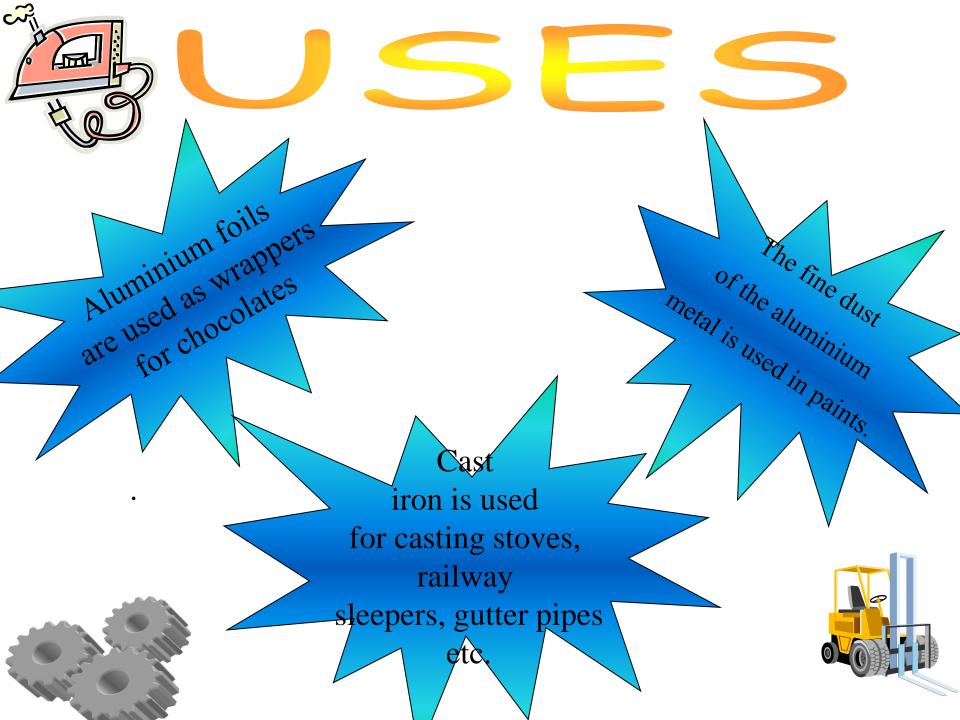
 $CaO_{(s)} + SiO_{(s)} \rightarrow CaSiO_{3(l)}$

•Both the slag and iron are drained from the bottom of the furnace.

•The slag is mainly used to build roads.

•The iron whilst molten is poured into moulds and left to solidify - this is Called Cast iron and is used to make railings and storage tanks.

•The rest of the iron is used to make steel.





Chalcopyrite



Open Pit mining

Wrought Iron

 Wrought iron: The product of the blast furnace is pig iron, which contains 4–5% carbon and usually some silicon. To produce a forgeable product a further process was needed, usually described as *fining*, rather than *refining*. At the end of the 18th century, this began to be replaced by puddling (in a puddling furnace.

Refined iron

• **Refined iron:** To use grey pig iron, a preliminary refining process was necessary to remove silicon. The pig iron was melted in a *running out furnace* and then run out into a trough. This process oxidised the silicon to form a slag, which floated on the iron and was removed by lowering a dam at the end of the trough. The product of this process was a white metal, known as *finers metal* or *refined iron*.

Purpose of alloying

- Strengthening of the ferrite
- Improved corrosion resistance
- Better hardenability
- Grain size control
- Improved mechanical properties like ductility, strength, toughness, etc.
- Improved Cutting ability
- Better wear resistance

Major alloying elements

- Carbon:
- Imparts hardness Tensile strength Machinability Melting point
- Nickel:

Increases toughness and resistance to impact. Lessens distortion in quenching Strengthens steel

• Chromium:

Joins with carbon to form chromium carbide, thus adds to depth hardenability with improved resistance to abrasion and wear.

Improves corrosion resistance.

• Silicon:

Improves oxidation resistance Strengthens low alloy steels Acts as deoxidisers

SOME ALLOY STEELS

- Nickel steels
- Chrome steels
- Chrome -Nickel steels
- Chrome Vanadium steels
- Manganese steel
- Silicon steels

CARBON STEEL

• LOW CARBON STEELS :

Carbon %----- 0.05 to 0.30%

APPLICATIONS: Connecting rods, valves, gears, crankshafts.

• MEDIUM CARBON STEELS: Carbon %-----

- 0.3 to 0.7%

APPLICATIONS: Die blocks, Clutch discs, Drop forging dies.

Plain Carbon Steel

Low carbon

- Good formability and weldability
- Strengthening by coldwork
- Structure usually pearlite and ferrite

Medium carbon

- Can be quenched to form martensite or bainite
- Compromising structure between ductility and strength

High carbon

- Low toughness and formability
- Good hardness and wear resistance
- Can form martensite by quenching but risk of cracking

Compare to other engineering materials

- High strength and stiffness, reasonable toughness, easy to recycle and low cost
- Rust easily, require surface protection

CHROME STEELS

- Composition:
- Carbon- 0.15 to 0.5%
- Chromium- 0.7 to 11%

Mostly widely used in chemical industries because of its resistance to corrosion.Very good strength. High resistance to wear.Cr increases tensile strength and corrosion

resistance.

NICKEL STEELS

- Composition:
- Carbon --- 0.35%
- Nickel----- 3.5%
- Addition of nickel increases strength withouta proportionality great decrease of ductility.
- Applications:
- Storage cylinder for liquefied gases and for low temperature applications.
- Turbine blades, highly stressed screws

CHROME- NICKEL ALLOYS

- Composition:
- Carbon- 0.35%
- Nickel 1.25%
- Chromium 0.6%
- Chrome-nickel steel will have ,after heat treatment, almost the same strength and ductility as 3.5% Nickel steel which has also been- treated.

- Nickel increases the toughness and ductility
- Chromium- improves hardenability and wear resistance.

MANGANESE STEELS

- Composition :
- Carbon 0.18 to 0.48%
- Manganese 1.6 to 1.9%
- Silicon 0.2 to 0.35%
- Manganese increases hardness and tensile strength.
- Increased resistance to abrasion and shock
- Applications: Grinding crushing machinery, railway tracks, etc.

CHROME VANADIUM STEELS

- Composition:
- C 0.26%, Cr- 0.92%, V 0.2%
- Chromium and vanadium increases hardenability and impart a finer grain structure.
- Applications:
- Shafts of automobiles, aeroplanes, locomotives.

SILICON STEELS

- Composition:
- C 0.1%, Mn- 0.6%, Si -1%
- Silicon imparts Strength and fatigue resistance and improves electrical properties of steel.
- Many bridges are constructed with Silicon Structural steel which is stronger than carbon steel of equal ductility.
- Silicon steels with greater than 4%silicon called electrical steels.

METALLURGY OF COPPER

Metallurgy of copper means

EXTRACTION OF COPPER From its ore.

OCCURRENCE OF METAL

- NATIVE OR FREE STATE
- MINERAL
- ORES

(4) LEACHING

- (3) MAGNETIC SEPARATION
- (2) FROTH FLOATATION
- (1) LEVIGATION
- CONCENTRATION
- CRUSHING AND GRINDING

GENERAL METHODS FOR EXTRACTION

EXTRACTION OF METAL FROM ORE

1.CONVERSION OF ORE IN METAL OXIDE(ROASTING,CALCINATION)

2.CONVERSION OF OXIDE IN METAL
(1) SMELTING
(2) REDUCTION BY HYDROGEN OR ALUMINIUM
(3) ELECTROLYTIC REDUCTION
(4)AUTO REDUCTION <u>PURIFICATION</u>

- LIQUATION
- DISTILLATION
- POLING
- CUPELLATION
- ELECTRO REFINING
- ZONE REFINING

OCCURRENCE OF COPPER

- Copper pyrite or chalcopyrite (CuFeS₂).
- Chalocite (Cu 2 S) or copper glance.
- Malachite green [CuCO₃.Cu(OH)₂
- Azurite blue [2CuCO₃.Cu(OH)₂].
- Bornite (3Cu₂S.Fe₂S₃) or peacock ore.
- Melaconite (CuO) etc.

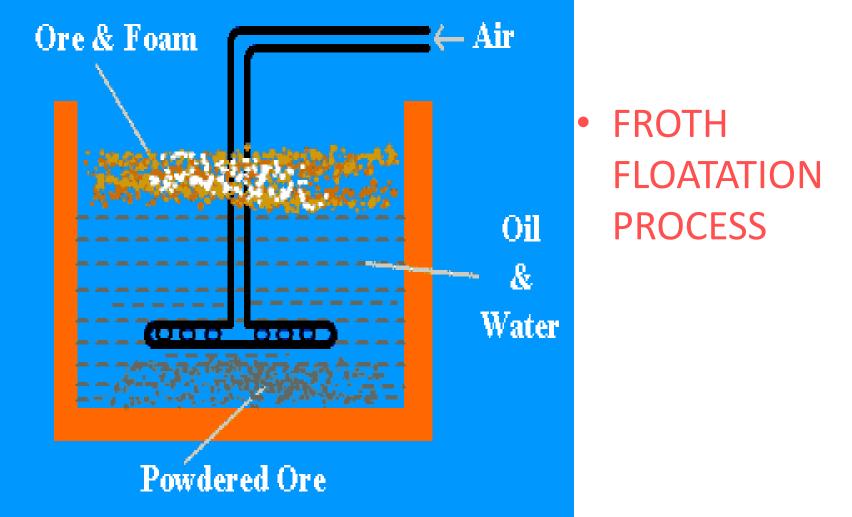
STEPS INVOLVED IN EXTRACTION

- CONCENTRATION
- ROASTING
- SMELTING
- BESSEMERIZATION
- REFINING

CONCENTRATION OF ORE

The finely crushed ore is concentrated by Froth-Floatation process. The finely crushed ore is suspended in water containing a little amount of pine oil. A blast of air is passed through the suspension. The particles get wetted by the oil and float as a froth which is skimmed. The gangue sinks to the bottom.

CONCENTRATION OF ORE



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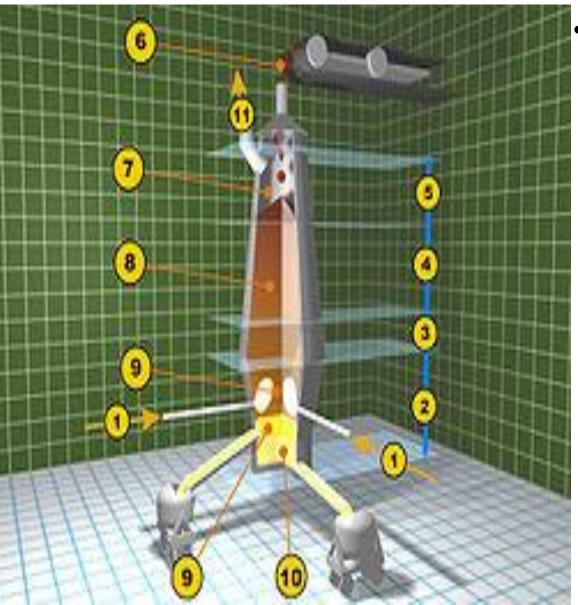
ROASTING

The following reaction takes place. $2CuFeS_2 + O_2 \rightarrow Cu_2S + 2FeS + SO_2$ $S + O_2 \rightarrow SO_2$ $4As + 3O_2 \rightarrow 2As_2O_3$ $4Sb + 3O_2 \rightarrow 2Sb_2O_3$

Cuprous sulphide and ferrous sulphide are further oxidized into their oxides.

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

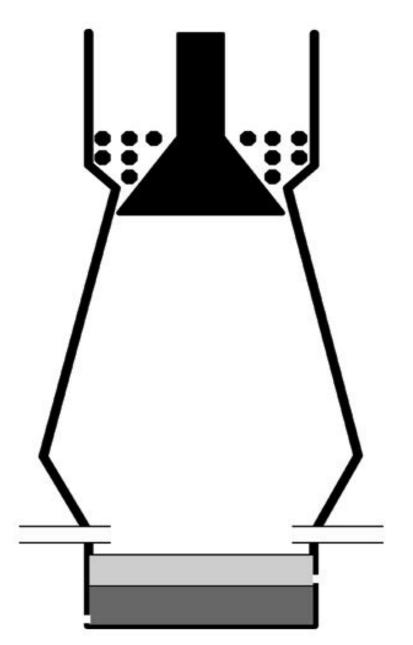
SMELTING PROCESS (REDUCTION BY CARBON)



SMELTING IS CARRIED **OUT IN BLAST FURNACE 1 HOT AIR BLAST** 2 MELTING ZONE **3, 4 REDUCTION ZONE 5 PREHEATING ZONE** 6 ORE, SILICA, COKE 7 EXHAUST GASES **8COLUMN OF ORE, SILICA, COKE 9 REMOVAL OF SLAG 10 MOLTEN MATTER 11COLLECTION OF WASTE** GASES

PROCESS OF SMELTING

The roasted ore is mixed with coke and silica (sand) SiO₂ and is introduced in to a blast furnace. The hot air is blasted and FeO is converted in to ferrous silicate FeSiO₃



BESSEMERIZATION

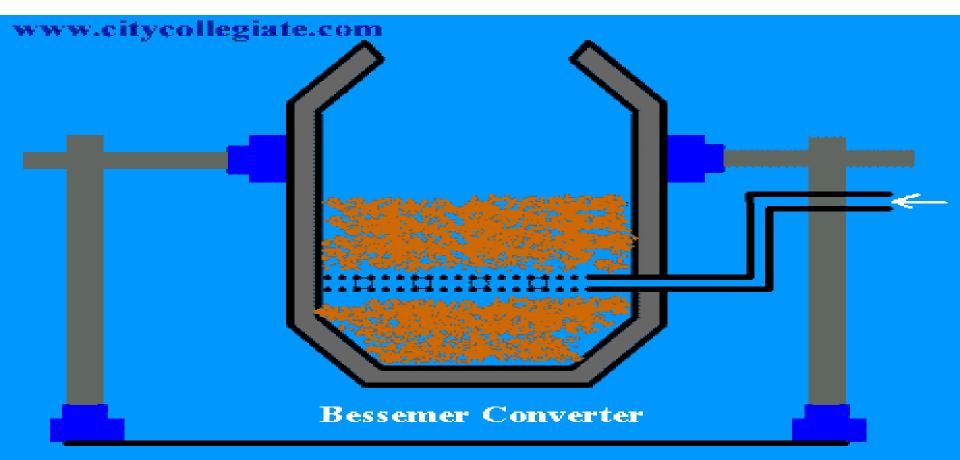
Copper metal is extracted from molten matte through bessemerization. The matte is introduced in to Bessemer converter which uphold by tuyers. The air is blown through the molten matte. Blast of air converts Cu₂S partly into Cu₂O which reacts with remaining Cu₂S to give molten copper.

SMELTING

The roasted ore is mixed with coke and silica (sand) SiO_2 and is introduced in to a blast furnace. The hot air is blasted and FeO is converted in to ferrous silicate (FeSiO₃).

FeO + SiO₂ \rightarrow FeSiO₃ Cu₂O + FeS \rightarrow Cu₂S + FeO FeSiO₃ (slag) floats over the molten matte of copper

BESSEMERIZATION



• $2Cu_2S + 3O_2 \rightarrow 2Cu_2O + 2SO_2$ $2Cu_2O + Cu_2S \rightarrow 6Cu + SO_2$

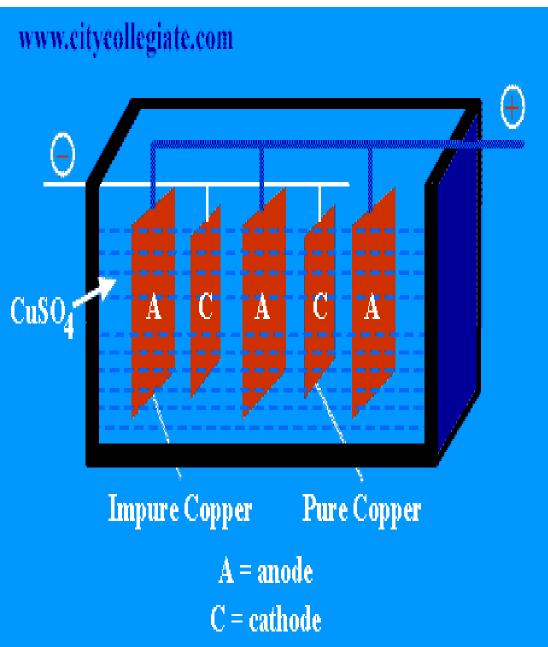
<u>REFINING OF COPPER</u>

Blistercopper is refined by electrolysis. Blocks of blister copper are used as anodes and thin sheets of pure copper act as cathodes. The cathode plates are coated with graphite in order to remove depositing copper. The electrolyte is copper sulphate ($CuSO_4$) mixed with a little amount of H_2SO_4 to increase the electrical conductivity. Optimum potential difference is 1.3 volt for this electrolytic process

During electrolysis, pure copper is deposited on the cathode plates and impurities which are soluble and fall to the bottom of the cell as anode mud or sludge.

REFINING OF COPPER

•



Cu → Cu⁺² + 2e- (at the anode) Cu⁺² +2e-→ Cu (at the cathode) This electrically refined copper is 100% pure

Metal	Main Occurrence	Main method of Extraction
Sodium	Common Salt,	Electrolysis of fused with
Magnesium	Carnallite, Magnesite	Electrolysis of fused with
Calcium	Lime stone, Gypsum,	Electrolysis of fused and
Aluminium	Bauxite,	Electrolysis of in molten (cryolite)
Copper HgS +	$O_2 \longrightarrow Hg + SO_2 + CO_2; + 2Ag$ te,	Partial oxidation of sulphide ore
Silver	Argentite, Native silver	Hydrometallurgy
Zinc	Zinc Blende, Calamine,	Reduction of with carbon or electrolysis of
Lead	Galena,	Reduction of with carbon
Tin	Cassiterite,	Reduction of with carbon
Iron	Haematite, Magnetite,	Reduction of oxide with carbon monoxide
Chromium	Chromite,	Reduction of with
Nickel	Millerite,	Reduction of with
Mercury	Cinnabar,	Direct reduction of HgS by heat alone