Welcome to

# Aakash Bryu's LIVE

General Principles and Processes of Isolation of Elements



#### Introduction



**Elements** in earth crust occurs in **free** as well as in **combined state**.

#### **Pure state**

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Examples: C, S, Au, noble gases, etc.

As oxides, halides, sulphides, etc.

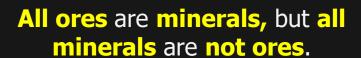
Examples: Fe, Cu, etc.

The metals in the combined state involve various processes for their extraction and isolation.

#### Minerals and Ores

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Minerals	Ores
The compounds of metal which are naturally available in earth's crust and can be obtained by mining	The minerals from which a metal can be extracted economically and conveniently
Example: FeS <sub>2</sub> (Iron pyrite)	Example: Galena (PbS), fluorspar (CaF <sub>2</sub> ), dolomite (CaCO <sub>3</sub> .MgCO <sub>3</sub> ), anglesite (PbSO <sub>4</sub> ), bauxite ore (Al <sub>2</sub> O <sub>3</sub> .2H <sub>2</sub> O), hematite (Fe <sub>2</sub> O <sub>3</sub> )



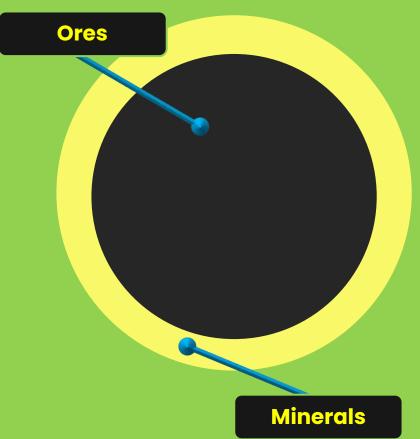


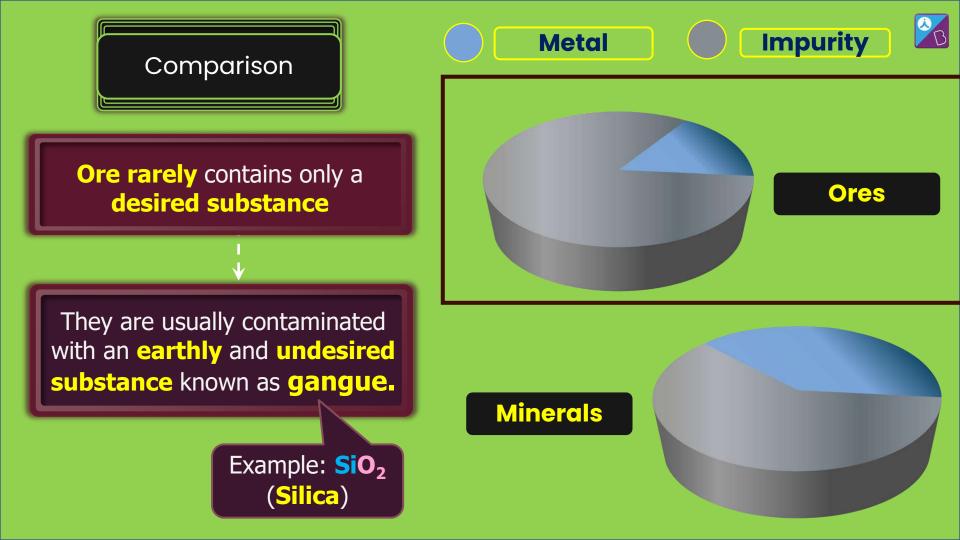
FeS<sub>2</sub> Mineral

**Abundantly present** in earth's crust

But **cannot** be used as an **ore** 









### **Occurrence of Metals**

Among metals, aluminium (Al) is the most abundant followed by iron (Fe) and third most abundant metal is Calcium(Ca) in earth's crust.



#### Occurrence of Aluminium



Third most abundant element in earth's crust

Among all the metals, aluminium is the most abundant.

| | |

Major component of igneous minerals including mica and clays

Many **gemstones** are **impure** forms of **Al<sub>2</sub>O<sub>3</sub>**.

The impurity ranges from **Cr** (in **ruby**) to **Co** (in **sapphire**).

#### Occurrence of Iron



Iron forms a variety of compounds.

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Iron is also essential in biological systems.

Haemoglobin

#### Occurrence of Calcium



**Calcium** is vital for **teeth** and **bones**.



It is an **essential** component for **cement** and **glass industry.** 

# Principal Ores of Some Metals



Metal	Ore	Composition
Alexadada	Bauxite	$AIO_x(OH)_{3-2x}$ [Where o< x <1]
Aluminium	Kaolinite (a form of clay)	[Al <sub>2</sub> (OH) <sub>4</sub> Si <sub>2</sub> O <sub>5</sub> ]
	Haematite	Fe <sub>2</sub> O <sub>3</sub>
Iron	Magnetite	Fe <sub>3</sub> O <sub>4</sub>
	Siderite	FeCO <sub>3</sub>
	Iron pyrites	FeS <sub>2</sub>

### Principal Ores of Some Metals

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Metal	Ore	Composition
Copper	Copper pyrites	CuFeS <sub>2</sub>
	Malachite	CuCO <sub>3</sub> ,Cu(OH) <sub>2</sub>
	Cuprite	Cu <sub>2</sub> O
	Copper glance	Cu <sub>2</sub> S
Zinc	Zinc blende or sphalerite	ZnS
	Calamine	ZnCO <sub>3</sub>
	Zincite	ZnO

# Principal Ores of Some Metals

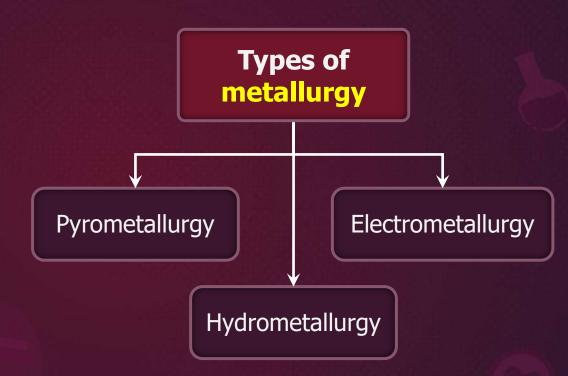


Metal	Ore	Composition
Silver	Silver glance or Argen	Ag <sub>2</sub> S
	Ruby silver	3Ag <sub>2</sub> S.Sb <sub>2</sub> S <sub>3</sub>
Magnesium	Kieserite	MgSO <sub>4</sub> .H <sub>2</sub> O
	Magnesite	MgCO <sub>3</sub>

### Metallurgy



Metallurgy is the subject that deals with the science and technology for the extraction of metals economically.



### **Pyrometallurgy**



Type of **metallurgy** which involves extraction and purification of metals by **processes** involving the **application** of **heat.** 



Ores of **less reactive** elements like **iron**, **zinc**, and more

### Hydrometallurgy



from its ore by preparing an aqueous solution of a salt of the metal and recovering the metal from the solution.



Ores of Cu, Au, Ag, and more

#### Electrometallurgy



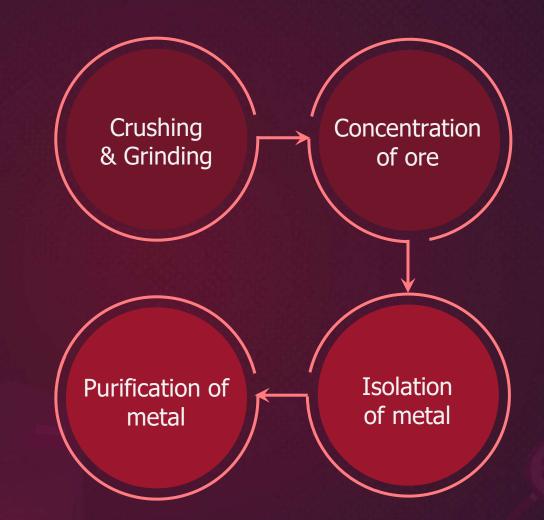
Metallurgy that deals with the application of electric current either for electrolytic deposition or as a source of heat.



Ores of Na, Mg, Al, and more



Steps involved in extraction and isolation of metals from ores!



### **Crushing and Grinding**



Also known as **pulverisation** of ore

The ore is first **crushed** by **jaw crushers.** 

-

And ground to **powder** in **ball mills** and **stamp mills**.

#### **Concentration of Ore**



Removal of unwanted material from ore

Also known as dressing or benefaction

Concentration of ore depends on the difference in the physical properties of:

Components
of metal

Concentration of ore depends on the difference in the physical properties of:

Gangue

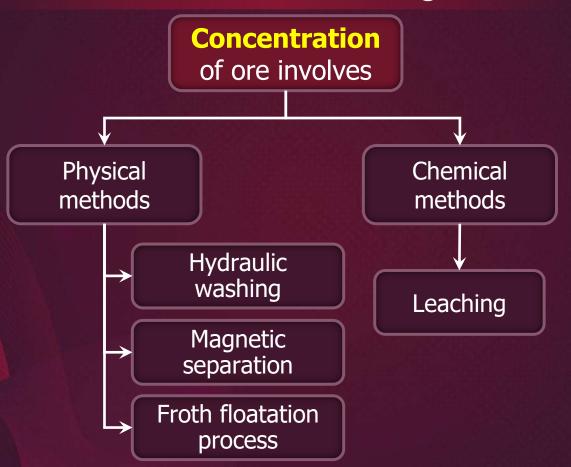
#### Gangue



An ore usually contaminated with earthly or undesired materials known as gangue.

#### Concentration or Dressing of Ore





## **Hydraulic Washing**



#### **Principle**

This method is based on **differences** in the **gravity** of **ore** and the **gangue** particles.

Also known as gravity separation method

An upward
stream of running
water is used to
wash the
powdered ore.

Lighter gangue particles are washed away

**Heavier ores** are **left** behind

#### **Magnetic Separation**



**Principle** 

This method is based on the differences in the magnetic properties present in the ore particles.

It is generally used to separate magnetic impurities from non-magnetic ores.



Tin stone, SnO<sub>2</sub> (non-magnetic) is separated from magnetic impurity FeWO<sub>4</sub> + MnWO<sub>4</sub>.

**Wolframite** 





Powdered ore is allowed to move over magnetic roller and falls down.

| | |

Magnetic material makes a new heap.

Because it is held to roller for longer time



#### Froth Floatation Process

**Principle** 

This method is based upon differential wetting of:

It is generally used to **remove** gangue from sulphide ores.





- Preparation of suspension of powdered ore
- Addition of collectors and froth stabilisers

Agitation of mixture

# Preparation of Suspension of Powdered Ore





#### **Collectors and Froth Stabilisers**



Collectors are the compounds that **enhance non-wettability** of mineral particles.

Froth stabilisers are the compounds that reduce the surface tension of water. They also produce a stable froth.

Examples: Pine oil, crude coal, tar, and more

Examples: **Aniline, cresol,** and more





A **rotating paddle** agitates the mixture and **draws air** in it.

It forms **froth** that causes **ore** particles

Froth is **light** and can be skimmed off.

**Dried** and **ore** particles are **recovered** 





If two sulphide ores are present, a particular ore can be obtained by using depressants.

Depressants are **substances** that are added to **suppress** the **floating characteristic** of the ore particles. Example: NaCN/KCN

#### **Froth Floatation Process**



#### **Example**

In this example, NaCN or KCN helps to keep ZnS in aqueous solution by forming a water soluble complex while PbS can be obtained in the froth.

Froth containing ZnS and PbS

Depressant Soluble complex of ZnS

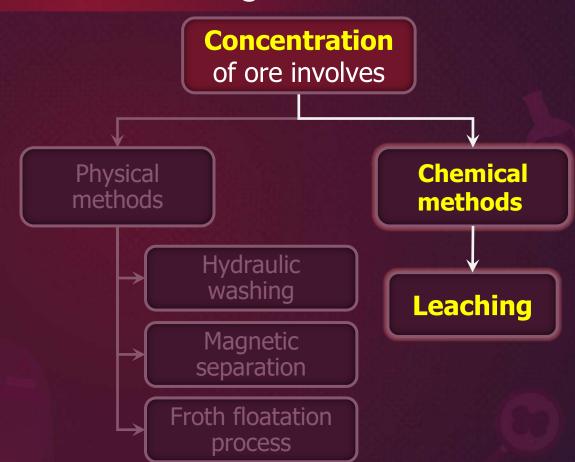
NaCN/KCN

**PbS**(s) + NaCN 
$$\longrightarrow$$
 No reaction

ZnS (s) + 4NaCN 
$$\longrightarrow$$
 [Zn(CN)<sub>4</sub>]<sup>2-</sup> + 4Na<sup>+</sup> + S<sup>2-</sup>

### **Concentration or Dressing of Ore**





### **Chemical Methods: Leaching**



It is generally used if the ore is soluble in a suitable solvent.



### Leaching of Alumina



From bauxite (Al<sub>2</sub>O<sub>3</sub>.2H<sub>2</sub>O)

Principal ore of aluminium

Impurities
present in
bauxite

SiO<sub>2</sub>, TiO<sub>2</sub>,
and Fe
oxides

#### **Leaching of Alumina**



Step 1

**Digesting** powdered ore with **aqueous** NaOH

At **473-523 K** and **35-36 bar** 

#### **Impurity**

$$Al_2O_3$$
 (s) +  $Fe_2O_3$  +  $SiO_2$  +  $TiO_2$  +  $2NaOH$  +  $3H_2O(I)$ 

**Sodium aluminate** 

**Impurities** 

 $2Na[Al(OH)_4](aq)$ 

### **Leaching of Alumina**



Step 2

Aluminate is neutralised by passing CO<sub>2</sub>

$$2Na[Al(OH)_4](aq) + 2CO_2(g) \rightarrow Al_2O_3.xH_2O \downarrow + 2NaHCO_3$$

**Precipitate** 

# **Leaching of Alumina**



Step 3

**Sodium silicate** remains in the **solution** 

Hydrated alumina is **filtered**, **dried** and **heated**.

$$Al_2O_3.xH_2O \xrightarrow{1470K} Al_2O_3 (s) + xH_2O (g)$$

**Pure alumina** 

# Leaching of Gold and Silver



Step 1

Metal is **leached** with dil. **NaCN** or **KCN**.

In the presence of **O**<sub>2</sub>

4M (s) + 8CN (aq) + 2H<sub>2</sub>O (aq) + O<sub>2</sub> (g) 
$$\longrightarrow$$
 4[M(CN)<sub>2</sub>] + 4OH (aq)

M = Ag or Au

# Leaching of Gold and Silver



Step 2

Pure metal is obtained by replacement.

$$2[M(CN)_2]^- (aq) + Zn (s) \longrightarrow [Zn(CN)_4]^{2-} (aq) + 2M(s)$$

#### **Isolation of Metal**



For **isolation**, concentrated ore must be converted to a **particular form**.

Which is **suitable** for **reduction** 

# Steps Involved in the Isolation of Metal



Step 1

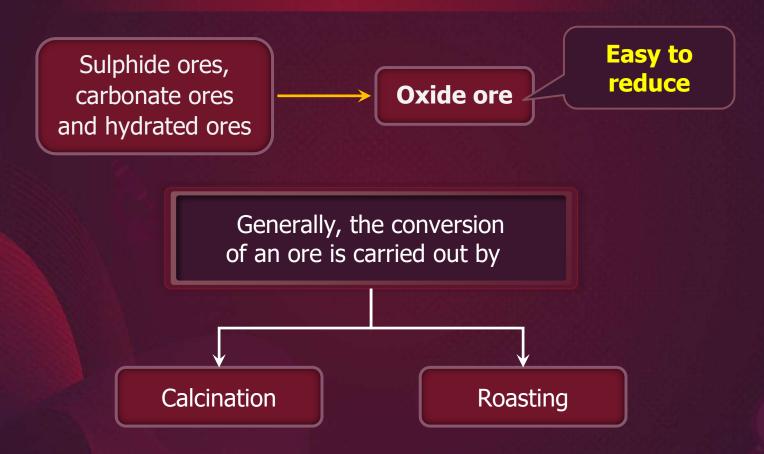
Conversion of ore to oxide

Step 2

Reduction of oxide to metal

#### **Conversion of Ore to Oxide**

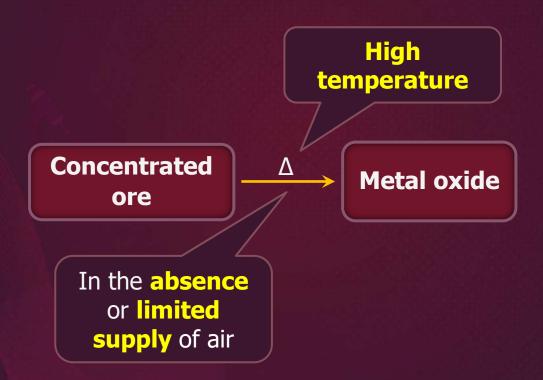




#### Calcination



Generally used for carbonate ores



#### Calcination





$$ZnCO_3$$
 (s)  $\stackrel{\triangle}{\longrightarrow}$   $ZnO$  (s) +  $CO_2$  \(\frac{1}{2}\)(g)

**Calamine** 

CaCO<sub>3</sub>.MgCO<sub>3</sub> (s) 
$$\stackrel{\triangle}{\longrightarrow}$$
 CaO (s)+ MgO (s) + 2CO<sub>2</sub>↑(g) Dolomite

#### Calcination





2

Hydrated ores

 $\longrightarrow$ 

Anhydrous oxides

$$Fe_2O_3.3H_2O \xrightarrow{\Delta} Fe_2O_3 + 3H_2O\uparrow$$

$$AI(OH)_3 \xrightarrow{\Delta} AI_2O_3 + 3H_2O^{\uparrow}$$

**Limonite** 

Impurities like S, As, and Sb are removed in the form of elemental vapours.

4

The products of **calcination** are always **porous**.





Generally used for sulphide ores

High temperature below melting point of metal

**Concentrated** ore

Excess air

**Metal oxide** 

Roasting occurs in reverberatory furnaces

# Roasting





2ZnS (s) + 
$$30_2 \xrightarrow{\Delta}$$
 2ZnO (s) +  $2SO_2 \uparrow$  (g)

2PbS (s) + 
$$30_2 \xrightarrow{\Delta}$$
 2PbO (s) +  $2SO_2 \uparrow$  (g)

$$\frac{2Cu_2S(s) + 3O_2 \xrightarrow{\Delta} 2Cu_2O(s) + 2SO_2\uparrow(g)}{}$$

Occurs in **reverberatory furnaces** 

# Roasting





2 Sometimes,

**Lower** oxidation state

**Higher** oxidation state

# Roasting



The impurities like organic matter, S,

As are removed by roasting in the form of their volatile oxides.

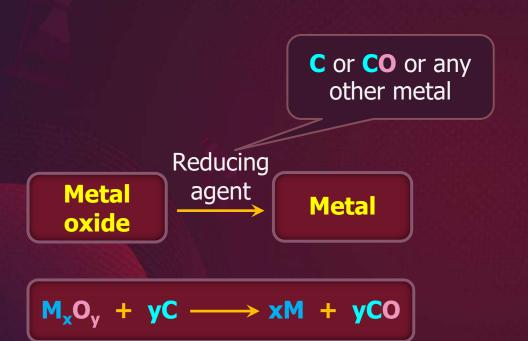
The product of **roasting** are always **porous** 

5

**Hydrous** ores become **anhydrous** through roasting.

#### Reduction of Oxide to Metal





Some metal oxides get **reduced** easily while others are **difficult** to **reduce**,

But **heating** is required in any case.



#### Recall



Gibb's energy change

=

=

ΔH: Enthalpy change

ΔS: Entropy change

T: Temperature

k: Equilibrium constant

=

- ->

Reaction proceeds (spontaneous)

$$\Delta G$$

=

-->

Reaction at equilibrium

+ve

Reaction does **not** occur **(non-spontaneous)** 



Now Let's Study a
Diagram which Helps
in Predicting
the Feasibility of
Thermal Reduction
of an Ore!



It is a graph that provides the basis for considering the choice of reducing agent in reduction of oxides.



Generally, it consist of the plots of

The slope of the graph of  $\longrightarrow$   $M_{x}O$  is **positive**.

Δ<sub>f</sub>G<sup>o</sup> vs T

For formation of oxides

$$\frac{2xM(s) + O_2(g)}{2M_xO(s)}$$

As AG increases with **increases** in temperature.

Slope of the line of carbon is unique due to entropy factor.

3

Generally, free energy follows a straight line, except when the material melt or vaporise when there is large change in entropy associated with change in state.

**Slope** of line **changes** 



Hg → HgO line changes slope at 356 °C

**Hg boils** 

Mg → MgO line changes slope at 1120 °C

Mg boils



Below which  $\Delta G = -ve$ 

There is a **point** in the curve of the graph above which M<sub>x</sub>O decomposes on its own.

So, M<sub>x</sub>O is stable



5

In most of the processes, one metal is used to reduce the oxide of another metal at particular temperature



So, any metal can **reduce** the oxide of another metal which **lies above** it in the **Ellingham diagram**.



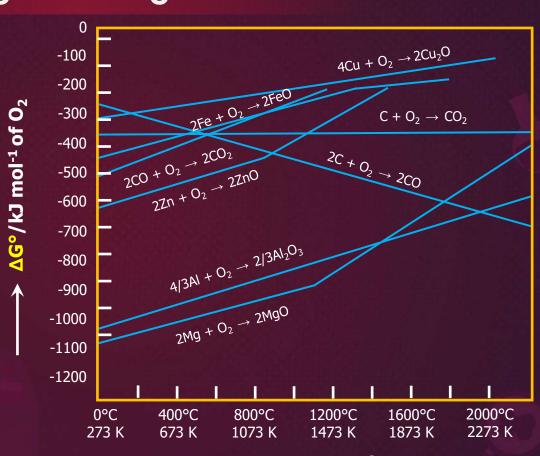
Al reduces the oxides of Zn, Fe, Ti

BUT,

It cannot reduce MgO at a temperature below 1500°C



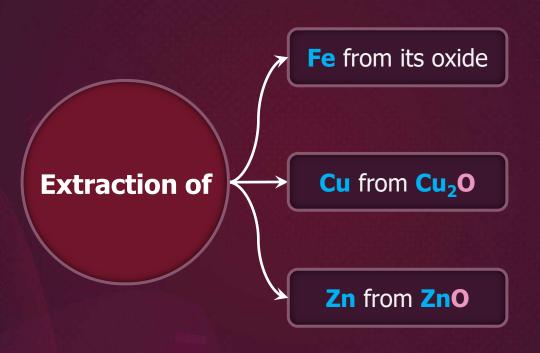
Larger the
difference between
the upper and lower
lines, easier the
reduction.



──→ Temperature in °C

# **Applications of Ellingham Diagram**





#### **Extraction of Fe from Its Oxides**



**Crushing** and **grinding Concentration** By **Isolation/Extraction** calcination of metal or **roasting** 

The ore is mixed with limestone and coke

In blast furnace



#### **Blast Furnace**

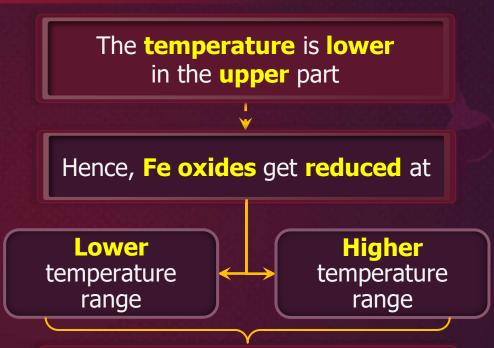


Hot air is blown in from the **bottom** of **blast furnace** 

Coke is burnt to produce a high temperature at the lower portion of furnace only

Up to **2200K** 

**CO** and **heat** move to the **upper** part of the furnace



Depending upon the **point of intersection** in the **Ellingham diagram** 

#### **Blast Furnace**



# At **500-800K (lower temperature),** the following reactions occur

$$3Fe_2O_3 + CO \longrightarrow 2Fe_3O_4 + CO_2$$

$$Fe_3O_4 + 4CO \longrightarrow 3Fe + 4CO_2$$

$$Fe_2O_3 + CO \longrightarrow 2FeO + CO_2$$

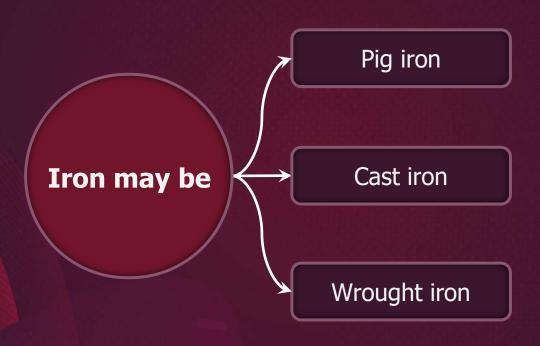
# At 900-1500K (higher temperature), the following reactions occur

$$C + CO_2 \longrightarrow 2CO$$

FeO + CO 
$$\longrightarrow$$
 Fe + CO<sub>2</sub>

# Types of Iron







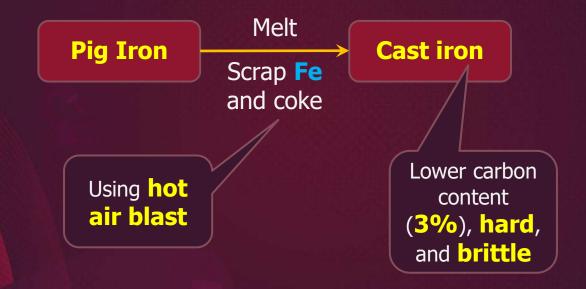


The **iron** obtained from **furnace** P, S, Si, Mn Contains 4% carbon and a small amount of **impurities** Can be cast into a variety of **shapes** Known as Pig iron

#### **Cast Iron**



#### **Preparation**



# Wrought Iron



Prepared from cast iron

By **oxidising impurities** in a **reverberatory** furnace lined with **haematite** 

**Haematite** oxidises **C** to **CO** 

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

**Limestone** is added as **flux** 

**S, Si, P** are **oxidised** and passed into **slag** 

Hence, iron metal is removed

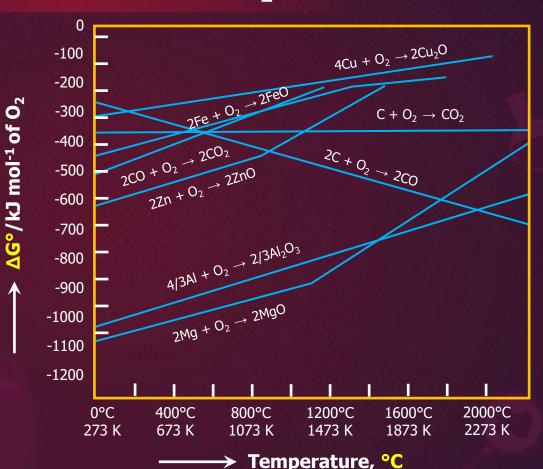
It consists of around **99.4% iron** by mass.

#### Extraction of Cu From Cu<sub>2</sub>O



The **sulphide ores** of **Cu** are **roasted** as

 $\frac{2Cu_2S + 3O_2}{2Cu_2O + 2SO_2}$ 



#### Extraction of Cu From Cu<sub>2</sub>O



Hence, it is easy to **reduce** the oxide ores of **copper** directly to the **metal** 

By just **heating** with **coke** 

$$Cu_2O + C \longrightarrow 2Cu + CO$$

Actually, the ore is **heated** in a **reverberatory furnace** after mixing with **silica**.

$$\begin{array}{ccc} \textbf{FeO} + \textbf{SiO}_2 & \longrightarrow & \textbf{FeSiO}_3 \\ \textbf{Impurity} & & & & & & & & \\ \end{array}$$

#### Extraction of Cu From Cu<sub>2</sub>O



Copper ore is produced as **copper matte.** 

Cu<sub>2</sub>S and FeS.

**Copper matte** is then charged to a silica-lined **convertor** with the addition of some **silica** 

After that, hot air blast is blown to convert the remaining FeS, FeO, and Cu<sub>2</sub>S/Cu<sub>2</sub>O to Cu

#### Reactions Involved in the Extraction of Cu



$$2FeS + 3O_2 \longrightarrow 2FeO + 2SO_2$$

$$FeO + SiO_2 \longrightarrow FeSiO_3 (Slag)$$

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

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





#### Extraction of Zn from ZnO



Requires **higher temperature** than **Cu** 

**Reduction** of **ZnO** is done using coke

For **heating** oxide, it is made into **brickettes** with **coke** and **clay**.

Reaction

$$ZnO + C$$
  $Coke$   $Zn + CO$ 

Distilled off and collected by rapid chilling





The theory assumes (often incorrectly) that the reactants and products are in equilibrium

Although the Ellingham diagram predicts the feasibility of the reaction, it does not give any data regarding competing alternative reactions

Also the Ellingham diagram does not predict the rates of the reactions

# **Electrolysis**





Electrochemical principles are governed by the given **equation**.

$$\Delta G^{\circ} = -nE^{\circ}F$$

Where, n = Number of electrons  $E^{o} = Electrode potential$ of redox couple

Less reactive metal would come out of the solution.

More reactive metal will go to the solution.

#### **Electrode Potential**





$$E_{Cu}^{\circ}^{2+}(aq)/Cu(s) = 0.34 \text{ V}$$

$$E_{Fe}^{\circ} ^{2+}(aq)/Fe (s) = -0.41 \text{ V}$$

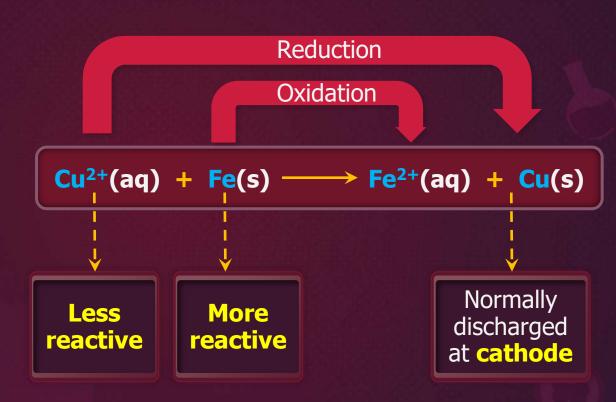
$$E_{\text{cell}}^{\circ} = E_{\text{Cu}}^{\circ} {}^{2+}_{(\text{aq})/\text{Cu(s)}} - E_{\text{Fe}}^{\circ} {}^{2}_{(\text{aq})/\text{Fe(s)}}$$
$$= 0.34 \text{ V} - (-0.41) \text{ V}$$

+ve E°

#### **Electrode Potential**

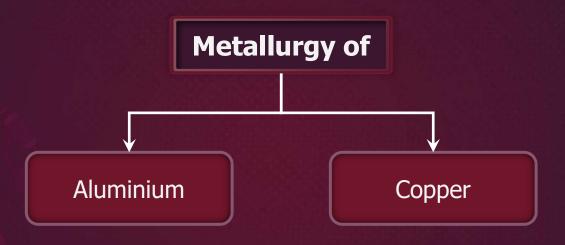






# Metallurgy of Some Important Metals





## **Electrometallurgy of Aluminium**



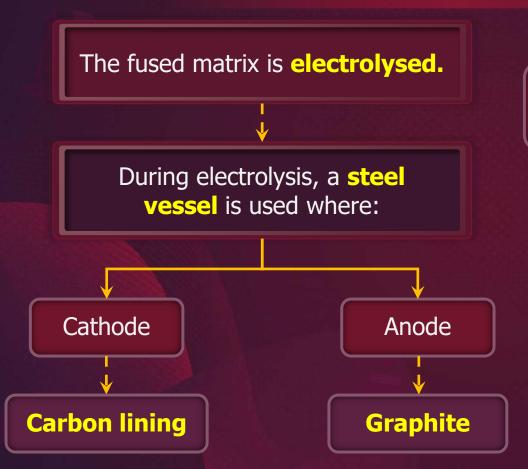
In the metallurgy of **aluminium** 

Purified Al<sub>2</sub>O<sub>3</sub> is mixed with Na<sub>3</sub>AlF<sub>6</sub> or CaF<sub>2</sub>

Na<sub>3</sub>AlF<sub>6</sub> or CaF<sub>2</sub> lowers the melting point of the mixture and brings conductivity.

## **Electrometallurgy of Aluminium**





$$2Al_2O_3 + 3C \longrightarrow Al + 3CO_2$$

The electrolysis is known as **Hall-Heroult** process.

## **Electrometallurgy of Aluminium**



Reaction

At cathode:

At anode:

$$C(s) + O^{2-} \longrightarrow CO(g) + 2e^{-}$$
(melt)

$$C(s) + 20^{2-} \longrightarrow CO_2(g) + 4e^{-}$$
(melt)

Formed by the reaction between C and O<sub>2</sub> liberated from anode

## **Hydrometallurgy of Copper**







**High-grade** ores

First ore is **leached**.

Solution containing Cu<sup>2+</sup> is treated with scrap Fe or H<sub>2</sub>.

By using acid or bacteria

$$Cu^{2+}(aq) + H_2(g) \longrightarrow Cu(s) + 2H^+(aq)$$

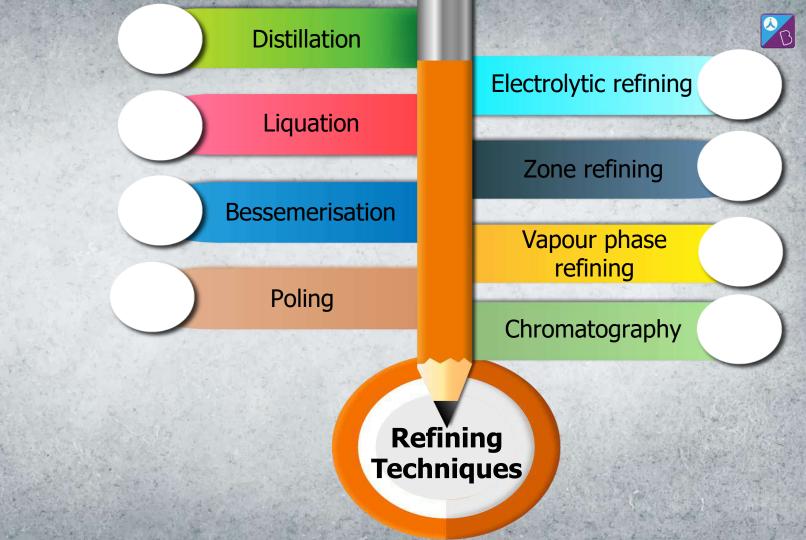
#### **Purification of Metals**



A metal **extracted** by any method is usually contaminated with some **impurities** 

• • •

To obtain a metal of **high purity**, several **techniques** are required.



#### **Distillation**



It is very useful for metals with **low boiling** points.

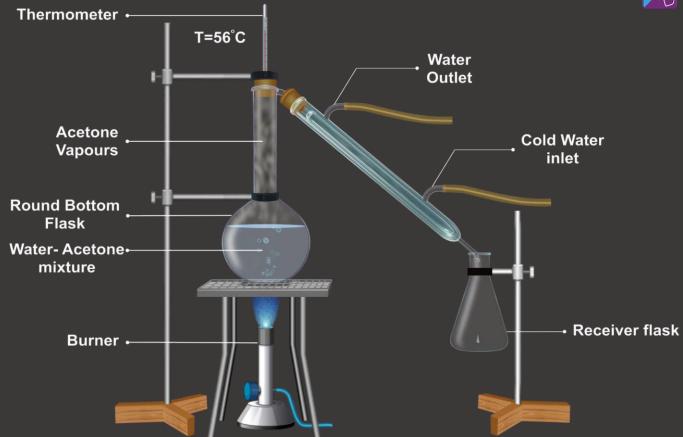
Like **Zn** and **Hg** 

An impure metal is **evaporated** to obtain a **pure metal**.

**Distillate** 

# Distillation 🕏





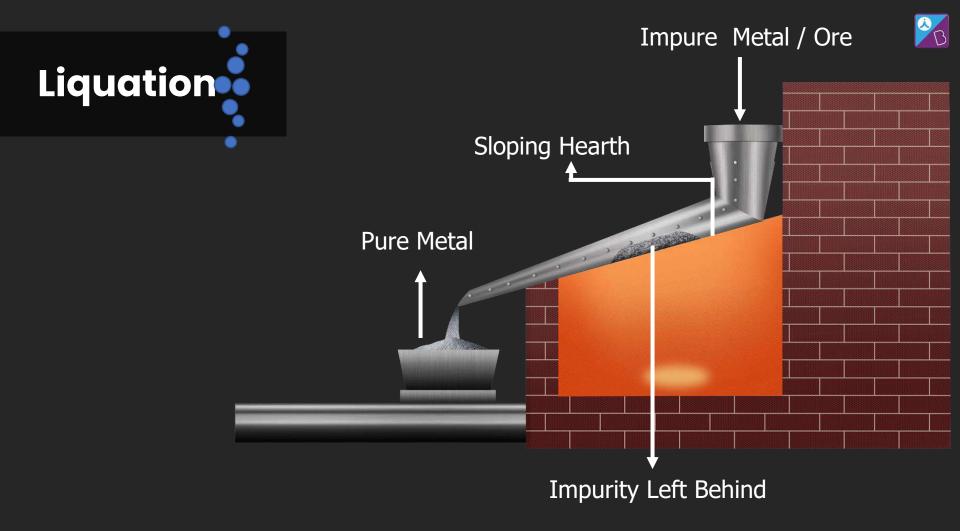
#### Liquation



Liquation is used for metals with **low melting points.** 

Like **Sn** 

Metal is made to flow on sloping surface; this is how it separates from impurities with higher melting points.



#### **Bessemerisation**



Method in which **air** is **blown** into **molten metal** mat

Deposited in the bessemer converter

In the final stage of smelting, other products (FeS) are oxidized (FeSiO<sub>3</sub>) and removed as slag. **Copper metal** 

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

Step 2

Cu<sub>2</sub>O reacts with the remaining molten Cu

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



# **Poling**



Used for Cu and Sn

**Molten Cu** contains **impurity** 

Cu<sub>2</sub>O

**Molten Cu** is treated with powdered **anthracite**.

Then stirred with a pole of green wood.

## **Poling**



Green wood at higher temperature liberates hydrocarbon gases.

These gases are converted into methane.

Reaction

Reduces CuO to Cu

Green wood 
$$\longrightarrow$$
 Hydrocarbon  $\longrightarrow$   $\leftarrow$  CH<sub>4</sub>

$$4CuO + CH_4 \longrightarrow 4Cu + CO_2 + 2H_2O$$

99.5% pure --

**Tough pitch copper** 

# **Electrolytic Refining**



In this method

Anode

**Impure** metal

Cathode

Strip of the **same** metal in its **pure form** 

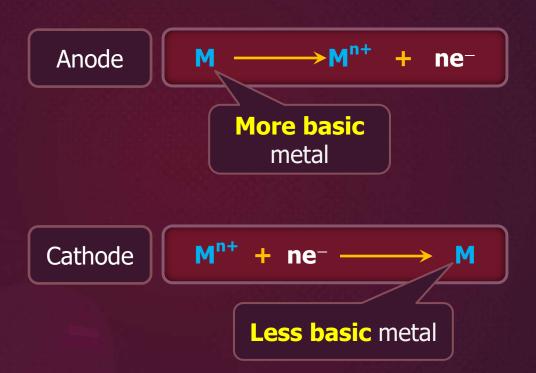
Both the electrodes are put in a suitable electrolytic bath.

Containing **soluble salt** of same metal

# **Electrolytic Refining**



General reaction



## **Copper Refining**



Anode

**Impure** copper

Cathode

Pure copper strips

Electrolyte

Acidified solution of CuSO<sub>4</sub>

Reactions involved

Anode

Cathode





Impurities from blister copper deposit as anode mud

Contains Se, Te, Ag, Au, Pt

**Recovery** of these metals may meet the **cost** of **refining**.

Zn can also be refined from electrolytic refining.

#### **Zone Refining**



**Principle** 

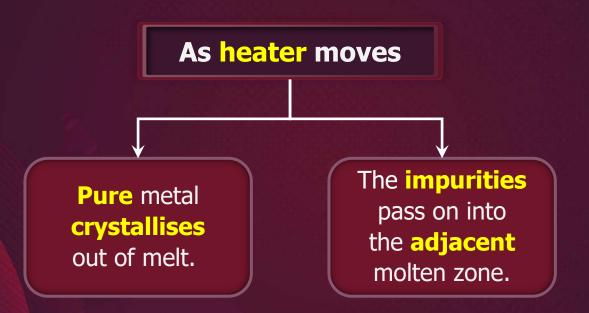
Impurities are more soluble in the molten state than in the solid metal.

A circular mobile heater is fixed at one end of a rod of the impure metal.

The molten zone **moves** along with the **heater** that moves **forward**.

## **Zone Refining**





## **Zone Refining**



Process is **repeated** several times and the heater is moved in the **same direction**.

1 1

**Impurities** get concentrated at **one end.** 

This end is **cut off** 



Ge, Si, B, Ga, In, etc.

Semiconductors and other metals

# Requirements of Vapour Phase Refining



A metal should form a volatile compound with a reagent.

The volatile compound should be **easily decomposable.** 

For easy recovery

## Vapour Phase Refining





**Requirements** of vapour phase refining

A metal should form a volatile compound be easily decomposable for easy recovery.

#### Van Arkel Method



Van Arkel method is useful for removing impurities from metals like Zr, Ti.

Oxygen and nitrogen

#### Van Arkel Method



Step 1

**Crude metal** is heated in an evacuated vessel with **iodine**.

Step 2

Metal iodine is decomposed on tungsten filament.

volatilises

 $Zr + 2I_2 \longrightarrow ZrI_4$ 

More covalent

Heated to about 1800 K

$$ZrI_4 \longrightarrow Zr + 2I_2$$

Pure metal

#### **Mond's Process**



Step 1

Ni is heated in a stream of CO to form nickel tetracarbonyl.

Step 2

The volatile compound is subjected to **higher temperature.** 

$$Ni + 4CO \xrightarrow{330-350 \text{ K}} Ni(CO)_4$$

**Volatile** 

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

**Pure metal** 

## Chromatography



In chromatography, a column of Al<sub>2</sub>O<sub>3</sub> is prepared in a glass tube

The moving medium containing a solution of components is in liquid form.

**Column chromatography** 

It is very useful for the purification of elements that are available in minute quantities

**Impurities** are **not** very different in chemical properties from the element to be **separated**.



