

Basic Principle of Extraction

NEEDS FOR EXTRACTION OF METALS

Section - 1

We all use metals in our day to day life sometimes directly and sometimes indirectly. For example, Iron is used making electromagnets, chains, etc. Steel is used in making machinery parts, household utensils. Silver and gold are used in making jewellery. We can find numerous examples where we use metals. Since metals do not occur in pure form in earth's crusts, we need to extract metals from their ores or minerals.

Occurrence of Metals :

Metals occur in various forms. Some in native form, some in carbonate form and some in oxide form. Those metals that are least reactive and have very little affinity for oxygen, moisture and other chemical reagents occur in free or metallic or native state.

- Natural substances in which metals or their compounds occur in earth are called *minerals*.
- Those minerals from which metals can be extracted conveniently and profitably are known as *ores*.

Illustration :

A certain metal M occurs in three compounds namely A, B, C. A has 15% of M, B has 66% of M and C has 71% of M. If we extract M from A, it costs Rs 35 per kg, if we extract it from B, it costs Rs 45 per kg and if we extract from C, it costs Rs 1110 per kg.

Now both A, B, C are minerals as they contain M, but all cannot be called ores. Extraction of M from mineral A would cost less but would result in a very less amount. Similarly, extraction from C would result in large amount but it will also cost a large sum. Hence, B is the appropriate mineral from which M should be extracted as it would give sufficient amount and would not even cost much. In that case, B is the ore of M. for example : Bauxite ($\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$) and Clay ($\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$) both are minerals of Aluminium. But still Bauxite is appropriate ore but not Clay since we can extract Aluminium more profitably and quantitatively from Bauxite.

Commercially Important Ores :

1. Native Ores :

These ores contain metals in the free state. They exist in free state because they are very unreactive. Some of important metals are :

2. Sulphurised and Arsenical ores :

These ores consist of sulphides and arsenides in simple and complex forms of metals.

Metal	Name of the ore	
Pb	Galena	PbS
Zn	Zinc blende	ZnS
Hg	Cinnabar	HgS
Ag	Argentite or Silver glance	Ag ₂ S
Fe	Iron pyrites	FeS ₂
Cu	Copper pyrites	CuFeS ₂
	Chalcocite or Copper glance	Cu ₂ S

3. Oxidised Ores

In these ores, metals are present as their oxides or oxy-salt as carbonates, nitrates, sulphates, phosphates, silicates, etc.

Oxides :

Haematite	Fe ₂ O ₃
Magnetite	Fe ₃ O ₄
Bauxite	Al ₂ O ₃ .2H ₂ O
Corundum	Al ₂ O ₃
Chromite	FeO.Cr ₂ O ₃
Tinstone (Cassiterite)	SnO ₂
Pyrolusite	MnO ₂

Carbonates :

Magnesite	MgCO ₃
Lime stone	CaCO ₃
Dolomite	CaCO ₃ .MgCO ₃
Calamine	ZnCO ₃
Malachite	CuCO ₃ .Cu(OH) ₂
Azurite	Cu(OH) ₂ .2CuCO ₃
Cerussite	PbCO ₃
Siderite	FeCO ₃

Nitrates :

Chile saltpetre	NaNO ₃
Salt petre	KNO ₃

Sulphates :

Epsom salt	$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$
Gypsum	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$
Glauber's salt	$\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$

Phosphates and Silicates :

Fluor-apatite	$3\text{Ca}_3(\text{PO}_4)_2 \cdot \text{CaF}_2$
Felspar	KAlSi_3O_8

4. Halide Ores :

Metallic halides are very few in nature. Chlorides are most common ores.

Common salt	NaCl
Horn silver	AgCl
Carnallite	$\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$
Fluorspar	CaF_2
Cryolite	Na_3AlF_6

Note : You Don't need to cram all these compounds in one go. As you will read the chapter these compounds will slowly set in your mind.

METALLURGY

Section - 2

The complete process of obtaining a pure metal from one of its ores is known metallurgy. The method to extract a metal is generally not universal, as it depends upon a number of factors such as its chemical nature and reactivity, nature of ore, nature of impurities and local conditions, etc. But still in general, metallurgy is divided into following three steps.

- I. Concentration of the Ore
- II. Obtaining Crude Metal from Concentrated Ore
- III. Refining of Crude Metal

Different methods are available for each of these stages. Choice of any method depends upon the nature of metal and type of impurity present in the ore.

I. Concentration of the Ore :

Concentration of an deals with removal of unwanted impurities. Ores usually contain soil, sand, stones and other useless silicates. These unwanted impurities are named gangue or matrix. For concentration, metal is crushed and powdered and then it undergoes concentration. Concentration of ore involves physical as well as chemical methods. It is also known as *Dressing or Benefication of the ore*.

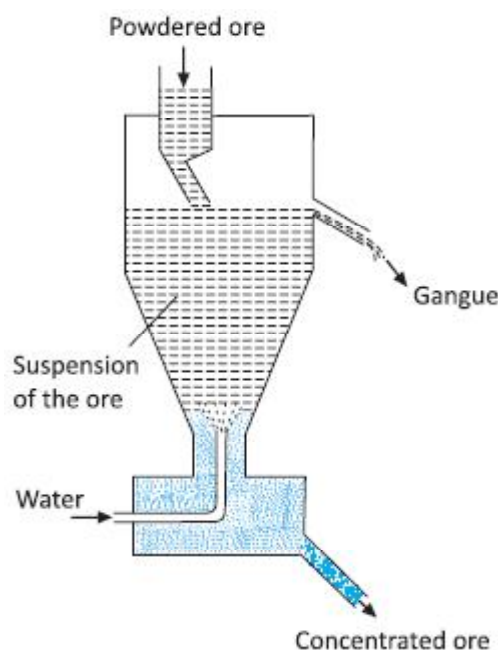
(i) Hydraulic Washing (Gravity Separation)

Principle :

It is based on the difference in specific gravity of ore and gangue particles.

Working :

Powdered ore is agitated with running water which carries lighter particles like sand, clay away with it.



Type of Ore :

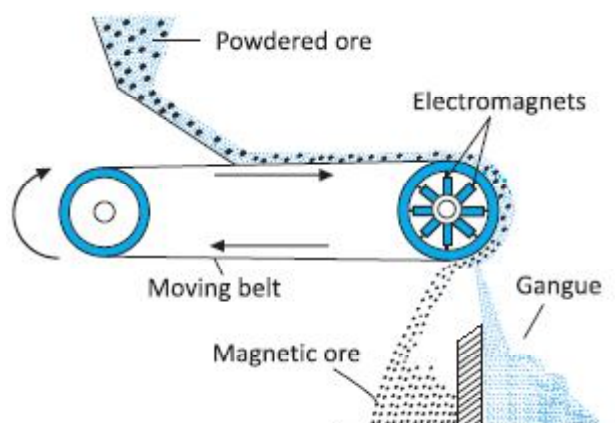
The oxides and carbonates type of ores are suitable for this method. For example : Tin's ore **Cassiterite** (SnO_2), Iron's ore **Haematite** (Fe_2O_3).

(ii) Magnetic Separation**Principle :**

It is based on the magnetic and non-magnetic properties of ore and gangue.

Working :

A magnetic separator consists of a belt which moves on two rollers, one of the roller being a strong magnet. Now, the powdered ore is dropped on the belt near the non-magnetic roller and as the ore reaches the magnetic roller the magnetic particles get attracted and fall nearer to the roller while the non-magnetic particles fall away from the rollers.

**Type of Ore :**

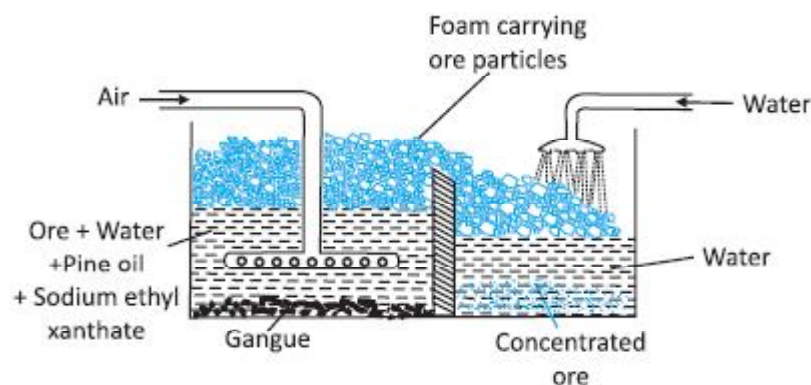
Separating Wolframite (Tungsten) ore from Cassiterite (Tin) ore, separating transition metal ores such as Magnetite (Fe_3O_4), Pyrolusite (MnO_2) and Chromite (FeO , Cr_2O_3) from unwanted gangue.

(iii) Froth Floatation**Principle :**

Mineral particles are wetted by oils and the gangue particles are welled by water.

Working :

Collectors, frothing agents and froth stabilisers are added to the ore which mixed water. Collectors enhance the non-wettability of mineral particles and froth stabilizers stabilize froth. Mineral particles become wet by oils while gangue particles by water. Liquid mixture is agitated and air blown. Froth is formed which carries off with it mineral particles. Light froth floats at the surface which is taken off and from this froth mineral is recovered.



Frothing agents : Pine Oil

Collectors : Fatty acids, Sodium Ethyl Xanthate

Froth Stabilizers : Cresols and Aniline

Depressants :

These are those chemicals that are used to prevent certain type of particles from forming the froth with the bubbles. For example : NaCN (sodium cyanide) acts as a depressant in preventing ZnS from forming the froth as it forms a layer of $\text{Na}_2\text{Zn}(\text{CN})_4$ on surface of ZnS in concentration of zinc blende (ZnS). This is also known as selective frothing.

Type of Ore :

Sulphide ores eg: Galena (Pbs), Zinc blenda (ZnS), Cinnabar (HgS).

(iv) Chemical Separation (Leaching)

Principle :

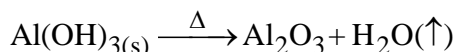
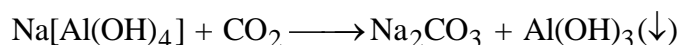
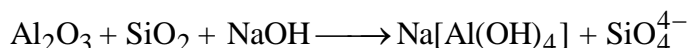
It is based on the differences in the chemical properties of the ore and the gangue.

Working :

Ore is made soluble in a solvent and is then separated from the gangue. The solvent's choice depends upon the ore and gangue's chemical properties.

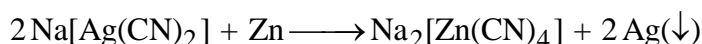
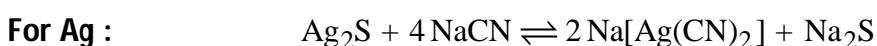
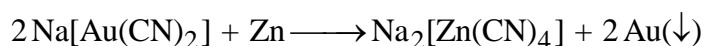
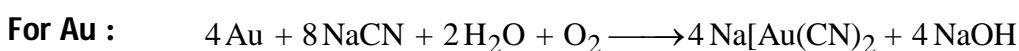
Example :

1. In Bayer's process, the impurities of iron and silicon are removed from the bauxite ore. NaOH is added to the ore and as Al is amphoteric it dissolves forming sodium aluminate. SiO_2 being acidic oxide also dissolves as silicate ions. The insoluble iron impurities are removed by filtering. Next, CO_2 is bubbled through the solution lowering the pH. This enables the precipitation of $\text{Al}(\text{OH})_3$ (silicate ions remain dissolved). The $\text{Al}(\text{OH})_3$ precipitated is calcined (heated strongly) to give concentrated Al_2O_3 .



2. Cyanide's Process

Another example is the cyanide's process for extraction of Au (from native form) and Ag (from Ag_2S ore). The ore containing impurities is crushed and then treated with 0.1 – 0.2% solution of NaCN or KCN and aerated forming a soluble complex from complex which the metal is extracted by the addition of Zn powder in the solution.



II. Obtaining Crude Metal :

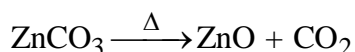
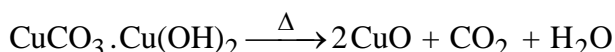
This step involves reduction of concentrated ore. The concentrated ore i.e. Metal oxides, Metal sulphides, Metal carbonates etc. are converted to metal in this step. $\text{M}^{n+} \longrightarrow \text{M}$ reduction occurs in this step. Metal carbonates and Metal sulphides are difficult to reduce than metal oxides therefore they are first converted to their oxides and then metal oxides is reduced to metal.

Conversion into Oxide Forms

Metallic ores are converted to metallic oxides by the two processes.

1. Calcination :

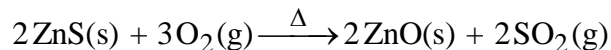
It involves heating of the ore below its fusion temperature in absence of air. It can remove moisture from hydrated oxides or carbon dioxide from carbonates. It is suitable for carbonate ores.



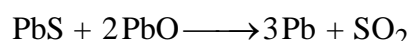
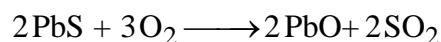
Calcination makes the ore porous. The step is generally performed in a reverberatory furnace.

2. Roasting :

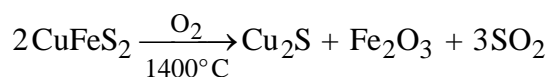
It involves heating of the ore strongly in the presence of excess of air below its fusion temperature. It is suitable for sulphide ores.



Sometimes, a part of sulphide may act as a reducing agent as in case of extraction of lead. PbO formed by roasting is reduced to lead by PbS.



Exception :



Note : Oxide ores are suitable for reduction. So, if we obtain ore in oxide form just after concentration as in case of aluminium, then this ore is not required to undergo calcination and roasting as it already exists in oxide form.

Reduction to Crude Metal

When the oxide form is obtained, then the metal has to be reduced. The choice of the reducing agent is decided by the factors of energetics and economics.

Three main categories of reduction processes are :

(A) Chemical Reduction (B) Hydrometallurgy (C) Electrolytic Reduction

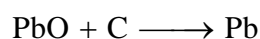
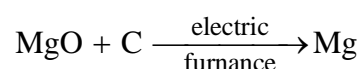
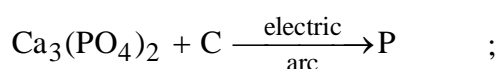
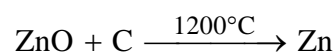
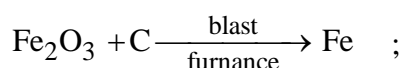
Now, we will discuss few important points of each category.

(A) Chemical Reduction Process

Carbon, Aluminium, Hydrogen and some other metals are used as reducing agents. These metals replace less electropositive metals from their oxides.

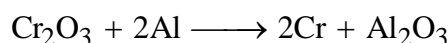
(i) Reduction by carbon :

Carbon can be used to reduce a number of oxides and other compounds, and because of the low cost and availability of coke this method is widely used. The disadvantages are that a high temperature is needed, which is expensive and necessitates the use of a blast furnace. Also, many metals combine with carbon, forming carbides, some examples are :

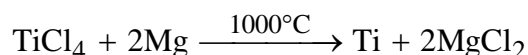


(ii) Reduction by another metal :

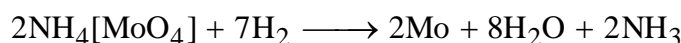
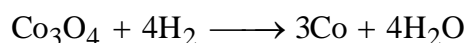
If the temperature needed for carbon to reduce an oxide is too high for economic or practical purposes, the reduction can be done by another highly electropositive metal such as Al, which liberates a large amount of energy on oxidation to Al_2O_3 . This is the bases of the thermite process : -



Magnesium being more electropositive metal as compared to Al is used to reduce halides.

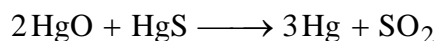
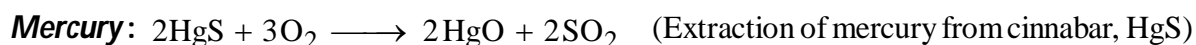
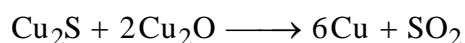
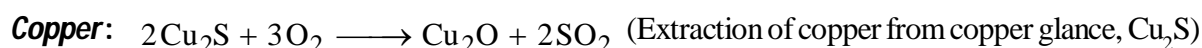
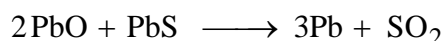
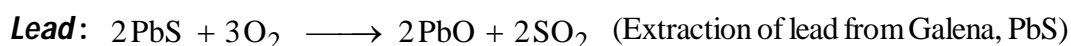
**(iii) Reduction of oxides with hydrogen**

This method is not widely used because many metals react with hydrogen at elevated temperatures, forming hydrides.

**(iv) Self Reduction Process**

The sulphide ore of less electropositive metals like lead, mercury, copper are heated in air as to convert part of the ore into oxide or sulphate which then reacts with the remaining sulphide ore to give the metal and SO_2 gas.

No external reducing agent is used in this process.



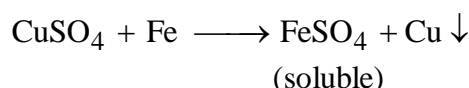
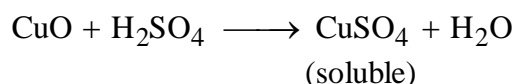
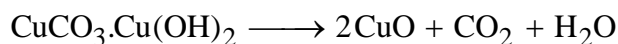
Another name for self reduction process is *auto reduction process* or air reduction process.

(B) Hydrometallurgy

This process is based on the principle that more electropositive metals can displace less electropositive metals from their salt solution. The ore is treated with such chemical reagents which convert it into soluble compound. By addition of more electropositive metals to the filtrate, the metal present in the ore can be precipitated.

Illustration :

Malachite ore is first calcined and the oxide obtained is dissolved in H_2SO_4 . To the solution of CuSO_4 , scrap iron is added which precipitates copper.



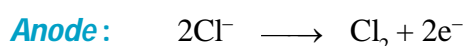
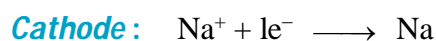
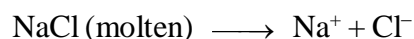
Similarly, silver can be obtained by cyanide process.

(C) Electrolytic Reduction

Oxide of highly electropositive metals like Na, K etc cannot be reduced with carbon at moderate temperature. So, for their reduction, a very high temperature is required, at which they may combine with carbon to form carbide. Thus, they are obtained by electrolysis of their oxides in fused or molten state.

Illustration :

Sodium is obtained by the electrolysis of fused mixture of NaCl and CaCl_2 (Down's Process) or by the electrolysis of fused NaOH (Castner's process).



Similarly aluminium is obtained by the electrolysis of alumina mixed with *cryolite*.

(III) Refining of Crude Metal

The crude metal obtained is impure. The impure metal is subjected to some purifying processes known as refining in order to remove the impurities. The processes used for refining depend upon the nature of the metal and the nature of impurities.

- | | | |
|---------------------------|-----------------------|---------------------------------|
| (A) Distillation | (B) Liquefaction | (C) Pyrometallurgical Oxidation |
| (i) Cupellation | (ii) Bessemerisation | (iii) Poling |
| (D) Electrolytic Refining | (E) Special Methods | |
| (i) Mond's Process | (ii) Van Arkel Method | (iii) Zone Refining |

(A) Distillation

This process is used for those metals which are easily volatile such as: Zn, Hg, Cd. The impure metal is heated in a furnace and its vapours are separately condensed in a receiver. The non-volatile impurities are left behind in the furnace.

(B) Liquation

This process is based on the difference in fusibility of metal and impurities. When the impurities are less fusible than the metal, this process is employed. The impure metal is placed on the sloping hearth of the furnace and gently heated. The metal melts and flows down leaving behind the impurities on the hearth. This method is used to purify Bi, Sn, Pb and Hg.

(C) Bessemerisation (Pyrometallurgical oxidation)

The impure metal is heated in a furnace and a blast of compressed air is blown through the molten mass. The impurities get oxidized. For example, the molten pig iron is taken in a Bessemer converter and compressed air is passed which oxidizes the impurities.

**(D) Electrolytic Refining**

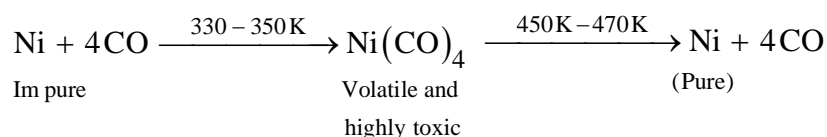
It is different from electrolytic reduction. The impure metal is made anode and a thin sheet of pure metal is made cathode.

As electrolysis proceeds, pure metal from anode is transferred to the cathode, whereas the impurities settle down as anodic mud or anodic sludge. For examples Cu, Ag, Au, Pb, Zn, etc. are refined by this method.

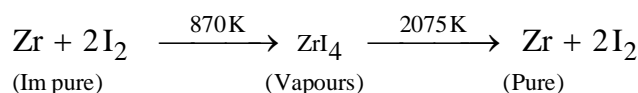
(E) Special methods for Refining**(i) Mond's Process**

It is used mainly for refining of nickel. Impure Ni is treated with carbon monoxide at 330K–350K, when volatile compounds $\text{Ni}(\text{CO})_4$ is formed.

The impurities are left behind and the volatile $\text{Ni}(\text{CO})_4$ is transferred into another container, where it is heated more strongly at 450 K to give pure Ni. The CO gas produced is used again.

**(ii) Van Arkel Method**

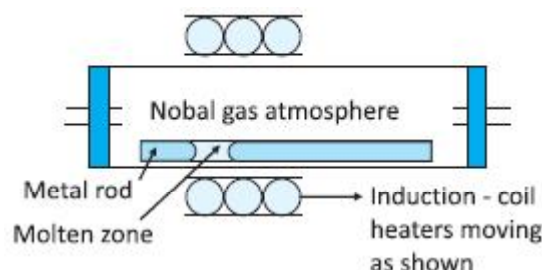
In this method, zirconium (or titanium) is heated in iodine vapour at about 870K to form volatile ZrI_4 . The vapours of volatile ZrI_4 are then decomposed electrically over tungsten filament to get pure metal, and iodine is recovered.



As Van Arkel method and Mond's process are quite related they are known as Vapour Phase Refining.

(iii) Zone Refining

This method is used for extracting ultra-pure metals. This method is based upon the principle that when a molten solution of impure metal is allowed to cool, the pure metal crystallizes out, while the impurities remain in the melt. A movable heater is fitted at one end of the rod of impure metal. The heater is slowly moved across the rod. The metal melts at the point of heating and as the heater moves on from one end of the rod to the other end, the pure metal crystallizes while the impurities pass into the adjacent melted zone. This process is repeated number of times unless metal of desired purity is obtained. The process is carried out in an inert atmosphere to prevent the oxidation of metal. For example, Germanium, Silicon and Gallium for being used in semiconductors are purified by this method.



Important Terms

1. Flux

Flux is a substance which is added to remove non-fusible impurities by forming slag and decrease the melting point of the melt during reduction. Flux can be of three types :

- (a) **Acidic flux** - It is used to remove basic impurities. Examples of acidic flux include SiO_2 (in smelting of Cu) and borax.
- (b) **Basic Flux** - It is added to remove acidic impurities. Examples include Fe_2O_3 , CaCO_3 (in blast furnace) etc.

2. Furnace

A furnace is a structure built to produce high temperature. Examples of some furnaces are reverberatory furnace, blast furnace and muffle furnace.

3. Refractory materials

These are compounds / mixtures which can withstand very high temperature without melting and are not affected by slags. They are used in the form of bricks for internal lining of furnaces.

Refractory materials may be of three types :

- (a) Acid Refractories - SiO_2 , quartz.
- (b) Basic Refractories - CaO (lime), magnesite, dolomite.(in blast furnace)
- (c) Neutral Refractories - Graphite (used in Hall Heroult Process), Chromite, bone ash.

IN - CHAPTER EXERCISE - A

1. List five ores which are smelted and give equations to show what occurs during smelting.
2. Name the process(es) used for concentration of tinstone.
3. Explain the role of collectors and froth stabilisers in Froth floatation process.
4. Why is reduction by hydrogen not widely used.
5. Name three ores which undergo autoredution give balanced equations.
6. Explain thermite process.

NOW ATTEMPT IN-CHAPTER EXERCISE-A REMAINING QUESTIONS IN THIS EBOOK

EXTRACTION OF IMPORTANT METALS

Section - 3



GROUP 1

LITHIUM

Sources :

Lithium occurs mainly as silicate minerals like spodumene ($\text{LiAlSi}_2\text{O}_6$), Lepidolite.

SODIUM

Sources :

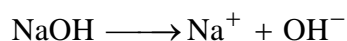
Sodium is the most abundant alkali metal. It is found in sea water, as rock salt (NaCl), Saltpetre (NaNO_3), Borax, Glauber's salt ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$), cryolite.

Extraction :

Sodium is obtained on large scale by two processes :

(A) Castner's process :

In this process, electrolysis of fused NaOH is carried out at 330°C using iron as cathode and nickel anode.



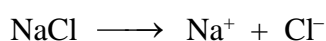
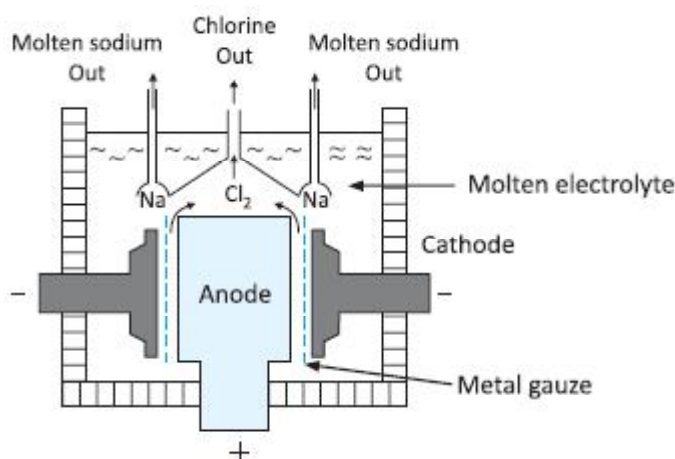
At Fe cathode: $\text{Na}^+ + \text{e}^- \longrightarrow \text{Na}$

At Ni anode : $4\text{OH}^- \longrightarrow 2\text{H}_2\text{O} + \text{O}_2 + 4\text{e}^-$

water formed at the anode gets partly evaporated and is partly broken down to form H_2 at cathode.

(B) Down's process :

Sodium metal is manufactured mainly by this process. It involves the electrolysis of fused sodium chloride (40%), calcium chloride (60%) and potassium fluoride using iron as cathode and graphite as anode at about 600°C .



The electrolysis of pure NaCl presents the following difficulties :

- The fusion temperature of NaCl is high, i.e., 803°C. At this temperature both sodium and chlorine are corrosive.
- Sodium forms a metallic fog at this temperature.

To remove above difficulties, the fusion temperature is reduced to 600°C by adding CaCl₂ and KF.

POTASSIUM

Sources :

Potassium occurs mainly as deposits of KCl and carnallite (KCl · MgCl₂ · 6H₂O)

Extraction :

A cell similar to down's cell can be used to obtain potassium by electrolysing fused KCl.

GROUP 2

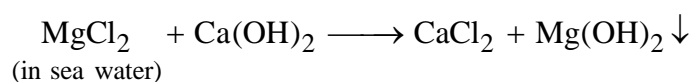
MAGNESIUM

Sources : Magnesium salts occur in sea water. Entire mountain ranges (eg Dolomites in Italy) consist of the mineral dolomite [MgCO₃ · CaCO₃]. It also occurs as magnesite (MgCO₃) and carnallite.

Extraction :

(A) Dow's sea water process :

Sea water contains MgCl₂. Water is treated with Ca(OH)₂ which precipitates MgCl₂ as Mg(OH)₂.

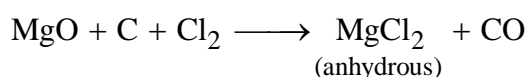
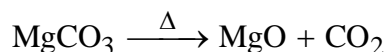


This is then converted back to MgCl_2 .



The obtained anhydrous MgCl_2 is then electrolysed in fused state.

(B) From magnesite

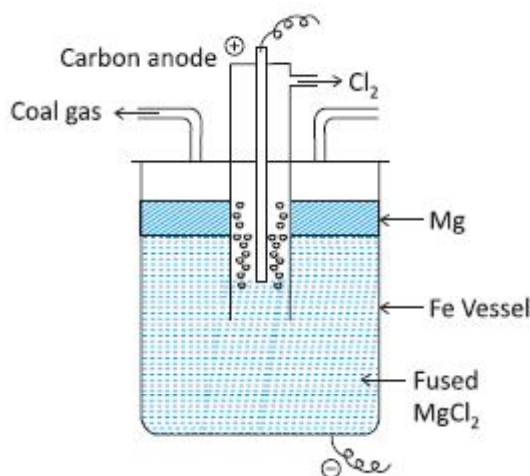


MgCl_2 is then electrolysed.

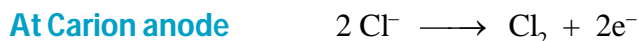
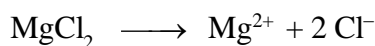
(C) Electrolysis of Fused Carnallite

Magnesium is prepared by electrolysis of fused MgCl_2 .

Anhydrous magnesium chloride is first prepared as in (A), (B) above

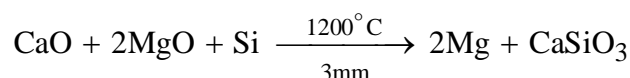


In order to lower fusion temperature of anhydrous MgCl_2 and to increase the conductivity of electrolyte NaCl or KCl (30%) is added. The electrolysis of MgCl_2 is carried out at 700°C . An air tight Iron vessel serves as cathode. A carbon rod serves as anode and is enclosed by a porcelain tube. This arrangement prevents the contact between magnesium and chlorine. Before starting the electrolysis, air above the electrolyte is replaced by coal gas. This precaution is necessary because at about 700°C magnesium reacts rapidly with O_2 , N_2 and CO_2 present in air.



(D) In silico-thermic process / Pidgeon process :

Here calcined dolomite ($\text{CaO} + \text{MgO}$) is reduced by ferrosilicon at about 1200°C in an electric furnace working under reduced pressure (3mm) where pure magnesium distils over.



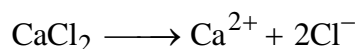
CALCIUM

Sources :

It occurs in many common minerals like limestne, marble and chalk (CaCO_3), dolomite, gypsum, Fluorspar and also as coral.

Extraction by Electrolysis :

Calcium is obtained by electrolysis of a fused mass consisting six parts calcium chloride and one part calcium fluoride at about 700°C in an electrolytic cell made of graphite which acts as anode and a water cooled cathode of iron which is suspended from the top in the fused mass. On passing current, calcium is discharged at cathode. It gets solidified as cathode is water cooled.



Since metallic calcium is soluble in fused CaCl_2 at electrolysis temperature, cathode is raised and Ca is removed as soon as it is deposited.

Note: Na or K is obtained by electrolysis of fused NaOH or KOH respectively but calcium cannot be obtained in the same manner as $\text{Ca}(\text{OH})_2$ decomposes into CaO (quick lime) which is difficult to fuse.



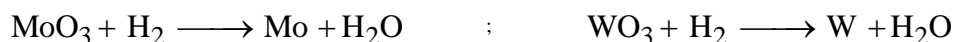
GROUP 3 - 7

➤ Ti is refined by Van Arkel - de-Boer method :



Note: TiO_2 is very stable and can't be reduced by C or CO as it forms carbides and hence is reduced by Na or Mg.

- Zirconium (Zr) is also refined by Van Arkel - de-Boer methods :
- Molybdenum and Tungsten are chemically reduced by H_2



GROUP 8

IRON

Sources :

Iron is the second most abundant metal and fourth most abundant element in the earth's crust. It is extracted from haematite (Fe_2O_3), magnetite ($Fe^{II}Fe^{III}O_4$) and iron pyrites (FeS_2) Famously called Fools Gold.

Extraction :

1. Crushing and Concentration :

The ore is crushed and washed with water (i.e., concentrated by levigating in a stream of water-gravity separation or hydraulic washing) and then concentrated by electromagnetic process.

2. Roasting :

The concentrated ore is roasted in shallow kilns in the presence of excess of air. In roasting,

- Most of the moisture is removed.
- Impurities (like C, S, P, As and Sb) are removed in the form of their volatile oxides.

$$S + O_2 \longrightarrow SO_2 \quad ; \quad 4As + 3O_2 \longrightarrow 2As_2O_3 \quad ; \quad P + O_2 \longrightarrow P_2O_3$$
- Carbonates and sulphides are converted into oxides.

$$FeCO_3 \longrightarrow FeO + CO_2 \quad ; \quad 4FeS_2 + 11O_2 \longrightarrow 2Fe_2O_3 + 8SO_2$$
- Ferrous oxide is oxidised to ferric and thus avoids formation of slag with sand in further processing.

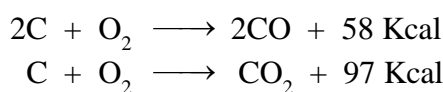
$$4FeO + O_2 \longrightarrow 2Fe_2O_3 \quad (\text{Otherwise } FeO + SiO_2 \longrightarrow FeSiO_3)$$
- The entire mass becomes porous which makes reduction easy.

3. Smelting or Reduction :

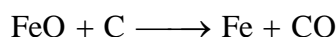
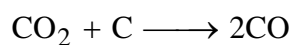
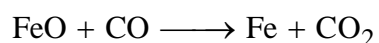
The roasted ore (8 parts) mixed with coke (C), a reducing agent (4 parts) and limestone, a flux (1 part) is smelted (reduced) in a blast furnace lined with dolomite. Hot air blast is introduced near the bottom of the furnace. Since the blast furnace has different temperature at different zones, different reactions take place at different zones.

(a) Zone of Combustion : ($1500^\circ C - 1600^\circ C$)

This zone is near the bottom of furnace and little above the tuyeres.



Both reactions are exothermic, a high temperature of about $1500^\circ C - 1600^\circ C$ is attained.



(b) Zone of Fusion : (1200°C -1500°C)

It is just above the zone of combustion. Here the iron produced in upper zones melts and trickles down in hearth while the slag being lighter floats over the molten iron and thus prevents oxidation of Fe by blast of hot air. The molten metal and slag are removed from different outlets.

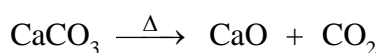
(c) Zone of Heat Absorption : (or middle zone) (800°C -1200°C)

In this middle part of furnace, rising CO_2 (produced in the zone of combustion) is reduced to carbon monoxide.

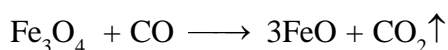


The reaction being endothermic lowers the temperature of the zone. In addition to this, following reactions also take place here.

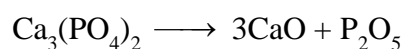
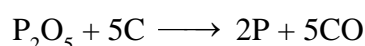
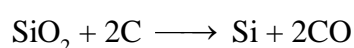
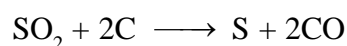
(i) Limestone decomposes forming CaO which reacts with SiO_2 forming slag.



(ii) Any Fe_3O_4 which escapes reduction in the zone of reduction is reduced in this zone.

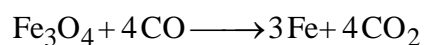
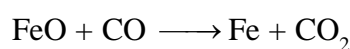
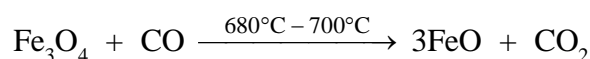
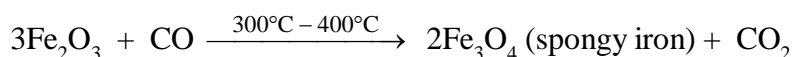


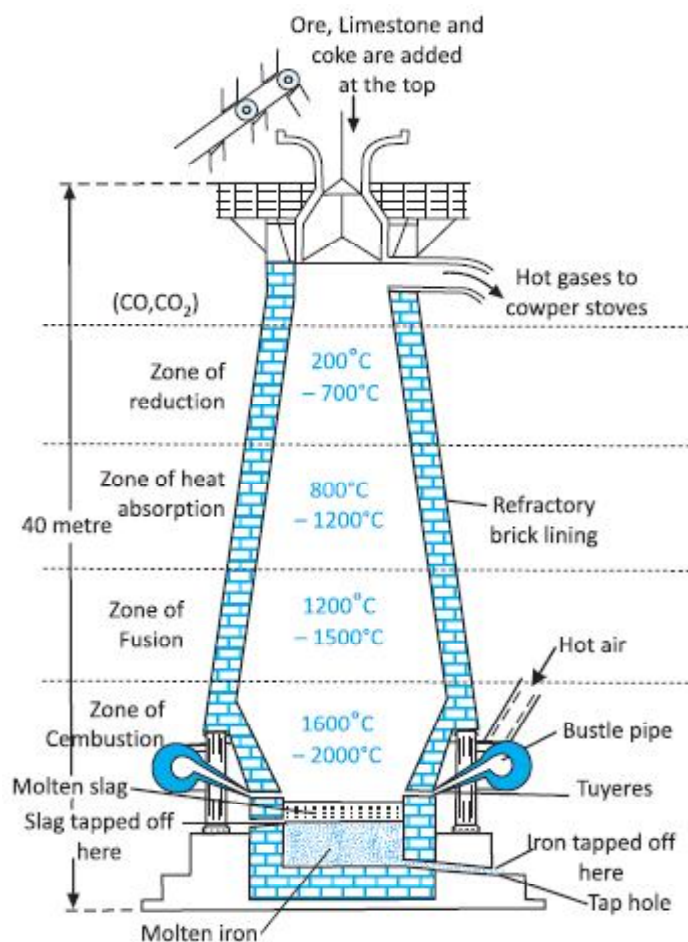
(iii) Some impurities are reduced and get mixed up with Iron.



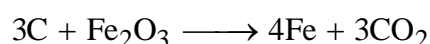
(d) Zone of Reduction : (300°C -700°C)

It is near the top of the furnace. Here the roasted ore is reduced by rising carbon monoxide CO. *The following reactions taking place in this zone are all reversible in nature.*





- Iron obtained is impure. The product from blast furnace is called as **Pig Iron**. The net product of blast furnace consists of Pig Iron, slag and fuel gases.
- The overall process for the extraction of Fe is thus :



Cast Iron : The cast iron is specially made by igniting Pig iron with scrap iron and coke in a specially designed furnace by blast of hot air. It contains 3% carbon in the form of graphite and carbide and is extremely hard and brittle.

GROUP - 11 COPPER

Sources :

The most common ore is chalcopyrites CuFeS_2 . Other ores include Cu_2S (Copper glance / chalcocite), basic copper carbonate $\text{CuCO}_3 \cdot \text{Cu(OH)}_2$ (called malachite and is green) and cuprite Cu_2O (is ruby red)

Extraction :

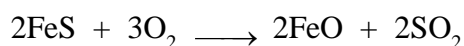
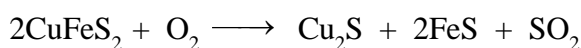
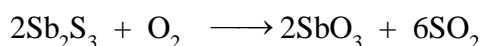
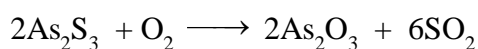
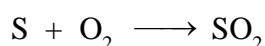
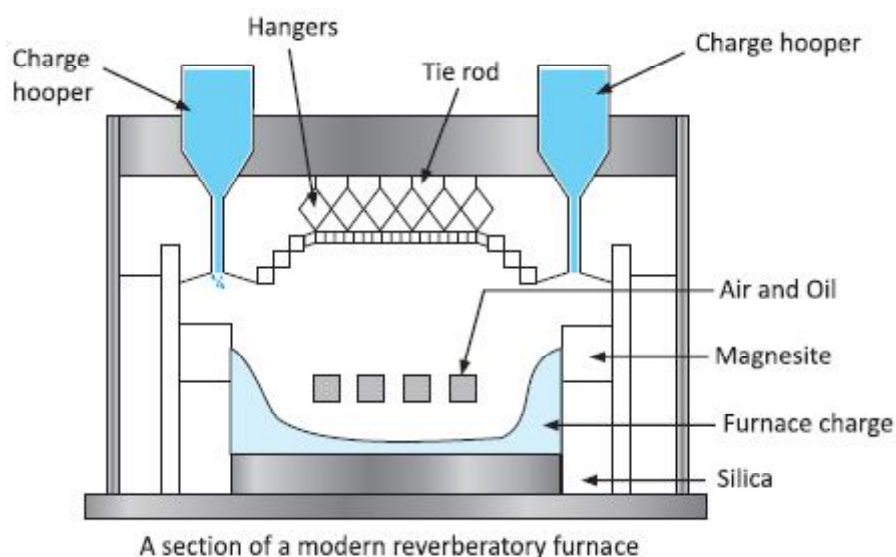
It is a **self reduction method**. It can be achieved by two ways.

I. Pyrometallurgical

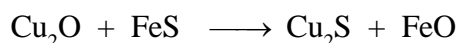
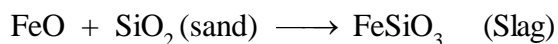
II. Hydrometallurgical

(A) Pyrometallurgical Method :

- 1. Concentration of Ore :** The ore is finely divided and concentrated by froth floatation method. Here froth is made from pine oil and water by bubbling air into the mixture. Concentrated ore adheres to the surface of froth leaving behind impurities.
- 2. Roasting :** The concentrated ore is heated strongly in presence of air in a reverberatory furnace. Sulphur, arsenic and antimony are removed in the form of their volatile oxides while the proper ore is converted into a mixture of cuprous and ferrous sulphides. These sulphides are partially oxidised to oxides.

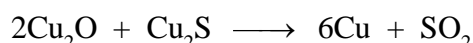
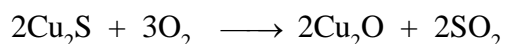


- 3. Smelting (Auto Reduction) :** The roasted ore is mixed with sand (flux) and coke (fuel) and then heated in water jacketed blast furnace called smelter. The oxidation of ferrous sulphide which started during roasting now goes up a step further, ferrous oxide, formed reacts with sand to form ferrous silicates (slag). Here some FeS reacts with Cu_2O to form Cu_2S again.

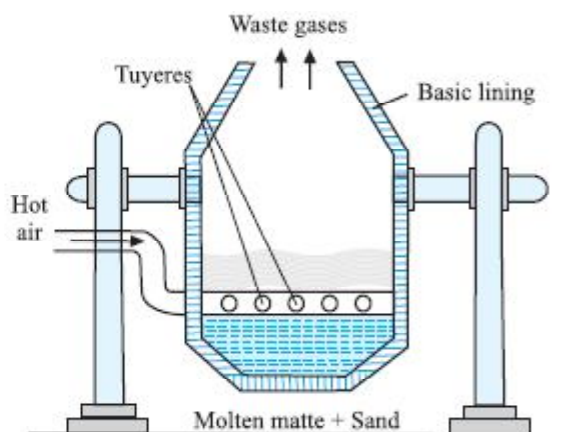
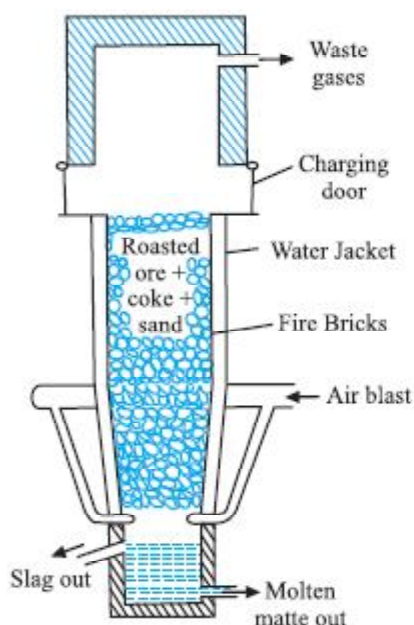


Slag, forming upper layer and molten mass consisting of Cu_2S and little FeS , forming lower layer called 'COPPER MATTE' are removed from separate holes.

4. **Bessemerisation** : Molten matte is heated in Bessemer converter and blast of air mixed with sand is blown through the molten mass. Here Iron (FeS) is completely removed as slag. A part of Cu_2S is oxidised to Cu_2O and a part of Cu_2S reduces Cu_2O to metallic copper.



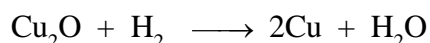
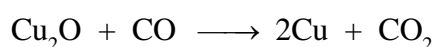
The molten copper is poured off into sand moulds. As it cools, it gives up dissolved SO_2 which forms blister on the metal surface. The copper thus obtained is called as BLISTER COPPER (98% Cu).



5. Refining of Copper :

- (a) **Furnace or thermal Refining** : Blister copper is melted in a reverberatory furnace provided with silver lining and air is blown in where the impurities oxidise. Some of oxides escape and other form a slag with silica. The slag is removed.

- (b) **Poling** : Molten Cu is stirred with poles of green wood to reduce Cu_2O to Cu by CO and H_2 from green wood.



- (c) **Electrorefining** : The electrolyte bath contains an acidified solution of copper sulphate, impure copper (blister copper) acts as anode while pure copper strip acts as cathode. The cathode grows in thickness and pure Cu is scraped off.

Anode : Impure Cu

Electrolyte: 3.55% CuSO₄ + 15% H₂SO₄ : $\text{Cu} \longrightarrow \text{Cu}^{2+} + 2\text{e}^-$

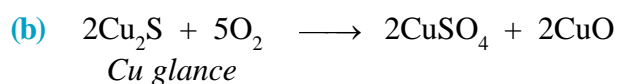
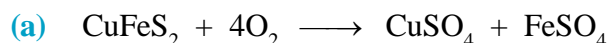
Cathode : Pure Cu

Temperature: 50°C : $\text{Cu}^{2+} + 2\text{e}^- \longrightarrow \text{Cu (Pure)}$

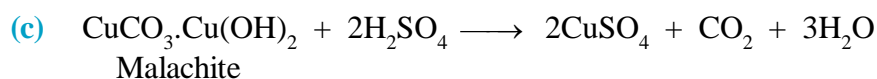
Note : The impurities (Au, Ag, Pb) collect below the anode and is called anode mud.

(B) Hydrometallurgical Method :

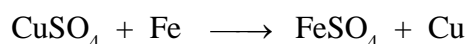
Low grade ore is crushed and exposed to air and water when copper sulphide is oxidised to copper sulphate. Some iron sulphate and sulphuric acid is also produced. This process takes one year.



In NON-SULPHIDE ores, the crushed ore is leached with dilute H₂SO₄.



The pale green liquor draining from the bottom to the heaps is collected in pans and treated with iron scraps which precipitate out copper.



The precipitated copper is dried, melted and refined.

SILVER AND GOLD

Sources :

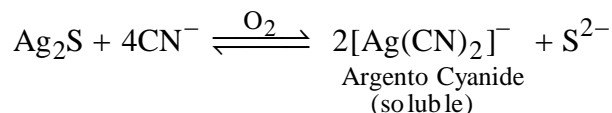
Silver is mainly found as sulphide ore Ag₂S (argentite) Gold occurs mainly as grains of metal disseminated in quartz veins.

Extraction :

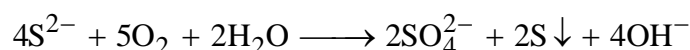
Au, Ag are both first crushed and concentrated by froth floatation. Silver then directly undergoes leaching while gold is leached after roasting.

Leaching is done by Cyanide process.

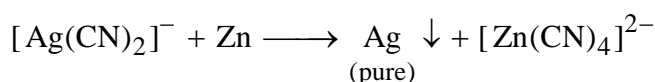
1. Ag ore is leached with NaCN (or KCN) solution in presence of air when silver and its salt are converted to soluble complex.



O₂(air) is pumped to force the reaction in forward direction.

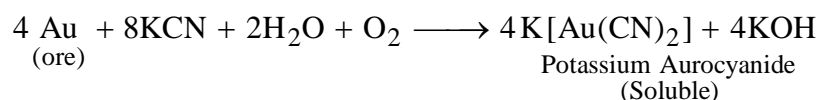


Zinc dust is then added to precipitate Ag.

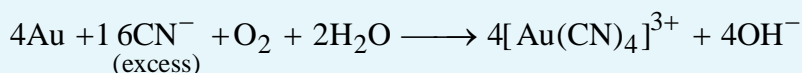


2. The leaching process used for Au is called **Mac Arthur Forest Cyanide Process** :

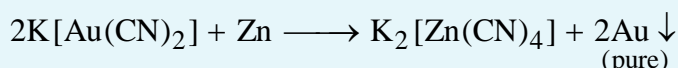
Concentrated ore is taken in large vats made of cement or iron. It is then treated with dilute (0.5%) solution of KCN in presence of air to form a soluble complex.



Note: If excess conc. KCN is used then



Zinc dust is then added :



The obtained Gold (or Silver) still contains traces of impurities and thus electrolytic refining is performed. The electrolyte used is AgNO₃ + 10% HNO₃ (for silver) and AuCl₃ + 10% HCl (for gold). Anode is the impure metal while cathode is made of pure metal.

- Ag is also obtained from argentiferous lead (PbS . Ag₂S) by *Parke's Process* or *Pattinson's Process* :
- Ag, Au can also be extracted from anode mud formed during electrolytic refining of copper.
- Another method of extraction is amalgamation. Powdered ore is first converted to its amalgam and then distilled to remove Hg in the form of vapour leaving behind pure metal.

GROUP - 12

ZINC

Sources :

Zinc is found as Zinc Blende (ZnS), Colomine (ZnCO₃) and zincite (ZnO)

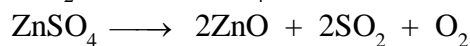
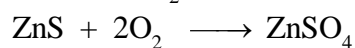
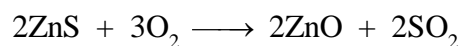
Extraction :

1. Concentration

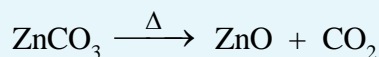
The ore is concentrated first by gravity method and then by froth floatation process. If Fe₂O₃ is present as an impurity, it is removed by magnetic separation.

2. Roasting

The concentrated ore is then roasted at 900°C – 1000°C to convert ZnS and ZnSO₄ to ZnO.

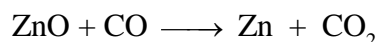
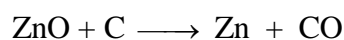


Note: If calamine is used as the source, only calcination is required at high temperature.



3. Reduction by coke

The oxide, ZnO is reduced with coke at about 1500°C to obtain metallic zinc which is distilled off and rapidly cooled.



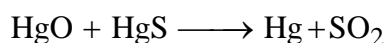
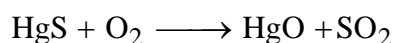
4. Electrolytic Refining

Zn thus produced contains impurities like Pb, Cd, and Fe. These impurities are removed by *liquation*. The pure zinc is obtained by electrolysis of the Zinc in presence of acidified ZnSO₄ (ZnSO₄ + dil H₂SO₄) as electrolyte. Impure zinc is made the anode and pure zinc, the cathode.

Note: Zinc can also be extracted by electrolytic method. ZnS is first roasted at 700°C to produce ZnO. Then, the oxide ZnO is leached with H₂SO₄ to convert to sulphate (ZnSO₄). After removing impurities by treating with milk of lime, ZnSO₄ is acidified and electrolysed to give pure zinc on cathode.

MERCURY

The most important ore is cinnabar (HgS) which is bright red coloured. The ore is first crushed and concentrated by froth floatation method. It then undergoes Auto / self reduction



Refining is done by either liquation or distillation.

**GROUP - 13****ALUMINIUM :****Sources :**

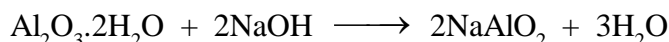
Aluminium is the most abundant metal and is commercially important. The most important ore of aluminium is bauxite. This is a generic name for several minerals with formulae varying between $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ and $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$

Extraction (Electrolytic method from Bauxite) :**1. Purification of Bauxite**

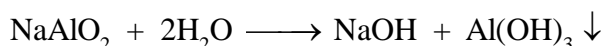
Bauxite contains mainly Iron oxide (Fe_2O_3) and silica as impurity. If iron oxide is the main impurity, it is called red bauxite and if SiO_2 is the main impurity, it is called white bauxite. It is difficult to remove iron or silicon from aluminium, so the ore is purified before hand. It can be achieved by either of the following processes.

(a) Bayer's Process (for ores containing iron oxide as major impurity) :

Finely grounded ore is roasted at a low temperature to convert FeO to Fe_2O_3 and digested with a concentrated solution of NaOH in an autoclave. Al_2O_3 (Amphoteric) dissolves forming NaAlO_2 , while Fe_2O_3 (basic) remains undissolved. Fe_2O_3 is removed by filtration.



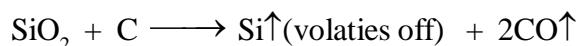
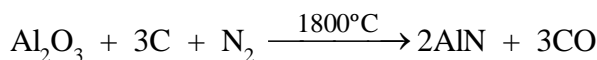
The filtrate containing sodium aluminate is diluted, treated with a seed crystal of pure $\text{Al}(\text{OH})_3$ and then agitated, when pure $\text{Al}(\text{OH})_3$ is precipitated.



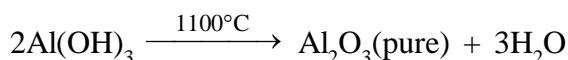
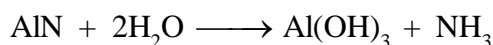
The precipitated $\text{Al}(\text{OH})_3$ is filtered, washed and ignited to give pure alumina, Al_2O_3 .

**(b) Serpek's Process (For ores containing silica, SiO_2) :**

The powdered ore is mixed with carbon and heated to 1800°C in a current of nitrogen, where aluminium nitride is formed. SiO_2 is reduced to silicon, which volatilises away.

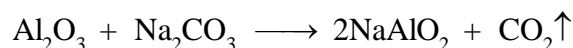


Aluminium nitride is hydrolysed by water to $\text{Al}(\text{OH})_3$ which on ignition gives pure alumina.

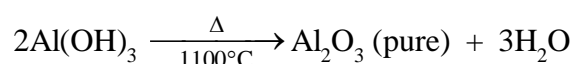
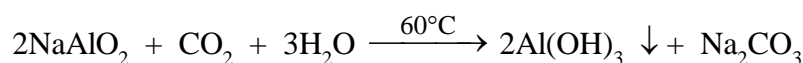


(c) Hall's Process [mainly for Red Bauxite] :

Crude bauxite reacts with Na_2CO_3 at 1000°C to give sodium aluminate and impurities Fe_2O_3 and SiO_2 form NaFeO_2 and Na_2SiO_3 respectively.

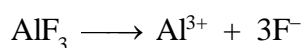
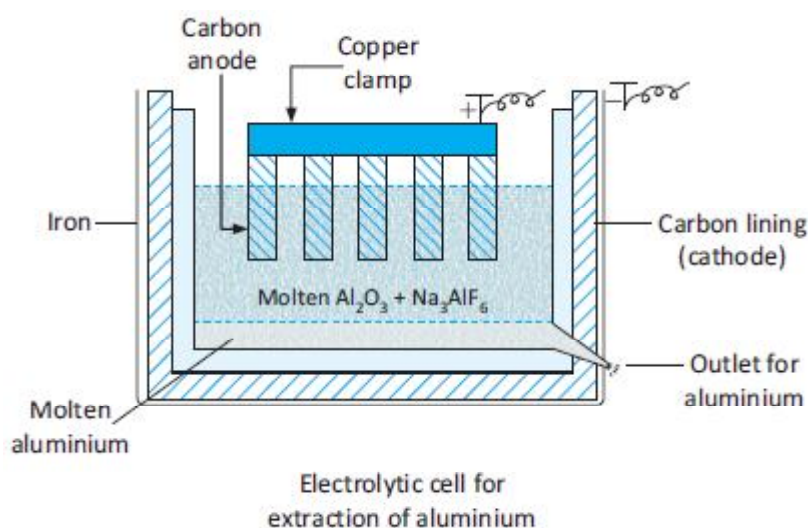


CO_2 at a temperature of around 60°C is passed into sodium aluminate solution producing $\text{Al}(\text{OH})_3$.

**2. Electrolytic reduction of alumina (Hall - Heroult Process)**

Aluminium can't be isolated by electrolysis of aqueous solution of Al_2O_3 , since aluminium is more electropositive than hydrogen, so its electrolysis gives H_2 at cathode.

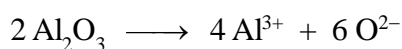
Al_2O_3 is infusible (M.P. = 2050°C), so it can't be electrolysed. So pure alumina, dissolved in molten Cryolite (Na_3AlF_6) containing some CaF_2 or NaF is electrolysed at about 800°C – 1000°C . Cryolite decreases melting point and increases conductivity while CaF_2 and NaF are added only to increase conductivity. The electrolysis is carried out in an *iron cell* lined with *graphite* (cathode). The anode is a series of *graphite rods*.



At cathode : $\text{Al}^{3+} + 3\text{e}^- \longrightarrow \text{Al}$

At the same time, Al_2O_3 dissociates into Al^{3+} and O^{2-} .

Since 'O' is below F in the electronegativity series, O^{2-} ions are selectively discharged at the anode as oxygen.



At anode : $6\text{O}^{2-} \longrightarrow 3\text{O}_2 + 12\text{e}^-$

The oxygen liberated at anode combines with carbon of anode to form CO and CO₂ so anode, which burn away have to be replaced periodically. Molten Al collects at the bottom of cell (99% pure)

3. Electrolytic Refining

The cells layers contain three fused layers.

- (a) The bottom anode layer of an alloy of Al, Cu, Si
- (b) The middle layer of Cryolite and BaF₂
- (c) The top cathode layer of pure aluminium.

When a current is passed, Al³⁺ ions from the fused middle layer get discharged at the cathode, while an equivalent amount of aluminium moves into the middle layer. Impurities (Cu etc) remain at the bottom.



GROUP - 14

TIN :

Sources :

It is mainly obtained from Cassiterite (SnO₂) which contains Wolframite (FeWO₄ · MnWO₄) as an impurity.

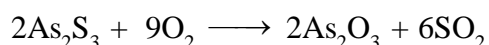
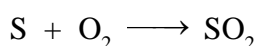
Extraction :

1. Concentration of ore :

Ore is crushed to a fine powder and concentrated by gravity process. Ore is washed with the stream of water to remove gangue and other silicon impurities. Tinstone and wolframite are left. Wolframite is then removed by magnetic separation.

2. Roasting :

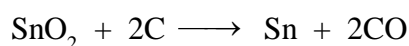
The ore is roasted to remove volatile impurities.



The roasted ore is washed with water to remove soluble impurities and dried. It contains 60 – 70% of tin as SnO₂ called *Black Tin*.

3. Smelting :

The ore is mixed with 1/5 th of its weight of powdered anthracite and a little limestone and heated in reverberatory furnace. SnO₂ is reduced to metallic state and silica is removed as slag.



4. Refining :

It is refined by any of the following processes.

- (a) **Liquation** : The crude tin is melted on the sloping hearth of a reverberatory furnace when tin alone melts and flows out. The process is called *sweating* and the impure tin left is called *dross*.

- (b) **Electrolytic Refining** : The electrolyte consists of hydrofluorosilicic acid (H_2SiF_6) containing stannic sulphate (SnSO_4) and H_2SO_4 . A block of impure tin is anode and a thin strip of pure tin the cathode.

LEAD

Sources :

Galena (PbS) is the principal ore.

Extraction :

(A) Self Reduction or Air reduction process :

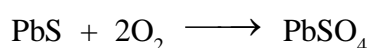
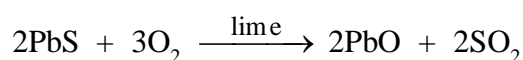
This is used for samples of galena rich in lead. In this process roasting and smelting are done in same furnace, but at different temperatures.

(i) Crushing and Concentration

The ore is crushed, finely powdered and concentrated by froth floating process. NaCN is used as a depressant to prevent ZnS (if present) from coming out as froth. The concentrated ore contains 50 – 60% of lead.

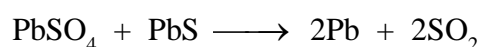
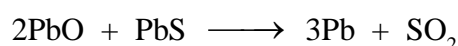
(ii) Roasting

The concentrated ore is roasted at a moderate temperature in a reverberatory furnace and in a limited supply of air.



(iii) Reduction (Smelting)

Air supply is cut off, fresh galena is added to roasted ore and the temperature is raised. Galena reduces lead oxide and lead sulphate to metallic lead.



Molten lead is drawn from time to time and purified.

(B) Carbon Reduction Process :

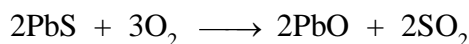
This process is suitable when the ore contains more impurity (silica) and has low amount of lead. Here roasting and smelting are done in different furnaces.

(i) Crushing and Concentration

This is done as in above process.

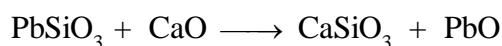
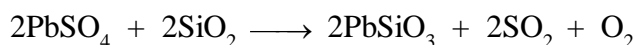
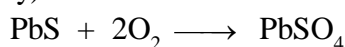
(ii) Roasting

Concentrated ore is mixed with lime (CaO) and heated in presence of air when PbS is oxidised mainly to PbO.

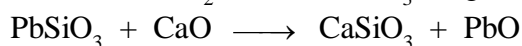
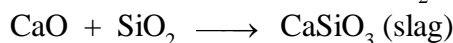
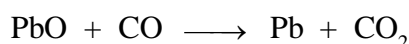
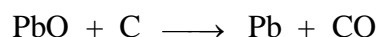


Lime performs two important functions.

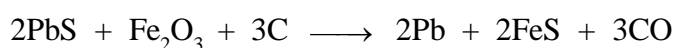
- (a) Being more basic than PbO, lime preferentially reacts with SO₂ (formed in the above oxidation) to form calcium sulphite and thus favours the oxidation of galena in the forward direction.
- (b) It decomposes lead silicate (formed by reaction of PbSO₄ with silica present as impurity) to PbO which would otherwise have gone as slag.

**(iii) Smelting**

The roasted mass is mixed with coke and lime (flux) and smelted in a blast furnace. Following reactions occur.



Little hematite is added to reduce any unchanged PbS to Pb.

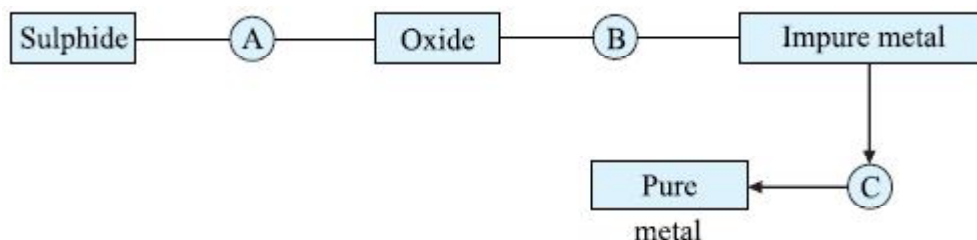
**(iv) Refining**

Impurities are Cu, As, Sb, Fe, Zn, Bi, Ag and sulphur. These are refined by either of following processes :

- (a) Oxidation or softening where impure metal is heated in current of air where Cu, Fe, Sn etc are oxidised before lead.
- (b) Desilverisation by Parke's or Pattinson method to remove Ag.
- (c) **Electrorefining** : Electrolysis of 1-15% Lead silica fluoride (PbSiF₆) and 5-10% (hydrofluorosilicic acid, H₂SiF₆) is carried out between pure lead sheets serving as cathode, and crude impure lead as anode.

IN - CHAPTER EXERCISE - B

1. Cinnabar (HgS) and galena (PbS) on roasting often give their respective metals but zinc blende (ZnS) does not.
Explain :
2. A metal is in combined state as sulphide. Identify the steps (A), (B) and (C)



3. Why Zinc and not copper is used for the recovery of metallic silver from the complex $[\text{Ag}(\text{CN})_2]^-$
4. Describe the extraction of magnesium from sea water.

NOW ATTEMPT IN-CHAPTER EXERCISE-B REMAINING QUESTIONS IN THIS EBOOK

NOW ATTEMPT OBJECTIVE WORKSHEET BEFORE PROCEEDING AHEAD IN THIS EBOOK

SOLUTIONS - IN - CHAPTER EXERCISE - A

1. $\text{Fe}_2\text{O}_3 + \text{C} \longrightarrow \text{Fe}$; $\text{ZnO} + \text{C} \longrightarrow \text{Zn} + \text{CO}_2 + \text{CO(gases)}$
(haematite) (zincite)
- $\text{PbO} + \text{C} \longrightarrow \text{Pb}$; $\text{MgO} + \text{C} \longrightarrow \text{Mg}$; $\text{Ca}_3(\text{PO}_4)_2 + \text{C} \longrightarrow \text{P}$
2. Tinstone is concentrated first by gravity separation and then magnetic separation is used to remove magnetic impurities like wolframite.
3. **Collectors** enhance the non wettability of mineral particles and froth - stabilizers stabilize the froth.
4. Reduction by hydrogen is not widely used because many metals react at elevated temperatures, forming hydrides. There is also a risk of explosion.
5. Galena (PbS), Chalcocite (Cu_2S) and cinnabar (HgS).
6. In the thermite process, Al is used to reduce metal oxide to metal while it itself gets oxidised to Al_2O_3 which produces a large amount of heat (1675 kJ/mol). This is utilised to join broken railway tracks.

SOLUTIONS - IN - CHAPTER EXERCISE - B

1. This is because HgS and PbS can undergo self reduction while ZnS doesnot.
2. A = roasting, B = reduction, C = refining
4. Sea water contains MgCl_2 which is precipitated as Mg(OH)_2 (using Ca(OH)_2). This is then converted back to MgCl_2 (by HCl) and dried. MgCl_2 is then electrolysed.

My Chapter Notes

